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Tel: 0 (288) 246 15 16
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İçindekiler / Contents

KINETIC CHARACTERIZATION OF GAG:CE PHOSPHOR

Sibel UYSAL SATILMIŞ[1], Arzu EGE[1*], Levent TÜRKLER[2], Zekai TEK[1], Elizabeth J. POPOVICI[3]

[1] *Manisa Celal Bayar University, Faculty of Science and Letters, Department of Physics, Manisa, Turkey*

[2] *Ege University, Bergama Technical and Business College, İzmir, Turkey*

[3] *Raluca Ripan Institute for Research in Chemistry, Babes Bolyai University, Cluj-Napoca, Romania*

Abstract

Thermoluminescence (TL) kinetic characterization of cerium (Ce^{3+}) doped gadolinium aluminum garnet (GAG) prepared by wet chemical synthesis method is presented in this study. Thermoluminescence glow curve of GAG phosphor after UV irradiation has two peaks at about 350 and 501 K with a heating rate of 2 Ks^{-1}. Thermoluminescence kinetic parameters such as order of kinetics, frequency factor and activation energy associated with the main glow peak of the GAG:Ce phosphor have been calculated using various heating rates (VHR) computerized glow curve deconvulation (CGCD) and peak shape (PS) methods in this study. The activation energies obtained by VHR, PS and CGCD methods were calculated as 1.24, 1.11 and 1.14 eV, respectively. The frequency factors attained by these methods were found as $3.41x10^{11}$, $1.80x10^{10}$ and $2.63x10^{10}$ s^{-1}, respectively. Results acquired using all methods are discussed and compared.

Keywords: Gadolinium aluminum garnet, Thermoluminescence, Kinetic parameter

GAG:CE FOSFORUNUN KİNETİK KARAKTERİZASYONU

Özet

Bu çalışmada, ıslak kimyasal sentez metodu ile hazırlanmış seryum (Ce^{+3}) katkılı gadolinyum alüminyum garnetin termolüminesans (TL) kinetik karakterizasyonu sunulmuştur. UV ile ışınlanmasının ardından GAG fosforunun, termolüminesans ışıma eğrisi 2 Ks^{-1} ısıtma hızı ile yaklaşık olarak 350 ve 501 K de iki pike sahiptir. Çalışmada GAG:Ce fosforunun ana ışıma piki (501 K) ile ilişkili kinetik derece, frekans faktörü ve aktivasyon enerjisi gibi termolüminesans kinetik parametreleri, çeşitli ısıtma hızları (VHR), bilgisayarlı ışıma eğrisi dekonvulasyonu (CGCD) ve pik şekli (PS) metotları ile hesaplanmıştır. VHR, PS ve CGCD metotları ile elde edilen aktivasyon enerjileri sırasıyla 1,24, 1,11 ve 1,14 eV olarak hesaplanmıştır. Bu metotlarla ulaşılan frekans faktörleri $3,41x10^{11}$, $1,80x10^{10}$ ve $2,63x10^{10}$ s^{-1} olarak bulunmuştur. Tüm metotlardan elde edilen sonuçlar kıyaslanmış ve tartışılmıştır.

Anahtar Kelimeler: Gadolinyum alüminyum garnet, Termolüminesans, Kinetik parametre.

[*] *arzu_aegean@hotmail.com*

1. INTRODUCTION

Garnet crystal is commonly used at high temperatures due to their high chemical and thermal stability. Moreover, it is used in the solid-state laser as host materials, the refractory coating fillers, magnetic materials, and phosphor powders [1-3]. The optical properties of Ce-activated garnet series used in white light emitting diodes have been remarkable in recent years [4]. Gadolinium aluminate is nowadays being investigated quite interesting as a material for, electronic, optical, magnetic and structural applications [5]. Information on the luminescence properties of cerium doped gadolinium aluminum garnet is limited to a few studies. The researches were related to gadolinium aluminum garnet preparation methods and their luminescent properties [1-8].

The recent increase in solar ultraviolet (UV) radiation reaching the Earth's surface due to the depletion of stratospheric ozone has been a major concern, due to the harmful effects on living organisms associated to the UVB (320–290 nm) and UVA (400–320 nm) components of the solar spectrum. Additionally, UVB may have several adverse influences on planktons in sea ecosystem [9, 10].

Thermoluminescence dosimeters have some superior characteristics such as their availability, being cheap and easy to use in the determination of exposed dose to living organisms. Recently, studies related to UV radiation measurement by thermoluminescent dosimeters were increased due to being cheap and easy technique in the UV measurement. This has led us to examine the usability of GAG:Ce phosphor in the measurement of UV radiation dose. The determination of the trapping parameters from thermoluminescence glow curves is an important research subject to improve the properties of the material as dosimetric usage.

In the present study, cerium-doped gadolinium aluminate phosphor prepared by a wet chemical synthesis route was used. The thermoluminescence kinetic characterization of the material was investigated after UV irradiation. It was observed that glow curve of the phosphor was consisted of two peaks at about 353 and 501 K. The kinetic parameters such as kinetic order (b), activation energy (E), and frequency factor (s) were calculated using various heating rates (VHR), Chen peak shape methods and computerized glow curve analysis (GCGD) were used.

2. MATERIAL AND METHODS

The cerium-doped gadolinium aluminate phosphor used in this study was synthesized by wet-chemical route via the reagent simultaneous addition (WCS-SimAdd) technique. All experimental details can be found in our earlier works [8]. A Harshaw 3500 TLD reader was used for recording TSL glow curves. All TSL measurements were carried out immediately after irradiating using UV light (Philips UV 100 lamp) with 311 nm wavelength.

TSL kinetic parameters of activation energy (E), frequency factor (s) and kinetic order have a sensible impact on the TSL characterization of a phosphor. Therefore, the knowledge of kinetic parameters has critical importance for understanding the thermoluminescence phenomenon in the phosphor, and there have been many methods for determining these parameters experimentally [11].

In this study peak shape (PS), various heating rates (VHR) methods and computerized glow curve deconvulation (CGCD) analysis were used to analyze the kinetic characterization for GAG:Ce phosphors.

In the peak shape method developed by Chen [12], the shape of the glow curve is used to calculate E, s and b parameters. The peak temperature T_m and two temperatures (T_1 and T_2) on ascending and descending side of T_m at the half of maximum intensity, the half width parameters (ω, δ, τ) and the symmetry factor ($\mu_g = \frac{\delta}{\omega}$) were used in the calculation of the kinetic parameters in the peak shape methods. Following equations (1-3) were applied in the Peak shape method.

$$E_\alpha = c_\varepsilon\left(\frac{kT_m^2}{\alpha}\right) - b_\alpha(2kT_m) \qquad (1)$$

Where α is $\omega = T_2 - T_1$, $\delta = T_2 - T_m$ and $\tau = T_m - T_1$,

$$\begin{aligned} c_\tau &= 1.51 + 3.0\,(\mu_g' - 0.42) & b_\tau &= 1.58 + 4.2\,(\mu_g' - 0.42) \\ c_\delta &= 0.976 + 7.3\,(\mu_g' - 0.42) & b_\delta &= 0 \\ c_\omega &= 2.52 + 10.2\,(\mu_g' - 0.42) & b_\omega &= 1 \end{aligned} \qquad (2)$$

The frequency factor can be evaluated using the Equation

$$s = \frac{\beta E}{kT_m^2}\exp\left(\frac{E}{kT_m}\right)\left[1 + (b-1)\Delta_m\right]^{-1} \qquad (3)$$

Where b is the order of the kinetics and $\Delta_m=2kT_m/E$.

The VHR method is based on the recording the maximum temperatures of the glow peak with using different heating rates [13, 14]. The maximum temperature T_m is associated with the heating rate β, this relation could be described in equation (4):

$$\ln(T_m^2/\beta) = E/kT_m + \ln(E/ks) \tag{4}$$

Where k is Boltzmann's constant, T_m is the maximum temperature of the glow peak, E is the activation energy (eV) and s is the frequency factor (s^{-1}). After recording T_m with a number of different heating rates, E could be calculated from the slope of the straight line obtained from the ln (T^2_m/β) versus $1/T_m$ plot. The intercept of the slope of this plot gives the value of frequency factor. Kitis and Tuyn proposed a model to correct for the temperature lag based on TSL measurements [15]. This model is given as an equation (5):

$$T_m^b = T_m^a - c\ln\left(\frac{\beta_a}{\beta_b}\right) \tag{5}$$

Where c is a constant and T_m^a and T_m^b are the maximum temperatures of glow peaks with heating rates β_a and β_b, respectively.

The fitting of the glow curves was carried out the CGCD analysis program designed using Pascal programming language by Turkler [16]. The equation (6) given by Kitis et al [17] for the general order kinetic glow peak was used in the CGCD analysis.

$$I(T) = I_M (b)^{-\frac{b}{b-1}} \exp\left(\frac{E}{kT}\frac{T-T_M}{T_M}\right) \left[(b-1)(1-\Delta)\frac{T^2}{T_M^2}\exp\left(\frac{E}{kT}\frac{T-T_M}{T_M}\right)+Z_M\right]^{-\frac{b}{b-1}} \tag{6}$$

Where $\Delta_M = 2kT_M/E$, $\Delta_M = 2kT_M/E$ ve $Z_M = 1+(b-1)\Delta_M$

3. RESULTS AND DISCUSSION

The dose response of a dosimeter should have linear or a well known function to be used in dosimetric purpose. TL glow curves of the GAG:Ce phosphors were recorded after irradiated with UV at different duration between 1 and 20 min. (Figure 1). The temperature of the main peak shifted to the low temperature side while the duration of irradiation was increased. This result indicates that the glow peaks of phosphor should not have first-order kinetics.

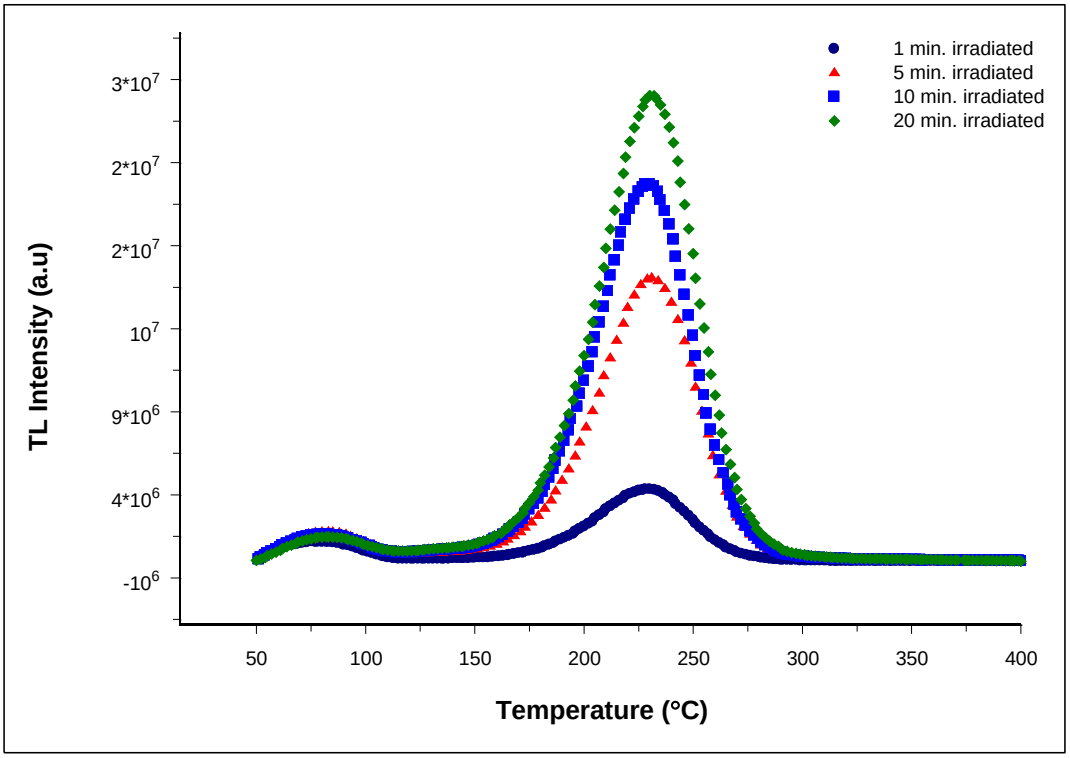

Figure 1. TL glow curves of the GAG:Ce phosphor exposed to UV irradiation at different duration.

The glow curve of the GAG:Ce phosphor is well defined so the various heating rate method was applied for kinetic characterization of the phosphor. Glow curves of UV irradiated GAG:Ce phosphors were recorded using different heating rates between 1 and 40 Ks^{-1} (Figure 2). If the glow curves are investigated, the peak temperatures of GAG:Ce phosphor glow peaks shifted to the high temperature with the increasing heating rates. This is an expected phenomenon.

The kinetic parameters are calculated by taking into consideration of the obtained peak temperatures in VHR method. However, the obtained results require some corrections due to the occurrence of some systematic errors during thermoluminescence measurements. It has been well established that temperature lag (TLA) and thermal gradient (TG) have an important role in the kinetic parameter analysis [18-22]. The TLA and TG of all measurements are evaluated using the method recommended by Kitis and Tuyn [23, 24].

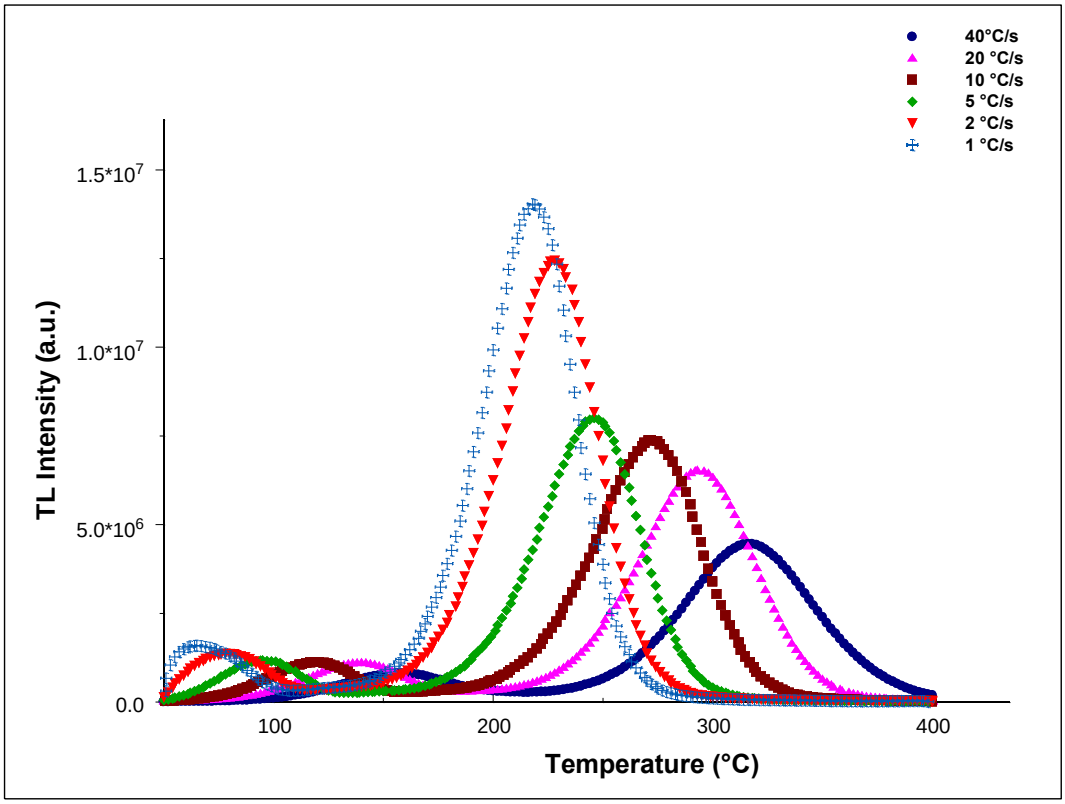

Figure 2. Glow curves of GAG:Ce irradiated with a UV. The glow curves were recorded at different heating rates, namely 1, 2, 5, 10, 20 and 40 Ks^{-1} respectively.

The peak temperatures of the glow curves obtained with each heating rates were used to plot the graph of ln (T^2_m/β) versus ($1/T_m$) (Figure 3). This graph should be a straight line since heating rates in the system is linear. The activation energy is determined from the slope of this line and the frequency factor is attained from the intercept of this line. Data (□) and data (▼)

correspond to the peak temperatures as attained from experiments and to the peak temperatures corrected for the temperature lag in figure 3, respectively. According to this method E and s parameters are calculated as 1.24 eV and $3.41x10^{+11}$ s^{-1}, respectively.

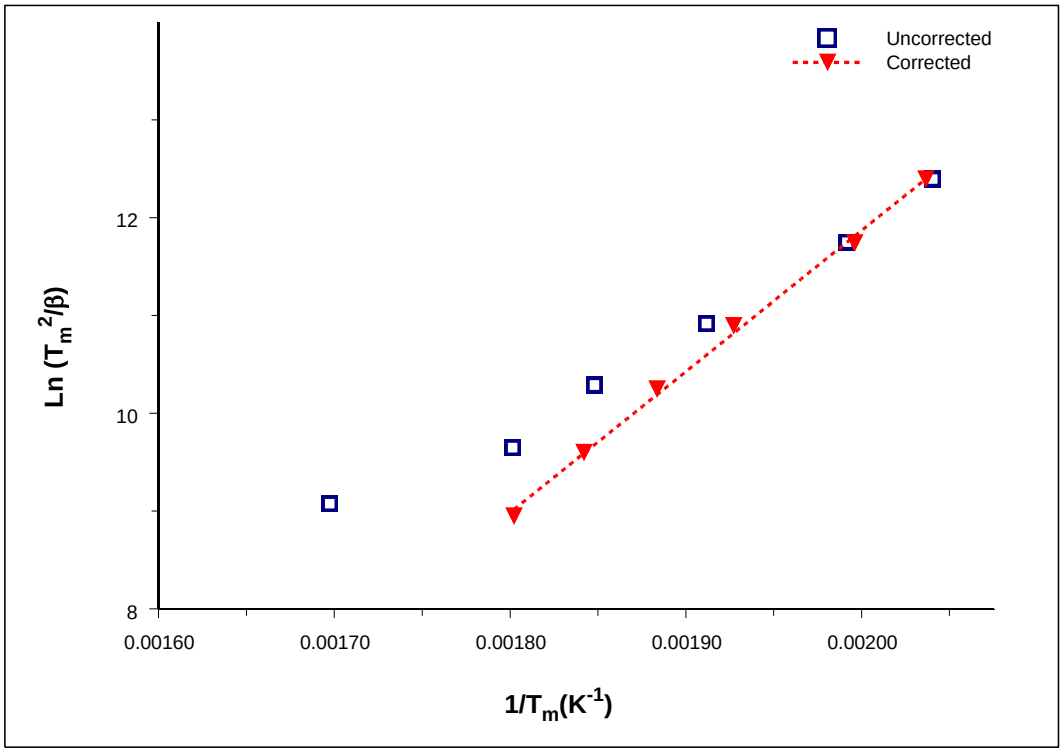

Figure 3. The plot of Ln (T^2_m/β) versus (1/T_m) values of the glow peaks attained at each heating rate.

The Peak Shape method which takes into account the peak shape or geometrical properties of a well known method of TL glow curve analysis has been applied [12]. According to this method, the average activation energy (E) was found to be 1.11 eV and average frequency factor (s) $1.80x10^{+10}$ s^{-1} of high temperature peak (501 K) which can be taken as a dosimetric peak using equations (1-3).

Table 1. The kinetic parameters of the glow peak at about 501 K attained by PS methods.

	Activation Energy (E)	(eV)	Frequency Factor (s)	(s^{-1})
PS Method	E_δ	1.13	s_δ	$2.57x10^{10}$
	E_τ	1.09	s_τ	$9.85x10^{9}$
	E_ω	1.11	s_ω	$1.83x10^{10}$

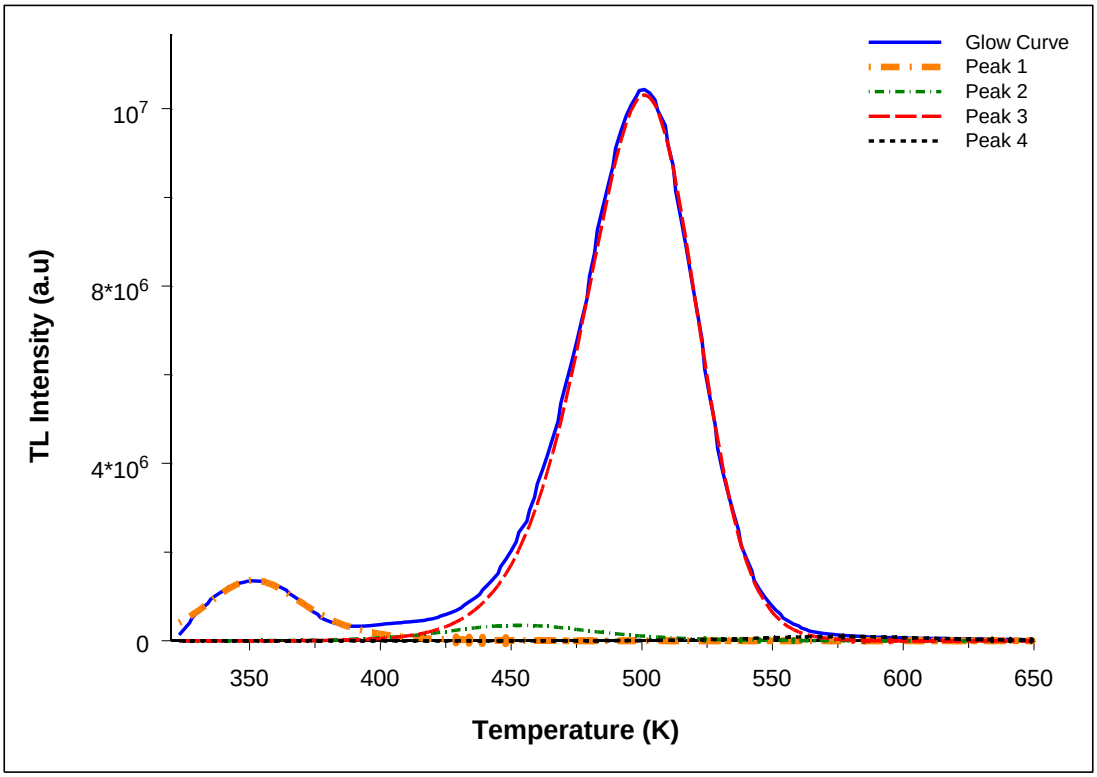

Figure 4. The computerized glow curve analysis of the GAG:Ce phosphor.

Glow curve deconvulation analysis of the phosphor GAG:Ce after exposing to UV irradiation by using the deconvulation program [16] was indicated in Figure 4. The most appropriate deconvoluted peak was taken into consideration by deciding the figure of merits (FOM). The physically calculated kinetic parameter by using FOM was in between 0.0% and

2.5% [25]. The FOM value of the current deconvulation process of the GAG:Ce glow curve was found as 2.05%. As a result of the analysis, it was observed that the glow curve is composed of four peaks at about 351, 452, 501 and 575 K. Although, phosphor has composed of four peaks, only the peak 3 could be used as dosimetric purposes. The kinetic parameters for all the above peaks were also calculated and are summarized in Table 2. The activation energy and frequency factors of the main peak at 501 K were obtained as 1.14 eV and $2.63x10^{+10}$ s^{-1} respectively. The kinetic order of the peak was founded as the general order.

Table 2. The kinetic parameters of the glow curve of GAG:Ce phosphors were obtained in CGCD analysis.

Peak	I_m	T_m (K)	E (eV)	b	s (s^{-1})
1	1362844	351	0.80	2	$3.51 x10^{+10}$
2	348461	452	0.85	1.87	$2.05 x10^{+8}$
3	12312130	501	1.14	1.31	$2.63x10^{+10}$
4	98729	575	1.26	2	$8.39 x10^{+9}$

4. CONCLUSION

Investigation of thermoluminescence properties of cerium-doped gadolinium aluminate phosphor subject is an original work. The literature review shows that so far no work has been done about the thermoluminescence kinetic characterization studies of cerium doped gadolinium aluminum garnet phosphor. Keeping this in view, an attempt has been made to study about the thermoluminescence properties of this material. The kinetic parameters of Ce doped gadolinium aluminum garnet phosphor were analyzed using the various heating rates, Chen's peak shape and computerized glow curve deconvulation methods. The obtained E, s and b parameters determined by all methods were found in good agreement with each other. The results show that the main dosimetric peak of GAG:Ce phosphor being at 501 K has a general order kinetic model. A whole knowledge of the thermoluminescence processes, determining the kinetic parameters is worth further investigation in order to design the most suitable dosimeter suitable for UVB.

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ULTRASONIC-PROMOTED SYNTHESIS OF FUNCTIONALIZED TETRAHYDROPYRIDINES USING TRIFLATE

Emel PELİT[1], Zuhal TURGUT[2,*]

[1]*Kirklareli University, Faculty of Art and Sciences, Department of Chemistry, Kayali Campus, Kirklareli, Turkey*
[2]*Yildiz Technical University, Faculty of Art and Sciences, Department of Chemistry, Davutpasa Campus, Istanbul, Turkey*

Abstract

An easy, and effective multicomponent synthesis of a highly substituted tetrahydropyridines has been achieved by reaction of different substituted aromatic aldehydes, β-ketoester (methyl acetoacetate), and p-methoxyaniline, in the presence of ytterbium (III) trifluoromethanesulfonate, $Yb(OTf)_3$, as an efficient catalyst under ultrasound irradiation. This method has supplied a different approach for the synthesis of highly substituted tetrahydropyridines in moderate to good yields.

Key words: Heterocycles, tetrahydropyridine, triflate, ultrasound, β-ketoester

TRİFLAT KULLANARAK İŞLEVSELLEŞTİRİLMİŞ TETRAHİDROPİRİDİNLERİN ULTRASONİK DESTEKLİ SENTEZİ

Özet

Yüksek derecede sübstitüe edilmiş tetrahidropiridinler, iterbiyum(III)triflorometansülfonat $Yb(OTf)_3$ katalizörlüğünde, farklı sübstitüe aromatik aldehitler, β-ketoester (metil asetoasetat) ve p-metoksianilinin kolay ve etkili reaksiyonuyla ultrason ışıması altında elde edilmiştir. Bu yöntem yüksek derecede sübstitüe edilmiş tetrahidropiridinlerin iyi verimlerle sentezi için farklı bir yaklaşım sağlamıştır.

Anahtar kelimeler: Heterosiklikler, tetrahidropiridin, triflat, ultrason, β-ketoester

**Corresponding author e-mail: zturgut@yildiz.edu.tr*

1. INTRODUCTION

Substituted tetrahydropyridines are significant heterocycles, which form the core part of various natural products and synthetic drugs [1-2]. Numerous compounds carrying this heterocyclic part have showed varied and attractive biological activities, such as antibacterical, antimalarial, anticonvulsant, anti-inflammatory, antihistamic properties, as well as anti-hypertensive activities [3-8].

Multicomponent reactions (MCRs) are placed one of the most significant reaction in the synthetic organic chemistry. They have been known as one of the key means to form highly efficient, atom economic and environmental friendliness. The synthesis of tetrahydropyridine compounds using MCRs is a domain of classical carbonyl condensation chemistry [4-8].

In the recent times, one-pot synthesis of substituted tetrahydropyridines have been reported in the presence of molecular I_2 [2, 9, 10], $LaCl_3$ [11], sulfamic acid [12], p-TsOH.H_2O [13], cerium ammonium nitrate (CAN) [14], oxalic acid dihydrate [15], tetrabutylammonium tribromide (TBATB) [16], $Bi(OTf)_3$ [17], $Ce(OTf)_4$ [3], $B(C_6F_5)_3$ [18], PEG-embedded KBr_3 [19] and $ZrCl_4$ [20] as efficient catalysts. However, the above deliberated processes have some drawbacks, such as the use of pricey and excessive amount of catalysts or long reaction times. Therefore, efficacious new approaches for the preparation of tetrahydropyridines are gaining great significance. Nowadays, triflates M(OTf)x have been employed as efficient catalysts for a wide variety of synthetic organic reactions [3, 17, 21]. During the last two decades, much attention has given to improving rare earth metal triflates particularly $Yb(OTf)_3$ catalyzed organic reactions. The features of these are low toxicity, moisture stability, commercial availability and recyclability [22, 23].

Ultrasonic irradiation is widely used in synthetic organic chemistry as it is associated with a series of key characteristics such as safety, energy savings, waste prevention and the use of ambient conditions. Therefore the usage of ultrasound to accelerate classical organic reactions has been significant. This procedure can be used to various organic reactions to perform better yields, under mild reaction circumstances and shorter reaction times [23]. The particular and interesting characteristics of ultrasound waves in chemical reactions arise from the physical phenomenon known as acoustic cavitation. Cavitation is the production, growth, and collapse of microbubbles in a liquid when a large negative pressure is applied to it. The formation of

cavitation bubbles is initiated during the rarefaction cycle. This phenomenon supplies the main mechanism for sonochemical effects. For the period of cavitation, bubble collapse or implosion releases enormous amounts of energy and produces strong local heating, high pressures, and very short lifetimes. Ultrasonic irradiation decreases reaction times, gets better yields and reduces side product construction by giving the activation energy contrast to classical conventional heating that gives thermal energy to the reaction [24].

Herein we report on the preparation of functionalized tetrahydropyridines under conventional conditions and ultrasonic conditions in the presence of $Yb(OTf)_3$ as a catalyst.

2. EXPERIMENTAL

^1H NMR and ^{13}C NMR spectrums were recorded on "Inova 500" and "Bruker 400" spectrometers, in the presence of TMS as an internal standard in $CDCl_3$ or DMSO solvents. FT-IR spectra were recorded on a "Philips PU 9714 ATR spectrophotometer", and using the "Perkin-Elmer Spectrum One" program. Mass Spectrums were obtained using a "Finnigan Trace DSQ" instrument. GC/MS spectra were recorded on an Agilent 6890N GC system-5973 IMSO instrument. TLC was carried out on silica gel 60 F254 precoated plates. The ultrasonication was performed in an "Intersonik ultrasound cleaner" (model: MIN4) with a frequency of 25 kHz, an US output power of 100 W and, a heating of 200 W. The temperature of the water bath was controlled by an automatic constant temperature cooling circulatory system. All of the chemical reagents were commercially available and were used without any purification.

2.1 General experimental procedures for the preparation of functionalized piperidines

Method A:

A mixture of p-anisidine (aromatic primer amine) **1** (2 mmol), methyl acetoacetate (β-ketoester) **2** (1 mmol), and 5 % mol $Yb(OTf)_3$ in 5 mL MeOH was stirred for 30 min at room temperature. Afterward the aldehyde **3** (2 mmol) was added to the reaction mixture and stirred for the time indicated in Table 2. The progress of the reaction was checked by thin-layer chromatography (TLC) at regular intervals. After the completion of the reaction, the raw product was filtered off and washed with water and then crystallized from EtOH to give pure product **4a-4j**.

Method B:

A mixture of p-anisidine (aromatic primer amine) **1** (2 mmol), methyl acetoacetate (β-ketoester) **2** (1 mmol), and 5 % mol $Yb(OTf)_3$ in 5 mL MeOH was sonicated at 60 ºC in an ultrasound cleaner for 30 min. Afterward the aldehyde **3** (2 mmol) was added and the reaction mixture was sonicated for the time indicated in Table 2. The progress of the reaction was checked by thin-layer chromatography (TLC) at regular intervals. After the completion of the reaction, the mixture was cooled to room temperature, the raw product was filtered off and washed with water and then crystallized from EtOH to give pure product **4a-4j**.

2.1.1. Methyl 2,6-bis(phenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino)-1,2,5,6-tetrahydropyridine-carboxylate (4a)

White solid, mp. 223-225 º C. FTIR (ATR): υ= 3258, 3058, 2949, 1648, 1589, 1509, 1176, 808 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ: 2.51-2.65 (dd, J_1= 12.50 Hz, J_2= 2.55 Hz, 1H), 2.72-2.86 (dd, J_1= 15.15 Hz, J_2= 2.50 Hz, 1H), 3.67 (s, 3H), 3.72 (s, 3H), 3.90 (s, 3H), 5.05 (br s, 1H), 6.14-6.19 (d, J= 8.50 Hz, 2H), 6.32 (s,1H), 6.41-6.46 (d, J= 8.50 Hz, 3H), 6.59-6.67 (dd, J_1= 8.80, J_2= 9.01 Hz, 4H), 7.13-7.32 (m, 9H), 10.02 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 33.74, 50.56, 54.72, 55.66, 55.66, 55.75, 55.94, 56.08, 58.21, 96.92, 113.53, 114.12, 114.33, 114.82, 126.03, 126.46, 126.72, 127.68, 127.99, 128.19, 128.19, 128.60, 128.81, 130.60, 141.53, 143.24, 144.23, 150.82, 157.09, 157.79, 168.67 ppm. MS m/z: 520, Anal. Calcd. for $C_{33}H_{32}N_2O_4$: C, 76.13; H, 6.20; N, 5.38. Found: C, 75.93; H, 5.98; N, 5.12.

2.1.2. Methyl 2,6-bis(4-methylphenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino)-1,2,5,6-tetrahydropyridine- carboxylate (4b)

White solid, mp. 225-226 º C. FTIR (ATR): υ= 3245, 2948, 2914, 1655, 1595, 1509, 1176, 808 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ: 2.20 (s, 3H), 2.35 (s, 3H), 2.59-2.68 (dd, J_1= 12.60 Hz, J_2= 2.50 Hz, 1H), 2.73-2.82 (dd, J_1= 15.20 Hz, J_2= 5.70 Hz, 1H), 3.65 (s, 3H), 3.75 (s, 3H), 3.90 (s, 3H), 5.01 (br s, 1H), 6.14-6.24 (d, J= 8.70 Hz, 2H), 6.35 (s,1H), 6.40-6.46 (d, J= 9.10 Hz, 1H), 6.59-6.67 (dd, J_1= 8.80, J_2= 9.01 Hz, 4H), 6.85-7.35(m, 7H), 7.75 (d, J= 8.00 Hz, 2H), 10.02 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.33, 21.55, 33.62, 50.52, 51.29, 55.13, 55.67, 55.76, 56.09, 57.94, 97.04, 113.51, 114.11, 114.82, 121.99, 122.37, 126.21, 126.66, 127.60,

128.19,128.03, 129.03, 129.48, 129.68, 130.74, 133.86, 135.69, 136.54, 140.16, 141.52, 145.11, 150.73, 157.79, 158.57, 168.67 ppm. MS m/z: 548, Anal. Calcd. for $C_{35}H_{36}N_2O_4$: C, 76.62; H, 6.61; N, 5.11. Found: C, 76.53; H, 6.70; N, 5.13.

2.1.3. Methyl 2,6-bis(4-bromophenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino)-1,2,5,6-tetrahydropyridine- carboxylate (4c)

White solid, mp. 177-179 º C. FTIR (ATR): υ= 3173, 3086, 2961, 1661, 1597, 1253, 838cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.51-2.55 (dd, J_1= 15.00 Hz, J_2= 2.00 Hz, 1H), 2.62-2.66 (dd, J_1= 15.00 Hz, J_2= 5.00 Hz, 1H), 3.68 (s, 3H), 3.75 (s, 3H), 3.80 (s, 3H), 4.88 (br s, 1H), 6.14-6.19 (d, J = 8.75, 1H), 6.58-6.68 (dd, J_1= 8.50 Hz, J_2= 2.00 Hz, 2H), 6.84-6.86 (d, J= 9.00 Hz, 2H), 6.92-7.52 (m, 10 H), 7.67-7.68 (d, J= 8.50 Hz, 2H), 10.02 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.60, 51.07, 55.45, 55.53, 55.64, 57.39, 96.42, 114.13, 114.40, 114.44, 114.58, 120.17, 120.86, 122.27, 127.80, 128.32, 128.63, 129.94, 130.38, 131.24, 131.69, 132.00, 135.37, 140.92, 141.94, 143.15, 144.43, 151.39, 156.71, 156.82, 158.00, 158.52, 168.38 ppm. MS m/z: 678, Anal. Calcd. for $C_{33}H_{30}Br_2N_2O_4$: C, 58.42; H, 4.46; N, 4.13. Found: C, 58.64; H, 4.61; N, 4.02.

2.1.4. Methyl 2,6-bis(4-*iso*propylphenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino)-1,2,5,6-tetrahydropyridine- carboxylate (4d)

White solid, mp. 230-232 º C. FTIR (ATR): υ= 3249, 3050, 2957, 1651, 1593, 1512, 1176, 805 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.07-1.14 (d, J= 16.50 Hz, 12 H), 2.49 (d, J= 16.50 Hz, 1H), 2.67 -2.71 (dd, J_1= 12.60 Hz, J_2= 2.50 Hz, 1H), 2.77-2.86 (m, 2H), 3.65 (s, 3H), 3.75 (s, 3H), 3.85 (s, 3H), 4.95 (br s, 1H), 5.96 (d, J= 8.56 Hz, 2H), 6.25 (s, 1H), 6.38-6.41 (d, J= 9.10 Hz, 2H), 6.45-6.59 (dd, J_1= 8.80, J_2= 9.01 Hz, 2H), 6.85-7.35, (m, 10H), 10.01 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 24.02, 24.07, 24.13, 24.30, 33.61, 33.84, 50.88, 55.36, 55.64, 58.32, 97.20, 113.67, 113.81, 114.49, 120.11, 123.44, 124.36, 126.21, 126.33, 126.65, 126.68, 127.57, 128.06, 130.73, 132.84, 135.20, 140.89, 141.47, 141.72, 146.55, 147.78, 150.62, 155.94, 157.28, 158.45, 168.70 ppm. MS m/z: 604, Anal. Calcd. for $C_{39}H_{44}N_2O_4$: C, 77.45; H, 7.33; N, 4.63. Found: C, 77.83; H, 7.20; N, 4.51.

2.1.5. Methyl 2,6-bis(4-methoxyphenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino)-1,2,5,6-tetrahydropyridine- carboxylate (4e)

White solid, mp. 217-219 º C. FTIR (ATR): υ= 3233, 3033, 2952, 1658, 1580, 1505, 1171, 832 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.60-2.65 (dd, J_1= 19.00 Hz, J_2= 3.50 Hz, 1H), 2.73-2.79 (dd, J_1= 19.00 Hz, J_2= 5.50 Hz, 1H), 3.66 (s, 3H), 3.74 (s, 3H), 3.79 (s, 3H), 3.82 (s, 3H), 3.89 (s, 3H), 4.97-4.98 (d, J= 2.00 Hz, 1H), 6.23 (s, 1H), 6.29-6.31 (d, J= 11.00 Hz, 2H), 6.44-6.46 (d, J= 1.50 Hz, 2H), 6.63-6.67 (m, 3H), 6.79-6.83 (m, 3H), 6.91-6.94 (dd, J_1= 8.00 H, J_2= 2.50 Hz, 1H), 6.96-6.99 (dd, J_1= 8.00 H, J_2= 2.50 Hz, 1H), 7.05-7.08 (d, J= 10.50 Hz, 1H), 7.19-7.22 (m, 2H), 7.82-7.85 (dd, J_1= 8.00 H, J_2= 2.50 Hz, 1H), 10.13 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.67, 50.85, 55.19, 55.29, 55.38, 55.47, 55.62, 57.42, 97.04, 113.43, 113.94, 114.14, 114.35, 122.05, 127.57, 127.82, 129.48, 130.23, 130.75, 135.10, 136.17, 141.60, 145.25, 150.89, 157.08, 157.75, 157.87, 157.98, 158.62, 161.98, 168.66 ppm. Ms m/z: 580, Anal.Cal. for $C_{35}H_{36}N_2O_6$: C, 72.39; H, 6.25; N, 4.82, Found: C, 72.01; H, 6.03; N, 4.71.

2.1.6. Methyl 2,6-bis(3,4-dimethoxyphenyl)-1-(3,4-dimethoxyphenyl)-4-(3,4-dimethoxyphenylamino) -1,2,5,6-tetrahydropyridine- carboxylate (4f)

White solid, mp. 221-223 º C. FTIR (ATR): υ= 3242, 3053, 2988, 1652, 1589, 1510, 1189, 795 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.62-2.66 (dd, J_1= 19.00 Hz, J_2= 4.00 Hz, 1H), 2.79-2.84 (dd, J_1= 19.00 Hz, J_2= 7.00 Hz, 1H), 3.65 (s, 3H), 3.73 (s, 6H), 3.77 (s, 3H), 3.83 (s, 3H), 3.85 (s, 3H), 3.86 (s, 3H), 4.91-4.93 (d, J= 4.00 Hz, 1H), 6.18 (s, 1H), 6.32-6.35 (d, J= 11.00 Hz, 2H), 6.44-6.47 (d, J= 11.50 Hz, 2H), 6.63-6.70 (m, 6H), 6.73-6.77 (m, 3H), 6.87 (s, 1H), 10.12 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.82, 50.78, 55.39, 55.58, 55.69, 55.80, 55.91, 55.97, 57.59, 95.55, 109.46, 110.47, 111.10, 113.92, 114.31, 114.72, 118.69, 127.95, 130.70, 135.49, 136.53, 141.56, 147.42, 147.88, 148.65, 149.01, 151.10, 157.31, 157.84, 168.57 ppm. MS m/z: 640. Anal.Calcd. for $C_{37}H_{40}N_2O_8$: C, 69.36; H, 6.29; N, 4.37. Found: C, 68.98, H, 6.46, N, 4.24.

2.1.7. Methyl 2,6-bis(3-nitrophenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino)-1,2,5,6-tetrahydropyridine- carboxylate (4g)

White solid, mp. 250-251 º C. FTIR (ATR) υ: 3216, 3007, 2916, 1645, 1610, 1584, 1508, 1343,

1185, 810 cm^{-1}. ^{1}H NMR ($CDCI_3$, 500 MHz) δ: 2.74 (dd, J_1= 15.00 Hz, J_2= 2.86 Hz, 1H), 2.82 (dd, J_1=15.53 Hz, J_2= 2.81 Hz, 1H), 3.69 (s, 3H), 3.74 (s, 3H), 3.83 (s, 3H), 5.19 (br s, 1H), 6.31 (s, 1H), 6.38-6.41 (m, 3H), 6.65-6.68 (d, J= 2.50 Hz, 1H), 7.24-8.17 (m, 12H), 10.16 (s, 1H) ppm. ^{13}C NMR ($CDCI_3$, 125MHz) δ: 33.78, 51.28, 55.46, 55.58, 56.26, 56.97, 95.68, 114.27, 114.80, 115.20, 121.64, 121.73, 125.04, 126.36, 127.67, 129.20, 129.63, 130.75, 132.87, 134.93, 140.12, 141.29, 144.86, 146.49, 148.53, 148.54, 152.17, 156.24, 157.61, 158.32, 168.16 ppm. MS m/z: 610. Anal.Calcd. for $C_{33}H_{30}N_4O_8$: C, 64.91; H, 4.95; N, 9.18. Found: C, 65.13; H, 5.01; N, 4.86.

2.1.8. Methyl 2,6-bis(4-benzyloxyphenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino) -1,2,5,6-tetrahydropyridine- carboxylate (4h)

White solid, mp. 166-168 º C. FTIR (ATR) υ: 3242, 3034, 2913, 1650, 1574, 1247, 840 cm^{-1}. ^{1}H NMR ($CDCI_3$, 500 MHz) δ: 2.51 (dd, J_1= 15.00 Hz, J_2= 2.86 Hz, 1H), 2.69 (dd, J_1= 15.53 Hz, J_2= 2.81 Hz, 1H), 3.56 (s, 3H), 3.65 (s, 3H), 3.80 (s, 3H), 4.98 (d, J= 5.00 Hz, 1H), 5.03 (s, 1H), 6.15-6.22 (m, 4H), 6.38-6.60 (m, 2H), 6.63-6.88 (m, 6H), 6.95 (d, J= 9.20 Hz, 2H), 7.12-7.39 (m, 14H), 7.78 (d, J= 5.02 Hz, 2H), 10.11 (s, 1H) ppm. ^{13}C NMR ($CDCI_3$, 125 MHz) δ: 33.78, 50.91, 55.26, 55.52, 55.67, 57.48, 70.00, 70.04, 70.11, 97.00, 114.00, 114.24, 114.38, 114.49, 114.94, 115.08, 118.31, 122.12, 123.57, 126.26, 127.47, 127.58, 128.17, 128.65, 128.69, 129.74, 130.29, 132.46, 136.53, 138.04, 140.31, 140.87, 141.28, 144.83, 145.27, 152.41, 157.33, 157.86, 158.01, 161.17, 168.70 ppm. MS m/z: 732. Anal. Calcd. for $C_{47}H_{44}N_2O_6$, C, 77.03; H, 6.05; N, 3.82. Found: C, 77.42; H, 6.14; N, 3.90.

2.1.9. Methyl 2,6-bis(2-thiophenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino) -1,2,5,6-tetrahydropyridine- carboxylate (4i)

White solid, mp. 190-192 º C. FTIR (ATR) υ: 3258, 3002, 2948, 1655, 1594, 1511, 1189, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.75-2.80 (dd, J_1= 13.00 Hz, J_2= 4.50 Hz, 1H), 2.95-3.00 (dd, J_1= 13.00 Hz, J_2= 6.50 H, 1H), 3.69 (s, 3H), 3.77 (s, 3H), 3.86 (s, 3H), 5.25-5.27 (d, J= 5.50 Hz, 1H), 6.26 (s, 1H), 6.55-6.56 (d, J= 2.50 Hz, 1H), 6.56-6.57 (d, J= 2.50 Hz, 1H), 6.70-6.71 (d, J= 1.00 Hz, 3H), 6.72-6.73 (d, J= 3.00 Hz, 1H), 6.74-6.75 (d, J= 3.00 Hz, 1H), 6.77-6.79 (dt, J_1= 4.00 Hz, J_2= 1.00 Hz, 1H), 6.80-6.82 (dt, J_1= 4.50 Hz, J_2=1.50 Hz, 1H), 6.86-6.89 (m, 2H), 7.11-

7.13 (m, 3H), 10.29 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 34.19, 37.08, 51.07, 53.66, 55.41, 56.98, 60.81, 96.12, 114.04, 114.16, 115.78, 118.98, 123.37, 124.41, 126.15, 126.32, 126.49, 127.71, 130.79, 131.11, 140.56, 144.57, 147.53, 148.75, 149.59, 151.99, 156.78, 157.84, 168.24 ppm. MS m/z: 532. Anal. Calcd. for $C_{29}H_{28}N_2O_4S_2$, C, 65.39; H, 5.30; N, 5.26. Found: C, 65.58; H, 5.21; N, 5.08.

2.1.10. Methyl 2,6-bis(5-methyl-2-thiophenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino) -1,2,5,6-tetrahydropyridine- carboxylate (4j)

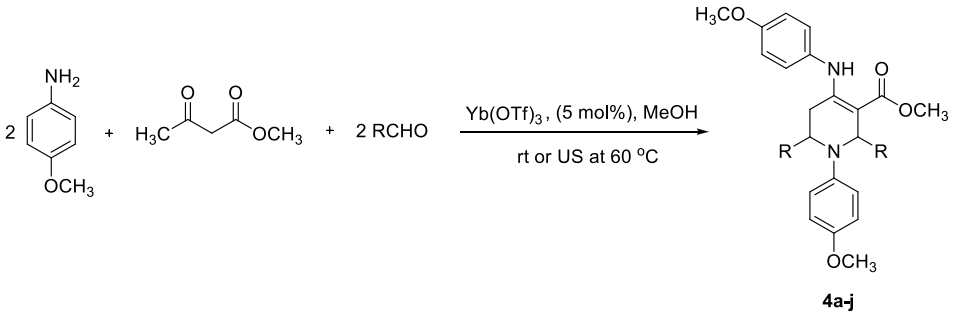
White solid, mp. 196-198 º C. FTIR (ATR) υ: 3244, 3059, 2951, 1659, 1610, 1581, 1508, 1376, 1242, 1179, 807 cm^{-1}. ^{1}H NMR ($CDCI_3$, 500 MHz) δ: 2.38 (s, 3H), 2.41 (s, 3H), 2.75 (dd, J_1= 14.98 Hz, J_2=2,01 Hz, 1H), 2.96 (dd, J_1= 15.03 Hz, J_2= 2.20 Hz, 1H), 3.70 (s, 3H), 3.76 (s, 3H), 3.85 (s, 3H), 5.14 (br s, 1H), 6.12 (br s, 1H), 6.47-7.22 (m, 12H), 10.28 (s, 1H) ppm. ^{13}C NMR ($CDCI_3$, 125 MHz) δ: 15.41, 15.46, 33.90, 50.81, 53.57, 55.44, 55.54, 96.10, 114.13, 114.26, 114.32, 114.46, 115.54, 122.21, 123.84, 124.02, 124.31, 124.46, 126.15, 127.73, 130.96, 132.13, 137.79, 138.49, 140.75, 144.99, 146.91, 151.78, 156.87, 157.77, 168.33 ppm. MS m/z: 560, Anal. Calcd. $C_{31}H_{32}N_2O_4S_2$, C, 67.86; H, 5.88; N, 6.81. Found: C, 67.69; H, 5.97; N, 6.70.

3. RESULTS AND DISCUSSION

In this study, we investigated the three component one-pot reaction of aromatic aldehydes and aromatic amine (p-anisidine) with methyl acetoacetate (2:2:1 ratio) using $Yb(OTf)_3$ as catalyst under stirring at room temperature and ultrasonic irradiation methods (Scheme 1).

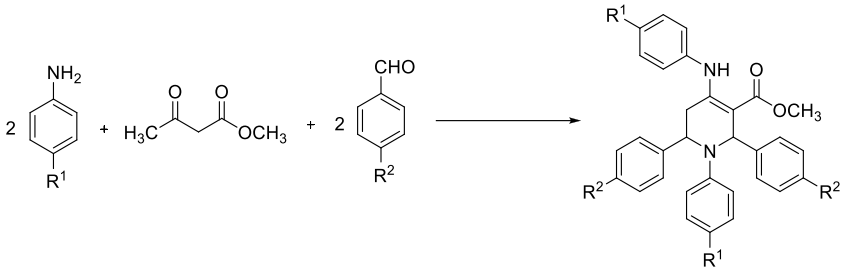
For the initial the identification of the suitable solvent and the appropriate concentration of catalyst, $Yb(OTf)_3$, were examined with the reaction of methyl acetoacetate (1 mmol), benzaldehyde (2 mmol), p-anisidine (2 mmol) to obtained the **4a**.

We have observed that 5 mol % of the catalyst gives the satisfactory results for the reactions. Selections of solvents also play an important role in one-pot reactions. For this reason, we also examined the effect of solvents in the reaction. A variety of solvents, such as EtOH, MeOH, AcOH and ILs (IL 1: 8-ethyl-1,8-diazobicyclo[5.4.0]-7-undecenium trifluoromethane sulfonate, and IL 2: 1-Ethyl-2,3-dimethylimidazoliumtetrafluoroborate) have been investigated. Among the selected solvents MeOH was the best of them in the synthesis of tetrahydropyridines showed in Table 1.



Scheme 1. Multicomponent synthesis of substituted piperidines.

Table 1. Effect of different catalysts, solvents, and conditions on construction of **4a**



Entry	R^1	R^2	Product	Catalyst/ Conditions	Yield (%)
1	$-OCH_3$	-H	**4a**	$Yb(OTf)_3$ (5%)/MeOH, rt, stirring, 20h	83
2	$-OCH_3$	-H	**4a**	$Yb(OTf)_3$ (5%)/ AcOH, rt, stirring, 20h	74
3	$-OCH_3$	-H	**4a**	$Yb(OTf)_3$ (5%)/MeOH, US, 3h	70
4	$-OCH_3$	-H	**4a**	$Yb(OTf)_3$ (5%)/EtOH, US, 60^0C, 3h	76
5	$-OCH_3$	-H	**4a**	$Yb(OTf)_3$ (5%)/MeOH, US, 60^0C, 3h	80
6	$-OCH_3$	-H	**4a**	$Yb(OTf)_3$ (5%)/ CH_3CN, US, 60^0C, 3h	72
7	$-OCH_3$	-H	**4a**	$Yb(OTf)_3$ (5%)/IL 1 , US, 60^0C, 3h	30
8	$-OCH_3$	-H	**4a**	$Yb(OTf)_3$ (5%)/IL 2, US, 60^0C, 3h	63

IL 1: 8-ethyl-1,8-diazobicyclo[5.4.0]-7-undecenium trifluoromethane sulfonate (DBU)
IL 2: 1-Ethyl-2,3-dimethylimidazoliumtetrafluoroborate (EDIMIM BF_4)

All stirring at the room temperature reactions were performed in the presence of 5 mol amount of the catalyst for 20 h (method A). We decided to perform this reaction under ultrasonic irradiation to get a shorter reaction time, and higher yield (method B). First the model reaction was examined under US with different solvents and temperature. The reaction was completed in 3 h with a yield of 70 %. When the temperature was increased from room temperature to 60^0C, the yield of the products was better, as indicated in Table 2.

A number of aromatic aldehydes were checked to study the majority and range of this synthetic procedure. Quite a lot of aromatic aldehydes with different substituents for instance Me, Br, NO_2, $OCH_2C_6H_5$ and $CH(CH_3)_2$ were reacted with p-anisidine and methyl acetoacetate in the same reaction conditions. The functionalized piperidines were formed in moderate yields at all these reactions.

Table 2. Synthesis of 2,6-bis(substitutedphenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino) -1,2,5,6-tetrahydropyridine- carboxylate

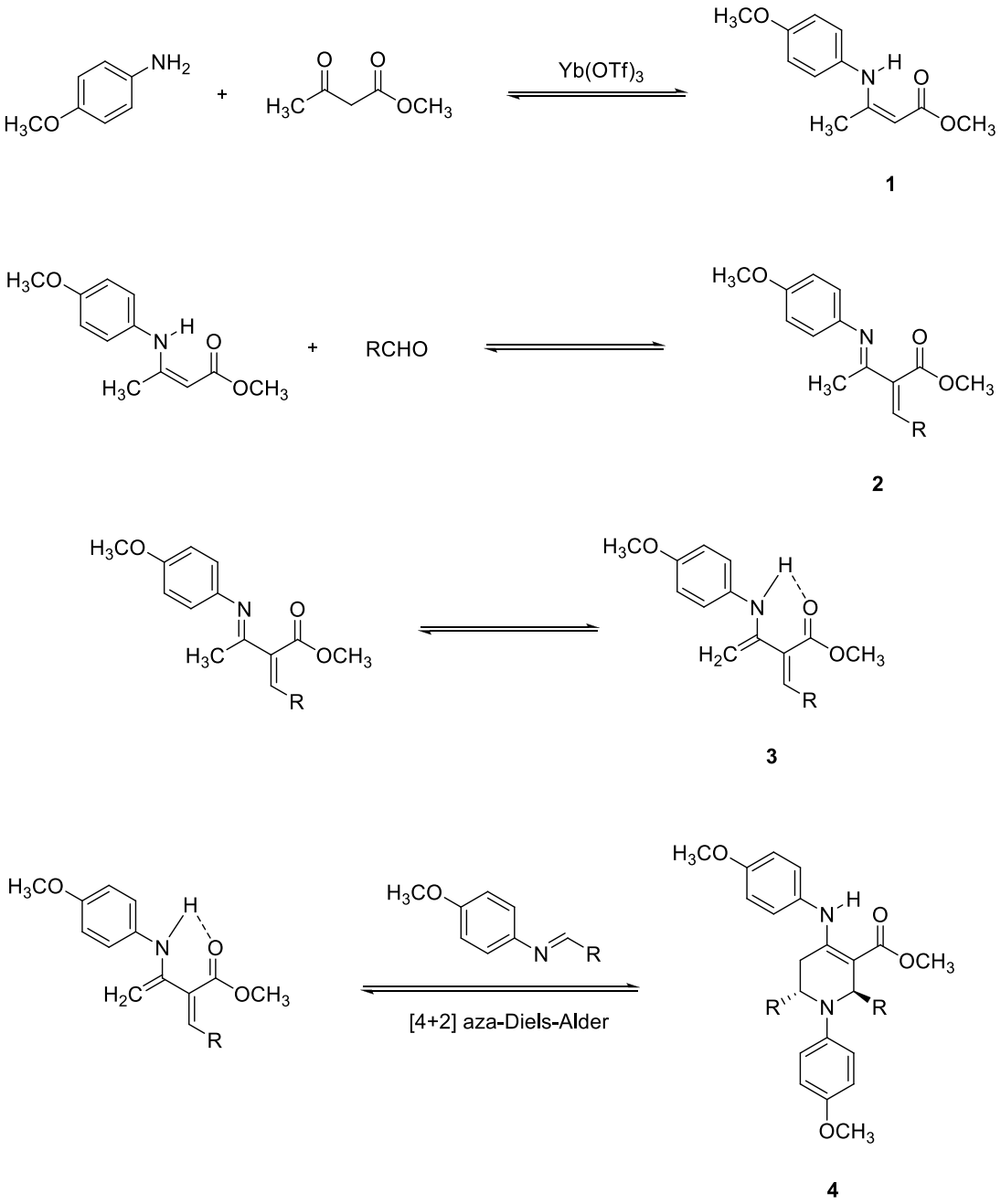
Entry	R	Product	Method A Yield (%)/Time (h)	Method B Yield (%)/Time (h)
1	C_6H_5	**4a**	83/20	80/3
2	4-Me-C_6H_5	**4b**	78/20	76/3
3	4-Br- C_6H_5	**4c**	83/20	82/3
4	4-$CH(CH_3)_2$-C_6H_5	**4d**	90/20	86/3
5	4-OMe-C_6H_5	**4e**	81/20	78/3
6	3,4-diOMe-C_6H_4	**4f**	76/20	72/3
7	3-NO_2- C_6H_5	**4g**	87/20	83/3
8	4-benzyloxy-C_6H_5	**4h**	88/20	85/3
9	2-thiophenyl	**4i**	90/20	87/3
10	5-Me-thiophen-2-yl	**4j**	86/20	83/3

Method A: $Yb(OTf)_3$ (5%), 5 mL MeOH, rt, stirring.

Method B: $Yb(OTf)_3$ (5%), 5 mL MeOH, 60 ^{o}C, US.

Furthermore, the structure of all products was approved by spectrophotometric methods (FTIR, ^{1}H NMR, ^{13}C NMR, EA and MS). **4a**, **4b**, **4c**, **4e** and **4i** have been synthesized before with the other methods [5, 7, 14, 19, 27].

A possible mechanism for the generation of these functionalized piperidines is outlined in Scheme 2. A similar mechanism was postulated in some literatures [25, 26, and 3] before. In the first step, $Yb(OTf)_3$ be able to act as a Lewis acid catalyst for the reaction of the p-anisidine (4-methoxyaniline) and methyl acetoacetate (1,3-dione) to give the β-enamine **1**. After the addition of aromatic or hetaryl-aldehyde, this enamine **1**, gives the Knoevenagel-type product **2**. The intermediate **2** undergoes catalyzed imine-enamine tautomerization to form **3**, which becomes stable by intramolecular hydrogen bonding. $Yb(OTf)_3$ facilitates the constitution of imine besides that enamine **1** in the multicomponent reaction. This imine form and the intermediate **3** undergo a [4+2] Aza-Diels-Alder reaction to give the polysubstituted piperidine derivatives [10, 17] (Scheme 2).



Scheme 2. A plausible mechanism for the synthesis of piperidines

4. CONCLUSIONS

We have demostrated a remarkable and practical one-pot procedure for synthesis of Methyl 2,6-bis (substitutedaryl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino) -1,2,5,6-tetrahydropyridine- carboxylate compounds via various aldehydes, p-anisidine and metyl acetoacetate. This reaction has been carried out under ultrasound irradiation is the first report of synthesis of tetrahydropyridine compounds catalyzed by $Yb(OTf)_3$ under ultrasonic irradiation. This method has approached several advantages such as short reaction times and good yields.

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MECHANICAL PROPERTIES OF FLY ASH AND BLAST FURNACE SLAG BASED ALKALI ACTIVATED CONCRETE

Saadet Gökçe GÖK*[1], Kadir KILINÇ[1]

[1] *Kırklareli University, Faculty of Engineering, Department of Civil Engineering, Kayalı Campus, Kırklareli, Turkey*

ABSTRACT

Cement is one of the commonly used materials in construction projects. In manufacture of Portland cement, clinker, which is the essential component of cement, is ground into smaller particles. During the formation of clinker, limestone ($CaCO_3$) is converted to lime (CaO) and carbon dioxide is emitted as a by-product of this chemical reaction. Cement production is an environmentally hazardous process due to high carbon dioxide emission during clinker production and fossil-fuel consumption for providing energy in production. Alternative construction materials which are more energy efficient and environmentally friendly can be preferred for sustainability. In order to use alternative materials and production methods, mechanical and physical properties of these materials should be examined thoroughly. In concrete production, strength, durability and workability should be in proper limits as well as considering economical factors. In this study, geopolymeric materials were used as an alternative to conventional concrete, and alkali activated concrete was produced. In this process, no cement was used. Pozzolanic materials such as fly ash and blast furnace slag were activated with alkaline liquids and gained binding property. In production of geopolymer concrete, pozzolanic materials, aggregates and alkaline activators were used. Mechanical properties of fly ash and blast furnace slag based geopolymer concrete were investigated. Compressive strengths of the cubic concrete specimens at the ages of 7 and 28 days were determined and the effect of ambient conditions on geopolymer concrete was examined. As a consequence, it was found that the increase in the amount of blast furnace slag resulted in higher compressive strength values.

Keywords: Alkali activated concrete, cement-free concrete, geopolymer, sustainability, waste management.

**saadet.gokce.gok@klu.edu.tr*

ALKALİ İLE AKTİVE EDİLMİŞ UÇUCU KÜL VE YÜKSEK FIRIN CÜRUFU ESASLI BETONLARIN MEKANİK ÖZELLİKLERİ

ÖZET

Çimento, inşaat projelerinde en çok kullanılan yapı malzemelerinden biridir. Portland çimentosunun üretiminde, çimentonun temel bileşenlerinden biri olan klinker öğütülerek daha ince parçacıklar haline getirilir. Klinker oluşumu esnasında kireçtaşı ($CaCO_3$), kirece (CaO) dönüştürülür ve bu kimyasal reaksiyonun yan ürünü olarak karbondioksit açığa çıkar. Klinker üretimi sırasında açığa çıkan karbondioksitin yanı sıra üretim aşamasında kullanılan fosil yakıtların tüketimiyle de yüksek miktarda karbondioksit salımı gerçekleştiğinden, çimento üretimi çevreye zarar veren bir süreçtir. Sürdürülebilirlik açısından bakıldığında, enerji verimliliği daha fazla ve çevreye dost alternatif yapı malzemelerinin tercih edilmesi daha uygun olacaktır. Alternatif malzemelerin ve üretim yöntemlerinin kullanılabilmesi için, bu malzemelerin mekanik ve fiziksel özellikleri kapsamlı olarak incelenmelidir. Beton üretiminde dayanım, dayanıklılık ve işlenebilirlik özelliklerinin uygun sınırlarda olması gerekirken ekonomik faktörler de göz önünde bulundurulmalıdır. Bu çalışmada, geleneksel beton üretimine alternatif olarak geopolimer malzemeler kullanılmış ve alkali ile aktive edilmiş beton üretimi gerçekleştirilmiştir. Bu üretim sırasında çimento kullanılmamıştır. Uçucu kül ve yüksek fırın cürufu gibi puzolanik malzemeler, alkaliler ile aktive edilerek bu malzemelere bağlayıcı özellik kazandırılmıştır. Geopolimer beton üretimi sırasında, puzolanik malzemeler, agregalar ve alkali aktifleştiriciler kullanılmıştır. Üretilen uçucu kül ve yüksek fırın cürufu esaslı geopolimer betonların mekanik özellikleri incelenmiştir. Küp şeklinde dökülmüş beton numunelerin 7 ve 28 günlük basınç dayanımları belirlenmiş ve ortam koşullarının geopolimer beton üzerindeki etkisi gözlenmiştir. Çalışma sonucunda, yüksek fırın cürufu miktarındaki artışın beton basınç dayanımını arttırdığı görülmüştür.

Anahtar kelimeler: Alkali ile aktive edilmiş beton, çimentosuz beton, geopolimer, sürdürülebilirlik, atık yönetimi.

1. INTRODUCTION

The annual consumption of Portland cement in the world reaches 4-5 billion tonnes per year and there is an increasing demand of 5% per year. Taking into consideration that the other components of concrete production such as aggregates and water, it can be observed that the annual consumption of concrete reaches more than thirty billion tonnes. Besides, one tonne of carbon dioxide is released per one tonne of cement production, and other greenhouse gases are emitted during production. The other factors damaging environment are the depletion of stone quarries and water in conventional concrete production. All these factors make the sustainability of conventional concrete as a construction material questionable [1].

By taking concrete produced with Portland cement into account as a waste management issue, it can be seen that by-products such as fly ash and blast furnace slag are used in concrete as 40-60% by weight of cement for economic and recycling purposes. On the other hand, only 35% of fly ash released by thermal plants can be reused in this way [2]. The developing technologies should make cement production cleaner and more energy-efficient.

It is possible to produce energy-efficient, low cost building materials with geopolymers, which is the main element of this study. Geopolymers are produced with processing natural geological minerals' chemical composition. Geopolymers are used in a wide variety of applications for different purposes such as refractory building materials having high thermal resistivity, high-strength concrete, bricks, mortar based strengthening materials, electrical fuse and radioactive waste storage units [1].

Geopolymers are obtained by activating binders such as fly ash, slag, kaoline, metakaolin, etc. For activation process, alkaline solutions like sodium silicate, sodium hydroxide and potassium hydroxide are used. Alkali activated pozzolanic material can also be called as geopolymer paste. Silicate and aluminate which are contained in fly ash based geopolymers, are activated by alkaline. The main material used for geopolymerisation can be one, or a combination of different materials [3]. The commonly used alkaline are sodium silicate-sodium hydroxide and sodium silicate-potassium hydroxide [4-7].

The chemical composition of geopolymers is similar to the zeolites, but geopolymers have amorphous microstructure [5]. The molecule groups of geopolymers are as follows [1, 7 and 8]:

- Si-O-Si-O-siloxo, poly(siloxo)
- Si-O-Al-O- sialate, poly(sialate)
- Si-O-Al-O-Si-O- sialate-siloxo, poly(sialate-siloxo)
- Si-O-Al-O-Si-O-Si-O- sialate-disiloxo, poly(sialate-disiloxo)
- P-O-P-O- phosphate, poly(phosphate)
- P-O-Si-O-Al-O-P-O- phospho-sialate, poly(phospho-sialate)
- (R)-Si-O-Si-O-(R) organo-siloxo, poly-silicone

Fly ash is a by-product which is released from thermal plants, having hollow circular particles. Fly ash particles contain amorphous silicate structured crystals such as mullite, hematite and quartz. Fly ash transforms into fine crystals having large amounts of silicate, aluminate and iron oxide with the effect of high temperature in thermal plants, and an efficient raw material for geopolymerisation process is obtained [9].

Fly ash balances the hydration energy and increases the amount of silicate hydrate (binder) with the silicate contained in fly ash, when it is used as pozzolans in conventional concrete. It also prevents alkali-aggregate reaction and provides toughness.

The advantage of fly ash in geopolymer production is the composition of large amounts of Al_2O_3 and SiO_2. Especially F-type fly ash contains large amounts of these components. Fly ash having fine, hollow and circular particles and having large amounts of silicate is convenient for geopolymerisation. These particles can be obtained when the temperature is higher than 1200ºC in a thermal plant.

The first product which is produced with fly ash and alkali silicate, is CAFA cement and it is patented in US [10]. Concrete specimens cured at 90ºC temperature for 18 hours had compressive strength values reaching 85 MPa. Zeolite matrixed geopolymers can also be synthesised with solutions containing only alkaline salts, instead of soluble silicates but this casting process is harmful for producer because of the high alkaline media [1].

The main properties of fly ash composition to produce high-strength and durable geopolymeric materials are stated as follows [11]:

- SiO_2/Al_2O_3 compounds should exist in fly ash composition in the range between 2-3.5% by weight.
- CaO amount should be limited just like pozzolans.
- There should not be sulphite compounds and metals in composition.
- Fe_2O_3 compound, and crystals of hematite and magnetite decelerate the geopolymerisation process and decrease the compressive strength.
- The amount of unburnt carbon particles in coal should be in minimum because of their negative effects on material properties.

2. MATERIALS & METHODS

In this experimental study, fly ash, blast furnace slag, fine aggregate (sand), coarse aggregate with maximum aggregate size of 20 mm (crushed stone II), coarse aggregate with maximum aggregate size of 12 mm (crushed stone I) and alkaline activators were used. 12 Molar potassium hydroxide solution was prepared and this solution was used after 24 hours. Then, potassium hydroxide solution and liquid sodium silicate were mixed and this new solution was used as alkaline activator. Blast furnace slag was used as a weight of 4, 10 and 20 percents of total binder. Pozzolanic binders were activated with alkaline activator for geopolymer concrete production and 15 cm × 15 cm × 15 cm cubic concrete specimens were produced. Concrete specimens were left in outdoor and in laboratory conditions without any curing, before compressive strength test was applied. Compressive strengths of specimens were determined at the ages of 7 and 28 days. The geopolymer concrete mix design was shown in Table 1.

Table 1. The geopolymer concrete mix design.

	Component amount (kg/m^3)								
	Fly ash	Blast furnace slag	Fine aggregate (Natural sand)	Coarse aggregate (20 mm) Crushed limestone II	Coarse aggregate (12 mm) Crushed limestone I	Sodium silicate solution	12 Molar potassium hydroxide solution	Alkaline activator-fly ash ratio	Sodium silicate solution-potassium hydroxide solution ratio
4% BFS	643	27	600	320	650	121	121	0.37	1
10% BFS	603	67	600	320	650	121	121	0.40	1
20% BFS	536	134	600	320	650	121	121	0.45	1

BFS: Blast furnace slag

3. RESULTS & DISCUSSION

Compressive strength test results of geopolymer concrete at the ages of 7 and 28 days were indicated in Table 2 and Table 3. For each sample group, six cubic specimens at the sizes of 15 cm × 15 cm × 15 cm were prepared and tested under compressive loads. As it can be seen from tables below, outdoor conditions provided an increment on early age compressive strength of alkali activated concrete while laboratory conditions provided higher 28-day compressive strength. It was found that blast furnace slag provided higher compressive strength values of alkali activated concrete.

Table 2. Compressive strength test results of geopolymer concrete specimens which were left in laboratory conditions without curing.

Mixture Code	*Compressive Strength (MPa)*	
	In laboratory conditions	
	7-days	*28-days*
4% BFS	6.60	15.40
10% BFS	12.34	28.20
20% BFS	21.53	42.70

Table 3. Compressive strength test results of geopolymer concrete specimens which were left in outdoor and in laboratory conditions without curing.

Mixture Code	*Compressive Strength (MPa)*			
	In outdoor conditions		*In laboratory conditions*	
	7-days	*28-days*	*7-days*	*28-days*
15% BFS	27.07	38.25	18.90	45.74
25% BFS	37.26	49.29	27.75	67.00

4. CONCLUSIONS

The main outcomes of this research can be summarized as follows:

- As the amount of blast furnace slag increased, compressive strength of geopolymer concrete increased.
- When blast furnace slag was used at 25% by weight of cement, it was reached higher compressive strength values such as 67 MPa without using cement. This indicates that geopolymer can be used for specific-targeted projects in future.
- The use of geopolymers is substantial in concrete production as lowering energy consumption and decreasing carbon dioxide emission.
- Environmentally friendly concrete can be produced by using waste materials. With alkaline activators and recycled materials, and by using different methods (pressurized forming, extrusion, etc.) in designs of semi-dry mix, the prefabricated elements, paving

stones, curbs, decorative tiles, facing tiles, concrete pipes, bricks and refractory building materials can be produced.

- For future research, the use of geopolymers in buildings placed in highly seismic zones can be investigated. The following methods can be suggested for future studies: Obtaining alkaline activators from industrial wastes can be a beneficial study for environmentally friendly concrete production processes. Geopolymer concrete can be produced with different pozzolanic binders such as silica fume. Facing tiles in different sizes can be produced with geopolymeric materials. Instead of using commercial silicate chemicals, solid silicate resources can be investigated to reduce the cost of geopolymer production. The use of solid silicate resources can lower the cost of production.

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TERMOLÜMİNESANS DOZİMETRELER İLE DOZ DAĞILIMLARININ İNCELENMESİ

Zeynep Açelya KURT[1], Serpil AKÖZCAN[*1],

Kırklareli Üniversitesi, Fen Edebiyat Fakültesi, Fizik Bölümü, Kırklareli

ÖZET

İyonlaştırıcı radyasyon uzun süredir kanser tedavisinde kullanılmaktadır. Radyoterapi, radyasyon tedavisi veya radyasyon onkolojisi olarak da ifade edilen kanser tedavisinde kullanılan temel yöntemlerden biridir. Termolüminesans dozimetreler (TLD) küçük boyutları ve yüksek hassasiyetleri sebebiyle radyoterapi kaynaklarının çevresindeki doz ölçümlerinde rutin olarak kullanılırlar. Bu çalışmada Bezmiâlem Vakıf Üniversitesi Tıp Fakültesi Hastanesi Radyasyon Onkolojisi Kliniğinde bulunan Lineer hızlandırıcı ve ^{60}Co kaynağı kullanılarak alınan radyasyon dozu termolüminesans dozimetre ile belirlenmiştir. Çalışmada 3.2 x 3.2 x 0.89 mm boyutlarında LiF : Mg , Ti (TLD - 100) çip dozimetreler, 2 Gy'lik ışınlama dozu için Harshaw TLD 3500 okuyucu sistemi ile değerlendirilmiştir. Çalışmada elde edilen sonuçlardan en yüksek radyasyon dozlarının hasta yastığı altı ve gözlere ait olduğu tespit edilmiştir.

Anahtar kelimeler: TLD, Dozimetri, Doz, Lineer Hızlandırıcı, ^{60}Co

RESEARCH OF DOSE DISTRIBUTION BY THERMOLUMINESCENCE DOSIMETRIES IN RADIOTHERAPY APPLICATIONS

ABSTRACT

Ionizing radiation has been used for therapy of cancer for a long time. Radiotherapy referred to as radiation therapy or radiation oncology, is one of the principal modalities used in the treatment of cancer. Thermoluminescent dosimeters (TLD) are routinely used to measure the dose around radiotherapy sources due to their small size and high precision. In this study, we were determined the radiotion doses received from Bezmiâlem University Faculty of Medical Hospital Clinic of Radiation Oncology linear accelerator and ^{60}Co Source using thermoluminescent dosimeter. In the present work the precision of LiF:Mg,Ti (TLD-100) chip dosimeters with dimensions of 3.2 x 3.2 x 0.89 mm was evaluated in Harshaw TLD 3500 reader, for 2 Gy irradiation dose. The results which obtained from the current study were showed that the highest radiation doses were received by patient pillow down and her eyes.

Key words: TLD, Dosimetry, Dose, linear accelerator, ^{60}Co

**serpil.akozcan@klu.edu.tr*

GİRİŞ:

Radyasyon terimi 1895 yılıda Wilhelm Röntgen'in X-ışınlarını keşfi ile hayatımıza girmiş ve kullanılmaya başlanmıştır. Radyasyon, dalga, parçacık veya foton şeklinde yayılan bir enerji türüdür ve hayatımızda daima var olan ve birlikte yaşadığımız bir olgudur. Radyasyon, "İyonlaştırıcı Radyasyon" ve "İyonlaştırıcı Olmayan Radyasyon" olmak üzere ikiye ayrılır. İyonlaştırıcı olmayan radyasyon türleri arasında görünür ışık, radyo ve mikro dalgalar sayılırken, gama ve X-ışınları, alfa, beta parçacıkları ve nötronlar iyonlaştırıcı radyasyon grubuna girmektedirler [1,2].

Nükleer teknolojinin gelişmesine paralel olarak, son yıllarda özellikle kanser teşhis ve tedavisinde kullanılan pek çok yeni cihaz geliştirilmiştir. Tedavilerin başarılı bir şekilde yapılabilmesi için kullanılan tedavi düzeyli dozimetre sistemlerinin belirli aralıklarla, standart radyasyon kaynakları veya standart dozimetreler kullanılarak kalibre edilmesi önemlidir. Günlük hayatımızda radyasyon ile çalışan görevliler diğer kişilere göre daha fazla radyasyon dozuna maruz kaldıkları için radyasyon doz limitleri dünya sağlık örgütlerince belirlenmiş olup, hekim ve diğer tıp personelinin alacakları radyasyon dozlarının müsaade edilen limitler aralığında olması zorunlu hale getirilmiştir [1]. Bunun için de gerekli dozimetrik ölçümlerin radyasyonla çalışan kişilerde ve çalıştıkları alanlarda rutin olarak yapılması gerekmektedir. Bunun için insan duyu organları ile algılanamayan iyonlaştırıcı radyasyonların varlığını tespit etmede ve seviyesini ölçmede, korunma amaçlı dozimetre ve radyasyon doz hızı ölçer olarak isimlendirilen cihazlar geliştirilmiş ve yaygın şekilde kullanılmaya başlanmıştır.

Termolüminesans dozimetre (TLD), radyoaktif bir kaynaktan çıkan ışınları ve bu kaynaklar çevresinde çalışan insanların aldıkları radyasyon miktarını belirlemek için kullanılan küçük boyuttaki dedektörlerdir. TLD ler teşhis, tedavi veya her ikisinde birden yapılan uygulamalar sırasında hastanın vücudu üzerine yerleştirilerek maruz kalınan iyonlaştırıcı radyasyon miktarının belirlenmesi için sıkça kullanılmaktadır [3,4]. TLD'lerin dozimetre aracı olarak kullanılmasının en önemli sebeplerinden biri absorbe edilen doz ile ışınlama sonrası malzeme tarafından yayılan ışığın yoğunluğu arasındaki ilişkidir. Aynı zamanda yüksek hassasiyetleri, geniş bir doz aralığında doğrusal doz cevabına sahip olmaları ve küçük boyutları nedeniyle doz ölçümlerinde sıklıkla tercih edilmektedirler [5]. TLD olarak kullanılan kristallerden bazıları arasında

magnezyum (Mg) ve titanyum (Ti) ile katkılanmış lityum florür (LiF:Mg,Ti), manganez (Mn) ile katkılanmış kalsiyum florür (CaF_2:Mn), disprozyum (Dy) ile katkılanmış kalsiyum florür (CaF_2:Dy), karbon (C) ile katkılanmış alüminyum oksit (Al_2O_3:C), manganez ile katılanmış lityum borat ($Li_2 B_4 O_7$:Mn) sayılabilir. Bunlar arasında personel dozimetri çalışmalarında en sık kullanılanı, TLD-100 olarak isimlendirilen ve etkin atom numarası (Z_{eff} =8.14) dokuya eşdeğer olan LiF:Mg,Ti'dir

1940 yıllarında nükleer reaktörlerin geliştirilmesi ile yüksek enerjili gama ışınları yayan yapay radyoaktif maddeler elde edilmiş ve ilk radyoaktif kobalt (^{60}Co) kaynağı 1951 yılında Kanada'da teleterapi ünitesi olarak kullanılmaya başlanmıştır. ^{60}Co teleterapi cihazları radyasyon kaynağı olarak ^{60}Co kullanılan cihazlardır. ^{60}Co teleterapi cihazı kaynağın bulunduğu kafa, ışının hastaya gönderildiği kolimatör, kafanın 80 ya da 100 cm'lik izomerkez etrafında dönmesini sağlayan gantry, hastanın tedavi edildiği masa ve cihazın uzaktan kontrolünü sağlayan konsoldan oluşmaktadır [2, 6].

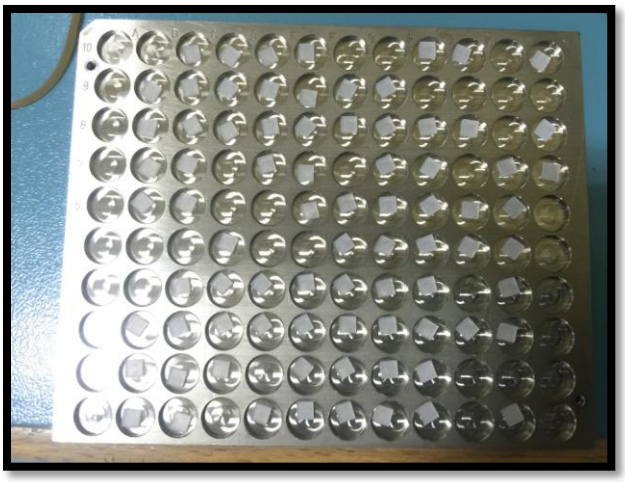
Nükleer tıp ve radyoloji alanında çalışan tıp personelleri ve tedavi gören kanser hastaları iyonlaştırıcı radyasyona yüksek ölçüde maruz kalmaktadır. Bu çalışmanın amacı iyonlaştırıcı radyasyon ve etkilerine karşı çalışanların, hastaların ve çevrenin belirlenen bir süre içinde, maruz kalınan radyasyon dozlarının ölçümünün yapılmasıdır. Bu amaçla Bezmiâlem Vakıf Üniversitesi Tıp Fakültesi Hastanesi Radyasyon Onkolojisi Kliniği'nde lineer hızlandırıcı cihazı odasında ve dışında bir dozimetre yerleşim planı oluşturulmuştur.

MATERYAL VE METOT

Bu çalışmada Bezmiâlem Vakıf Üniversitesi Tıp Fakültesi Hastanesi Radyasyon Onkolojisi Kliniği' nde, PET/BT odasında insan benzeri fantom kullanılarak, hem fantomun üzerine hem de odada cihazdan belirli mesafede bulunan yerlere ve kumanda odasına TLD-100 dozimetreler yerleştirilmiş ve PET/BT'den kaynaklanan saçılan radyasyon dozu tespit edilmiştir. Bu işlem için 104 adet TLD-100 dozimetre kullanılmıştır (Şekil 1). Her bir TLD-100 dozimetre 3.2 mm x 3.2 mm, kalınlığı 0.89 mm boyutlarında ve LiF:Mg,Ti içeriğinde olup insan dokusu eşdeğerine yakın olmasından dolayı çalışma için seçilmiştir.

Çalışmada daha önce hiç işlem görmemiş 104 adet TLD, kalibrasyon işlemi için Kırklareli Üniversitesi Merkezi Araştırma Laboratuvarı'nda bulunan PROTHERM PLF 120/7 model

fırında ilk önce 400°C'de 1 saat 10 dakika, daha sonra 100°C'de 2 saat tavlanmış ve tüm bu tavlama işlemlerinden sonra seçilen 104 adet TLD kalibrasyon işlemi için hazır duruma getirilmiştir.



Şekil 1. Çalışmada Kullanılan TLD-100 Dozimetreler.

Kullanılan dozimetrelerin kalibrasyonu için Trakya Üniversitesi Tıp Fakültesi Hastanesi Radyasyon Onkolojisi Kliniği'nde bulunan Cyrus marka lineer hızlandırıcı ve insan dokusu eşdeğerine sahip bolus kullanılarak 80 cm SSD değerinde, 20 cm x 20 cm matriks alanda, yüzeyden 0.5 cm derinlikte her biri 1 Gy doz alacak şekilde ışınlanmıştır.

Şekil 2. TLD Okuyucu Sistemi

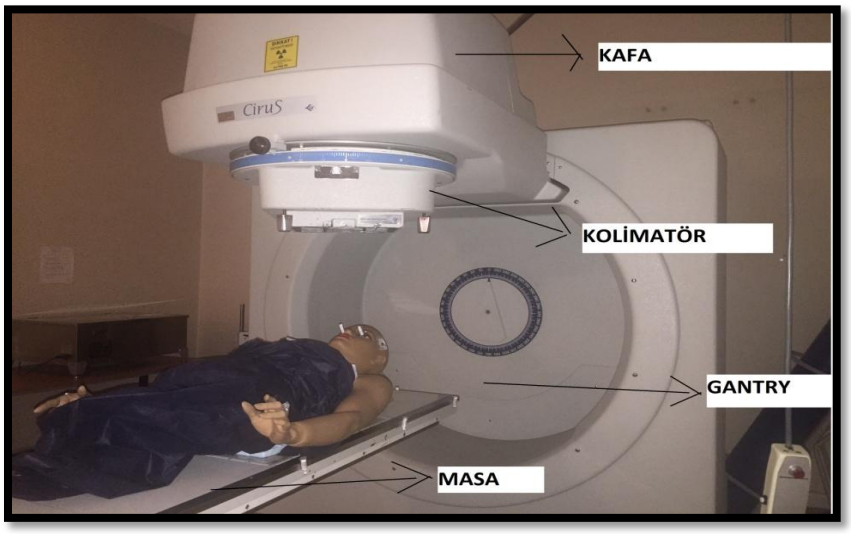
Tüm termolüminesans ölçümleri Harshaw Model 3500 TLD okuyucu kullanılarak yapılmıştır (Şekil 2). Dozimetre kalibrasyonu sonucunda 79 adet TLD-100 çalışmada kullanılmak üzere belirlenmiştir.

Kalibre edilen dozimetreler Bezmiâlem Vakıf Üniversitesi Tıp Fakültesi Hastanesi Radyasyon Onkolojisi Kliniği'nde PET/BT odasında insan benzeri rando fantom kullanılarak, fantom üzerinde, yattığı masa etrafında, ışınlama ve kumanda odasında 36 farklı noktaya yerleştirilmiştir. Rando materyalleri radyasyon emilimi açısından, foton ve elektronlar için insan dokularına eşdeğeridir olmakla beraber, rando plastiği radyasyon ve fiziksel değişimlere karşı çok duyarlıdır. Çalışmada radyoterapi merkezlerinde doz ölçümleri için kullanılmak üzere üretilen 100 cm uzunluğunda ve 50 kg ağırlığındaki kadın fantom kullanılmıştır (Şekil 3).

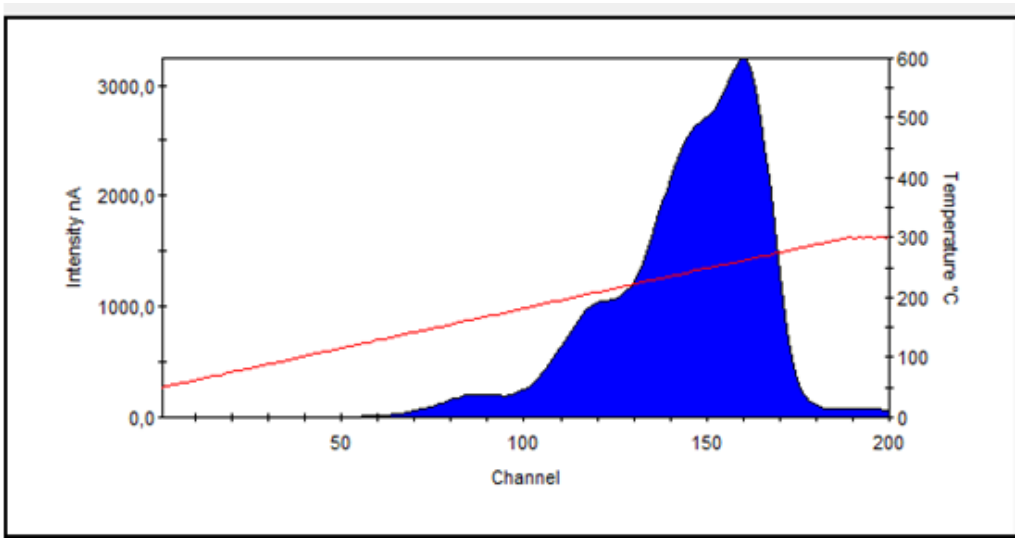
Çalısmada TLD'lerin kalibrasyonu için Trakya Üniversitesi Tıp Fakültesi Hastanesi Radyasyon Onkolojisi Birimi'ne ait ^{60}Co teleterapi cihazı (CIS-B10, CYRUS, 1996) kullanılmıştır (Şekil 3). Terapi kafası kurşun kılıf içine yerleştirilmiş 2 cm çapında ^{60}Co kaynak içermekte olup ±180°'lik açı ile hareket etme yeteneğine sahiptir. Kaynak-aks mesafesi (SAD) 80 cm olup cihazda birbirinden bağımsız hareket eden ve kolimatör alan boyutları 3.5x3.5 cm'den 32x32 cm'ye kadar açılabilen iki kolimatör sistemi bulunmaktadır.

Çalışmada içerisinde ^{60}Co kaynak bulunan Cyrus marka model Lineer Hızlandırıcı kullanılarak kadın fantoma 2 Gy' lik total kranium (kafa) ışınlaması yapılmıştır (Şekil 3). Aynı sıralamada ve aynı yerleşimlerle ölçümler 3 kez tekrar edilmiştir.

Her ışınlanma sonrası TLD okuyucu yardımıyla ışıma ölçümleri alınmış ve ışıma eğrilerinden yararlanarak TLD'lere ait doz değerleri hesaplanmıştır (Şekil 4).



Şekil 3. Co-60 Teleterapi Cihazı.



Şekil 4. Çalışmada elde edilen örnek ışıma eğrisi.

SONUÇLAR VE TARTIŞMA

Bu çalışmada, içinde ^{60}Co kaynağı bulunan lineer hızlandırıcı cihazı kullanılarak tüm vücut ışınlama pozisyonunda 2 Gy şiddetinde ışınlama işlemi gerçekleştirilmiş ve bu işlemin belirli konumlarda yarattığı etkilerin incelenmesi amaçlanmıştır. Çalışmada kullanılan TLD'ler ilk olarak tavlama prosedürlerine uygun olarak tavlandıktan sonra kalibre edilmiş ve 36 ayrı noktaya ikişer tane TLD yerleştirilmiştir. Her bir konumlama ve ölçüm için elde edilen ortalama sonuçlar Tablo 1'de verilmiştir.

Çalışmada üç ayrı ölçüm sonucunda elde edilen değerlerin ortalaması alınmış ve TLD-100'lerden hesaplanan soğurulan doz şiddetlerinin 0.05 ile 1.6 Gy değer aralığında değiştiği görülmüştür. Bu değişim literatürde de belirtildiği gibi dozimetrelerin konumlandırılmasındaki farklılıktan kaynaklandığı düşünülmektedir. En yüksek doz değeri rando fantomun kafasının altındaki yastık bölgesinde hesaplanmış olup, üç ölçüm için ortalama 1.59 Gy şiddetinde bulunmuştur. Konumlandırılan TLD-100 dozimetreleri arasında ölçülen en düşük şiddet zırhlı kapı karşısında yer alan koridorda bulunmuştur.

Bu konuda dünyada yapılmış başka çalışmalarda hesaplanan değerler ve çalışmamızda ölçülen dozlar arasında oluşan farkların nedenlerinden birinin de kalibrasyon ve okuma prosedüründen kaynaklanan hatalardan ve TLD'leri fantoma yerleştirirken yapılan hatalardan kaynaklanabileceği ve özellikle yüksek doz değişimi olan noktalarda, TLD ile elde edilen hesaplarda doz farklılığının olabileceği belirtilmiştir [7,8,9].

Tablo 1. 36 ayrı noktaya yerleştirilen TLD-100'lerin ortalama sonuçları

Dozimetre Yeri	Hesaplanan Ortalama Doz (mGy)	Dozimetre Yeri	Hesaplanan Ortalama Doz (mGy)
Masa Başı fantom kafa hizası sağ taraf	5.83±0.78	Kapı girişi sol duvar	0.16±0.05
Masa Başı fantom kol hizası sağ taraf	4.89±0.51	Sol duvar	0.22±0.03
Masa sağ taraf	0.85±0.10	Fantom karşısı sol duvar	0.28±0.12
Masa sağ taraf	0.22±0.05	Cihazın arkası sağ taraf	0.18±0.05
Masa sağ taraf	0.19±0.06	Fantom sağ el	0.76±0.08
Masa ucu fantom ayak hizası	0.25±0.05	Cihazın arkası sol taraf	0.21±0.04
Masa sol taraf	0.20±0.07	Fantom karşısı sağ duvar	0.27±0.04
Masa sol taraf	0.26±0.08	Sağ duvar	0.17±0.04
Masa sol taraf	0.80±0.12	Cihazın karşısındaki duvar	0.21±0.11
Masa Başı fantom kol hizası sol taraf	4.49±0.73	Merkez-Masa altı	265±229
Masa Başı fantom kafa hizası	7.19±0.11	Zırhlı Kapı-iç kısım	0.15±0.05
Masa Başı fantom kafa hizası sol taraf	6.50±1.97	Zırhlı Kapı-yan kısım	0.18±0.05
Hasta Yastığı	1.6 Gy±0.1	Zırhlı Kapı-dış kısım	0.18±0.04
Göğüs	14.77±4.80	Koridor-Zırhlı Kapı karşısı	0.13±0.01
Fantom sağ göz	279±108	Kumanda odası yan duvar	0.20±0.04
Fantom sol göz	301±71	Kumanda odası karşı duvar	0.16±0.06
Fantom sol el	1.31±0.06	Kumanda odası dolap	0.22±0.06
Fantom Boyun	22.68±2.38	Koridor (Background)	0.23±0.09

Bu tür çalışmalarda tüm vücut ışınlamasında şartlar farklıdır. Hasta vücudunun tedavi alanı içerisine konumlandırılmasının hatasız olması için hasta tedavisinde birkaç metre uzaklıktaki alanlar kullanılır. Çalışmamızda farklı mesafelere yerleştirilen TLD-100 dozimetrelerinden alınan sonuçlar, hesaplanarak beklenen sonuçlarla uyumlu bulunmuştur.

TEŞEKKÜR

Bu çalışmanın yapılmasında yardımlarından dolayı Bezmiâlem Vakıf Üniversitesi Tıp Fakültesi Hastanesi Radyasyon Onkolojisi Bölümüne ve Trakya Üniversitesi Tıp Fakültesi Hastanesi Radyasyon Onkolojisi Bölümüne teşekkürü bir borç biliriz. Ayrıca Kırklareli Üniversitesi Rektörlüğü'ne de tüm desteklerinden dolayı teşekkür ederiz.

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MODELS FROM NATURE FOR INNOVATIVE BUILDING SKINS

Gülcan MİNSOLMAZ YELER[1*], Soner YELER

Kırklareli University, Faculty of Architecture, Department of Architecture, Kırklareli

ABSTRACT

The general aim of this research is to transform the knowledge of biological systems (natural solutions) into architectural knowledge for the design of innovative building skins. The basic questions for research are formulated as follows: What are the best skin models in nature? How are these models utilized in the best way for building skin? What kind of building skins can be improved to adapt to changing conditions? In this context, the study aims to determine with a literature review, effects of biological paradigm to building skin design, innovative ideas and concepts produced in this process; how biological principles used in design on conceptual/experimental and applied projects by analysis study, what kind of solutions are produced. The analysis study reveals that an approach based on the principles of the models in the nature is a unique resource for presenting innovative ideas to architects and for solving problems experienced today.

Keyword: Nature, Biologic Principles, Biomimicry, Building Skins

YENİLİKÇİ YAPI KABUKLARI İÇİN DOĞADAN MODELLER

ÖZET

Bu araştırmanın genel amacı, yenilikçi bina kabukları tasarımı için biyolojik sistemler bilgisini (doğadaki çözümleri) mimarlık bilgisine dönüştürmektir. Araştırmaya temel olan sorular şu şekilde formüle edilmiştir: Doğadaki en iyi kabuk modelleri nelerdir? Bu modeller yapı kabuğu oluşturmak için en iyi şekilde nasıl kullanılır? Değişen koşullara uyum sağlamak için hangi tür yapı kabukları geliştirilebilir? Bu bağlamda, çalışma bir literatür taraması ile biyolojik paradigmanın yapı kabuğu tasarımına, bu süreçte üretilen yenilikçi fikirlere ve kavramlara etkilerini belirlemeyi; kavramsal/deneysel tasarımlar ve uygulanan projeler üzerinden, biyolojik ilkelerin nasıl kullanıldığını, ne tür çözümler üretildiğini analiz etmeyi amaçlamaktadır. Analiz çalışması, doğadaki modellerin ilkelerini esas alan bir yaklaşımın, mimarlara yenilikçi fikirler sunması ve günümüzde yaşanılan sorunlara çözüm üretmesi bakımından eşsiz bir kaynak olduğunu ortaya koymaktadır.

Anahtar Kelimeler: Doğa, Biyolojik İlkeler, Biyomimikri, Yapı Kabukları

gulcan.yeler@klu.edu.tr[1],

1.INTRODUCTION

1.1. Problem Statement

The awareness about environmental issues like climate cahange, has attracted interest on buildings energy consumption. Building skin is mostly responsible for building's energy consumption. Because, building skin is one of the most important design parameters determining indoor physical environment related to thermal comfort, visual comfort and even occupancy working efficiency, thus affecting energy usages in buildings [1] for lighting, mechanical systems, and maintenance. Also, building skin is harmful to the environment due to their manufacturing, installation and maintenance. There are many problems of current building skins. The current building skins static. A static building or skin can not guarantee an optimal level of performance, and this will lead to a discrepancy between the building and the environment [2]. With seasonal variations, shifting weather patterns, and the ever-changing comfort needs and energy requirements of indoor occupants, static passive building skin design can not provide consistent climate control due to daily, even hourly changes in the weather [3]. The another problem with current building skins is that they are constructed from multiple dissimilar components. Which creates too many opportunities for material failure and leads to condensation, thermal bridging and wasteful material use [4]. Moreover, the perception of a building's identity is possible through its skin, making it a significant communication component. These are a few reasons why the challenges in the skin are a contemporary proble.

Considering the aforementioned problems, target for today and the future is, instead of the static building skins, new skin formation provide more comprehensive space activity, increase comfort of user, climate compatible, sustainable for people and environment, energy-effective and energy-active, multi-functional, modular, at the same time smart and communicative.

1.2. Solution for Problems: Nature/Biology

To solve problems, designers need new solutions. In this context, focus on biological solutions is important in terms of acquiring new perspective for building skins.

Eilouti [5] states that solutions which are produced according to the suggestion of natural organisms and such information described as biomimetic establishes the connection between building man-made products and solving design problems within the new perspectives models:

The "Biomimicry" term represents a concatenation of "bio" which means life and "mimesis" meaning imitation. Janine Benyus' [6] book "Biomimicry: Innovation Inspired by Nature" published in 1997 refers to a new scientific field that studies nature, its models, systems, processes and elements, and then imitates or takes creative inspiration from them to solve human problems sustainably. Biologists and ecologists have studied the environmental influences on animal and plant physiology and behaviour, but translating these observations and analysis into architecture has been largely unexplored. The resilience of species in a particular habitat can provide valuable lesson for long-lasting design. Mazzoleni state that just as animals have systems, such as skeletal, circulatory, immune, digestive, communication, and sensory, so too do buildings have systems of structure, circulation, protection, energy and water use, communication, and thermal regulation [7]. So, researches in biomimetic has encouraged architects, scientists and designers to dig deeper into the natural world-even to microscopic levels in a bid to seek answers to sustainable design questions by mimicking biological systems that have already solved them, solutions developed over billions of years of evolution [8].

2. MATERIALS AND METHODS

2.1. The process of the research

Firstly, by using the archive method, problems about building skin will be expressed and in order to solve these problems, the necessity of applying to nature's solutions will be discussed in the framework of biomimicry. Then, skin types in the nature which are prominent in today's building skins researches and their solutions when confronted with different environmental conditions will be expressed. Twenty designs were analyzed in order to create building skins inspired from the nature. In the results section, the results of the analysis are shown in tables and the concepts resulting from the natural solutions are discussed.

2.2. Research samples

In literature, there are a lot of projects created inspired from the nature. However, in this study, different sources were searched and especially the building skin designs inspired from the principles of natural skins were chosen. In the study, 20 other studies, which are applied today and were developed concept/experimentally, were included.

3. PRINCIPLES IN NATURAL SKINS

The term "skin" is used in this research on a general level to refer to any human, plant and animal coverings, including skin, hair, fur, feathers, scales, exoskeletons, and shells. Skin is a complex and incredibly sophisticated organ that performs various functions, including protection, sensation and heat and water regulation [7]. Yowel [4] stated that natural skins are an organism's first line of defense to protect its interior from the exterior environment. But, a natural skin can regulate temperature and humidity, is often waterproof, yet permeable when needed, integrates systems in a very thin membrane, protects from sunlight, can repair itself and is beautiful. Plus it does all this with environmentally friendly manufacturing, done at the local level and will not be harmful to the environment at the ends of its life.

The harsh environmental characteristics create difficult conditions for living organisms. Living systems are not static. They constantly need to adapt themselves to changing internal and external conditions [9].

For example, some animals have thick coat with dense hair, it does not only protect animals from cold winter, but it insulates them from summer heat. A **polar bear's fur** consists of three main layers: the clear hollow hair, a dark color skin, and a wooly fur layer underneath it all. Light penetrates the clear hollow hair, while the dark skin increases heat absorption and after that, the heat is preserved in the wooly fur layer and insulated by the 10cm layer of fat underneath it all [10].

Polar bear's fur changes color in summer due to the structure of each hair and the dark color of the underlying layer of skin. Each hair is clear and hollow to allow light in [10]. Coloration is also an important factor in reducing of heat absorption in desert animals [11]. A desert **chameleon** becomes darker in the morning to increase its heat absorption and lighter during the day to reflect light [10]. Their colors are used for communication between other chameleons, and as camouflage from predators.

Sand lizard has hygroscopic skin to absorb moisture from the air and to produce enough water [11]. The **Namib desert beetle** is able to capture moisture however from the swift moving fog that moves over the desert by tilting its body into the wind. Droplets form on the alternating hydrophilic-hydrophobic rough surface of the beetle's back and wings and roll down into its mouth [12]. **The thorny devil** (Moloch horridus) can gather all the water it needs directly from

rain, standing water, or from soil moisture, against gravity without using energy or a pumping device [10]. Ribs or grooves are morphological adaptation for water transportation, e.g. barrel cactus. Besides the importance of ribs in allowing the **cactus** to shrink and swell, they provide channels fort he collected water to reach the roots [13]. Also, the cactus' spines serve is to help shade the plant from the intense sun.

Plant surfaces provide more than one solution for environmental conditions and can include, for example, light reflection, superhydrophobic or superhydrophilic surfaces [14,15]. For example, **lotus leaf** is the most superhydrophobic, hence it always remain clean in muddy and dirty ponds. In the rainy season, when the raindrops fall on the surface of lotus leaves, they immediately bead up like shiny spherical balls and quickly roll off the surface collecting dirt and debris along the way [17,18]. Koch and Barthlott [19] stated that superhydrophobicity is also a protection against plant pathogens such as fungi and bacteria, because germination of many microorganisms such as fungi and reproduction of bacteria are limited by water access. Animals such as **water stride, water spider** and **mosquito** exhibit excellent water repellent, superhydrophobic properties.

Dynamics in plants are generated due to their nastic structure [20]. **Heliotropism** is the movement of leaves following the sun and it is one of the ways to regulate light intensity on the surface. For example, **sun flower** track sun path throughout the day by bending towards light and maintaining radiation perpendicular surface [13]. Most plants must open and close their **stomata** during the daytime in response to changing conditions, such as light intensity, humidity, and carbon dioxide concentration. Also, some plants like **mimosa** fold its leaves when touched or exposed to heat. Many other plants also fold their leaves in the evening [21]. Flexibility is an important feature for protection in animals. For example, the **armadillo** has a hard outer shell and can curl up into a ball leaving no soft body parts exposed to danger (a bit like a woodlouse) [22]. Also, the **pangolin**'s scaly body can curl up into a ball when threatened, with its overlapping scales acting as armour. The scales are sharp, providing extra defense against unwary paws [23]. The **balloon fish** can triple its body volume by pumping water into its stomach for the purpose of defended itself against predators. Then, it shows off the pointy spines that cover their skin. So, fish skin exhibits striking structural and functional specialization for inflation [24]. Some animals respond to different conditions with specially designed nests. For example, **termits** construct their mounds to maintain a constant temperature. The insects do this by constantly opening and

closing vents throughout the mound to manage convection currents of air-cooler air is drawn in from open lower sections while hot air escapes through chimneys [25].

4. TRANSLATING NATURAL PRINCIPLES FOR BUILDING SKINS

Those mentioned above shows that natural skins are good models for how building skins should behave. However, current building skin are seen as barriers from the outside world, instead of filters like a natural skin [4]. It is seen that when evaluating natural skins in a similar way building envelopes serve multiple roles, as they are the interface between the building inhabitants and environmental elements. [26]. Wigginton and Harris [27], in their book Intelligent Skins, argue that the use of the term "skin" is more than merely a metaphor; the building's envelope can be considered quite literally as a complex membrane capable of energy, material and information exchanges. Emulating nature's strategies to innovate design for building skin could be successful. The skin of nature's organisms has similarities with the building skin and that makes it interesting to look to their strategies. The transformations of the strategies from biology to architecture is possible in different ways. Eilouti [5] states that nature can be imitated directly or indirectly as a metaphor to solve design problems and to develop environment-friendly functions, systems and solutions. According to the Gruber [28], abstraction is the key to transferring ideas from one discipline to another. Maibritt Pedersen Zari [29] stated that Biomimicry is the mimicry of an organism, an organism's behaviour or an entire ecosystem in terms of its form, material, construction method, process, strategies or function.

4.1.Case Studies: Applied Designs

This part of the study, ten works that come to the fore in the literatüre are analyzed inspired by natural skins.

4.1.1. The Esplanade Theater: The Esplanade Theater in Singapore, designed by DP Architects and Michael Wilford. It was inspired by the durian plant while the shell of this building was designed. The thorny, multi-layered and semi-rigid pressurized shell of the plant protects the seeds inside. Similarly, with a layered shading system that resembles the shell of the plant from the outside, the building skin also prevents overheating of the interiors while allowing the sunlight to be taken from the interior [30] (Figure 1).

Figure 1. Durian plant and The Esplanade Theater [3]

4.1.2. The Minister of Municipal Affairs&Agriculture (MMAA) in Qatar: This building is designed by Aesthetics Architects. The skin of the desert cactus is applied to the design of the skin of a desert building. The cactus plant is exposed to more night sweats than the daytime to hold the water. Likewise, intelligent sun shading elements in windows are also opened and closed in response to heat. Thus saving energy [30] [31] (Figure 2).

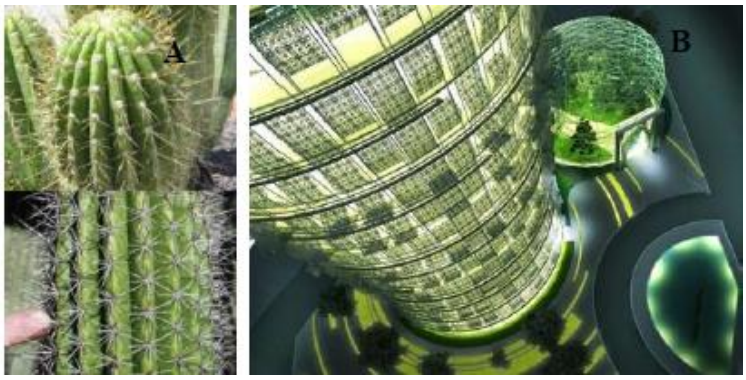

Figure 2. Cactus plant and MMAA Building [30] [31]

4.1.3. Al Bahar Towers: In Abu Dhabi, towers' facade is designed by Aedas Architects. The façade has an interactive relationship to the environment which is reminiscent to the opening of a **morning glory flower** to the sun. Flower-like shading elements in building skin are managed by the building automation system and are opened and closed in response to the sun [32] (Figure 3).

Figure 3. Morning glory flower and Al Bahar Towers [32]

4.1.4. Heliotrope House: Heliotrope House is designed by Architect Rolf Disch. This building is the first energy positive house in Germany. In the design of the house inspired by heliotropism, a phenomenon common to plants that live in the Arctic, where the growing season is short. During a never-ending summer day, Arctic poppies will follow the sun around and around, using its rays to warm their petals so as to attract insects. Similarly, Mounted on a pole, the house rotates (180 degrees) during the day depending on the direction of sunrise. The solar panels on top produce more than enough energy to make the home net energy positive. A unique hand railing system on the roof doubles as solar thermal tubing that heats the home's water and radiators [33, 34] (Figure 4).

Figure 4. Arctic popies and Heliotrope House [34]

4.1.5. Self-cleaning coatings: A self-cleaning effect which was first discovered by Prof. Barthlott at the lotus leaf. Dust and other pollutions are rinsed off by raindrops from a lotus leaf. Many institutes and suppliers try to apply this effect on textiles, plastics, glass or other materials. StoLotusan Color protection, dirt runs off each time it rains to leave a beautifully clean and dry façade [35]. BalcoNano® is a hard, durable protective coating. Dirt and other deposits cannot cling to the glass surface and either wash away easily or can be easily cleaned with water and a cloth [36] (Figure 5).

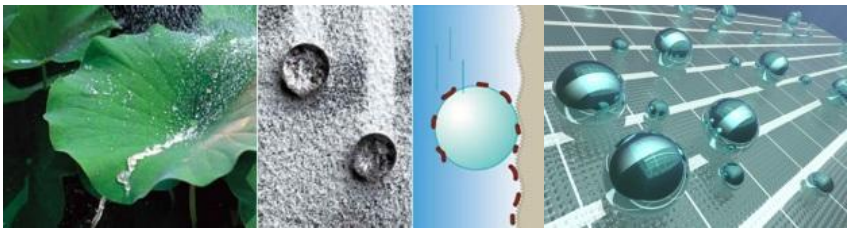

Figure 5. Lotus leaf and self-cleaning coatings [35] [36]

4.1.6. Waterloo International Terminal: This building was designed by Nicholas Grimshaw&Partners. The flexible skin of pangolin is imitated in the parts that fix the glass panels of the building so that the changes in the air pressure caused by the trains entering and leaving the terminal do not damage the building. So that the glass skin of the building can move in response to applied air pressure forces [37, 38] (Figure 6).

Figure 6. Pangolin and Waterloo International Terminal [37]

4.1.7. The Swiss Re (Gherkin) Tower: Tower was designed by Sir Norman Foster in London. It was inspired by the venus flower basket sponge. This special sponge hosts a lattice-like exoskeleton that appears glassy and glowing in its underwater environment. The various levels of fibrous lattice work help to disperse stresses on the organism in various directions and its round shape reduce forces due to strong water currents, both of which were applied to Foster's design of the tower [39]. The steel spiral "diagrid" structure creates an aerodynamic form that provides the lowest resistance to wind [40] (Figure 7).

Figure 7. Venus flower basket and Swiss Re Building [8]

4.1.8. Eastgate Tower: The architect Mick Pearce was inspired termit mound to design the Eastgate center In Zimbabwe where the temperature outside can vary from 3 °C up to 43 °C and where the air condition plays a significant role. The innovative building uses similar behavior in the design, and air circulation planning it stays cool without air conditioning and uses less than 10% of the energy used in similar sized conventional buildings. His solution was to have specially designed hooded windows, variable thickness walls and light colored paints as a part of a passive-cooling structure to reduce heat absorption. By doing so Eastegate uses 90% less energy for ventilation than conventional building [25] (Figure 8).

Figure 8. Termit mound and Eastgate Tower [25]

4.1.9. Council House 2 (CH2) Building: The ten storey building was designed by Architect Mick Pearce in Melbourne, Australia. The climate control of this building mimics the ventilation system of a termite mound. CH2 includes many innovative and technological features such as photovoltaic cells, chilled ceilings, blackwater sewage recycling systems. But by far the most striking features of CH2 are its recycled timber louvers controlled by photovoltaic cells and the five shower towers, in which water droplets evaporate slightly as they use up energy and thus cool the air. Other features worthy of notice are wind-powered turbines which will help cool the building at night, internal thermal mass, a gas fired co-generation plan, as well as the recycling of the waste heat generated inside the building for their heating/cooling system [41] (Figure 9).

Figure 9. Termit mound and CH2 Building [41]

4.1.10. Q1 Building: Q1 building was designed by JSWD Architetken in Germany. This building is not just a feathery design element- it also serves as a sophisticated sun shading system. The metal feather elements vary in shape from trapezoids to triangles and rectangles. Aside from the shading benefits, the different feather-like elements create a dazzling façade that sparkles like a fish's scales when the sun catches them just right. The metal elements block of the harsh sun while keeping the interior cool, reducing the need for air conditioning and climate control [42] (Figure 10).

Figure 10. Feather and Q1 Building [42]

4.2. Case Studies: Concept/Experimental Designs

Knaack [43] stated that every solution begins with a concept. The idea is the starting point for progress: concepts are visionary thougts, developed from a certain way of perception. The following ideas provide an extreme approach to solutions that are conceivable, yet far from realization. However, this can change over time and these ideas might be taken into consideration. So, this part of the study place is given to concept projects. These projects are selected from studies of researchers and acedemicians mentioned below and other studies in the literatüre.

One of the studies in recent years was investigated analogies between the biological skin and the technical skin at the TU (Vienna University of Technology) student's project. Now, these projects under the leadership of AIT (Austrian Institute of Technology), is being developed at a later stage as BioSkin. "BioSkin–Research aimed at the identification of potentials from nature for climate-adaptive energy efficient facades of the future. The study was conducted at the AIT Austrian Institute of Technology, Energy Department [44][45]. Prof. Dr. Ulrich Knaack founder the Facade Research Group and his team at the Chair Design of Construction in Technical University of Delf concentrates on exploring future possibilities for the building envelope. Key topics for this group are energy consumption and sustainability, typology, materialization, fabrication and assembly of facades. The ideas discussed by the group were collected in the book, "Facades" [43]. Also, Ilaria Mazzoleni and her students at the Southern California Institute of Architecture focused on the analysis and understanding of different types of animal skins [46] and translated the learned principles into the built environment These related to the topics of

sensation, coloration, energy regulation, water management, and the use of local and renewable resources [40]. In her recently published book Architecture Follows Nature: Biomimetic Principles for Innovative Design, she presented twelve case studies about animal skins for the design of building skins [7].

4.2.1. The Habitat 2020: This skin was designed by Philips Design and was envisioned for China. The skin has been designed as a living skin, rather than a system of inert materials used only for construction and protection. The skin behaves like a membrane which serves as a connection between the exterior and interior of the habitat. Alternatively, the skin may be considered as the leaf surface having several stomata cellular openings involved in gaseous exchange and transpiration in plants. The surface would allow the entry of light, air and water into the housing. It would automatically position itself according to the sunlight and let in light. The air and wind would be channeled into the building and filtered to provide clean air and natural airconditioning. The active skin would be capable of rain water harvesting where water would be purified, filtered, used and recycled. The skin could even absorb moisture from the air. The waste produced would be converted into biogas energy that could be put to diverse uses in the habitat [47] (Figure 11).

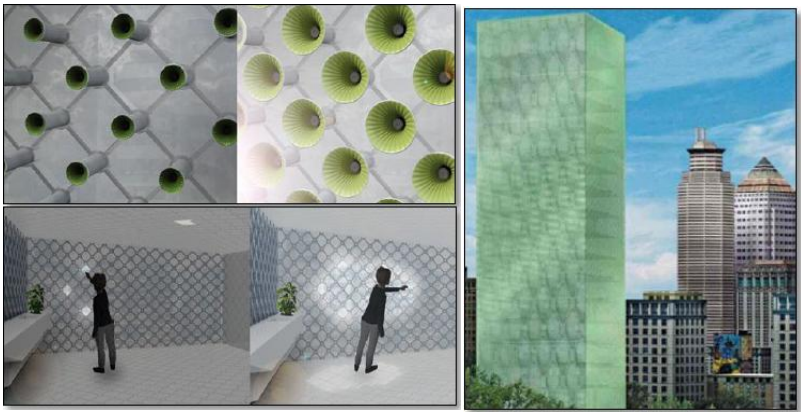

Figure 11. The Habitat 2020 [47]

4.2.2. Stoma brick: This evaporative cooling system (SB) for building skin was designed by L. Badarnah, N. Y. Farchi and U. Knaack (The Facade Research Group). It was designed based on principles of several natural systems. These include stoma of a plant, pine cones, hair protecting

eyes in the desert, and human skin. The system consist of four integrated parts. Stoma brick: made of porous material. It has outer layer of hairy structure to filter the air passing through the envelope. A veneer shutter to control opening/closing in accordance to humudity gradient. The most inner layer is spongy to hold moisture for evaporation. The mono-brick: it includes an irrigation cycle that irrigates through holes the SBs, which are inserted into the mono-brick to allow a continuous performance vertically. The steel framing: is load bearing structure of the cooling system. Th inner layer: filter fora ir cleaning or a double acrylic glass for lightening and visual contact with the exterior environment [48] (Figure 12).

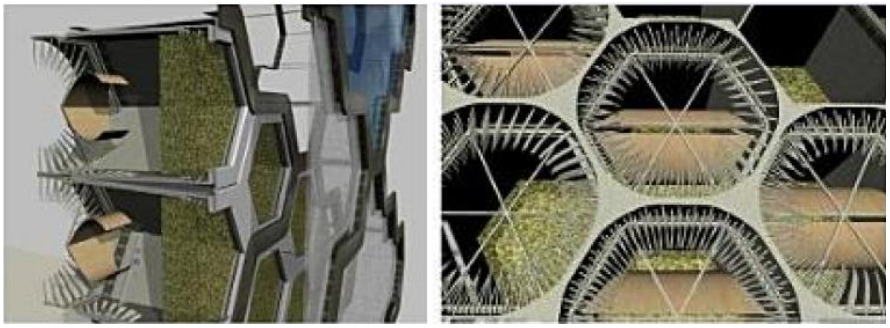

Figure 12. Details of stoma brick [48]

4.2.3. Foliage façades: This facade was designed by Ulrich Knaack (Facade Research Group). Integrating fern of foliage from other deciduous plants into the space between two glass panels will function as periodic sun shading. In winter, the plant has shed its foliage and lets the sun penetrate, but in summer there is good shading. The elements have to fill a reservoir with rainwater to let the plants grow [43] (Figure 13).

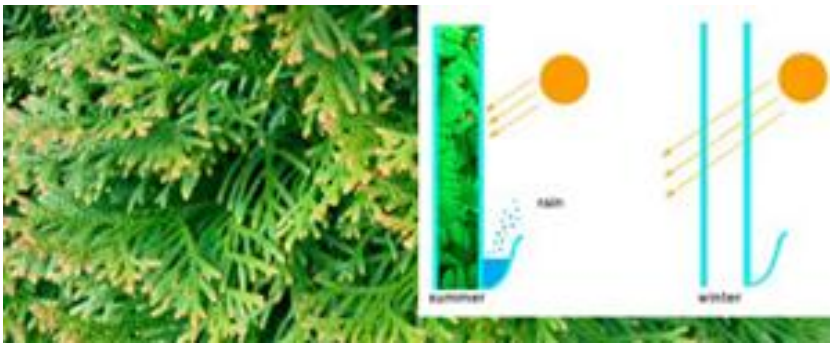

Figure 13. Fern and foliage façade [43]

4.2.4. AeroDimm: This facade was designed by Stefan Pfaffstaller and conducted by Petra Gruber in Vienna University. In the design of pneumatic facade is inspired by the color changing skin of cephalopod. The color change in the two-layered facade is caused by the volume change of the elastic membranes by pneumatic pressure. This technique provides color change as well as darkening of the facade [49] [44] (Figure 14).

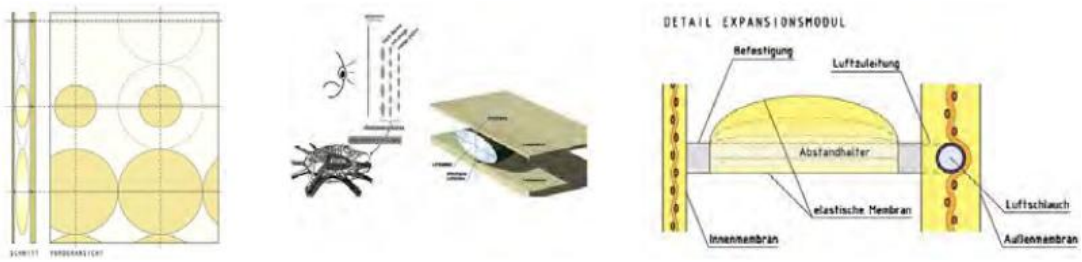

Figure 14. Cephalopods and AeroDimm [44,49]

4.2.5. S.C.A.L.E.S. (Smart, Continuous, Active, Layered, Environmental, System): This project was designed by Ilaria Mazzoleni and her students (Yuan Yuan and Juan San Pedro). It is a project that takes inspiration from the characteristics of the side-blotched lizard (uta stansburiana). The team created a residence in Palm Springs, California for the desert climate which mimics the behaviors and translated physiological characteristics of the lizard's skin. Scales in the skin of the lizard, number, shape and thickness according to function and position in the body and is also linked to a continuous surface. Similarly, flexible membrane used in walls of the house, special covered with photovoltaic panels. Also, similar to the lizard in the desert, the main concern of the design is the comfort of the residents in hot, arid days and cold nights. This example demonstrates how a user help meet their requirements and provide thermal regulation [46] (Figure 15).

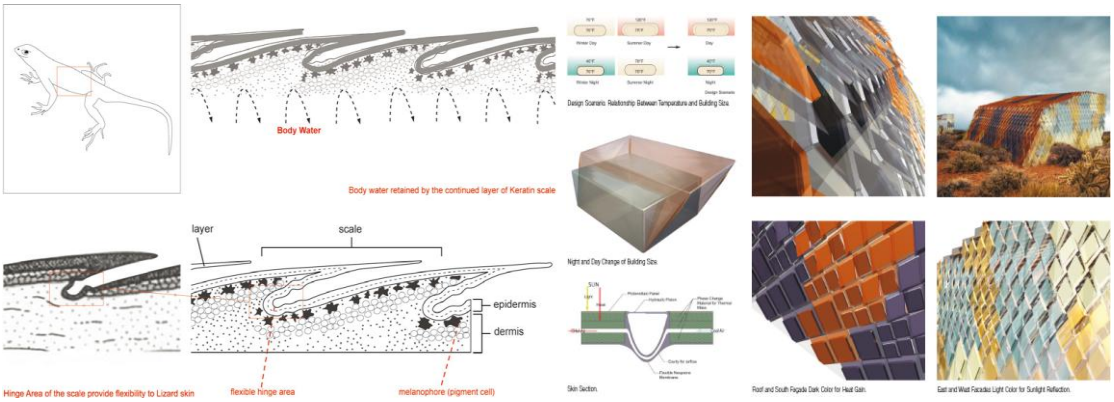

Figure 15. Lizard and S.C.A.L.E.S. project [46]

4.2.6. Polar bear-Keep It Warm: This project was designed by Ilaria Mazzoleni and her students. It mimics the polar bears physiological adaptation developed in order to survive to some of the planet's harshest weather conditions. The living units designed in the arctic region (0 ° C in the summer and -34 ° C in the winter) are partially buried in the earth, not dissimilarly from the bear's hibernation den. The units are also southwest oriented so that they can provide the most suitable heat gain from the sun. The solar energy (heat and light) is collected by an active shell consisting of glass tubes, such as hollow, steerable fur. The energy is conducted through the tube to the insulating strata where is stored, conserved and slowly released. Moreover, embedded in the phase changing material, phosphorescent cells allow the accumulation of light which then gets slowly released at night [50] (Figure 16).

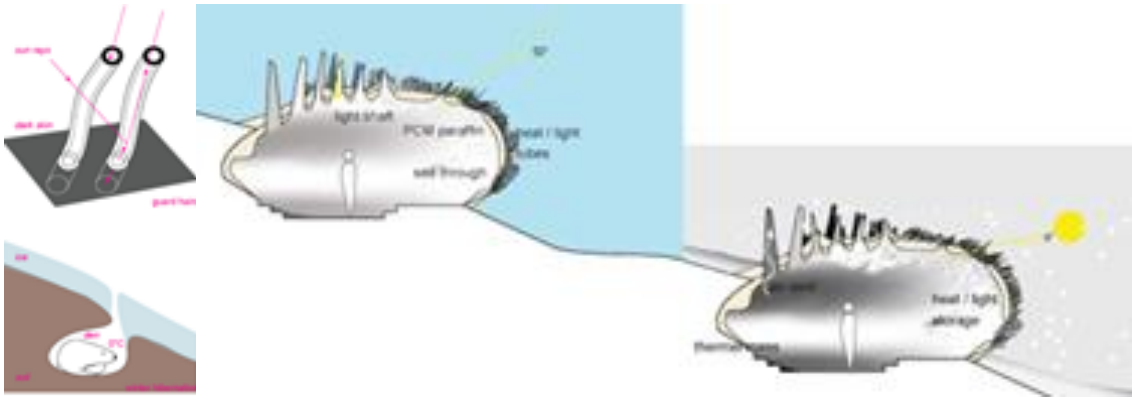

Figure 16. Building skin inspired by polar bear [50]

4.2.7. Porous wall claddings: These wall claddings was designed by S. Turner and R. C. Soar. They suggest porous wall coverings that act like a low-pass filter for turbulent winds, similar to the porous wall structure of termite nests. In this instance, an interior space of a building could be wind-ventilated without having to resort to tall chimneys, and without subjecting the inhabitants to the inconvenient gustiness that attends to the usual means of local wind capture, namely opening a window [51] (Figure 17).

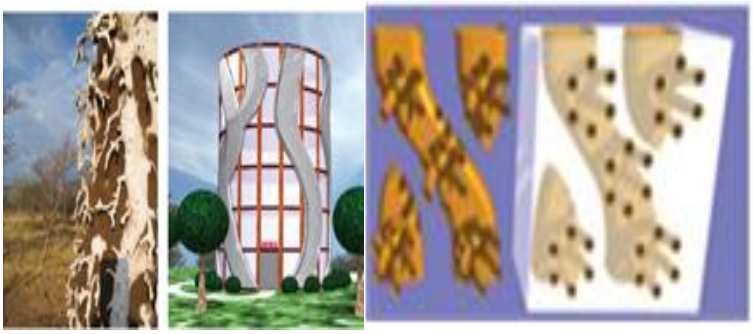

Figure17. Termit mound and porous wall claddings [51].

4.2.8. The Las Palmas Water Theatre: This theatre was proposal project for the city of Las Palmas in the Canary Islands and designed by Grimshaw Architects. Design follows the similar principles as the Namibian fog basking beetle. To heat the sea water going to the evaporators, solar thermal panels are placed in the roof of this structure. The wind brings moisture back to the theater. the air is condensed by the cooling and fresh water is collected. Then, it is used in drinking or irrigation [52] (Figure 18).

Figure 18. Namibian beetle and The Las Palmas W.Theatre [52]

4.2.9. Hydrological Center for the University of Namibia: This building was designed by Matthew Parkes of KSS Architects. In the design of the center that researches sustainable development and water use in West Africa, water collection technique of the Namibia Desert beetle is based. This technique is also called fog catcher [53]. The collects on the mesh screen and because of its shape and vertical orientation, the water naturally runs down the mesh into gutter system located at the bottom of the screens. The water is then transported through the gutters into large cisterns that keep the water at an appropriate cooler temperature so that the water does not evaporate [54] (Figure 19).

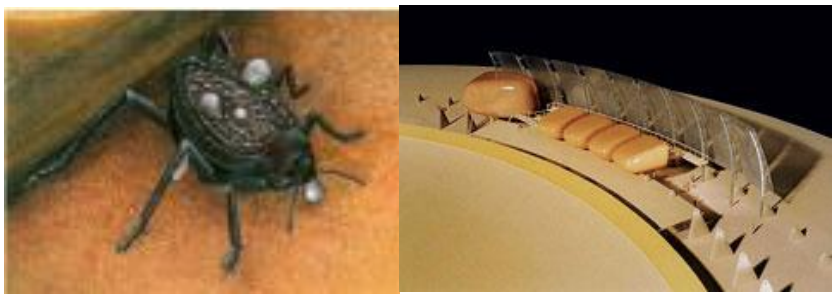

Figure 19. Namibian beetle and Hydrological Center [53]

4.2.10. Deep skin: The idea of "deep skin" is inspired by the skin of the shark for façade design of a tower in Manhattan, New York. The analysis of the configuration of a shark skin, especially how it is formed in macro and micro scales has led to the idea of deep skins in which, different inner volumes of the tower is derived from various skin types[55] (Figure 20).

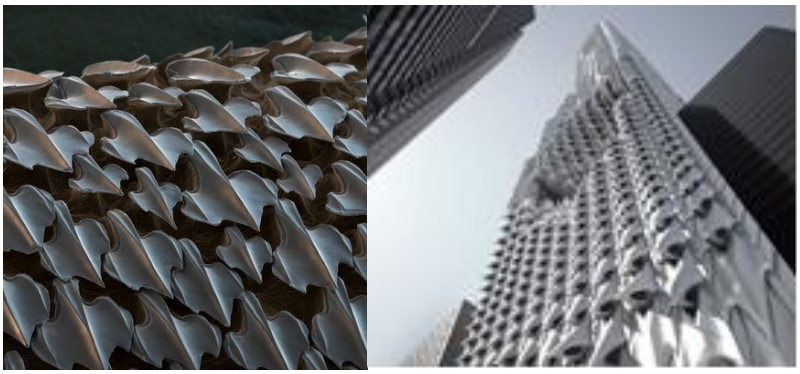

Figure 20. Building skin inspired by shark skin [55]

5. RESULTS AND DISCUSSION

In this section, Table 1 [56], which shows the skin systems of the organisms and the features of the building skins of today and future, was created.

Table 1. Properties of the skin systems in nature and the architectural medium [56]

PROPERTIES OF SKIN SYSTEMS			
NATURE	**ARCHITECTURE**		
	TODAY		**FUTURE**
	CONVANTIONAL	**INNOVATIVELY**	**CONCEPT/EXPERIMENTAL**
• **Adaptable** • **Growing** • **Changable** • **Responsive** • **Multi-functional** • **Dynamic** • **Flexible** • **Self-repair** • **Self-renewable** • **Sustainable** • **Minimum material** • **High-performance** • **Energi generating** • **Complex integrated systems**	• Non adaptable • Non growing • Unchangable • Unresponsive • Multi-functional • Static • Rigid • Non self-repair • Non self-renewable • Ephemeral • Maximum material • Low-performance • Energy comsumption • Simple relationship	• Adaptable • Modular growing • Changable • Smart and interactive • Multi-functional • Dynamic • Flexible • Non self-repair • Non self-renewable • Sustainable • Minimum material • High- performance • Energy generating • Complex integrated systems	• Adaptable • Growing • Changable • Responsive • Multi-functional • Dynamic • Flexible • Self-repair • Self-renewable • Sustainable • Minimum material • Maximum performance • Energy generating • Complex integrated systems

After the samples were analyzed, Table 2, which shows the solutions for building skins with the principles of natural skins, was created.

The tables clearly show that, organisms live in harmony with their environment by showing anatomical, physiological and behavioral features and sometimes by changing these features in order to survive. Adaptation principle of nature ensures that the building skin is flexible, transformable and responsive. This makes the building skin multifunctional and necessitates each system (function-form-structure-material) of the building skin to integrate. Moreover, change and transformation in the nature, along with the developments in technology and materials, lead to a change and transformation in concepts. Building skin which gained the feature of intelligence, as it reacts to its environment, can be programmed, arranged and controlled with digital technologies. The above mentioned features make the building skin very dynamic and free.

Table 2. Principles of natural skins and solutions for building skin (Created by authors)

	CASE STUDY	ORGANISM	NATURAL PRINCIPLES	SOLUTIONS FOR BUILDING SKIN
APPLIED DESIGN	**The Esplanade Theater**	Durian plant	Thorn-covered husk Multilayered, semi rigid skin Structural geometry	Effective shading systems Climate adaptive shading skin Deployable surfaces
	MMAA	Cactus	Responsive stomata permeability Self-shading ribbed morphology Water conservation	Folding systems on the windows Effective shading systems Wastewater management system
	Al Bahar Towers	Morning glory flower	Response to the sun's path Foldaple flowers	Deployable components Intelligent skin
	Heliotrope	Arctic poppies	Heliotropism Response to the sun's path	Rotatable, dynamic structure Responsive skin
	Self-cleaning coatings	Lotus leaf	Self-cleaning effect Water resistant	Self-cleaning material and skin Ice and snow free surface
	Waterloo International Terminal	Pangolin	Overlapping, flexible, sharp scale Extra defense Regulating the temperature Allow to air circulation	Flexible structure Movable panels Responsive skin Flexible skin materials
	Swiss Re Tower	Venus flower basket	Complex, lattice-like, glass skeleton Strong structural stability Round shape	Spiral, diagrid structures Aerodynamic skin Aerodynamic form
	Eastgate Tower	Termit mound	Passive ventilation Chimneys and air passages	Passive ventilating skin Climate adaptive skin
	CH2 Building	Termit mound	Passive ventilation Chimneys and air passages	Passive ventilating skin Climate adaptive skin Recycling materials and systems
	Q1 Building	Feather	Special morphological arrangements Regular division Low conduction	Modular elements Sophisticated sun shading system Effective shading systems
CONCEPT/EXPERİMENTAL DESIGN	**The Habitat 2020**	Living skin Stoma	Connection between the exterior and interior Elasticity and expansion	Active, breathing, living skin Interactive skin Flexible, dynamic skin
	Stoma brick	Stoma Pine cones Hair protecting eyes Human skin	Elasticity and expansion Response to changes in moisture Protection against dust, small particles Cooling through evaporation	Integration of multiple function Layered, deployable, dynamic skin A flexible perforated skin Climate adaptive skin
	Foliage façades	Fern	Sunlight interception capability	Effective sun shading systems
	AeroDimm	Cephalopod	Colour change Camouflage	Flexible, pneumatic, integrated skin Color-changing, communicative skin Responsive skin
	S.C.A.L.E.S.	Side-blotched lizard	Flexible, interconnected scales Colorful and textured skin Moisture harvesting	Smart sun tracking system Colorful and textured skin Water regulating skin
	Polar bear-Keep It Warm	Polar bear	Insulation Color change	Active skin Phase changing material and skin
	Porous wall claddings	Termite mound	Passive ventilation	Passive ventilating skin
	The Las Palmas Water Theatre	Namibian beetle	Collects water from fog Collecting water in driest weather	Water colleting skin
	Hydrological Center	Namibian beetle	Collects water from fog Collecting water in driest weather	Water colleting skin Fog and frost-free surfaces
	Deep skin	Shark	Micro and macro scales Aerodynamic Bacteria control	Adaptive skin Aerodynamic skin Bacteria, dirt, snow free surface

Building skin, which can adapt to all kinds of conditions with different techniques, can also integrate with its environment and therefore becomes sustainable as well. Principles, properties

and solutions of natural skins in Table 1 and Table 2 revealed the different concepts such as nature-inspired, biomimetic, bio-inspired, responsive, active, intelligent, (climate) adaptive, smart, interactive, high-performative, meteorsensitive, kinetic, dynamic, breathing, living skin and so forth. It is observed that these concepts are also used in the case studies. It is aimed that future building skin designs will have the features of natural skins.

As a result, natural world acts as a great idea bank for architectures to create ideas and to transform them into designs. In this context, biological solutions should be well identified and understood taking into account the problems in building skin designs. The architect should have the ability to interpret nature laws (from micro to macro levels) while creating the architectural object/building skin. Knowledge transformation process necessitates for architect to cooperate with various disciplines such as civil engineering, biology, physics, chemistry, climatology, physiology, psychology, ecology, computer engineering, cybernetics and artificial intelligence.

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BİYOÇEŞİTLİLİĞE DAİR KISA NOTLAR

Hakan BOZDOĞAN*

Ahi Evran Üniversitesi, Bitkisel ve Hayvansal Üretim Bölümü, Teknik Bil. MYO, Kırşehir

Özet:

Biyoçeşitlilik kavramı, her ne kadar üzerinde çokça konuşulan temel bir biyolojik kavram olsa da, böcek biyoçeşitliliğinin zihinlerde oluşturduğu belirsizlik henüz netlik kazanmamıştır. Yaşayan canlı türlerinin neredeyse 2/3'ünü oluşturan böcekler, doğanın baskın canlıları olma yolunda hızlı mesafe almaktadır. Bu açıdan bakıldığında böcek biyoçeşitliliği, entomolojinin diğer pek çok uğraşı dallarına ışık tutan zorunlu bir disiplindir. Eserde her bir böcek takımına ilişkin bölgesel tahmini ve yerli olmayan tür sayıları çıkarılmış, zoocoğrafik bölgelerin böceklerle ilgili olan floristik karakterleri tartışılmıştır. Her bir bölümün sonuç kısmında ise böcek bilimcilere ve diğer bilim insanlarına yönelik toplumsal farkındalık oluşturulmaya çalışılmıştır. Eserde ayrıca böceklerin besin ağı etkileşimi kapsamlı bir şekilde açıklanarak yakın gelecekte böcek taksonomistlerini bekleyen olası sorunlar ele alınmıştır. Bu çalışmada, editörlüğünü Robert G. Foottit ve Peter H. Adler'in üstlendiği Böcek Biyoçeşitliliği eserinin kısa değerlendirilmesinin yapılması amaçlanmıştır.

Anahtar Kelimeler: Robert G. Foottit, Peter H. Adler, Biyoçeşitlilik

**hakan.bozdogan@ahievran.edu.tr*

Analiz ve Değerlendirme

Kitap; Böcek Biyoçeşitliliği: Bölgesel Örnekler, takson örnekleri ve uygulamalar-yaklaşımlar olmak üzere 3 ana kısım ve 25 alt birimden oluşmuştur. İlk kısımda bölgesel (zoocoğrafik) farklılıkları yansıtan, ikinci kısımda ise takson düzeyinde örneklemeleri yansıtan biyoçeşitlilik kavramı anlatılmaya çalışılmıştır. 3. kısım olan son kısımda ise taksonominin araç ve yaklaşımlarına yer verilmiştir.

Bilindiği üzere, böcekler dünya üzerindeki diğer tüm canlı gruplarının global biyoçeşitliliğin % 58'inden fazlasını bünyesinde barındırmaktadır. Başta karasal ve akuatik olmak üzere tüm ekosistemlerde yaşam sürebilen canlılardır.

Böcek biyoçeşitliliği; şu an için kararsız ve muğlâk bir dönem yaşamaktadır. Taksonomist araştırıcı sayısında her geçen gün azalma gözlenmektedir. Bu durum zorunlu olarak birçok böcek grubunun taksonomik bilgisinin elde edilemeyeceği gerçeğini gözler önüne sunmaktadır. Özellikle biyoçeşitlilik yönetimi, koruma, sürdürülebilir gelişme, ekosistem yönetimi ve iklim değişikliği konularına getirilecek olan bakış açısının da o oranda azalmasına neden olmuştur.

Günümüzde böcek biyoçeşitliliğinin kantitatif değerlendirilmesi, böcek biyoçeşitliliğine ilişkin bildiğimiz ya da bilinmeyen yönlerin ve bilhassa insan etkisinin ya da ayak izinin bu çeşitliliğe olan etkisi önem arz etmektedir. Diğer yandan taksonomistin bilimsel anlamda eksiklikleri ve belirli böcek gruplarında sahanın genişliği, sözde taksonomistler kavramını gündeme getirmiştir.

Bu kitaptaki çoğu bölüm, modern dünyada böceklerin ve onların aktivitelerinin anlaşılmasını hız kazandıracaktır.

Ormanların çoğu Palearktik'te yer almaktadır. Anadolu; Akdeniz Altbölgesi ile Saharo-Gobian Çöl Bölgesi arasındaki zondur. Ancak sıklıkla step vejetasyonun hakim olduğu düşünülür. Yazar, eserinde Palearktikte yaşayan 5 böcek takımının (diptera, heteroptera, coleoptera, hymenoptera, lepidoptera) biyoçeşitliliğine ilişkin kısmi de olsa bilgi sunmuştur. Diğer yandan, Afro-Tropikal Bölgeye de habitat-yaşam döngüsü temelli yer vermiştir. Bu bölgedeki habitat transformasyonunda indikatör rol üstlenen gübre böceklerini, Afrika meyve sineklerinin ekonomik önemlerini ve koruyucu böcek gruplarını inceleyen araştırıcılardan eklentiler

yapmıştır.

Yazarlar, Hexapodların sadece tür bazında değil, birey olarak da sayı bakımından zengin olduğunu vurgulamaktadır. Örneğin Collembola yoğunluğunun karasal ekosistemlerde metrekarede 10^4 den 10^5'e kadar değiştiğini savunmuştur.

Eserde, eklembacaklılar ve kuş-memeli etkileşimi örgüsel olarak incelenmiştir. Örneğin, çoğu kuş familyaları yılın belirli dönemlerinde böcekleri zorunlu ve temel bir besin öğesi olarak alırlar. Bunun en belirgin örneği, British Columbia'nın Cariboo Bölgesindeki sarı başlı siyah kuşun, yaşamını ve hayat devrini önemli ölçüde yusufçuklara bağlı olarak geçirdiği gerçeğidir. Benzer şekilde, memeliler, örneğin, tamandua, tembel ayı, Afrika Oryantal pangolinleri ve çok sayıda predatör memeliler, karınca ve termit kolonileri böceklerini besin olarak tüketmektedirler.

Yazarlar, eserinde böcek bilimcilerce dikkat çekici bazı bilimsel realitelere de yer vermiştir. Örneğin, tüm dünyada %1-2'den daha az oranda fitofag böcek bulunsa da yine de fitofagların ciddi anlamda tahrip edici bir etkiye sahip olduğunu vurgulamıştır. Ayrıca üzerinde her ne kadar tartışmalar yürütülüyor olsa da bitki virüsü da taşıyabilen kahverengi bitki piresi *Nilaparvata lugens* (Stål), Güney Asya'da her yıl 1.23 milyar dolarlık pirinç kaybına neden olduğunu belirtilmiştir.

Farklı zoocoğrafik bölgelerdeki tür çeşitliliğini anlatırken, o sahadaki bilhassa doğa müzelerinde emeği geçen bilim insanlarının çalışmalarına başvurulması yerinde olmuştur. Yazar, belki de çok az eserde değinilen, böcek taksonomistlerinin açmazlarını, arazi çalışmalarındaki zor süreçleri ve taksonomistin ilerleyen yıllardaki durumunu açıklayıcı yönde bilgiler sunmuştur.

Yazar, Amazon yağmur ormanlarındaki tür çeşitliliğini, zonlaşma ve dağ oluşumlarındaki ilişki ve ilintiyi sayısal değerler kullanarak açıklamayı tercih etmiş ve bu yönüyle anlaşılırlığı kolay hale getirmiştir. Diğer yandan, içerik hem olgusal hem de teorik örneklerle verilmeye çalışılmıştır. Yazarın kullandığı kaynaklar içerikle direkt ilintili olmasına karşın, detaydan uzaktır. Diğer bir ifade ile daha fazla kaynak kullanımına gereksinim duyulmaktadır.

Yazarlar, tür ve tür altı taksonlarda doğru teşhisin yapılması adına mitokondrial rna'nın önemine de vurgu yapmışlardır. Araştırıcılar, mitokondrial gen sekansları ile morfolojik taksonomiden

moleküler taksonomiye geçişin çok daha kolay olacağını bildirmişlerdir. Pek çok araştırıcı, böcek türlerinin dörtte birinin mtDna sekansları ile karakterize olabileceği konusunda ittifak etmişlerdir. Dna barkot uygulamalarının Lepidoptera, Diptera, Coleoptera, Hymenoptera, Collembola ve Ephemeroptera takımlarındaki uygulamalarına kısmen yer vermiş; ancak bu konuyu işlerken resimlerden ziyade yazınsal anlatıya ağırlık vermiştir.

Yazar, Nearktik Bölge böcek biyoçeşitliliğini işlerken ilginç saptamalarda bulunmuştur. Nearktik böcek türlerinin % 35'inin hâlâ tanımlanmadığını, Nearktikteki 1000'den fazla böcek türünün tehlike altında olduğunu ve 160 türün ise Amerikan hükümeti tarafından korunduğunu göstermiştir. Nearktikte, Ekojeoklimatik faktörlere bağlı olarak değişkenlik gösteren biyoçeşitlilik güneyden kuzeye büyük bir azalma gösterir. Arizona ve Teksas gibi güneybatı eyaletlerdeki biyoçeşitlilik en fazla iken Kanada yakınlarında ve güneydoğudaki Kalifornia ile Florida'dır. Nearktik karasal faunasında 144 binden fazla böcek türü yaşadığı göz önüne alındığında bu türlerin ne acıdır ki çok azının larval durumuna ilişkin bilgi bulunmaktadır. Mevcut rakamın neredeyse yarısından fazlasının tanımlanması yapılmamıştır ve teşhisi yapılan türlerin bir kısmının tekrar değerlendirmeye ihtiyaç olduğu bilinmektedir.

Sonuç

Taracad Narayanan Ananthakrishnan tarafından 2010 yılında yazılan *"Böcek Biyoçeşitliliği: Fonksiyonel Dinamikler ve Ekolojik Perspektifler"* isimli biyoçeşitlilik kaybının günümüzde önemli bir dünya sorunu olduğu ifade edilmiş ve insan refahının tesis etmek için temel ekolojik kaynakları gerekliliği işaret edilmiştir. Öte yandan orman arazilerinin zarar görmesi ya da yok edilmesi gibi sorunların farklı ekosistemlerde biyoçeşitliliğin değerlendirilmesini zorunlu kıldığını vurgulamıştır. Ancak ne var ki bu eserde böcek takımları, *"Böcek Biyoçeşitliliği"* kitabında olduğu şeklinde alttakım, familya ya da cins düzeyinde irdelenmemiştir. Diğer yandan editörlüğünü Geoff M. Gurr, Steve D. Wratten ve William E. Snyder'in yaptığı *"Biodiversity and Insect Pests''* isimli eser içeriğinde her ne kadar böcek biyoçeşitliliğini işleyen kısımlar barındırsa da ekonomik ürün kaybına neden olan böceklerin biyoçeşitliliğine ışık tutmuştur ve bu yönüyle sistematik entomoloji çalışan araştırıcılara hitap etmemektedir. Bunun yanısıra Peter W. Price editörlüğünde kaleme alınan *"Böcek Biyoçeşitl*iliği'', *"Insect Ecology''* isimli eser ile

taksonomik benzerlik gösterse dahi daha güncel bir kaynak durumundadır.

Eserin önem derecesini artıran belki de en önemli faktör hiç şüphesiz yazarları olmuştur. Öyle ki Peter H. Adler böcekleri; davranış, ekoloji, genetik sistematik ve medikal yönleriyle araştıran yetkin bir araştırıcı konumundadır. Eserin diğer mimarı olan Robert G. Foottit ise, çok çeşitli habitatlarda yaprak bitlerini morfolojik ve içerisinde DNA mikrosatellitlerin de yer aldığı moleküler yönleriyle inceleyen Kanada Ulusal Böcek Koleksiyonu için Ulusal Eklembacaklı Bilgi Sistemi Projesi geliştiren girişimci bir entomologdur.

Eserde, üzerinde çokça çalışma yapılmış olan Amerika'nın tropik ve subtropik bölgelerinde yaşam süren pamuk kozası buğday biti *Anthonomus grandis grandis* türünün *22* milyon dolardan daha fazla ürün kaybına neden olduğu tespit edilmiştir. Benzer şekilde *Dendroctonus frontalis* türünün ise Amerika'nın güney kısmında sadece 18 ayda 10 milyon dolar değerindeki yaklaşık 40 bin ağacı öldürdüğü tespit edilmiştir. Kınkanatlı böceklerin biyomühendislik ve ilintili disiplinlerde geniş bir araştırma aracı olarak kullanılacağı eserde yer alan çarpıcı kısımlar arasındadır. Elitral açılış-kapanış mekanizması havacılık ve astronomi mühendisliği için ilham kaynağı durumundadır. Yaklaşık 1 cm uzunluğundaki fırıldak ya da deveran böcekleri (Gyrinidae), su yüzeyinde 55 cm $^{s-1}$ yüzerler ve saniyede 12 yatay rotasyon yaparlar. *Hydrobius fuscipes* (Hydrophilidae) akuatik larvası, suyun alt yüzeyinde uzuvsuz kayarak hayranlık oluşturucu bir davranış sergilemektedir.

Söz konusu eser, önlisans, lisans ve kısmi anlamda lisansüstü eğitimde temel başvuru kaynağı olarak kullanılmaya uygun olup biyoçeşitliliği genel hatlarıyla kavramada yeterlidir. Emek verilmiş ve üzerinde yoğunlaşılmış bir eserdir. Renkli anlatıların ve okuyucuyu yormayan sayfa dizaynının yapılması ile eserin okur kitlesinin artış gösterebileceği düşünülmektedir. Eser, dil ve anlatım özellikleri bakımından yalın ve anlaşılır bir çerçevededir.

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Kırklareli Üniversitesi Mühendislik ve Fen Bilimleri Dergisinde fen ve mühendislik alanında özgün araştırma makaleleri, derlemeler, kısa makaleler, teknik not, vaka takdimleri, kitap eleştirileri ve bilimsel nitelikli editöre mektuplar yayınlanır. Dergi Aralık ve Haziran aylarında olmak üzere yılda iki kez yayınlanır. Yayınlanmak üzere gönderilen eserlerin başka bir yerde yayınlanmamış veya yayınlanmak üzere gönderilmemiş olması gerekmektedir. Derginin yayın dili Türkçe ve İngilizcedir. Dergide yayınlanacak eserlerin her türlü sorumluluğu yazar/larına aittir. Makaleler, http://dergipark.ulakbim.gov.tr adresine gönderilmelidir. Makalenin hakem incelemesi için kabul edilmesi durumunda, Telif Hakkı Devir Formu tüm yazarlarca imzalanarak editörlüğe gönderilmelidir.
Dergiye gönderilen makaleler, öncelikle Dergi Yayın Kurulu tarafından bilimsel içerik ve şekil bakımından ön incelemeye tabii tutulur. Dergi Yayın Kurulu, yayınlanabilecek nitelikte bulmadığı veya yazım kurallarına uygun hazırlanmayan makaleleri hakemlere göndermeden red kararı verme hakkına sahiptir. Değerlendirmeye alınabilecek olan makaleler, incelenmek üzere iki ayrı hakeme gönderir. Dergi Yayın Kurulu, hakem raporlarını dikkate alarak makalelerin yayınlanmak üzere kabul edilip edilmemesine karar verir.

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2. Çizimler ve tablolarla birlikte, makaleler 25 sayfadan, teknik notlar 6 sayfadan daha uzun olmamalıdır.
3. Yazı, elektronik ortamda (CD veya e-posta eki) dergi e-posta adresine veya dergi yazışma adresine gönderilmelidir.
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5. Bölümler (i) özet ve anahtar kelimeler, (ii) abstract and keywords (İngilizce başlık, özet ve anahtar kelimeler), (iii) ana metin (giriş, materyal ve metod, sonuçlar vb.), (iv) semboller, (v) teşekkür (gerekliyse) ve (vi) kaynaklar sırası içinde düzenlenmelidir.
6. Başlık kısa ve açık olmalı, içeriği yansıtabilmelidir. Başlık büyük harfle ortalanarak yazılmalıdır.
7. Yazar/ların adları kısaltmasız, başlığın altına yan yana, soyadlar büyük harfle ortalanarak 11 punto boyutunda yazılmalıdır. Yazar isimlerinden sonra virgül ve adres belirtmek için üst simge olarak rakam kullanılmalıdır. Yazışmaların yapılacağı sorumlu yazar isminde mutlaka üst simge yıldız (*) sembolü olmalıdır. Adres/ler tam yazılmalı, kısaltma yapılmamalıdır. Sorumlu yazarın e-mail adresi dipnot olarak bulunmalıdır. Yazar adları yazılırken herhangi bir akademik unvan belirtilmemelidir.
8. Özet (ve Abstract) çalışmanın amacını, kapsamını, yöntemini ve ulaşılan sonuçları kısaca tanımlamalı ve 200 kelimeyi aşmamalıdır. En az üç tane anahtar kelime verilmelidir. Anahtar kelimeler, zorunlu olmadıkça başlıktakilerin tekrarı olmamalıdır. Başlık, Özet ve İngilizce başlıklı Abstract birinci sayfaya sığdırılmalı, birinci sayfanın altında on satır boş bırakılmalı ve ana metin ikinci sayfadan başlatılmalıdır.
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10. Semboller uluslararası kullanıma uygun seçilmeli; her bir sembol ve varsa kısaltmalar ilk kullanıldığı yerde tanımlanmalı, ayrıca metnin sonunda (Kaynaklardan önce) tüm semboller alfabetik sıra ile (önce Latin, sonra Yunan alfabesi) listelenmelidir.
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> *Örnek:* [2] Kraus. H., Thin Elastic Shells, New York. Wiley, 1967.

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> *Örnek:* [3] Cappleman. O., Communication in the Studio, FIDE'98 International Conference on First Year Architectural Design Education Proceedings, Faculty of Architecture İstanbul Technical University, Cilt V, S 48-54, 1998

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> *Örnek:* [4] Özşahin. B., Yalıtım Kalıplı Donatılı Beton Duvarlı Binaların Yapımsal ve Ekonomik Uygulanabilirliği, Doktora Tezi, Trakya Üniversitesi Fen Bilimleri Enstitüsü, S 5-9, 2011

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> *Örnek:* [6] Pieper. C. M., Introduction to Activity Based Costing, ATechnical Bulletin From ABC Technologies, www.abctech.com 1998, Erişim tarihi: 12.10.2014

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Example: [6] Pieper. C. M., Introduction to Activity Based Costing, A Technical Bulletin From ABC Technologies, www.abctech.com 1998, 12.10.2014

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