

## A NOVEL SURVEY ON SOLVENT BASED-DYES CONTAINING SHELLAC AND PUMICE

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**Abstract:** This study aimed the dyes as decorative usage and improving the physical properties by using solvent based-dye with additives to evaluate in construction and chemical applications. The physical tests as viscosity, hydrophobicity, drying time, gloss effect, hiding power/transparency were applied on surfaces. Taguchi Method was used as an optimization method and characterization of molecular bonds was investigated with FT-IR. Shellac was used for protection of metallic surfaces and pumice increased the adhesive effect of dye. The test results showed that the additives did not affect the glossiness, color availability and drying time as a negative result. When the prepared dyes compared reference dyes, it was seen that hydrophobicity and hiding power/transparency effects were increased. FT-IR spectra showed that the prepared dyes had similar bonds with reference dyes.

**Keywords:** Dye, Solvent, Taguchi, FT-IR

### Pomza ve Gomalak İçeren Solvent Bazlı Boyalar Üzerine Yeni Bir Araştırma

**Öz:** Bu çalışmada; inşaat ve kimya sektöründe kullanılmak üzere solvent bazlı boyaya çeşitli katkı maddeleri eklenerek fiziksel özelliklerin geliştirilmesi ve dekoratif amaçlı olarak kullanılması hedeflenmiştir. Yapılan çalışmada viskozite, parlaklık, kapaticılık, hidrofobiklik ve kuruma süresi gibi farklı fiziksel testler uygulanmıştır. Optimizasyon metodu olarak, Taguchi metodu kullanılmış ve FT-IR cihazı ile moleküler bağ karakterizasyonu incelenmiştir. Burada, gomalakın metal yüzeylerde koruma sağladığı ve pomzanın ise yapışma özelliğini arttırdığı gözlemlenmiştir. Yapılan testler sonucunda kullanılan katkıların, parlaklık, renk uygunluğu ve kuruma süresine olumsuz bir etkisinin olmadığı gözlemlenmiştir. Referans boyaya kıyasla, hazırlanan boyaların hidrofobikliği ve kapaticılığı arttırıcı etkisinin olduğu gözlemlenmiştir. Deneylerin FT-IR spektrumları incelendiğinde ise referans boyayla benzer bağ karakterizasyonu olduğu gözlemlenmiştir.

**Anahtar Kelimeler:** Boya, Solvent, Taguchi, FT-IR

## 1. INTRODUCTION

Boron is an element in rocks, soil, water and various sources. Economically sized deposits of boron minerals are generally seen in arid areas with volcanism. These deposits are being exploited in Turkey, the United States, and other countries (Woods, 1994). Boron compounds are important raw materials in many branches of industry (Kucuk and Kocakerim, 1994). Turkey has the 72% of world borate reserves which are able to use as important raw materials in many branches of industry, and used increasingly and expanding continuously in the production of medicines, disinfectants, cosmetics, detergent materials and in the glass, polymer, dye and plating, steel, refractory materials industries (Mergen et al., 2003). Important boron mineral

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reserves are gathered in most places around the world, especially in Turkey (Kalafatoglu and Örs, 2003). Increasing usage of additives as a flame retardant or smoke inhibitor in plastics, woods, textile products, dyes, and construction materials is expected to decrease the loss of life and material in fire disasters. (Durgun, 2010).

Shellac is a mixture of polyesters and single esters and it forms from a few hydroxyl and carboxyl groups. The number of carboxyl groups has an effect on the physicochemical properties of shellac film (Altinsoy and Caliskan, 2014).

Pumice is a cheap and readily available construction material (Kocadagistan and Kocadagistan, 2016). Pumice is a rock that has porous structure. Pumices have a porous structure due to the result of volcanic events. Thanks to pores, pumices provide high insulation (Kul et al., 2017). In literature, pumice was used as adsorbent for removing reactive azo dye from watery solutions (Veliev et al., 2006). In development of mechanical theory, it is seen that pumice has adhesive effect on various surfaces (Pizzi and Mittal, 2003).

Dyes are widely used in most of area in daily life. Not only decorative effect but also protective purposes are led to using of dyes (Panyakaew and Fotios, 2011). Dyes are named as water based and solvent based-dyes (Ozturk, 2015). Beside some disadvantages like long lasting drying period and strong odour, dyes provide a high gloss on metal surfaces (Moreno et al., 2015; Stoye and Freitag, 1998). Water-based dyes have lower levels of volatile organic compounds that makes water-based dyes environment friendly (Law et al., 2010; [http://ec.europa.eu/environment/air/pollutants/stationary/paints/paints\\_legis.htm](http://ec.europa.eu/environment/air/pollutants/stationary/paints/paints_legis.htm)). To eliminate the negative and enhance physical properties of dyes, some types of additives were used (Kowalczyk et al., 2013). Recent studies have focused on property enhancing and strengthening of dyes (Kymalainen and Sjöberg, 2008).

Taguchi is a statistical method to optimize the process parameters and improve the quality of components in production by reducing the cost. The graphs in method give optimum parameter values for experiments.

Taguchi method is based on orthogonal array of experiments which reduces number of experiments when compared with conventional factorial methods (Bayrak, 1996; Canyılmaz, 2001; Singaravel and Selvaraj, 2016).

In this study, unlike the studies in the literature, pumice, shellac and boric acid were grinded and homogenized with adding to dye by using an appropriate polymeric binder. Shellac, pumice and boric acid were used to improve the physical properties of dyes with triple effect. The optimum parameters were determined by using Taguchi method for 3 parameters and 3 levels. In conclusion, it was seen that the usage of additives effected the physical properties of solvent based-dyes.

## **2. EXPERIMENTAL METHOD- MATERIALS**

The materials and chemicals used in this study were pumice (from Nevsehir region), boric acid ( $H_3BO_3$ ) (Eti Maden), shellac (secretions of the lac insect, *Laccifer lacca*), solvent based-dye, aluminium plates (10x10 cm), applicator (TQC-Bird Film Applicators 4- Sided) and ethyl alcohol (Technical purpose).

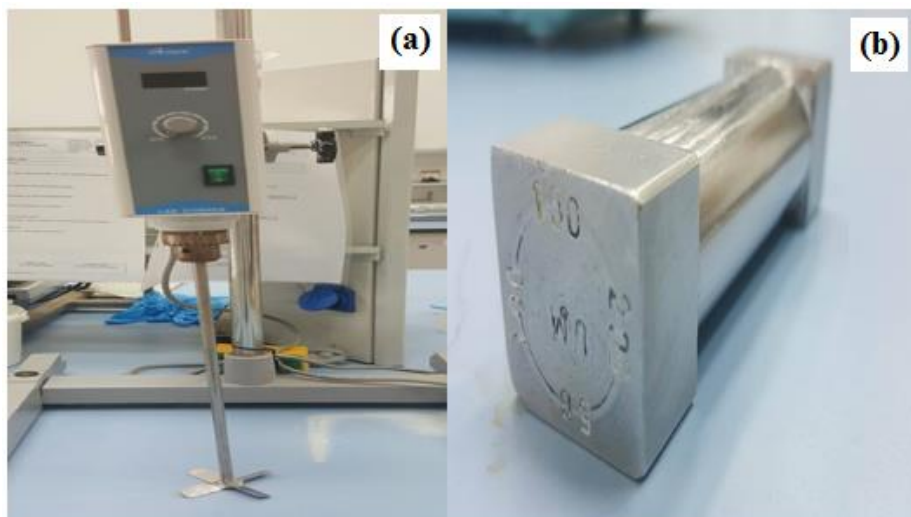
### **2.1. Additive Preparation**

Pumice, boric acid were brought to small particle size (+200 mesh) with using ball mill. Shellac, as dry flakes, was dissolved in ethyl alcohol (9%, w/w) at 96°C and added to dye as solution form.

### **2.2 Experimental Study**

The pumice, boric acid and shellac were used in range of 0-15% (in terms of dye, w/w). The dye, pumice, boric acid and shellac were stirred by using mechanical stirrer (1000 rpm-3 min). The applicator film thickness was used with 150  $\mu$ m (Figure 1).

Opacity charts (the surface chequered with black and white colours) were used for the visual tests. Dyes samples were prepared according to Taguchi optimization method. In this study, 3 parameters (boric acid, pumice and shellac) and 3 levels were used as given in Table 1.



**Figure 1:**  
Equipments: (a) Mechanical stirrer, (b) Applicator

**Table 1. Experimental parameters and levels**

	Parameters	Level 1	Level 2	Level 3
1	Shellac	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>
2	Boric Acid	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>
3	Pumice	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>

**Table 2. L-9 Orthogonal array for solvent based-dyes**

No	Shellac	Boric Acid	Pumice	Viscosity (cP)
1	1	1	1	1500
2	1	2	2	2900
3	1	3	3	3400
4	2	1	2	2300
5	2	2	3	2600
6	2	3	1	2200
7	3	1	3	2000
8	3	2	1	2000
9	3	3	2	2600

Letters in level section (S, B and P) represent amount of additives and changed 0-6% (w/w). Taguchi Optimization Method L-9 orthogonal array was given in Table 2 for additives. According to Table 2, sample 1 was reference solvent based-dye and other samples were prepared with additive agents.

### 2.3. Characterization

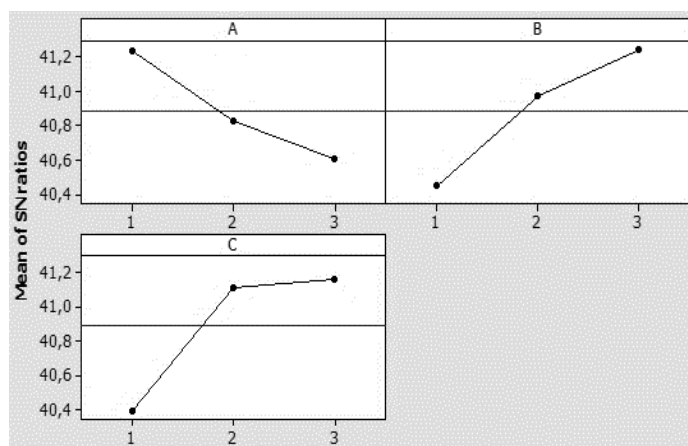
The FT-IR (Bruker–Tensor 27) analysis was performed to characterize the raw materials and compare the literature. The major structural groups were detected from their infrared patterns. The tests as cross-cut adhesion test, visual tests, hydrophobicity and gloss effect were carried out on metal surfaces.

## 3. RESULTS AND DISCUSSION

### 3.1. Optimization Results

Taguchi developed a special design of orthogonal arrays to study the entire parameter space with a small number of experiments only (Vankantia and Ganta, 2014). For the Taguchi design and analysis of results Minitab Release 13.20 Statistical Software was used after determined parameters. In this study, Taguchi’s L-9 orthogonal array table was used to carry out experiments by choosing three parameters at three levels (Table 2).

In the orthogonal array of L-9 type, L and subscript 9 means Latin square and the number of experiments, respectively. A full factorial approach will require 27 experiments to be conducted for optimizing a process while in fractional factorial using an L-9 orthogonal array the number of experiments is reduced to nine. The optimum experiment was No:3 as given in Table 2 and Figure 2.



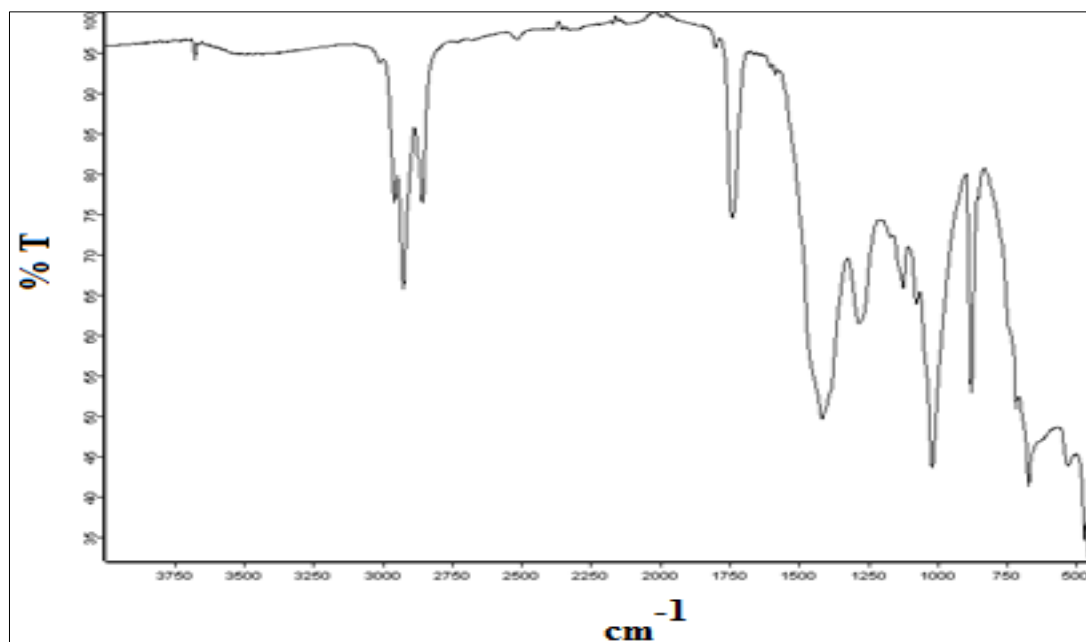
**Figure 2:**  
S/N ratio in Taguchi Method

### 3.2. The Results of FT-IR Analysis

Additives used in dyes are modified as hydrophobic. The system is immobilized with forming chemical bond between hydrophobic surfaces by interacting hydrogen bonds and other molecules in medium. Thereby, viscosity increases by using additives in dyes. For this purpose, FT-IR analysis was used to obtain the chemical structure in detail.

The infrared spectrum in the region of 1500-400  $\text{cm}^{-1}$  was a fingerprint of the region indicating structural features of pumice framework. The sharp peak around 1000  $\text{cm}^{-1}$  was

noticed in natural minerals as zeolit, pumice etc (Byrappa and Suresh Kumar, 2007). The peaks in range of  $1250\text{-}950\text{ cm}^{-1}$ ,  $720\text{-}650\text{ cm}^{-1}$ ,  $500\text{-}450\text{ cm}^{-1}$  were obtained due to asymmetric stretch, symmetric stretch and T-O bent, respectively. An FT-IR spectrum of pumice was shown in Figure 3. The C-O stretching band was observed at around  $1700\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$  in the FT-IR spectrum of pumice as specific two peaks (Ozturk Akbal et al., 2000). OH ( $3700\text{-}3000\text{ cm}^{-1}$ ) and aliphatic CH bands ( $3000\text{-}2800\text{ cm}^{-1}$ ). The quantity of the aromatic CH groups ( $1000\text{-}700\text{ cm}^{-1}$ ) was approximately the same as previous study (Varhegyi et al., 1998). In addition, it was seen that the chemical structure of dye prepared at optimum point was similar with reference solvent based-dye due to being physical mixture (Figure 3, Figure 4).



**Figure 3:**  
FT-IR spectrum of reference dye

### 3.3. Cross-cut Adhesion Test

Dyed surfaces were tested with adhesive tape and the results were evaluated according to flaked away from aluminium surfaces. According to the test results it was seen that the additives increased the resistance of the dye adhesion. The dye (No:3) showed the best adhesion resistance. Reference dye showed weak resistance to adhesion test compared to dyes including pumice and boric acid. Shellac didn't contribute to any properties related with adhesion. The results of experiments were given in Figure 5.

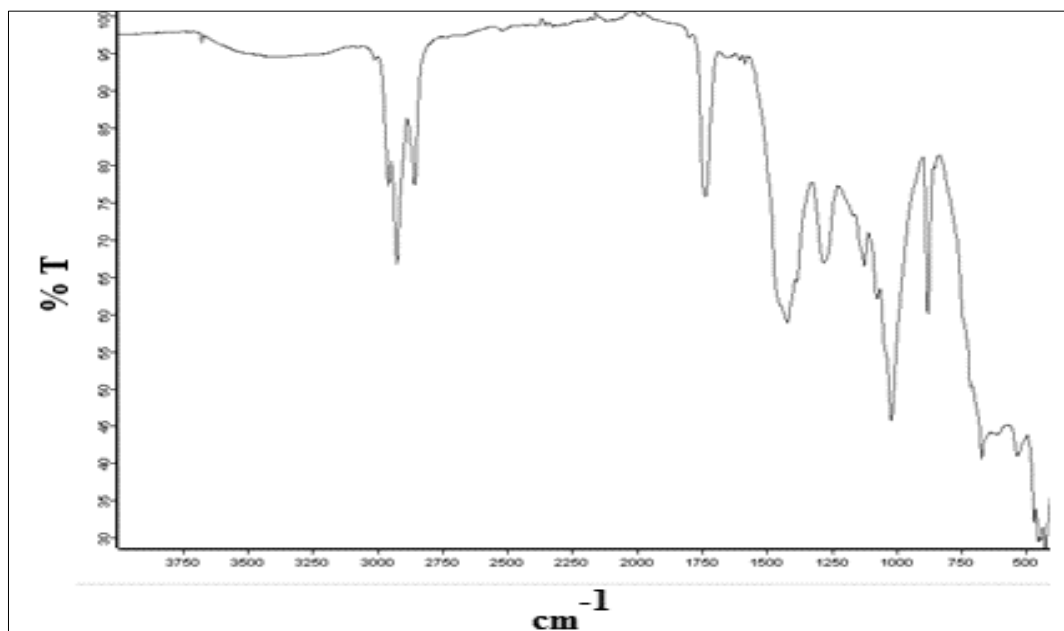
### 3.4. Visual Test

Opacity charts were used to determine a physical property. Visual test results showed that dyes prepared had concealer property for walls and decoratives due to its off-white colour when compared with reference dye (Figure 6).

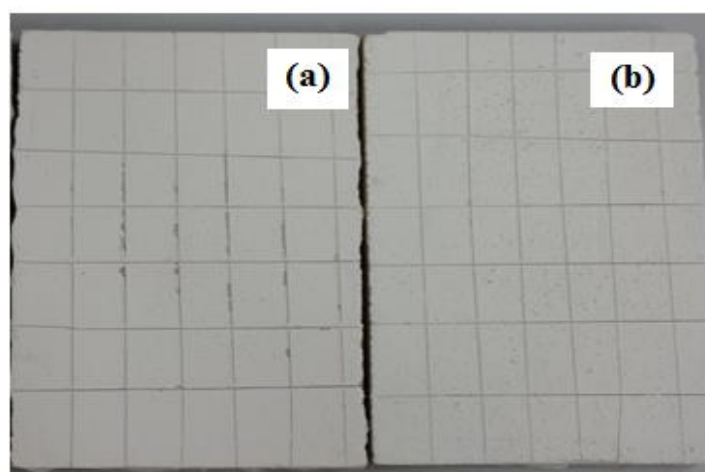
### 3.5. Hydrophobicity Test

Lipophilicity determinations for organic dyes used for natural fibres are relevant. Lipophilicity can be assessed from hydrophobicity studies for dyes (Seclaman et al., 2002). Wettability is an important property of solid surfaces from both fundamental and practical aspects. However, various industrial products require not only hydrophilicity but also hydrophobicity. Given the limited contact areas between solid surface and water, chemical

reactions or bonding formation through water are limited on a super-hydrophobic surface (Nakajima et al., 2001). Water was dropped on the dry coating film a period of time as a volume of 0,1 ml pipette. Then, the flowing of waterdrop was observed. As a result, surface was hydrophobic in the dry dye film (Figure 7).



**Figure 4:**  
FT-IR spectrum of dye (No:3)



**Figure 5:**  
Cross cut adhesion test: (a) Reference dye, (b) Dye (No:3)



**Figure 6:**  
Visual test: (a) Reference dye, (b) Dye (No:3)



**Figure 7:**  
Hydrophobicity test result for No:3

### 3.6. Gloss Effect

Dyes were dried in atmospheric conditions for 24 h which applied on metal surfaces with applicator. Gloss effect values of dyes dried were measured with gloss effect apparatus (micro-TRI-gloss, BYK) (Table 3). The glossiness of dye (No:3) was approximate value to reference dye.

**Table 3. Gloss effect for reference dye and optimum dye point (No:3)**

No	20°	60°	85°
Reference dye	1.4	3.7	4.9
Dye (No:3)	1.3	2.4	3.8

## 4. CONCLUSION

Consequently, the optimum parameters were determined by using Taguchi method for 3 parameters and 3 levels. The optimum mixture was experiment 3 for 1-3-3 in Taguchi method. According to classification of additives; pumice enhanced the adhesion strenght of dyes, shellac strengthened dye against harsh ambient conditions, boric acid did not improve significantly any physical properties of dyes. Using pumice and shellac as additives in suitable amounts according to usage area of dyes will enhance usage of dye in various applications and protect surfaces.

## REFERENCES

1. Altinsoy A.R. and Caliskan, S. (2014) *Investigation of thermal and physical properties for construction dyes containing different boron chemicals and shellac*, Yildiz Technical University, Istanbul.
2. Bayrak, Z. (1996) *Applying Taguchi method in the shield of practising quality control*, MSc Thesis. Kocaeli University, Kocaeli.
3. Byrappa, K. and Suresh Kumar B.V. (2007) Characterization of zeolites by infrared spectroscopy, *Asian Journal of Chemistry*, 19(6), 4933-4935.
4. Canıylmaz, E. (2001) *Taguchi method in quality improvement and an application*, MSc Thesis. Gazi University, Ankara.
5. Durgun, Z.G. (2010) *Çeşitli Kalsiyum Boratların Sentezi Karakterizasyonu ve Alev Geciktirici Etkinliklerinin İncelenmesi*, MSc Thesis. Ankara University.
6. [http://ec.europa.eu/environment/air/pollutants/stationary/paints/paints\\_legis.htm](http://ec.europa.eu/environment/air/pollutants/stationary/paints/paints_legis.htm), Accessed Date: 12.01.2017.
7. Kalafatoğlu, İ.E. and Örs, S.N. (2003) 21. yüzyılda bor teknolojileri ve uygulamaları, *BAÜ Fen Bilimleri Enstitüsü Dergisi*, 5(1), 59-71.
8. Kocadagistan, B. and Kocadagistan, E. (2016) Batch and column removal of the dye blue 3R over pumice, *Desalination and Water Treatment*, 57(58), 28042-28055. doi: 10.1080/19443994.2016.1184186
9. Kowalczyk, K., Łuczka, K., Grzmił, B. and Spychaj, T. (2013) Anticorrosive 2K polyurethane paints based on nano and microphosphates with high dispersing additive content, *Progress in Organic Coatings*, 76, 1088–1094. doi: 10.1016/j.porgcoat.2013.03.003
10. Kucuk, M. and Kocakerim, M. (2005) Optimization of dissolution of ulexite in water saturated with sulphur dioxide, *Chemical Engineering and Processing*, 44(9), 1005-1011. doi: 10.1016/j.cep.2004.11.006
11. Kul, A.R., Benek, V., Selçuk, A. and Onursal, N. (2017) Using natural stone pumice in Van region on adsorption of some textile dyes, 4 (2), 525-536. doi: 10.18596/jotcsa.292662
12. Kymalainen, H.R. and Sjöberg, A.M. (2008) Flax and hemp fibres as raw materials for thermal insulations, *Building and Environment*, 43, 1261-1270. doi: 10.1016/j.buildenv.2007.03.006
13. Law, C., Pathirana, S.C., Li, X., Anderson, A.Y., Barnes, P.R.F., Listorti, A., Ghaddar, T.H. and O'Regan, B.C. (2010) Water-based electrolytes for dye-sensitized solar cells, *Advanced Materials*, 22(40), 4505-4509. doi: 10.1002/adma.201001703
14. Mergen, A., Demirhan, M.H. and Bilen, M. (2003) Processing of boric acid from borax by a wet chemical method, *Advanced Powder Technology*, 14, 279-293. doi: 10.1163/15685520360685947
15. Moreno, M., Lampard, C., Williams, N., Lago, E., Emmett, S., Goikoetxea, M. and Barandiaran, M.J. (2015) Eco-paints from bio-based fatty acid derivative latexes, *Progress in Organic Coatings*, 81, 101–106. doi: 10.1016/j.porgcoat.2015.01.001
16. Nakajima, A., Hashimoto, K. and Watanabe, T. (2001) Recent studies on super-hydrophobic films, *Monatshefte für Chemie*, 132, 31-41.
17. Ozturk Akbal, F., Akdemir, N. and Nur Onar, A. (2000) FT-IR spectroscopic detection of pesticide after sorption onto modified pumice, *Talanta*, 53(1), 131-135.



18. Ozturk, A.B. (2015) *Investigation of thermal and physical properties for construction dyes containing different boron chemicals and shellac*, MSc Thesis. Yildiz Technical University, Istanbul.
19. Panyakaew, S. and Fotios, S. (2011) New thermal insulation boards made from coconut husk and bagasse, *Energy Buildings*, 43, 1732-1739. doi: 10.1016/j.enbuild.2011.03.015
20. Pizzi, A. and Mittal, K.L. (2003) *Handbook of Adhesive Technology*, Second Edition, Revised and Expanded, USA.
21. Seclaman, E., Sallo, A., Elenes, F., Crasmareanu, C., Wikete, C., Timofei, S. and Simon, Z. (2002) Hydrophobicity, protolytic equilibrium and chromatographic behaviour of some monoazoic dyes, *Dyes and Pigments*, 55, 69–77.
22. Singaravel, B. and Selvaraj, T. (2016) Application of Taguchi method for optimization of parameters in turning operation, *Journal for Manufacturing Science and Production*, 16(3), 1-5.
23. Stoye, D. and Freitag, W. (1998) *Paints, coatings and solvents*, Second Edition, Wiley-VCH.
24. Vankantia, V.K and Ganta, V.J. (2014) Optimization of Process parameters in drilling of GFRP composite using Taguchi method, *Journal of Materials Research and Technology*, 3(1), 35-41. doi: 10.1016/j.jmrt.2013.10.007
25. Varhegyi, G., Szabo, P., Till, F. and Zelei, B. (1998) TG, TG-MS and FTIR characterization of high-yield biomass charcoals, *Energy Fuels*, 12, 969-974. doi: 10.1021/ef9800359
26. Veliev, E.V., Öztürk, T., Veli, S. and Fatullayev, A.G. (2006) Application of Diffusion Model for Adsorption of Azo Reactive Dye on Pumice, *Polish Journal of Environmental Studies*, 15 (2), 347-353.
27. Woods, W.G. (1994) An introduction to boron: history, sources, uses, and chemistry, *Environmental Health Perspectives*, 102, 5-11. doi: 10.1289/ehp.94102s75

