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RESEARCH ARTICLE

REMOVAL of METHYLENE BLUE FROM AQUEOUS SOLUTIONS USING PINE CONE and STATISTICAL COMPARISON of ADSORBED MATERIAL

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ABSTRACT

In this study, pine cone, a previously unused biosorbent substance, was used to remove methylene blue from the aqueous solution. For this purpose, pine cones were first cut into pieces, then dried at room temperature, passed through a grinder, sieved in a 230 mesh sieve and brought to the appropriate dimensions and used in experimental processes. On pine cone and methylene blue biosorption; effects such as initial dye concentration, temperature, amount of biosorbent and equilibrium contact time were investigated. In the adsorption of methylene blue with pine cone, descriptive statistical analyzes and comparisons of time-dependent concentrations were made and the results were significant. Descriptive statistical analyzes and comparisons of the concentration were also made and it was seen that the adsorption did not varied depending on the temperature at different methylene blue concentrations.

Keywords: *Methylene Blue, Pine cone, Biosorbent*

1 .INTRODUCTION

Environmental pollution is one of the most important problems affecting human health in recent times. As a result of industrial processes, waste water is produced and most of them are produced as a result of the processes carried out in plants that do not have a treatment system such as paint and textile factory and are delivered directly to the receiving environment. This type of wastewater is continuously supplied to the environment such as rivers and lakes and prevents the transmission of these colored waters to sunlight, thus decreasing the dissolved oxygen concentration and photosynthetic activity. As a result, anaerobic conditions occur and aerobic organisms die [1,2].

Scientists are constantly working on the development of the most suitable methods for the removal of color and other impurities from dyes in waste water. Physical and chemical methods are generally used for this purpose, but these techniques have disadvantages such as being inexpensive in terms of facilities, equipment and materials and not completely eliminating the problem of environmental pollution. Methods used to remove harmful substances from water include ozonation, adsorption, chemical coagulation-flocculation, bio-absorption, chemical and photo-oxidation, nanotechnology and ion exchange. Color removal obtained by these methods varies according to the type of paint in the waste water, makes it difficult to choose the most appropriate method to be used for color removal from waste water [3].

Adsorption is one of the methods with high purification potential used to remove dyestuff organic substances from waste water [5, 6]. As an alternative to the expensive and complex activated carbon used in adsorption applications, which is one of the methods used in purification processes, many low cost and easily available materials are being searched. Among these biological adsorbents with high adsorption power, many microorganisms such as corn cob, peanut shell, sawdust, agricultural waste, rice waste, orange peel and fungus are used for color removal in dyestuff [7]. Numerous studies have been conducted among researchers on the removal of unwanted substances from wastewater. One of them is Özer et al. this is a study of dried peanut shells and the adsorption of methylene blue from aqueous solution. In this study, the effect of initial dye skin, temperature, particle size was investigated and optimum experimental conditions were determined. As a result of the study, it was concluded that dried peanut shells are a good adsorbent in removing methylene blue [8]. In addition, Faraco et al. in their study, they studied the color removal capacities of Pluerotus ostreatus and Phanerochaete chrysosporium fungi on 11 different dyes. As a result, they observed that pluerotus ostreatus on direct blue 1, and Phanerochaete chrysosporium on Reactive red 4, direct black 38 and disperse yellow 3 dyes provided 100% color removal [9]. In another study, Giahi et al. used waste tea as a biosorbent in the biosorption of methylene blue, a cationic dye from wastewater. In thermodynamic studies, it was observed that the adsorption equilibrium constant (KL) and maximum adsorption capacity (qmax) increased as the temperature increased. As a result of thermodynamic studies, the DH and DS values were calculated as 11,356 kJ/mol and 20.563 J/(mol K), respectively[10]. In this study, we investigated the statistical evaluation of some parameters such as initial dye concentration and temperature on the removal of methylene blue from wastewater by using natural pine cones as a biosorbent material.

In this study, we used natural pine cones as biosorbent material.Among the dyestuffs, methylene blue is a dark blue dye that is easily soluble in water (4g / L), ethanol and chloroform and has strong water retention[11,12]. This dye is of a cationic molecular structure with a molecular weight of 373.9 g mol-1. The molecular formula is ($C_{16}H_{18}ClN_3S.3H_2O$) (3,7-bis (dimethylamino) -phenazothium chloride). Methylene blue was chosen for this study because its adsorption ability was very strong. Although methylene blue is a weak antiseptic, it has a very effective use in combination with other antiseptic mixtures. One of the most common uses is its use as a redox indicator. As redox indicator in milk analysis and Au, B, Bi, Ce, Cu, Ga, Ge, Hg, In, Sb, Se, Sn, Tl, U, Zn, Pb, Fe, Cr, Ti, V, Mo, Sn and It is reported that it is used as a titrant or indicator in the determination of dissolved O2 [11, 13]. Methylene blue can be used to stain diphtheria bacterial cells and nerve tissue [12,14] or can be used to stain cotton in pure blue tones. In addition, the adsorption power of charcoal is measured using methylene blue [15]. Methylene blue is encountered in wastewater due to its use especially in textile sector and mentioned areas. Numerous studies are available in the literature on the determination and removal of toxic organic substances in waste water.

In this study, it is aimed to remove methylene blue dye from aqueous solutions by using pine cones obtained from natural environment. We also made descriptive statistics and comparisons of the adsorption of dye ions on the pine cone and the descriptive statistics and comparisons between the concentration amount and temperature.

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2.MATERIAL and METHOD

In the experimental stage, pine cone was used as adsorbent material (biosorbent) in adsorption studies.

2.1. Preparation of Pine cone:

The pine cone used in the study was collected from the campus area of Yüzüncü Yıl University in Van region. The pine cones (biosorbent) obtained therefrom were first cut into pieces by hand and kept at room temperature and removed from moisture. It was grinded into a powder, then it was brought to the appropriate dimensions using a 230 mesh sieve and used as such in the study.

2.2. Properties of Methylene Blue Dye:

Methylene blue; C16H18N3SCl.3H2O and a cationic dye with a molecular weight of 373.9 gmol-1. It has strong adsorption ability. In this study, it has been deemed appropriate to use this dyestuff. The following figure shows the chemical structure of Methylene Blue dye.

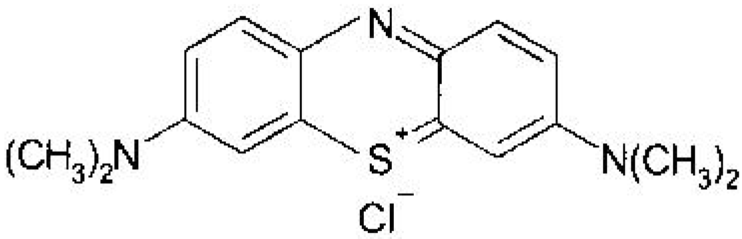

Figure 1. Chemical structure of methylene blue dye.

2.3. Statistical Analysis

Descriptive statistics for the feature emphasized;

Average; $\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$, Standard deviation;$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i-\bar{x})^2}{n-1}}$calculated worths ve minimum (x_{min}) ve maksimum (x_{max})values were determined. For the eight concentrations, one-way analysis of variance (ANOVA) was used to define whether there was a distinction between both time and temperature levels. Tukey multiple comparison test was used to define which group (s) the differentiation was caused by variance analysis. Statistical meaning level was taken as 5% in the calculations and SPSS statistical package program was used for the analyzes.

3. RESULTS

Descriptive statistics and comparison results of adsorption of methylene blue ions on pine cone; The concentration (100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm) and times were given in Table 1. According to Table 1; The variation between the timesand at the different concentrations were meaning ($p < 0.001$). According to a concentration of 100 ppm, methylene blue ions were adsorbed for an average of 57.99 units at 5 minutes, while 84.04 units were adsorbed at 300 minutes.Likewise, at a concentration of 150 ppm; 66.84 units were adsorbed on average at 5 minutes and 115.65 units were adsorbed on average at 300 minutes. In the 200 ppm concentration, 105.42 units of sample at 5 minutes and 139.28 units of sample were adsorbed at 300 minutes. For the other 250 ppm concentration studied, the adsorption amount of 125.61 units and 171.68 units, respectively, was found as a result of 5 minutes and 300 minutes of treatments. In the same way, in the 300 ppm concentration the adsorption amount of 134.46 units and 196.38 units , respectively, was found as a result of 5 minutes and 300 minutes of procedures.

Table 1. Descriptive statistics and comparison results of absorbance values for various time intervals

	Time	n	Mean	Std. D.	Min	Max	p		Time	n	Mean	Std. D.	Min	Max	p
100 ppm	5	3	57,99	6,02	51,276	62,884	0,001	250 ppm	5	3	125,61	3,47	121,96	128,876	0,001
	10	3	63,73	3,28	60,327	66,873			10	3	132,97	5,31	128,324	138,754	
	15	3	66,51	3,05	63,817	69,814			15	3	136,14	4,93	131,903	141,554	
	20	3	69,44	1,43	67,97	70,823			20	3	142,5	6,79	138,334	150,33	
	30	3	72,02	1,28	70,554	72,886			30	3	153,24	13,79	141,626	168,476	
	40	3	74,5	0,6	73,816	74,891			40	3	160,65	8,57	152,814	169,807	
	50	3	76	1,24	74,864	77,326			50	3	160,87	7	153,816	167,816	
	60	3	77,5	0,98	76,91	78,634			60	3	162,96	6,55	156,993	169,96	
	70	3	79,36	1,31	77,873	80,329			70	3	163,99	5,65	159	170,124	
	80	3	80,33	1,85	78,336	81,986			80	3	164,85	4,94	161,999	170,554	
	90	3	81,48	2,73	78,903	84,34			90	3	166,1	4,14	163,606	170,88	
	100	3	82,68	2,93	79,814	85,667			100	3	166,54	3,9	163,804	170,999	
	110	3	83,04	2,83	80,329	85,984			110	3	168,7	4,18	163,876	171,31	
	120	3	83,88	2,66	81,563	86,787			120	3	169,46	5,07	163,634	172,886	
	140	3	84,01	2,57	81,959	86,886			140	3	169,56	5,02	163,792	172,997	
	160	3	84,01	2,7	81,733	86,999			160	3	169,91	4,41	164,856	172,986	
	180	3	84,24	2,67	81,681	87,016			180	3	170,06	4,14	165,323	172,99	
	200	3	84,43	2,26	82,814	87,017			200	3	169,85	5,27	163,863	173,806	
	240	3	83,4	3,38	80,329	87,014			240	3	170,5	5,87	163,812	174,815	
	300	3	84,04	2,64	81,987	87,015			300	3	171,68	4,39	166,803	175,33	
150 ppm	5	3	66,84	2,67	63,814	68,864	0,001	300 ppm	5	3	134,46	3,77	130,816	138,336	0,001
	10	3	74,45	4,82	70,629	79,863			10	3	145,12	3,56	142,334	149,136	
	15	3	85,5	17,64	72,884	105,664			15	3	156,86	1,66	155,82	158,777	
	20	3	89,34	16,02	79,34	107,814			20	3	163,91	4,89	160,4	169,5	
	30	3	93,77	13,73	85,814	109,626			30	3	170,66	2,07	168,82	172,896	
	40	3	97,11	11,26	88,626	109,889			40	3	175,7	4,68	170,33	178,886	
	50	3	101,67	8,75	92,83	110,324			50	3	177,95	4,94	172,29	181,36	
	60	3	102,92	8,04	94,895	110,981			60	3	180,75	5,63	174,36	185	
	70	3	106,46	5,02	101,874	111,816			70	3	184,53	2,72	181,91	187,337	
	80	3	108,99	3,07	105,856	111,984			80	3	186,11	1,93	184,864	188,328	

	90	3	109,98	1,23	108,61	110,999	
	100	3	112,56	0,51	111,976	112,856	
	110	3	113,87	2,33	111,326	115,906	
	120	3	114,9	1,84	112,814	116,286	
	140	3	115,35	2,16	112,876	116,804	
	160	3	115,03	1,82	112,984	116,482	
	180	3	115,38	2,07	112,982	116,589	
	200	3	115,12	2,72	111,999	116,981	
	240	3	115,6	3,16	111,974	117,814	
	300	3	115,65	3,31	111,843	117,897	
200 ppm	5	3	105,42	4,5	100,814	109,814	0,001
	10	3	111,2	2,31	109,863	113,866	
	15	3	116,77	3,46	112,889	119,527	
	20	3	120,03	5,04	114,334	123,874	
	30	3	123,93	6,98	115,864	127,981	
	40	3	127,16	8,29	117,864	133,806	
	50	3	129,01	7,13	120,894	134,28	
	60	3	130,62	6,75	123	135,866	
	70	3	132,21	7,63	123,893	138,876	
	80	3	133,71	6,53	126,884	139,9	
	90	3	136,21	4,42	132	140,816	
	100	3	136,92	3,52	134,889	140,987	
	110	3	137,81	2,75	135,894	140,96	
	120	3	139,37	3,2	135,976	142,324	
	140	3	139,53	3,3	135,977	142,488	
	160	3	139,52	3,33	135,979	142,582	
	180	3	139,59	3,38	135,976	142,662	
	200	3	139,25	4,06	134,818	142,786	
	240	3	139,29	4,07	134,864	142,86	
	300	3	139,28	4,12	134,803	142,91	

90	3	188,27	2,9	186,336	191,6
100	3	191,02	1,63	189,85	192,88
110	3	193,09	1,26	191,886	194,403
120	3	195,5	3,57	191,782	198,903
140	3	195,56	3,56	191,885	198,986
160	3	195,78	3,87	191,887	199,633
180	3	195,5	4,47	190,874	199,786
200	3	195,76	4	191,724	199,716
240	3	195,58	4,89	190,56	200,333
300	3	196,38	6,18	190,479	202,803

The statistical results of the adsorption of methylene blue ions on pine cones at concentration (100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm) and temperature (25°C, 35°C and 45°C) values are shown in Table 2. According to Table 2, it was observed that the adsorption values of dye ions at different concentrations did not change depending on the temperature.

Table 2. Comparison of adsorption results at different temperatures and concentrations and descriptive statistics.

	^{0}C	n	Mean	Std. Deviation	Min	Max	p
100 ppm	25	20	75,527	8,412	51,276	82,814	0,231
	35	20	77,466	7,604	59,816	84,033	
	45	20	79,897	7,904	62,884	87,017	

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150 ppm	25 35 45	20 20 20	107,177 101,029 102,365	12,494 16,866 17,439	63,814 68,864 67,833	112,984 117,208 117,897	0,436
200 ppm	25 35 45	20 20 20	129,895 127,753 134,877	9,701 12,016 10,524	100,814 105,634 109,814	135,979 140,142 142,910	0,110
250 ppm	25 35 45	20 20 20	156,030 158,272 165,118	13,986 15,239 14,039	121,960 128,876 125,989	166,803 172,910 175,330	0,126
300 ppm	25 35 45	20 20 20	180,082 181,672 181,018	17,092 18,575 19,798	130,816 134,235 138,336	191,887 195,853 202,803	0,963

Figures 2-5, Adsorption of methylene blue dye on Pine Cone ; concentration (100 ppm, 150 ppm, 200 ppm, 250 ppm, 300ppm)

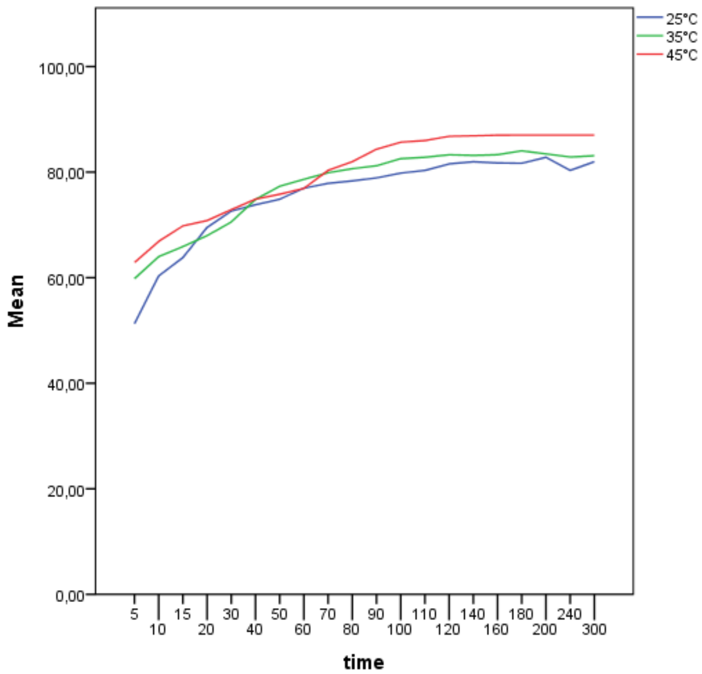

Figure 2. 100 ppm

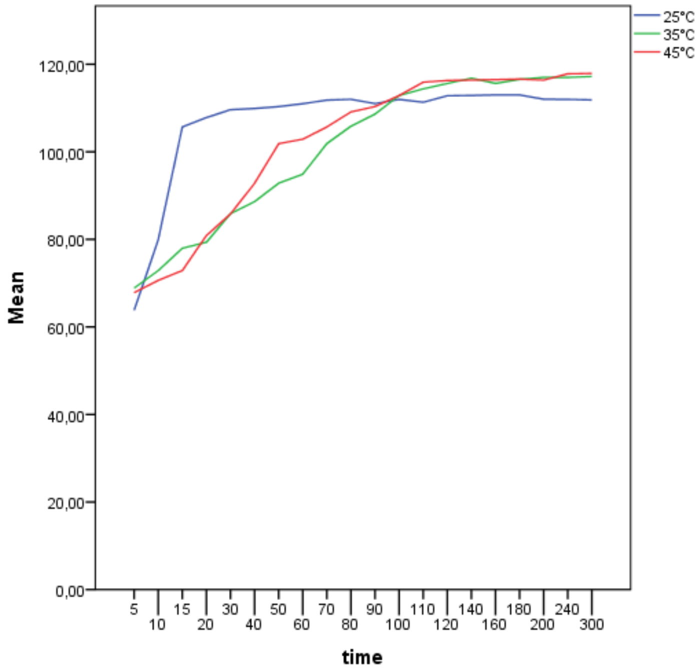

Figure 3. 150 ppm.

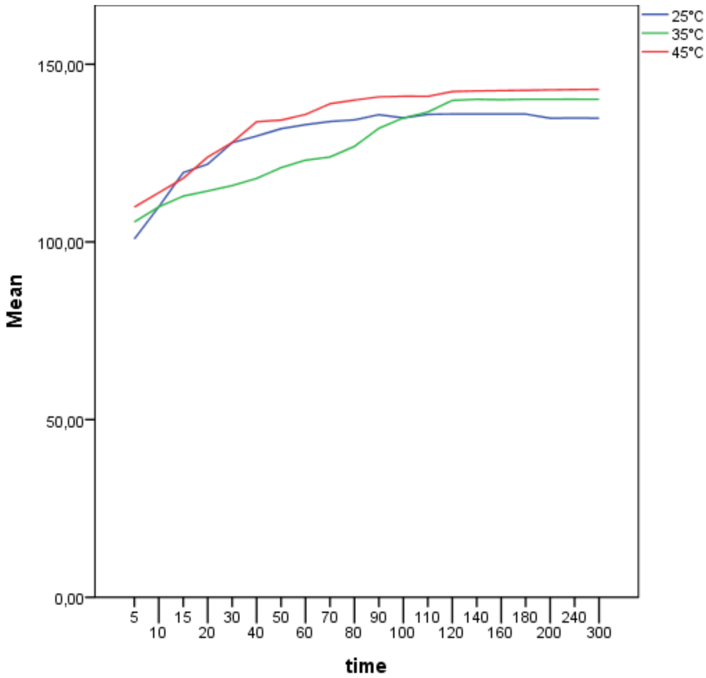

Figure 4. 200 ppm.

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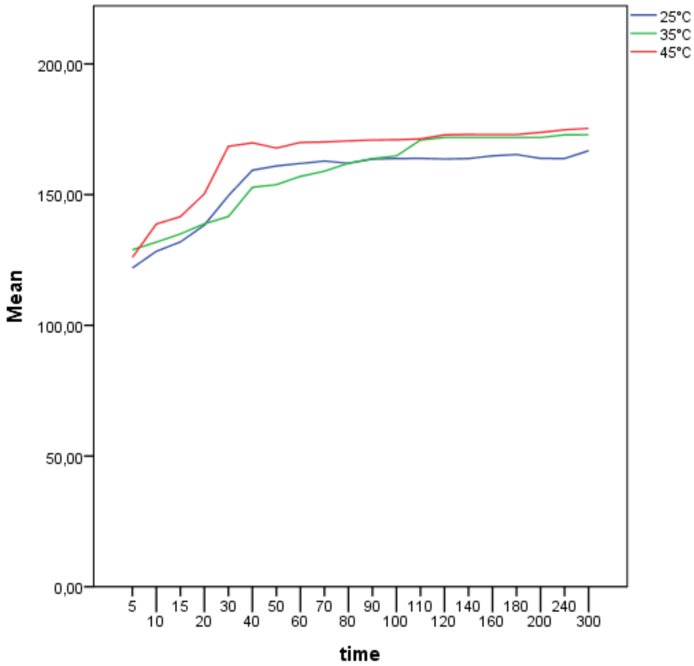

Figure 5. 250 ppm.

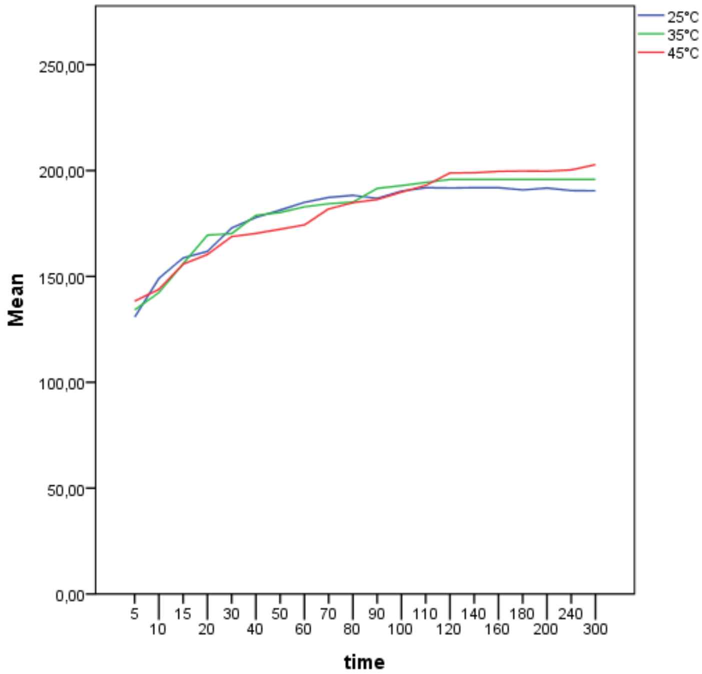

Figure 6. 300 ppm.

4. DISCUSSION AND CONCLUSION

In this study; natural pine cones obtained from the campus of Yüzüncü Yıl University in Van region were used as biosorbents and methylene blue, a dyed organic substance, was removed from the aqueous medium. In this study, the methylene blue solution prepared at various concentrations such as 100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm, at different temperatures (25^{0}C, 35^{0}C and 45^{0}C) and at various times (5,10,15,20,30,40, 50,60,70,80,90,100,120,140,160,180,200,240,300 min.), The change of adsorption of pine cone was examined. In the adsorption of methylene blue from the aqueous medium with pine cone, descriptive statistics and comparisons were made between concentration amounts and time. By increasing the concentration of methylene blue ions in the solution, the amount of adsorbed material was also increased. By increasing the contact time between the pine cone and the concentrations of methylene blue ions, it was found to increase significantly in adsorption. In this study on the adsorption of methylene blue with pine cone, the relationship between concentration amounts and temperature was also examined statistically. As a result, depending on the temperature, the adsorption of dye ions at various concentrations on the pine cone did not change.

Other studies, similar to this study, in which some parameters related to the initial dye concentration, time and temperature, which we examined on the removal of methylene blue with naturally occurring pine cones, were evaluated statistically, were also carried out by some researchers. In a study, the adsorption process for the removal of methylene blue using Van sour cherry pulp was investigated at pH = 5 according to different concentrations, temperatures and time. In this study, in which the adsorption of dye solution on adsorbent material was compared according to time, the differences between the times and concentrations were seen to be statistically important ($p < 0.001$). Consistent with our study, they observed that the adsorption of dye solution at various concentrations did not change with temperature (25oC, 35oC, 45oC) [16]. In another similar study, models were used to determine the adsorption of Basic Blue 41 (BB 41) dyestuff on activated carbon obtained from apple peel, and it was observed that the adsorption process mostly increased with the increase of BB 41 dye concentration in the solution and the contact time with activated carbon [17].

In recent years, there has been a lot of research on the elimination of waste materials from aqueous solutions by adsorption in order to protect the environment. In one study; color removal of the methylene blue and safranine dyes in the batch and filled column system was investigated by using activated sludge pyrolysis and chemicalactivation with activated carbon and it was found that methylene blue dye was adsorbed faster than safranine dye [18, 19]. In another study; observed that the removal of methylene blue from the aqueous medium using Platanus Orientalis L. Bioma increased the amount of adsorbed substance by increasing the concentration of dyes [20]. Using the data obtained as a result of the study; It is concluded that this material can be used as biosorbent because it is easy and inexpensive to obtain natural pine cone and high dye removal efficiency. We believe that the pine cone that we use in our study is an alternative biosorbent material because it will reduce the pollutant potential of environmental pollutants and it is economical and easily obtainable for the removal of paint pollution caused by industrial wastes. We believe that our study will support the information in the scientific literature and will shed light on other studies to be done from now on.

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