J. Int. Environmental Application & Science, Vol. 14(4): 177-182 (2019)

Research Paper

Batch Adsorption of Methylene Blue Dyestuff Using Van Sour Cherry Pulp and Statistical Comparison

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Received September 05, 2018; Accepted December 01, 2019

Abstract: Water contamination which is defined as change by physical, chemical and biological reasons causes environmental pollution. This pollution can be caused by both human wastes and industrial processes. Since dyestuffs are difficult to separate chemically and biologically, wastewater with dyestuffs damages the ecosystem and causes toxic affect to human life. Adsorption process is one of the alternative methods in the treatment of wastewater dyestuff. In this study, the use of Van sour cherry pulp without any chemical process, which is abundantly available in the city of Van, low-cost and plant waste, has been investigated as a bio adsorbent in treatment of methylene blue dyestuff. In order to obtain sour cherry pulp, the Van sour cherry was removed from stems, boiled in pure water with seeds and then strained to get the pulp. 1 gr of methylene blue dyestuff was dissolved in 1L distilled water and 1000 ppm solution stocks were prepared for the whole experimental study. One-way variance analysis (ANOVA) was utilized to determine whether there was a difference between both time and temperature levels for all concentrations. Tukey multiple comparison test was utilized to determine from which group (s) the difference was caused by variance analysis.

Keywords: *Bio adsorbent, Methylene Blue, Sour Cherry,*

Introduction

Water contamination which is defined as change by physical, chemical and biological reasons causes environmental pollution. This pollution can be caused by both human wastes and industrial processes (Gerçel & Seyidoğlu, 2015). The coloring substances (Uçar, 2009) which needed to color products used in textile, leather, cosmetics, printing, plastic, construction, pharmaceutical, food and other industries are synthetic and organic chemicals (Çay & Uyanık, 2002). Since dyestuffs are difficult to separate chemically and biologically, (Uslu *et al*., 2015) wastewater with dyestuffs damages the ecosystem and causes toxic affect to human life. One of these dyes being methylene blue, is widely used in the textile industry, belongs to the class of cationic dyes found in wastewater and has the general formula as $C_{16}H_{18}ClN_3S$ (Yaşar & Özcan, 2004). In dyestuff treatment of wastewater, highly efficient treatment methods such as; coagulation, flocculation, chemical oxidation, filtration, reverse osmosis etc., are used. However, the treatment efficiencies of these methods are limited (Angın *et al*, 2016, Gerçel & Seyidoğlu, 2015). Another method is adsorption process. Adsorption is the accumulation of dissolved substances in the solution on a boundary (liquid-gas liquid-solid or liquid-liquid). Adsorption method is easy, convenient to regeneration, inexpensive and effective, so it became a preferred method in recent years (Uslu *et al.,* 2015). In adsorption duration, among the parameters that can affect the treatment efficiency are adsorbed substance and properties of solvent, amount, surface area, pH and contact time, and temperature. In this process, usually active carbon is used as the adsorbent. However, production of active carbon is highly expensive, so other remedies are being sought (Gerçel & Seyidoğlu, 2015). In order to reduce the cost in wastewater treatment, industrial and plant wastes which are abundant and inexpensive, have been tested and are still being tested (Çay & Uyanık, 2002). In the literature, in dye adsorption, various wastes such as apple pulp, wheat husk, olive waste, almond shell, garlic husk, pomegranate peel, cherry stems and seeds are used as adsorbent (Savcı *et al,* 2017, Gerçel & Seyidoğlu, 2015). In this study, the use of Van sour cherry pulp without any chemical process, which is abundantly available in the city of Van, low-cost and plant waste, has been investigated as a bio adsorbent in treatment of methylene blue dyestuff.

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Materials and Method

In order to obtain sour cherry pulp, the Van sour cherry was removed from stems, boiled in pure water with seeds and then strained to get the pulp. The sour cherry pulp remaining on the strainer was dried on the blotting paper. It was then milled in a mill and passed through a 230 mesh sieve. After 5 days in the oven at 100 ^{O}C, it was placed in the desiccator for use in the experiment. 1 gr of methylene blue dyestuff was dissolved in 1L distilled water and 1000 ppm solution stocks were prepared for the whole experimental study. Adsorption operations were performed in intermittent processes. Water baths with temperature controls were used. Using magnetic stirrers, the system was expected to reach equilibrium concentration. Samples were taken at predetermined times during the experiments and centrifugation was performed. In adsorption equilibrium studies, 1 gram of sour cherry pulp was treated with 1000 ml methylene blue solution. Prepared methylene blue solution in the concentration of 15 ppm, 25 ppm, 35 ppm, 45 ppm, 55 ppm, 65 ppm, 75 ppm, 85 ppm and at pH = 5 and temperatures of 25 ^{o}C, 35^{O}C, 45^{o}C, was shaken with sour cherry pulp at different times (5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 180, 200 and 240 minutes). The adsorption of methylene blue in the sour cherry pulp sample at constant pH = 5, the concentration was examined with respect to temperature and time. All adsorption measurements were made by Termo Scientific brand ICE 300 Series AA model spectrometer (Benek, 2015).

Statistical Analysis

Descriptive statistics for the feature emphasized;

The mean; $\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$, standard deviation; $s = \sqrt{\frac{\sum_{i=1}^{n}(x_i-\bar{x})^2}{n-1}}$ values were calculated and the minimum (x_{min}) and maximum (x_{max}) values were determined. One-way variance analysis (ANOVA) was utilized to determine whether there was a difference between both time and temperature levels for all concentrations. Tukey multiple comparison tests were utilized to determine from which group (s) the difference was caused by variance analysis. Statistical significance level was taken as 5% in the calculations and SPSS statistical package program was used for analyses.

Findings

Descriptive statistics and comparison results of adsorption of methylene blue dye on Van sour cherry pulp; concentration (15 ppm, 25 ppm, 35 ppm, 45 ppm, 55 ppm, 65 ppm, 75 ppm and 85 ppm) and values with respect to time are presented in Table 1. As shown in Table 1; the difference between the times for each concentration was statistically significant ($p < 0.001$). With reference to this, while 15 ppm concentration of methylene blue, when shaken for 5 minutes, adsorbed an average of 3.92 units of substance, at the same concentration, when shaken for 240 minutes, an average of 12.99 units of substance were adsorbed (Figure 1). Similarly, at a concentration of 25 ppm; while an average of 7.93 units were adsorbed when shaken for 5 minutes, an average of 21.62 units were adsorbed when shaken for 240 minutes at the same concentration (Figure 2). Similarly, when it was increased to 35 ppm, it was adsorbed for an average of 15.24 units when shaken for 5 minutes and 28.94 units of material was adsorbed when shaken for 240 minutes (Figure 3). When it was increased to 45 ppm, the average of 20.56 units of substance was adsorbed when shaken for 5 minutes while it was shaken for 240 minutes and 37.93 units of material were adsorbed (Figure 4). When it was increased to 55 ppm, it was adsorbed on average of 26.56 units for 5 minutes and 45.22 units on average when shaken for 240 minutes (Figure 5). When it reached 65 ppm, it was adsorbed on average of 32.69 units when shaken for 5 minutes and 53.64 units when shaken for 240 minutes (Figure 6). Similarly, when it was increased to 75 ppm, it was adsorbed on average of 37.72 units when shaken for 5 minutes and 62.59 units of substance when shaken for 240 minutes (Figure 7). When methylene blue concentration increased to 85 ppm, 40.85 units of material were adsorbed for 5 minutes on shaking and 70.1 units of material were adsorbed on shaking for 240 minutes (Figure 8).

Descriptive statistics and comparison results of adsorption of methylene blue solution on Van sour cherry pulp; concentration (15 ppm, 25 ppm, 35 ppm, 45 ppm, 55 ppm, 65 ppm, 75 ppm and 85 ppm) values with respect to temperature are given in Table 2. When Table 2 is examined; it can be seen that adsorption of methylene blue solution at different concentrations on Van sour cherry pulp does not change with temperature (25^{o}C, 35^{o}C, 45^{o}C).

Figures 1-8. Adsorption of methylene blue dye on Van sour cherry pulp; concentration (15 ppm, 25 ppm, 35 ppm, 45 ppm, 55 ppm, 65 ppm, 75 ppm and 85 ppm)

Figure 1. 15 ppm

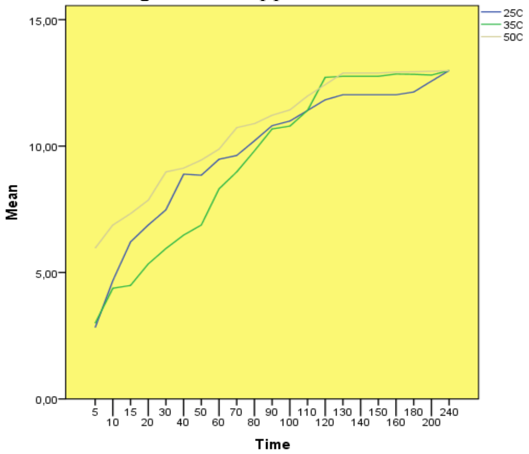

Figure 2: 25 ppm

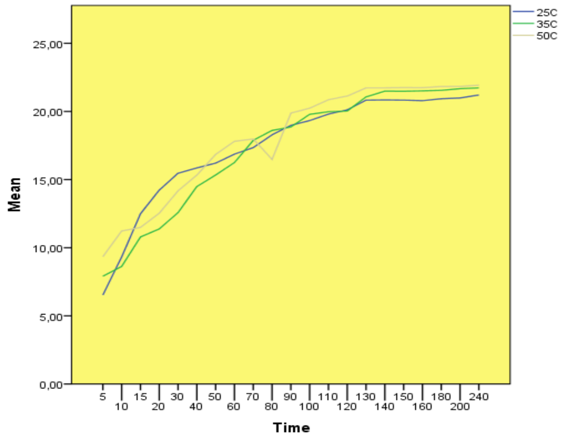

Figure 3. 35 ppm

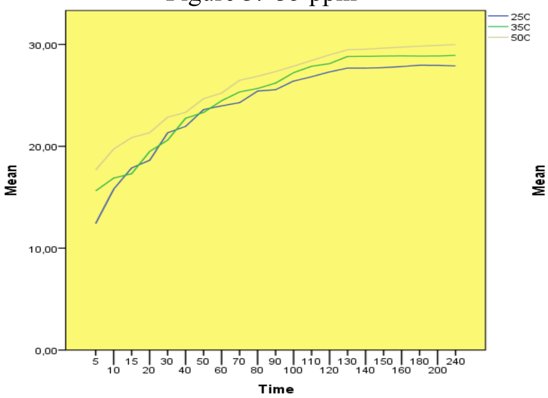

Figure 4. 45 ppm

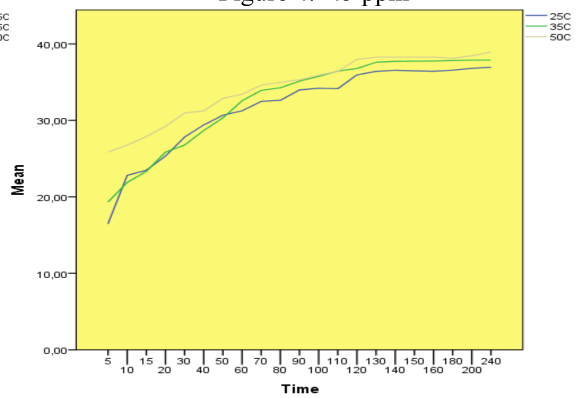

Figure 5. 55 ppm

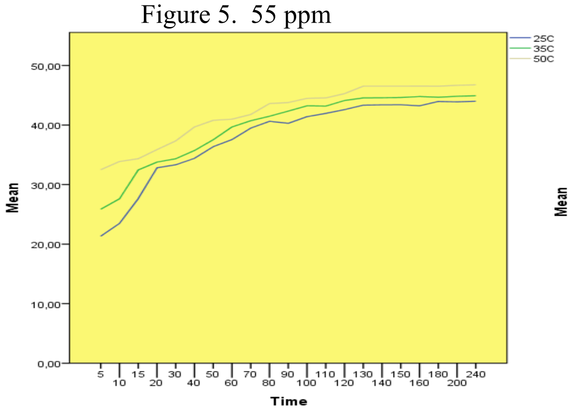

Figure 6. 65 ppm

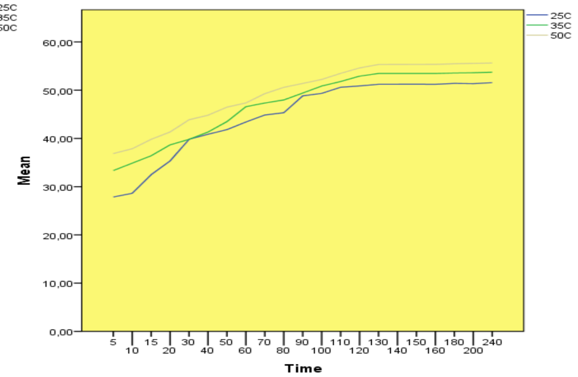

Figure 7. 75 ppm

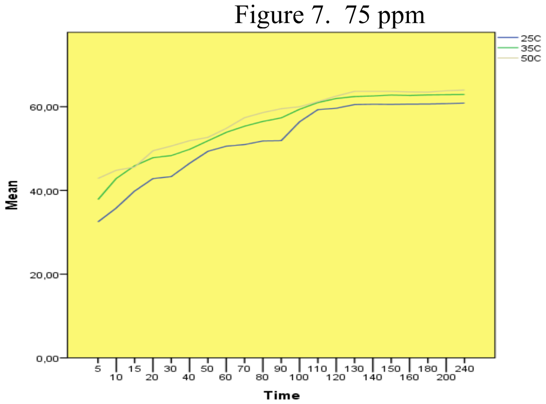

Figure 8: 85 ppm

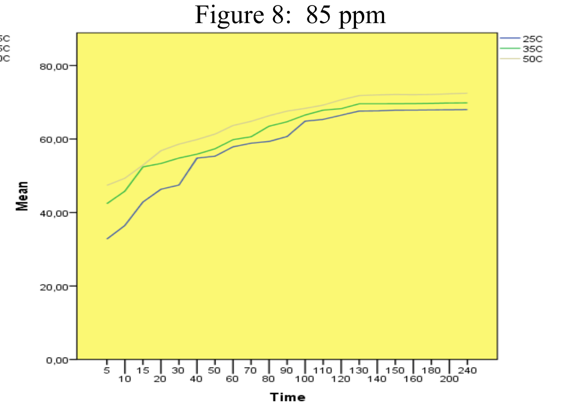

Table 1. Descriptive statistics and comparison results of absorbance values for various time intervals

		n	Mean	Std. Deviation	Min	Max	*p*			n	Mean	Std. Deviation	Min	Max	*p*
Ppm 15	5	3	3.923	1.766	2.82	5.96	0.001	Ppm 55	5	3	26.56	5.613	21.33	32.49	0.001
	10	3	5.313	1.365	4.38	6.88			10	3	28.32	5.241	23.47	33.88	
	15	3	6.01	1.431	4.49	7.33			15	3	31.48	3.456	27.64	34.34	
	20	3	6.693	1.27	5.34	7.86			20	3	34.16	1.565	32.82	35.88	
	30	3	7.47	1.515	5.95	8.98			30	3	35	2.086	33.33	37.34	
	40	3	8.167	1.466	6.48	9.13			40	3	36.61	2.742	34.41	39.68	
	50	3	8.393	1.344	6.88	9.45			50	3	38.23	2.29	36.37	40.79	
	60	3	9.223	0.816	8.31	9.88			60	3	39.41	1.731	37.56	40.99	
	70	3	9.78	0.885	8.98	10.73			70	3	40.67	1.146	39.49	41.78	
	80	3	10.3	0.546	9.81	10.89			80	3	41.91	1.535	40.63	43.61	
	90	3	10.9	0.282	10.68	11.22			90	3	42.14	1.754	40.29	43.78	
	100	3	11.07	0.327	10.79	11.43			100	3	43.04	1.548	41.41	44.49	
	110	3	11.6	0.329	11.41	11.98			110	3	43.23	1.301	41.96	44.56	
	120	3	12.33	0.454	11.83	12.72			120	3	44	1.349	42.59	45.28	
	130	3	12.56	0.464	12.03	12.89			130	3	44.81	1.61	43.34	46.53	
	140	3	12.56	0.464	12.03	12.89			140	3	44.83	1.585	43.39	46.53	
	150	3	12.56	0.464	12.03	12.89			150	3	44.86	1.572	43.41	46.53	
	160	3	12.6	0.498	12.03	12.93			160	3	44.85	1.656	43.23	46.54	
	180	3	12.64	0.436	12.14	12.94			180	3	45.05	1.32	43.96	46.52	
	200	3	12.78	0.197	12.57	12.96			200	3	45.13	1.42	43.89	46.68	
	240	3	12.99	0.006	12.98	12.99			240	3	45.22	1.4	44	46.75	
Ppm 25	5	3	7.927	1.405	6.53	9.34	0.001	Ppm 65	5	3	32.69	4.535	27.86	36.86	0.001
	10	3	9.73	1.345	8.63	11.23			10	3	33.79	4.715	28.63	37.87	
	15	3	11.59	0.854	10.79	12.49			15	3	36.24	3.668	32.49	39.82	
	20	3	12.71	1.434	11.38	14.23			20	3	38.45	3.006	35.34	41.34	
	30	3	14.08	1.448	12.58	15.47			30	3	41.17	2.344	39.82	43.88	
	40	3	15.23	0.691	14.49	15.86			40	3	42.34	2.163	40.86	44.82	
	50	3	16.13	0.758	15.34	16.85			50	3	43.94	2.362	41.83	46.49	
	60	3	16.98	0.785	16.25	17.81			60	3	45.78	2.092	43.41	47.36	
	70	3	17.74	0.339	17.35	17.98			70	3	47.16	2.22	44.86	49.29	
	80	3	17.79	1.149	16.48	18.61			80	3	47.97	2.63	45.33	50.59	
	90	3	19.24	0.557	18.86	19.88			90	3	49.88	1.357	48.82	51.41	
	100	3	19.79	0.455	19.33	20.24			100	3	50.81	1.446	49.34	52.23	
	110	3	20.22	0.564	19.81	20.86			110	3	51.96	1.448	50.61	53.49	
	120	3	20.43	0.611	20.03	21.13			120	3	52.8	1.867	50.88	54.61	
	130	3	21.21	0.466	20.83	21.73			130	3	53.34	2.053	51.23	55.33	
	140	3	21.35	0.46	20.84	21.73			140	3	53.35	2.058	51.23	55.34	
	150	3	21.35	0.473	20.83	21.75			150	3	53.35	2.057	51.24	55.35	
	160	3	21.35	0.496	20.79	21.74			160	3	53.35	2.073	51.22	55.36	
	180	3	21.44	0.461	20.93	21.83			180	3	53.48	2.036	51.41	55.48	
	200	3	21.5	0.45	20.99	21.84			200	3	53.51	2.102	51.36	55.56	
	240	3	21.62	0.372	21.21	21.93			240	3	53.64	2.036	51.56	55.63	
Ppm 35	5	3	15.24	2.661	12.41	17.69	0.001	Ppm 75	5	3	37.72	5.191	32.48	42.86	0.001
	10	3	17.47	2.034	15.79	19.73			10	3	41.17	4.733	35.82	44.82	
	15	3	18.68	1.906	17.31	20.86			15	3	43.78	3.398	39.86	45.89	
	20	3	19.82	1.385	18.63	21.34			20	3	46.71	3.461	42.83	49.48	
	30	3	21.6	1.149	20.61	22.86			30	3	47.42	3.735	43.31	50.61	
	40	3	22.69	0.693	21.96	23.34			40	3	49.4	2.724	46.49	51.89	
	50	3	23.87	0.712	23.33	24.68			50	3	51.3	1.729	49.36	52.68	
	60	3	24.56	0.634	23.97	25.23			60	3	53.09	2.232	50.57	54.82	
	70	3	25.37	1.1	24.29	26.49			70	3	54.56	3.285	50.96	57.39	
	80	3	26	0.775	25.43	26.88			80	3	55.64	3.474	51.82	58.61	
	90	3	26.37	0.901	25.56	27.34			90	3	56.25	3.934	51.89	59.53	
	100	3	27.17	0.732	26.41	27.87			100	3	58.6	1.917	56.41	59.99	
	110	3	27.71	0.811	26.83	28.43			110	3	60.5	1.039	59.31	61.21	
	120	3	28.14	0.835	27.31	28.98			120	3	61.37	1.536	59.63	62.53	
	130	3	28.66	0.911	27.68	29.48			130	3	62.21	1.597	60.51	63.68	
	140	3	28.68	0.934	27.68	29.53			140	3	62.28	1.564	60.59	63.68	
	150	3	28.74	0.96	27.73	29.64			150	3	62.34	1.613	60.55	63.68	
	160	3	28.82	0.957	27.83	29.74			160	3	62.28	1.492	60.63	63.53	
	180	3	28.88	0.935	27.96	29.83			180	3	62.31	1.486	60.64	63.48	
	200	3	28.91	0.981	27.95	29.91			200	3	62.47	1.581	60.73	63.82	
	240	3	28.94	1.05	27.89	29.99			240	3	62.59	1.59	60.86	63.99	

Ppm 45	5	3	20.56	4.808	16.48	25.86	0.001	Ppm 85	5	3	40.85	7.438	32.76	47.39	0.001
	10	3	23.83	2.6	21.88	26.78			10	3	43.88	6.635	36.49	49.33	
	15	3	24.91	2.585	23.34	27.89			15	3	49.38	5.654	42.86	52.88	
	20	3	26.81	2.112	25.34	29.23			20	3	52.16	5.343	46.33	56.82	
	30	3	28.53	2.186	26.78	30.98			30	3	53.64	5.659	47.48	58.61	
	40	3	29.78	1.315	28.69	31.24			40	3	56.85	2.663	54.81	59.86	
	50	3	31.3	1.386	30.33	32.89			50	3	58	3.059	55.33	61.34	
	60	3	32.42	1.093	31.26	33.43			60	3	60.46	2.951	57.88	63.68	
	70	3	33.68	1.082	32.49	34.61			70	3	61.43	3.058	58.86	64.81	
	80	3	33.96	1.21	32.63	34.99			80	3	63.06	3.52	59.34	66.34	
	90	3	34.82	0.725	33.99	35.33			90	3	64.32	3.47	60.68	67.59	
	100	3	35.3	0.948	34.21	35.93			100	3	66.58	1.74	64.86	68.34	
	110	3	35.67	1.317	34.15	36.45			110	3	67.48	1.973	65.34	69.23	
	120	3	36.91	1.021	35.96	37.99			120	3	68.47	2.103	66.48	70.67	
	130	3	37.43	0.938	36.42	38.27			130	3	69.67	2.106	67.61	71.82	
	140	3	37.52	0.874	36.56	38.27			140	3	69.74	2.174	67.65	71.99	
	150	3	37.5	0.915	36.49	38.27			150	3	69.85	2.142	67.85	72.11	
	160	3	37.49	0.95	36.43	38.27			160	3	69.85	2.109	67.86	72.06	
	180	3	37.51	0.824	36.57	38.12			180	3	69.91	2.112	67.91	72.12	
	200	3	37.72	0.838	36.81	38.46			200	3	70.01	2.178	67.95	72.29	
	240	3	37.93	0.996	36.96	38.95			240	3	70.1	2.242	68	72.46	

Table 2. Descriptive statistics and comparison results of absorbance values for various temperatures

	ºC	n	Mean±Std. Deviation	Minimum	Maximum	p
Ppm 15	25	21	9.8090±2.79397	2.82	12.99	0.370
	35	21	9.4752±3.43386	2.99	12.99	
	45	21	10.6967±2.28360	5.96	12.98	
Ppm 25	25	21	17.4900±4.07434	6.53	21.21	0.860
	35	21	17.2867±4.60952	7.91	21.73	
	45	21	17.9943±4.15802	9.34	21.93	
Ppm 35	25	21	24.1014±4.53139	12.41	27.96	0.292
	35	21	24.9038±4.47129	15.63	28.93	
	45	21	26.1829±3.83308	17.69	29.99	
Ppm 45	25	21	31.7614±5.68158	16.48	36.96	0.278
	35	21	32.6476±5.98935	19.34	37.89	
	45	21	34.3890±4.22175	25.86	38.95	
Ppm 55	25	21	38.0248±6.86974	21.33	44.00	0.086
	35	21	39.7652±5.93955	25.86	44.92	
	45	21	42.1414±4.78569	32.49	46.75	
Ppm 65	25	21	44.7300±7.89309	27.86	51.56	0.111
	35	21	47.1238±7.03597	33.34	53.73	
	45	21	49.4338±6.41651	36.86	55.63	
Ppm 75	25	21	52.1548±9.06658	32.48	60.86	0.133
	35	21	55.6595±7.67939	37.82	62.91	
	45	21	57.0414±7.09089	42.86	63.99	
Ppm 85	25	21	58.3014±11.06959	32.76	68.00	
	35	21	61.9519±8.50299	42.41	69.83	0.081
	45	21	64.8448±7.98858	47.39	72.46	

Results and Recommendation

In this study, adsorption of methylene blue dye solution onto Van sour cherry pulp was investigated at temperatures (25ºC, 35ºC, 45ºC), times (5, 10, 15, 20, 30, 40, …. 240 min) and concentrations (15, 25, 35, .. 85 ppm). In Table 1, the results of the comparison of the adsorption of methylene blue dye solution on Van sour cherry pulp with respect to time are given. The differences between the times for each concentration were found to be statistically significant (p <0.001). It is observed that the amount of adsorbed methylene blue increases after a certain period of time, depending on the ambient conditions and the amount of adsorbent surface, it reached saturation by the dyeing anions then the amount taken was approximately fixed. In Table 2, the results of the comparison of the adsorption of methylene blue dyestuff solution on Van sour cherry pulp with respect to temperature are given; it was observed that the adsorption efficiency did not change with temperature. Similar results were obtained in a study using banana peel as an adsorbent against Acid Blue 121 dyestuff (Uslu *et al*, 2015). There are many studies in the literature regarding the adsorption removal of dyes from aqueous solutions. In a study, the adsorption of methylene blue on bamboo-based activated carbon was investigated and it was stated that bamboos could be used as a raw material in the preparation of activated carbon (Hameed & Din, 2007). In a similar study, it was stated that coconut cored carbon may be preferred as an effective adsorbent for removing methylene blue from waste waters (Kavitha & Namasivayam, 2007). In a study by Dural et al., It was proved that *Posidonia oceanica* (L.) dead leaves could be used in the preparation of activated carbon for methylene blue adsorption. In another study, adsorbent material was produced from cotton stalk for adsorption of methylene blue and it has proved to have significant potential for removal of methylene blue dye from aqueous solutions (Deng *et al*., 2011).

This study shows that sour cherry pulp, which is abundant in the city of Van, is inexpensive agricultural waste and can be used as an effective bio adsorbent for the treatment of waste water containing dye.

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