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Adsorption of Astrazon red GTLN (AR) with volcanic tuff Bayburt Stone

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Abstract

The discharge of dyestuffs originating from the textile industries pollutes the natural waters. Therefore, the adsorption which used to remove dyestuffs from wastewater, is an effective, economical and successful method. Adsorption is a very effective, widespread, easy and inexpensive method used for textile dye removal from wastewater. Bayburt stone powders were used as adsorbent and Astrazon Red GTLN textile dye was used as adsorbate. According to the results of the study, the optimum pH value was 10, the initial dye concentration was 10 mg/L, the mixing speed was 200 rpm and the adsorbent amount was 10 g/L. Langmuir, Freundlich and Temkin isotherms were used to evaluate the adsorption dynamics. Langmuir isotherm was best fit and Astrazon Red removal efficiency was found to be 85% by using Bayburt stone under optimum conditions.

1. Introduction

With industrialization, the textile industry is also developing rapidly. Finishing processes such as dyeing, printing, washing and drying are commonly used in textile fabrics. Since textile dyes have the potential to pollute the receiving water environment, they are in the group of wastewaters that must be treated before discharge [1]. For this purpose, various treatment methods such as coagulation, flocculation, electrochemical processes, chemical oxidation, reverse osmosis, electrochemical filtration, aerobic and anaerobic treatment are used for textile dye removal from wastewaters. More economical and more suitable operating conditions are preferred in terms of the applicability and efficiency of the treatment methods used in dyestuff removal [2]. The adsorption of methylene blue dyestuff in aqueous solutions with pumice powder was investigated and it was revealed that as the amount of adsorbent and time increased, the adsorption increased, and the adsorption rate of the basic dye decreased with increasing concentration [3]. Wastewaters containing dyestuffs generally have a dark different colour and wide pH range, high temperature, COD (Chemical Oxygen Demand), BOD (Biological Oxygen Demand), total dissolved solids and high conductivity. Both physical, chemical and visual pollution occur in the discharge of dye-containing wastewater. The colour and density of wastewater containing dyestuffs may differ according to the type of dyestuff [4].

Adsorption is a frequently used, inexpensive and good method for the treatment of dyestuff-containing wastewater. Adsorption studies are carried out by altering the conditions such as different organic and inorganic materials and different pH, temperature, concentration, adsorbent amounts to optimise the conditions for adsorption. Adsorption continues until a balance that established between the concentration of the substance deposited on the surface of the adsorbent and the concentration of the substance remaining in the solution. At this equilibrium time, the relationship between the amount of substance adsorbed at constant temperature and the equilibrium pressure or concentration is called "adsorption isotherm" and gives information about the characterization of the experiment. In the study in which rice husk was used as adsorbent, it was observed that the adsorption process reached equilibrium at pH 7.87 and within 90 minutes [5]. In another study, the removal of ethylene blue dye from aqueous solutions with pine-magnetite composite as adsorbent was studied and its effects on the removal of methylene blue dyestuffs were investigated at different temperatures, adsorbent dose, adsorbate concentration and different temperatures [6].

2. Material and Method

The Bayburt stone used in this study is extracted from the provincial borders of Bayburt and brought to the laboratory in relatively large sizes to be used in the study. It was first grinded and cleaned by washing several times with the help of distilled water and left to dry in an oven at 105 °C for 24 hours and then ground into powder. Detailed technical analyse values of yellow Bayburt stone are given in Table 1 [7].

Table 1. Technical analysis values of Bayburt stone

MgO, %		0.5
SiO_2, %		4.80
CaO, %		7.30
Fe_2O_3, %		2.45
Spesific gravity, g/cm^3		2.71
Unit volume weight, g/cm^3		1.84
Water absorption at atmospheric pressure	By weight (%)	13.0
	By volume (%)	24.0
Apparent porosity, %		24.0
Pressure resistance, kgf/cm^2		282
Porosity degree, %		32.2
Average wear resistance, cm^3/50 cm^2		63.6

In order to investigate the zeta potential values, potential measurements were made at different pH values between 2 and 12 and the maximum value was obtained at pH 10 as -29.8 mV (Figure 1).

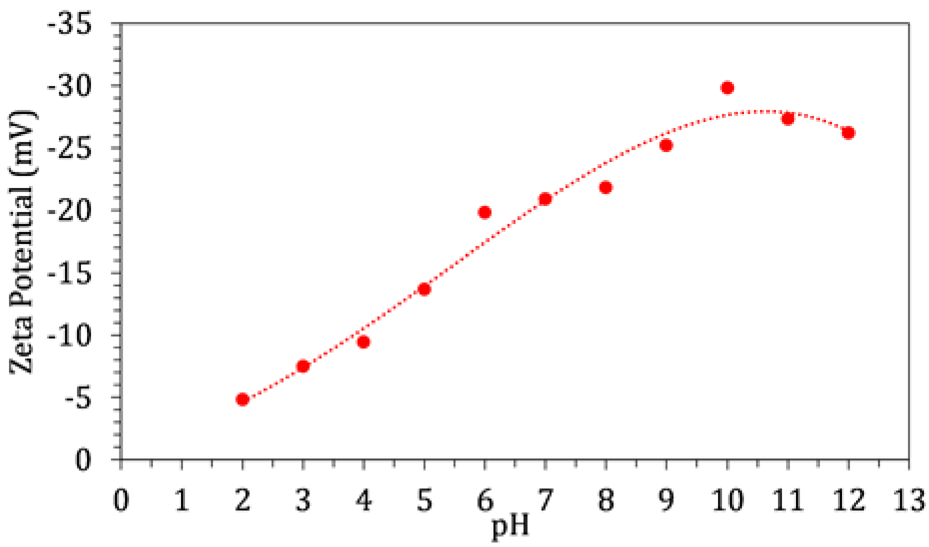

Figure 1. Zeta potential values versus pH

The wastewater used in the study was prepared synthetically with Astrazon Red GTLN textile dye. Astrazon Red GTLN textile dye has the chemical formula of $C_{19}H_{25}ClN_5O_2$. The chemical structure of it is given in Figure 2.

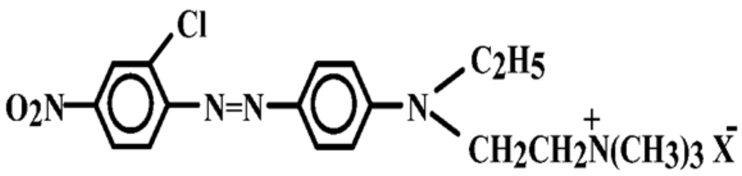

Figure 2. Chemical formula of Astrazon Red GTLN

In the study, different inlet dye concentration, adsorbent amount, contact time and different temperature values were tried to determine the adsorption efficiency for dyestuff removal in laboratory conditions.

1 N hydrochloric acid (HCl) and 1 N sodium hydroxide (NaOH) solution were used to bring the pH value to the desired values. The dyestuff stock solution prepared at 1000 ppm was diluted in the range of 10-200 mg/L and placed in 250 ml bottles and adsorbent was added in the range of 0.1-10 g/L. After centrifugation, it was heated and stirred at constant temperature for a certain period of time. The samples were filtered and read in the spectrophotometer.

Devices used in conducting experimental studies are in Atatürk University Environmental Engineering Department Laboratories. Axis 220 brand analytical balance was used for precision weighing, MikrotestTT104 brand oven and desiccator were used for the preparation of the samples, batch trials were carried out in Edmund Bühler Incubator HoodTH15 brand heater mixer. pH measurement was made with a CrisonpH25+ brand pH meter. Nuve NF 1200 R brand centrifuge device was used for solid-liquid separation. The concentrations of the samples were determined with the help of Merck Spectroquant prove 300-mark spectrophotometer device.

At the end of the experiment the adsorbent was separated from the solution with the help of filtration and then viewed with the Daytam ZEISS SIGMA 300 brand Scanning Electron Microscope (SEM) device. SEM photographs of Bayburt stone before and after adsorption are shown in Figures 3 and 4.

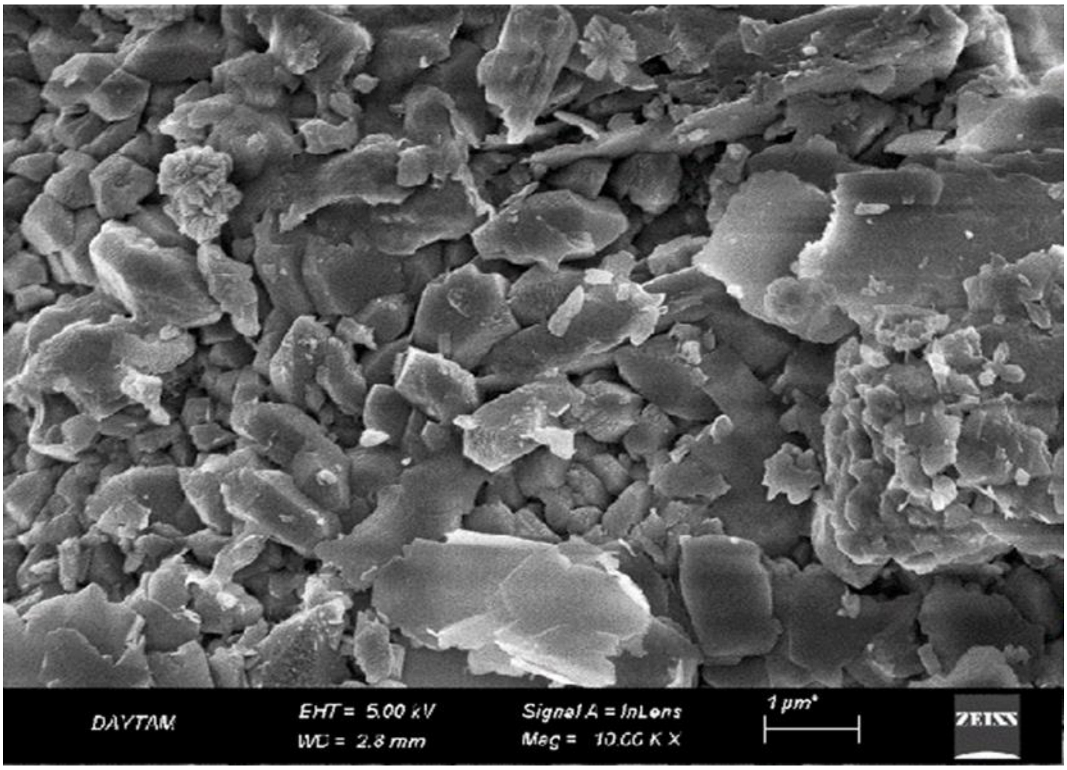

Figure 3. Before adsorption

Different inlet concentration, temperature and contact time values were tried to determine the optimum conditions.

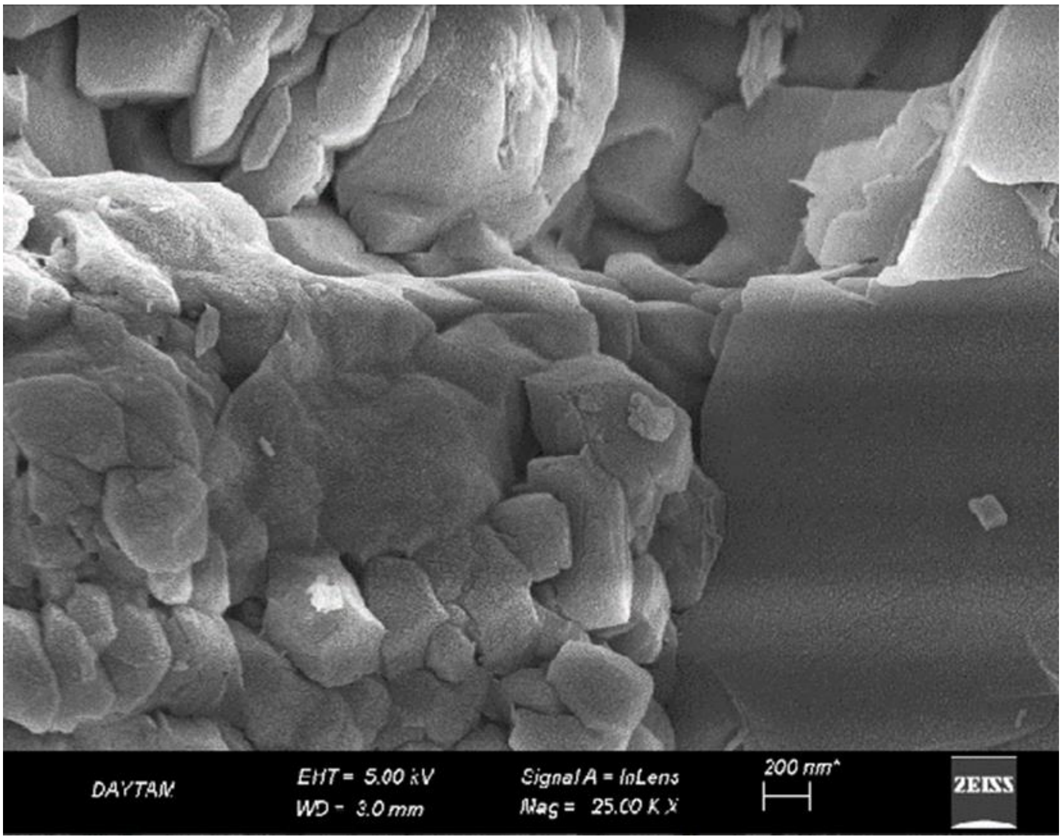

Figure 4. After adsorption

In order to calculate the adsorption efficiency for dyestuff removal in laboratory conditions, the adsorbent amount is taken as the basis in the inlet and equilibrium state, and the concentration and volume. The equilibrium amount of adsorbed substances (qe) and removal efficiency was calculated with the Equations (1) and (2):

$$qe= \frac{Co-Ce}{m}*V \tag{1}$$

$$\%R= \frac{Co-Ce}{Le}*100 \tag{2}$$

where Co and Ce are the liquid-phase concentrations of dye (mg/L) at initial and equilibrium state, respectively, V is the volume of the solution (L) and m is the mass of dry sorbent(g) [8].

3. Results

Adsorption experiments were carried out by using 250 mL Erlenmeyer flasks. Sorbent and Astrazon Red GTLN solutions were added to the flasks for each experiment. Flask content temperatures stabilized before the test within a range between 25 °C and 35 °C.

Adsorbed Astrazon Red GTLN amount onto per unit weight of adsorbent (mg/g) is calculated with Equation 1. Langmuir [9], Freundlich [10] and Tempkin [11] isotherm model equations are given below with the Equations of 3, 4 and 5, respectively.

$$\frac{1}{q_e} = \left(\frac{1}{K_L.q_m}\right)\left(\frac{1}{C_e}\right) + \left(\frac{1}{q_m}\right) \tag{3}$$

where q_m is the maximum adsorbate uptake capacity (mg/g) and K_L is the Langmuir constant related to the energy of adsorption (L/mg).

$$ln(q_e) = lnK_F + \frac{1}{n} lnC_e \tag{4}$$

where K_F is Freundlich constant related to biosorption capacity (L/g) and 1/n is the heterogeneity factor.

$$q_e = B\ ln\ A + B\ lnC_e \tag{5}$$

where $B = RT/b$, b is the Temkin constant related to heat of sorption (J/mol), A is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol.K) and T is the absolute temperature (K) of solution.

Langmiur, Freundlich and Tempkin isotherms were tested. Graphs are given in Figure 5.

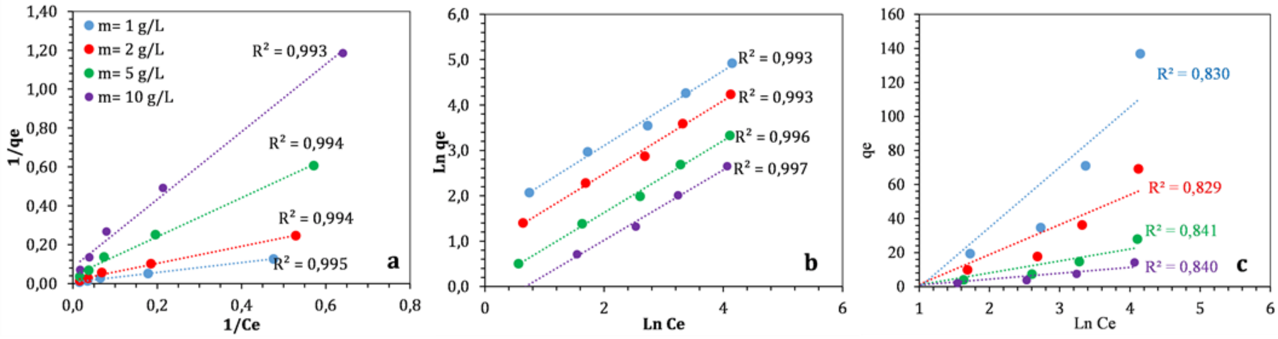

Figure 5. Langmuir (a), Freundlich (b) and Tempkin (c) isotherm model plots

The isotherm model constants are given in Table 2.

The study was carried out at 25°C, 30°C, 35°C conditions. In the study, the adsorption efficiency for dyestuff removal was calculated under different temperature laboratory conditions and it was observed that the adsorption rate increased with temperature. According to the results of the adsorption study, it was determined that the highest dye removal efficiency was at 35°C (Figure 6).

Table 2. Isotherm model constants

Temp.	m(g)	Langmuir			Freundlich			Temkin			
		q_m	B	R^2	K_F	n	R^2	A	B	b	R^2
25°C	1	75,864	0,055	0,973	4,143	1,312	0,987	0,347	29,935	86,931	0,809
	2	39,086	0,055	0,973	2,148	1,312	0,992	0,358	15,131	171,982	0,822
	5	17,266	0,050	0,980	0,891	1,308	0,995	0,369	6,158	422,619	0,843
	10	8,420	0,058	0,977	0,483	1,320	0,995	0,397	3,114	835,616	0,841
30°C	1	91,649	0,049	0,982	4,436	1,266	0,991	0,371	32,892	79,116	0,816
	2	45,533	0,051	0,981	2,305	1,272	0,993	0,384	16,497	157,741	0,821
	5	17,641	0,060	0,978	1,037	1,306	0,994	0,425	6,522	399,000	0,834
	10	9,506	0,057	0,981	0,531	1,290	0,996	0,434	3,358	774,912	0,841
35°C	1	147,833	0,027	0,995	4,298	1,214	0,993	0,362	35,360	73,593	0,830
	2	63,240	0,036	0,994	2,383	1,239	0,993	0,395	17,554	148,245	0,829
	5	24,920	0,040	0,994	1,047	1,261	0,996	0,428	6,994	372,054	0,841
	10	11,730	0,049	0,993	0,591	1,292	0,997	0,478	3,475	748,875	0,840

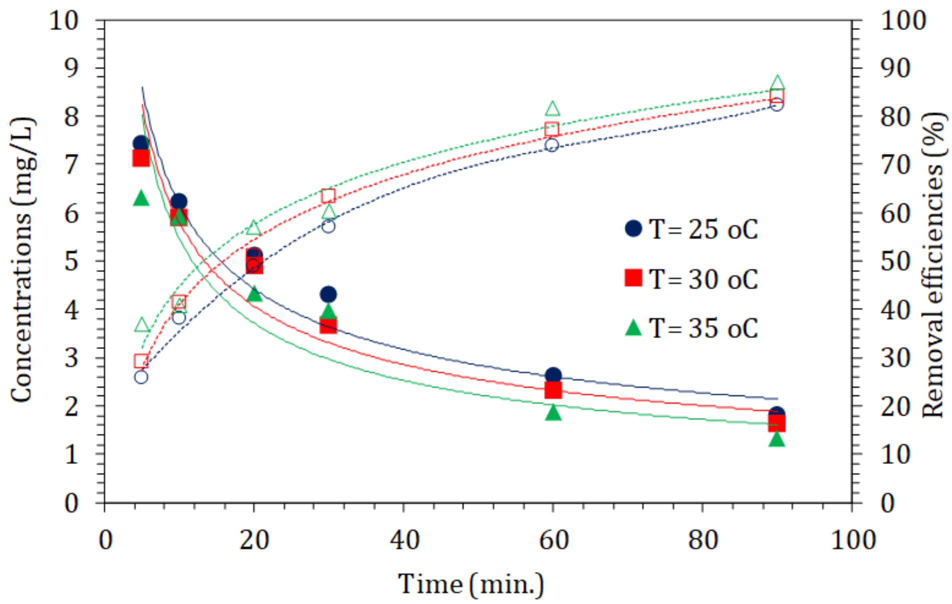

Figure 6. Concentrations with time for different temperatures

It was observed that as the inlet dye concentration increased, the removal efficiency decreased as it exceeded the adsorption capacity. Similarly, in a study which is on the removal of methylene blue, used pine leaves as adsorbent, it was observed that while the concentration was increased from 10 to 90 mg/L, the removal efficiency decreased from 96.5 to 40.9% [2].

The following experiments were carried out under different temperature and inlet concentration conditions and the dye removal efficiencies were investigated. It was observed that the adsorption efficiency decreased as the inlet concentration increased (Figure 7). In order to determine the adsorption efficiency and concentration behaviours in the adsorption process, experiments were carried out up to 90 minutes but the first 30 minutes were found to be the effective time.

The adhesion and contact of the dyestuff to be removed in the adsorbent substance yellow Bayburt stone surface area and pores should be homogeneously ensured. Therefore, since the mixing speed is effective in adsorption, the diffusion of the entire substance cannot fully adhere to the adsorbent surface in a low-speed mixing process. High mixing speed disrupts the adsorption mechanism and makes it difficult for adsorption to reach equilibrium [12]. In addition, when the mixing energy cost is considered, the mixing speed becomes even more important.

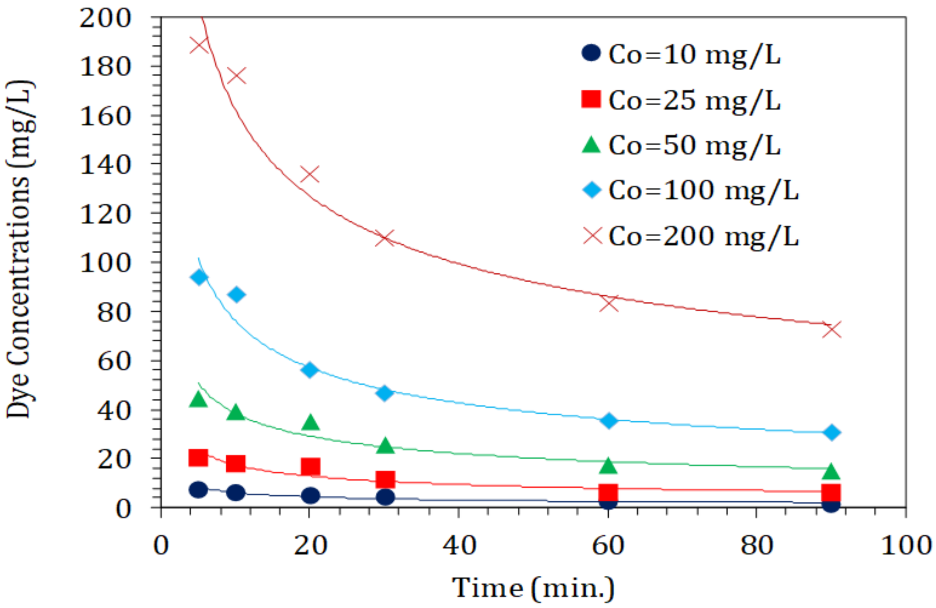

Figure 7. Concentrations with time for different initial dye concentrations

As can be seen in Figure 8, when the dye removal efficiency values were examined against different initial concentrations, the adsorption efficiency decreased as the concentration value increased.

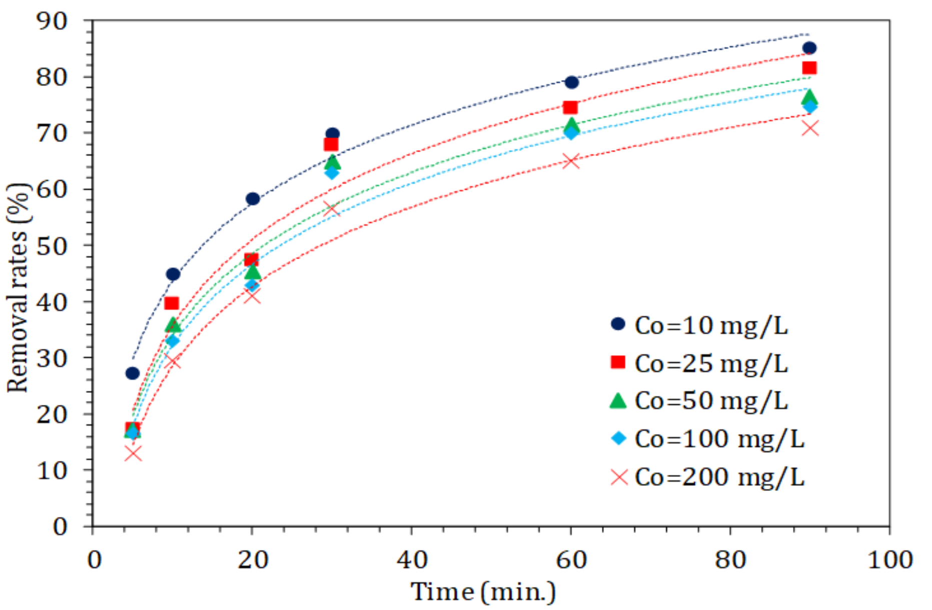

Figure 8. Removal rates for different initial dye concentrations

Considering these experimental data, it is seen that increasing the amount of Bayburt stone increases the adsorbing efficiency of the dyestuff. Since the surface area of the adsorbent will increase with the increase of the amount used, the amount of adsorbate adsorbed in the pores of the adsorbent also increases. Because the adsorption efficiency and intensity will increase proportionally with the increase in surface area, this ratio has been proven [13].

4. Conclusion

By using the yellow type of Bayburt stone, in this study, the removal of dyestuff in the aqueous solution, which is used in dyeing products in the textile industry, by adsorption method was investigated. In terms of parameters affecting adsorption, the effects of contact time, inlet adsorbate substance concentration, adsorbent substance dosage, mixing speed and temperature were investigated in batch system experiments. The results obtained in this study revealed that Bayburt stone, which is very cheap and easy to find, is an effective adsorbent material.

In order to determine the optimum dye concentration, experiments were carried out with concentrations of 10 mg/L, 25 mg/L, 50 mg/L, 100 mg/L and 200 mg/L. As the initial dye concentration increased, the removal efficiency decreased and the optimum value was determined as 25 mg/L. In addition, 1 g/L, 2 g/L, 5 g/L and 10 g/L adsorbent amounts were used to determine the most suitable adsorbent amount, and it was determined that 10 g/L adsorbent substance amount was the most appropriate. In order to determine the effective mixing speed in adsorption, studies were carried out at different mixing speeds. Stirring speeds of 100 rpm, 200 rpm and 300 rpm were tried. The optimum mixing speed was determined as 200 rpm. In the study; 85% adsorption efficiency was obtained by taking the temperature 35°C, inlet dye concentration 10 mg/L, stirring speed 200 rpm and adsorbent concentration 10 g/L. As a result, the results of the study showed that Bayburt stone is an economical, effective and suitable adsorbent that can be used in the adsorption method.

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Author contributions

Erdem Kocadağistan: Writing-Original drafting, Software, Validation. **Beyhan Kocadağistan:** Visualization, Analysis, Writing-Review and Editing.

Conflicts of interest

The authors declare no conflicts of interest.

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