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Removal of Bromophenol Blue from Aqueous Solution Using Bentonite, Zeolite and Graphene Oxide

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Research Article

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ABSTRACT

In this study, an anionic dyestuff bromophenol blue (BrPB) from the aqueous solution was removed by adsorption in the presence of bentonite (B), zeolite (Z) and graphene oxide (GO). The effects of pH, adsorbent amount, initial concentration of BrPB, temperature and time on adsorption were investigated. After the adsorption process, ultraviolet-visible region spectrophotometer (UV-VIS) was used to measure the amount of dyestuff remaining in the solution which is not adsorbed. It's found that; the optimum values obtained for the adsorption process; the optimum pH value 5 for B and Z, 4 for GO; 0.03 g amount of adsorbent and 60 minutes for the equilibrium time. The compatibility of Langmiur and Freundlich isotherm models was found as Z> GO> B and GO> B> Z respectively. In terms of kinetics aspect, it was observed that all adsorbents were comply with pseudo-second order reaction kinetics. To be positive of ΔG° value for B and Z is of physical nature of adsorption, to be negative of ΔG° value for GO requires to be chemical nature of adsorption. When the obtained ΔH° values were examined, it was observed that the reaction was endothermic for B and Z and exothermic for GO. The negative value of ΔS° for B and Z adsorbent species indicates that the randomness between solid and liquid decreases, whereas the positive ΔS° value for GO indicates that the randomness between solid and liquid increases. The highest adsorption capacity value obtained after the measurements made under optimum conditions is 589 mg g^{-1} for GO and 15.7 and 19.8 mg g^{-1} for B and Z, respectively.

Keywords: Adsorption, Bentonite, Bromophenol blue, Graphene oxide, Zeolite.

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Introduction

Today, water pollution is one of the main factors that adversely affect human health. The rapid increase in industrialization and urbanization have been effective in the rapid deterioration of water quality. Scientific studies suggest that different industrial wastes such as textile, leather, food, paint, etc. are composed of toxic compounds, some of which are carcinogenic [1]. Uncontrolled and untreated wastes containing dyestuffs can cause major environmental disasters even at low concentrations in receiving environments. Whether or not these dye-containing wastewaters are toxic and carcinogenic, they are characterized by a high chemical oxygen demand (COD) / biological oxygen demand (BOD) ratio, suspended solids and intense colour. In addition, these wastewaters prevent the self-treatment capacity of the receiving environment, cause colouration of the receiving water, decrease the light transmittance of the water, slow down the photosynthesis rate of aquatic flora [2].

Water is an indispensable need and source of life for all living things. Therefore, it is of great importance to protect our existing water resources and to make wastewater reusable. Among the impurities contained in wastewater, there are also dyestuffs that have toxic effects. Industrial wastewater contains large amounts of dyestuffs that are resistant to biodegradation and whose contents can vary greatly. These wastewaters containing dyestuffs, which also have toxic effects, have a high risk potential for receiving waters. Therefore, removal of industrial wastewater by simple, economical and effective methods is of great importance in terms of usable water resources.

Especially the discharge of wastewater containing dyestuffs from the textile industry to the aquatic environment without any treatment process is one of the main reasons for the formation of carcinogenic and toxic aromatic amines. The discharge of wastewater containing dyestuffs even at low concentrations into streams and river beds causes pollution in the waters [3]. Dyes discharged into receiving environments may cause irreversible problems in receiving environments by preventing sunlight from passing into water due to their structural properties. Dyes are resistant to biodegradation due to their chemical composition [4]. The release of aromatic amines during the anaerobic degradation of some azo dyes is another cause of pollution [4-5].

Significant researches are being carried out for the treatment of wastewater from dyestuffs. Among the methods used in the treatment of dyestuffs are chemical, biological, and physical methods. The methods used in treatment vary depending on the nature of the receiving environment [6].

It is known that adsorption method is an easy and very effective physical separation method in wastewater treatment. The most commonly used adsorbents in the adsorption method include zeolite, bentonite and carbon-based nano materials [7].

Adsorbents are porous solids that bind molecules on their surfaces that are liquid, gaseous or dissolved in water. In adsorption, they are generally used to remove heavy metals and dyestuffs from wastewater by binding them to adsorbents such as bentonite, zeolite, activated carbon or silica gel.

The majority of zeolites consist of natural aluminum silicates. Zeolites are alumina silicates formed by forming a network structure of tetrahedral $AlO4$ and $SiO4$, bonded to each other by oxygen atoms. Zeolites are widely used as ion exchange agents, catalysts and molecular filters in a number of industrial processes [8].

Bentonite is a widely available abundant natural clay mineral, known as a low-cost adsorbent for water and wastewater treatment. The chemical structure and pore structure of bentonite usually determine its adsorption capacities [9]. Bentonites exhibit high capacity adsorbent properties due to their colloidal structure, electrically charged particles, high liquid absorbency, high water retention capacity and large surface areas despite their small size. Bentonite has many advantages over other clay minerals due to its unique properties such as high cation exchange capacity, high specific surface area, excellent physical and chemical stability and surface properties.

Allotropes of carbon, which has a two-dimensional planar structure formed by the arrangement of carbon atoms in hexagons in a honeycomb structure, are called graphene. The modified Hummers method, one of the chemical methods, was used to obtain graphene oxide from graphite. When graphite layers are oxidized, the layers are opened thanks to oxide derivatives, and these opened layers are separated from each other by sonication. In this way, graphene oxide layers are obtained [10]. GO, which has many oxygen-containing groups such as hydroxyl, epoxide, carboxyl and carbonyl functional groups, is hydrophilic, negatively charged and can be easily dispersed in water to form a stable colloidal suspension [11].

GO and graphene, the newly discovered carbon nanoscale materials, interact strongly with organic molecules thanks to their characteristic structures and electronic properties and non-covalent forces such as Van der Waals interactions. They have many advantages for use as adsorbents, such as their nano-sized structure, rapid equilibration, high adsorption capacity and operation in a wide pH range [12].

A literature search revealed that bromophenol blue adsorption, despite its importance in water quality management, has not been reviewed. The purpose of this paper is to review the use of different adsorbents for the removal of bromophenol blue from contaminated water. The adsorption capacities of the adsorbents were compared under different experimental conditions. Due to their high specific surface area and various morphologies, carbon nanomaterials such as GO are a type of adsorbent with high efficiency in water treatment.

Materials and Methods

Instrumentation

Analytical signals at 610 nm were obtained using a UV-Vis spectrophotometer (Shimadzu UV-1800 PC, Kyoto, Japan). Phases separation was facilitated with the aid of a Universal Hettich centrifuge model (London, England). The pH was measured using a pH meter (pH-2005 model, JP Selecta, Spain).

Reagents and Standard Solutions

Analytical pure materials and double-distilled water were used throughout the analysis. A 50 mg L^{-1} solution of Bromophenol Blue (BrPB) dye (Merck, Germany) was prepared from 1000 mg L^{-1} BrPB stock solution. The clear molecular structure of BrPB is given in Figure 1.

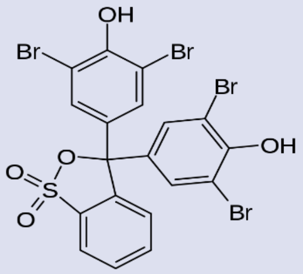

Figure 1. Molecular structure of BrPB

Dilute solutions of 1.0 mol L^{-1} HCl and NaOH (Merck, Germany) were used to adjust the solution pH. Bentonite (B) and Zeolite (Z) used as adsorbents were purchased. Graphene oxide (GO) was synthesised by oxidation of graphite using a modified Hummers method. Acid mixtures were added to the powdered graphite pieces and mixed in a sonification device at room temperature. The sonification process was continued by adding a certain amount of weighed $KMnO4$. After being kept at 55 ^{0}C for 30 minutes, it was taken from the sonification device and allowed to cool at room temperature. Ice water containing 30% H_2O_2 was added to the cooled mixture and sonification was continued. The solid obtained after this process was washed with distilled water until it reached pH 7 and dried in an oven at 60 ºC. GO was synthesised in the laboratory of Sivas Cumhuriyet University, Faculty of Engineering [13,14].

Adsorption Experiment

Certain volumes of BrPB solution, prepared daily at certain concentrations, were put into the test tube. By keeping the solutions in the natural pH environment, 0.1g B, 0.1g Z and 0.05g GO were added to the tubes containing BrPB solutions at different concentrations, and they were kept at room temperature for 24 hours to equilibrate. After 24 hours, each tube was centrifuged in a centrifuge device at 4000 rpm for 15 minutes to separate the adsorbent from the solution. After centrifugation, the phases were separated from each other and the absorbance value of the taken solutions was measured at 592 nm on a UV-VIS spectrophotometer in order to determine the concentration of dye remaining without adsorption on the adsorbent. After determining the equilibration time of the solution for each adsorbent, other experimental conditions were optimised. Adsorption capacity was calculated using Equation 1.

$$q_e = \frac{(C_0 - C)}{m} \times V(1) \qquad (1)$$

q_e = Amount of species adsorbed by adsorbent (mg g^{-1})
C_0 = Initial concentration of the species to be adsorbed (mg L^{-1})
C = Adsorbed concentration remaining in aqueous solution after adsorption (mg L^{-1})
m = Adsorbent amount (g)
V = Solution volume (L)

pH effect

Based on the adsorption processes mentioned above, 0.1g B, 0.1g Z and 0.05 g GO were added to 10 mL of 50 mg L^{-1} BrPB solution taken into separate tubes. The pH of the solution was adjusted to the desired pH value with dilute HCl and NaOH and kept at room temperature for 24 hours. After centrifugation for phase separation, absorbance values were measured at 592 nm. To determine the optimum pH value, simultaneous experiments were carried out in the pH range of 3-9.

Effect of Adsorbent amount

After the initial concentration and pH value were determined, the effect of the amount of adsorbent was investigated. The effect of the amount of adsorbent in the range of 0.01-0.7 g for B and Z in a 50 mg L^{-1} BrPB solution at pH 5 was investigated. For GO, since it is a more effective adsorbent by nature, the amount of adsorbent was reduced considerably and was kept in the range of 0.001-0.1 g.

Effect of initial concentration of BrPB

The effect of the initial concentration of BrPB in the BrPB solution of 5-100 mg L^{-1} was determined at the pH value determined in the previous step for each adsorbent type, by keeping the system pH constant, with 0.1 g B and Z, 0.05 g GO at 25 °C was investigated.

Temperature effect

In order to investigate the effect of temperature on the system under the optimum conditions determined in the previous experimental stages, a series of experiments were carried out in the range of 5-40 °C.

Examination of adsorption kinetics

Once the optimum experimental conditions were determined, the reaction kinetics were determined for each adsorbent species.

Investigation of adsorption thermodynamics

Examination of adsorption thermodynamics was also evaluated under determined optimum conditions; Thermodynamic parameters such as Kc, ΔG°, ΔH° and ΔS° were calculated.

Results

pH Effect

pH value is one of the most important parameters in changing the adsorption capacity since it affects the surface charge and ionization degree of the adsorbent. The effect of pH on adsorption capacity was investigated in the pH range of 3-9, 0.1 g B and Z, 0.05 g GO, 50 mg L^{-1} BrPB, 25 ∓ 1 °C, and the results are given in Figure 2.

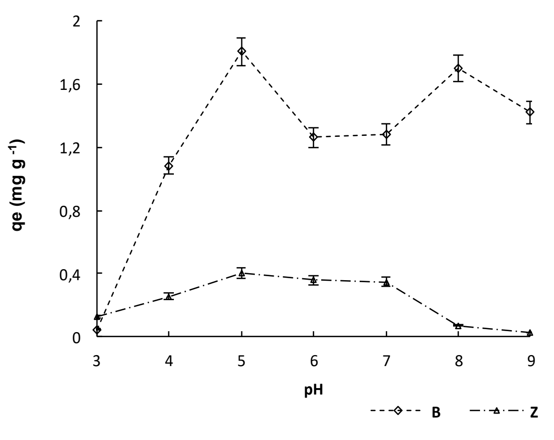

Figure 2. pH effect on the BrPB adsorption capacity of B and Z

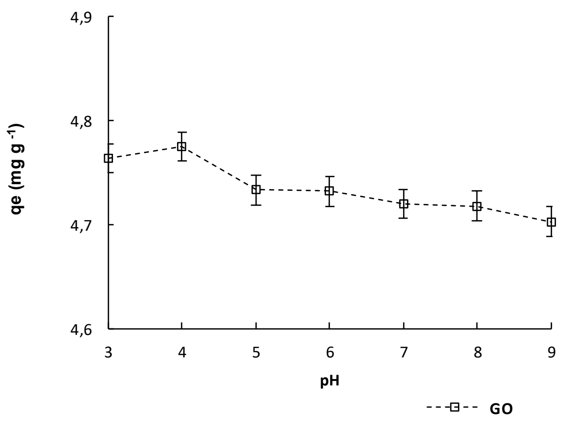

Figure 3. Effect of pH on the adsorption capacity of GO on BrPB

As can be seen in Figure 2 and Figure 3, the adsorption capacity of BrPB increased with increasing pH for all adsorbents up to a certain value and then remained at almost constant values. The best adsorption capacity for B and Z was observed at pH 5, while for GO at pH 4. BrPB is a weakly acidic anionic compound, so it exists in a neutral form at pH<7 and in an ionic form at pH>7 [15]. When the pH is above 7, the surface charge of the adsorbent becomes more negative and the electrostatic repulsion between the negative groups becomes effective due to the anionic state of BrPB [16].

Effect of Initial Concentration of Dyestuff

The effect of the initial concentration of 5-100 mg L^{-1} BrPB solution was investigated at pH 5 for adsorbent types B and Z, pH 4 for GO, at 0.1 g B and Z, 0.05 g GO adsorbent amount, at 25 ∓ 1 °C. The results obtained are given in Figure 4- Figure 5. As can be seen from Figure 4- Figure 5, for all adsorbent types, the adsorption capacity increased up to a certain value with the increase in the initial concentration of BrPB and then this value became almost constant when the system reached equilibrium. Increasing the initial concentration of BrPB means that the species to be adsorbed in the solution increases, but since the amount of adsorbent in the system is fixed, the maximum value that the adsorbent can adsorb does not change. After the equilibrium and saturation point, the remaining unadsorbed BrPB remains in solution and the adsorption percentage decreases or remains constant [17, 18].

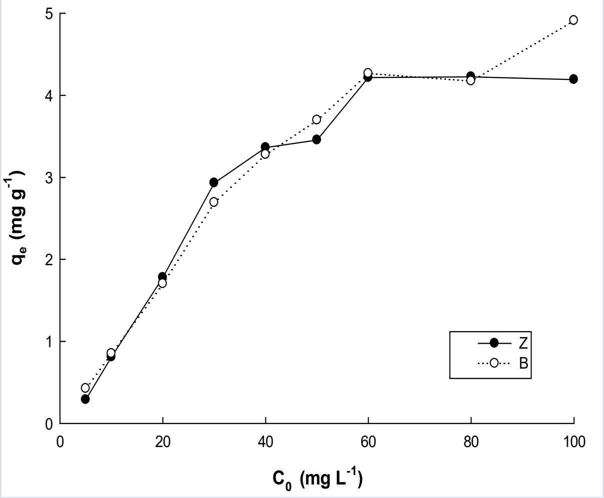

Figure 4. Effect of initial concentration of BrPB on B and Z adsorption capacities

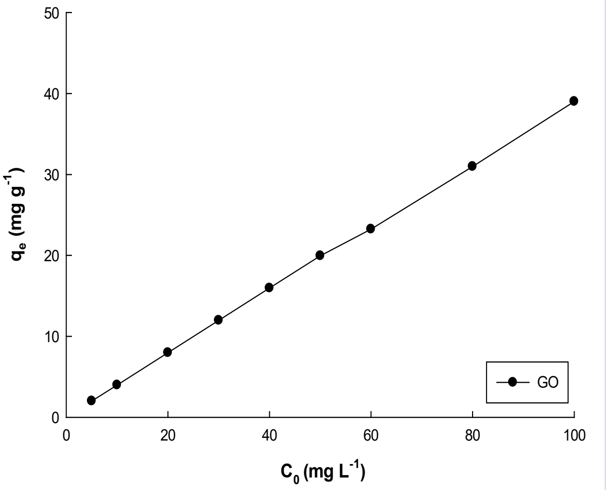

Figure 5. Effect of initial concentration of BrPB on GO adsorption capacity

Effect of Adsorbent Amount

The experiments were carried out at pH 5 for B and Z, pH 4 for GO, 50 mg L^{-1} BrPB, 25 °C, to investigate the effect of the amount of adsorbent taken in the range of 0.01-0.7 g for B and Z and 0.001-0.1 g for GO on the adsorption capacity. The results obtained are given in Figure 6.

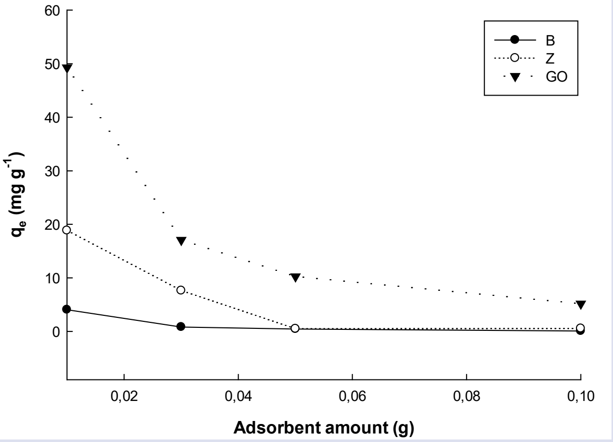

Figure 6. Effect of adsorbent amount on the BrPB adsorption capacity of different adsorbents

It can be seen in Figure 6 that, as the amount of adsorbent increases, the adsorption capacity for all adsorbent types initially increases and after a certain value it decreases. While the adsorption capacity was expected to increase with the increase in the amount of adsorbent, on the contrary, a decrease in adsorption was observed. On the one hand, while the amount of adsorbent increased, on the other hand, the amount of BrPB, the species to be adsorbed, was constant and the adsorption capacity decreased because the adsorbent surface became saturated [19-22]. Considering the values in Equation 2.3.1, it is expected that the adsorption capacity will decrease as the amount of adsorbent increases.

Temperature Effect

The pH of the solution was adjusted to 5 for B and Z and 4 for GO, the amount of adsorbent was taken as 0.1g for B and Z and 0.01g for GO and the effect of temperature on adsorption at an initial concentration of 50 mg L^{-1} for B and Z and 600 mg L^{-1} for GO BrPB was investigated at 5, 25 and 40 °C and the results are given in Figure 7- 8. It was observed that the adsorption capacities increased with the increase in temperature for B and Z adsorbents. The increase in adsorption capacity with increasing temperature shows that the system is an endothermic system.

For GO, on the contrary to B and Z adsorbents, the adsorption capacity started to decrease with the increase in temperature. Increasing the temperature may have a decreasing effect on the adsorption capacity, as it may cause the functional groups on GO to break off.

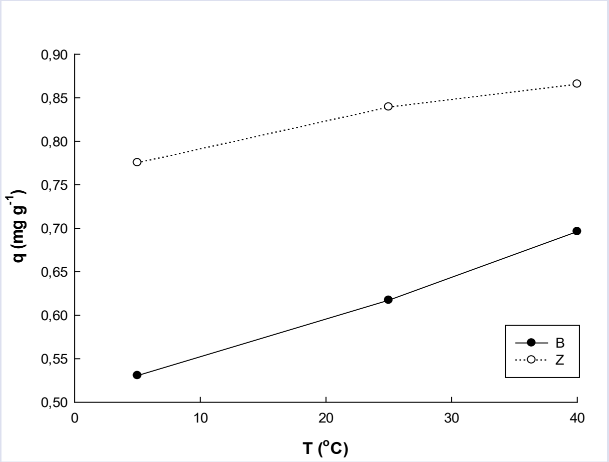

Figure 7. Effect of temperature on the adsorption of BrPB by B and Z

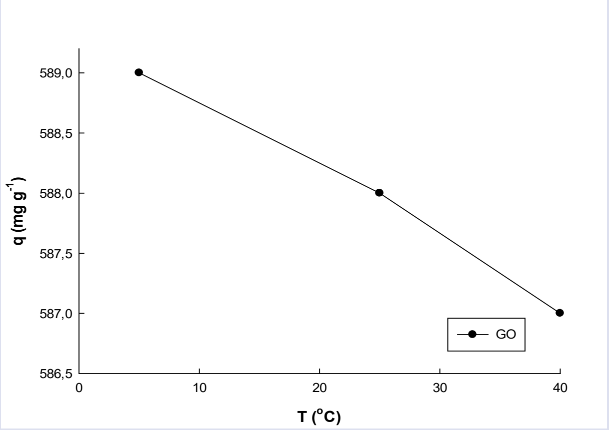

Figure 8. Effect of temperature on GO adsorption of BrPB

Evaluation of Isotherms

The Langmuir and Freundlich isotherm models are described in Equation 2- 3 respectively.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

C_e: Concentration of the substance remaining in the solution after adsorption (mg L^{-1})

q_e: Amount of material collected per unit adsorbent (mg g^{-1})

K_L: Constant that depends on the adsorptivity of the adsorbate (g^{-1})

q_m: Maximum adsorption capacity of the adsorbent (mg g^{-1})

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (3)$$

C_e: Concentration of the substance remaining in the solution after adsorption (mg L^{-1})

q_e: Amount of material collected per unit adsorbent (mg g^{-1})

K_F: (Adsorption capacity (g^{-1})

n: Adsorption intensity

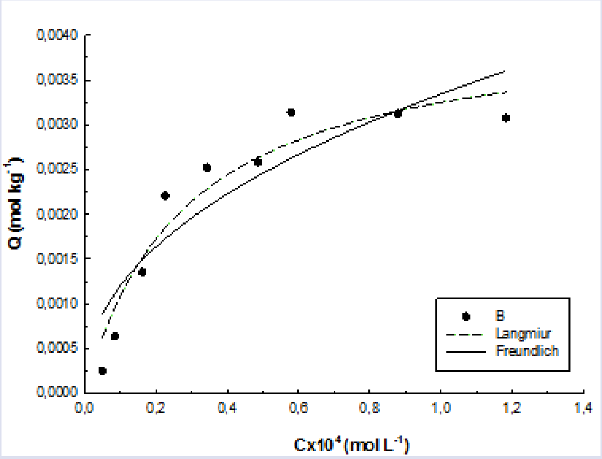

Figure 9. Langmuir and Freundlich isotherms of B

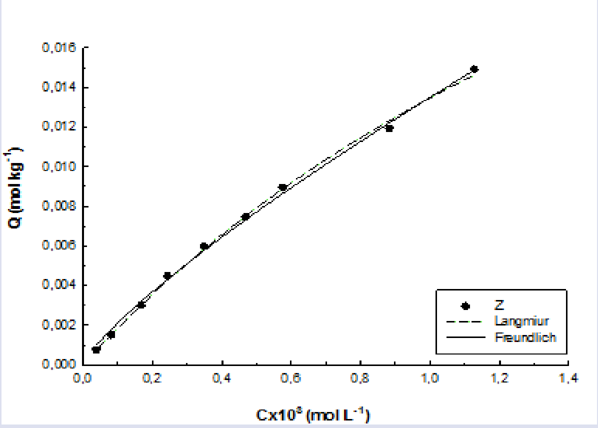

Figure 10. Langmuir and Freundlich isotherms of Z

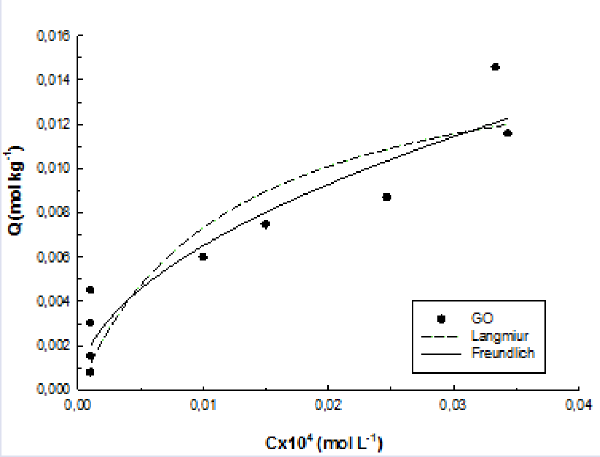

Figure 11. Langmuir and Freundlich isotherms of GO

Table 1. Langmuir and Freundlich parameters derived from BrPB adsorption isotherms to B, Z and GO

Material	Langmuir			Freundlich		
	X_L/molkg^{-1}	K_L/Lmol^{-1}	R^2	X_F	B	R^2
B	0.0042	35340	0.931	0.198	0.443	0.829
Z	0.045	4252	0.998	22.9	0.807	0.998
GO	0.02	464100	0.831	7.75	0.513	0.889

When the 'monolayer adsorption capacities, X_L' found from the Langmiur model are compared, it is seen that the order is Z>GO>B. The XF values found in the Freundlich and D-R models also confirm the result. The comparison of the KL values, which is a measure of the tendency of adsorption, was found to be in the order of GO>B>Z. The order of the heterogeneity measure β (decreasing value, increasing interest) in the Freundlich model is Z>GO>B.
As a result, when the adsorption capacities were evaluated, it was found that the adsorption capacity of Z for BrPB adsorbent had the highest value compared to B and GO, and in the comparison of adsorption tendency values, GO had the highest value compared to B and Z.

Evaluation of Kinetics

Pseudo-first order equation and pseudo-second order equation were used to evaluate the adsorption kinetics. The pseudo-first order kinetics equation and the pseudo-second-order kinetics are given by Equation 4-5 respectively.

$$\ln\left(1-\frac{q_t}{q_e}\right) = -k_1 t \qquad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

where q_t and q_e are the averaged current and equilibrium concentrations, respectively, in a sorbent; and k with different subscripts are rate constants.

Kinetic values were calculated for each adsorbent type, and the results are given in Figure 12-17 and Table 2. Pseudo-first-order and pseudo-second-order constants were calculated by plotting the $\ln(q_e-q_t)$ and t/q_t values separately against the t value, respectively. As a result of the examination of both kinetic values, the R^2 (correlation coefficient) values of B, Z and GO show that they conform to pseudo-quadratic rate kinetics. The rate constants for B, Z and GO were found in the order Z>B>GO. The results showed that adsorption was completed in about 30-60 minutes for all three materials.

Table 2. Pseudo-first order and pseudo-second order reaction kinetics constants of BrPB on adsorbents

Pseudo-first-order kinetic values			
Adsorbents	k_1(min^{-1})	q_e(mg g^{-1})	R^2
B	0,0207	6,638	0,9671
Z	0,0021	3,454	0,5621
GO	0,0256	15,706	0,8074
Pseudo-first-order kinetic values			
Adsorbents	k_2(g mg^{-1}min^{-1})	q_e(mg g^{-1})	R^2
B	0,0171	15,31	0,998
Z	0,253	17,0357	1
GO	0,00974	583,235	1

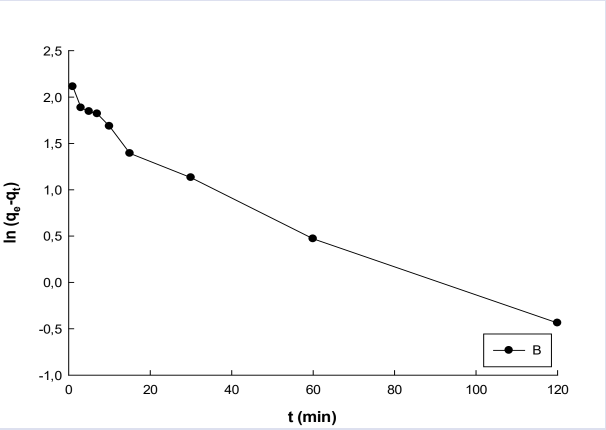

Figure 12. Pseudo-first-order kinetics of BrPB on B

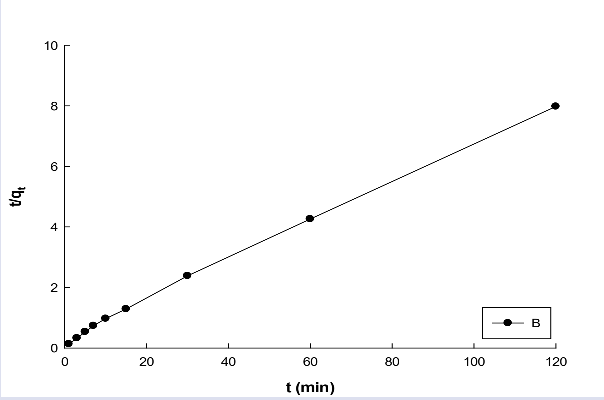

Figure 13. Pseudo second-order kinetics of BrPB on B

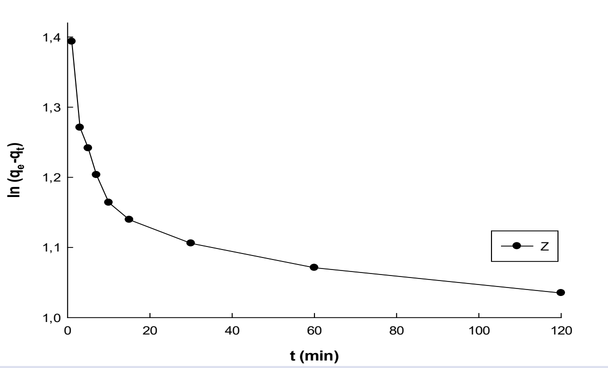

Figure 14. Pseudo-first-order kinetics of BrPB on Z

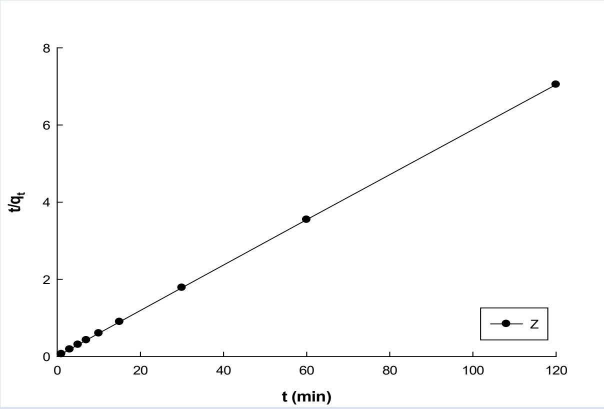

Figure 15. Pseudo-second-order kinetics of BrPB on Z

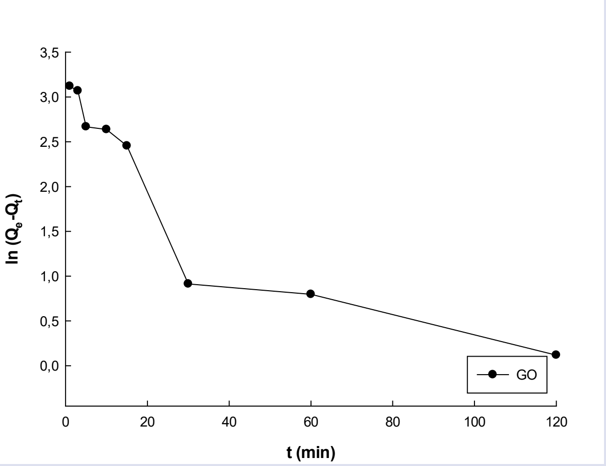

Figure 16. Pseudo-first-order kinetics of BrPB on GO

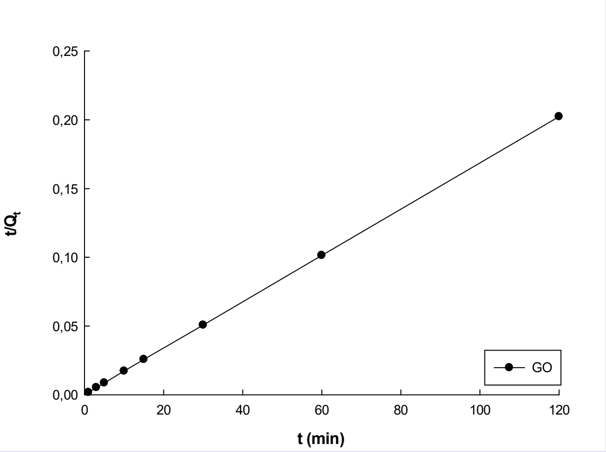

Figure 17. Pseudo-second-order kinetics of BrPB on GO

Evaluation of Thermodynamics

For each temperature value, Kc was calculated from Equation 6 and ΔG° from Equation 7. ΔH° and ΔS° values were calculated from the slope and intercept of the line formed by plotting the lnKc value against 1/T (Van't Hoff). The thermodynamic values obtained are given in Table 3.

$$K_c = \frac{C_a}{C_e} \qquad (6)$$

$$\ln K_c^0 = -\frac{\Delta S^0 - \Delta H^0}{R} x \frac{1}{T} \qquad (7)$$

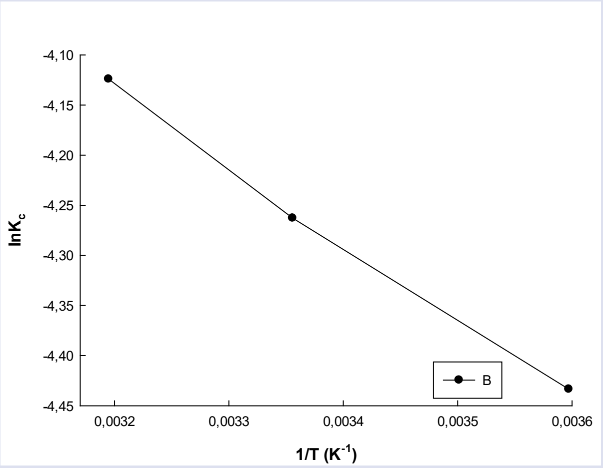

Figure 18. Thermodynamic parameters in B adsorption

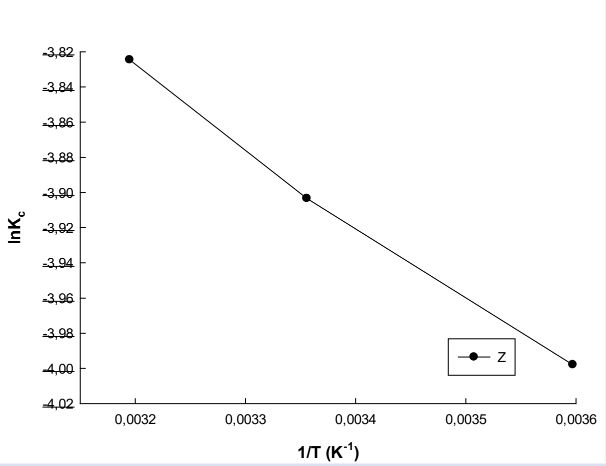

Figure 19. Thermodynamic parameters in Z adsorption

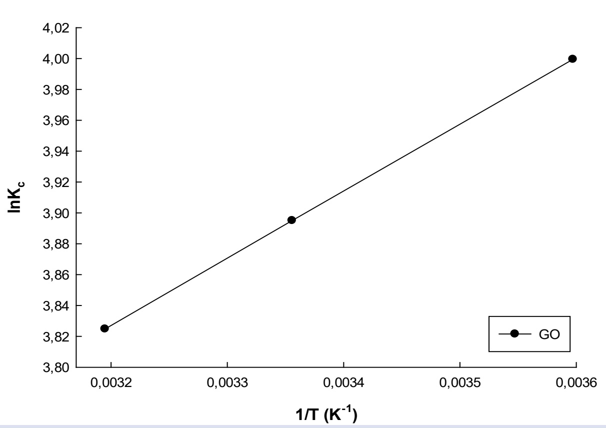

Figure 20. Thermodynamic parameters in GO adsorption

Table 3. Thermodynamic constants of adsorption of BrPB on B, Z and GO

	T(K)	ΔG°(kJ mol^{-1})	ΔH°(kJ mol^{-1})	ΔS°(J mol^{-1} K^{-1})
	278	10,25		
B	298	10,56	6,36	-14,03
	313	10,73		
	278	9,24		
Z	298	9,67	3,56	-20,46
	313	9,95		
	278	-9,24		
GO	298	-9,65	-3,61	20,27
	313	-9,95		
	278	10,25		
B	298	10,56	6,36	14,03
	313	10,73		
	278	9,24		
Z	298	9,67	3,56	-20,46
	313	9,95		
	278	-9,24		
GO	298	-9,65	-3,61	20,27
	313	-9,95		

Table 3. shows that a positive ΔG° value for B and Z indicates that the adsorption process is not spontaneous, while a negative ΔG° value for GO indicates that the reaction, i.e. adsorption, is spontaneous in the direction in which it proceeds. A positive ΔH° value for B and Z

indicates that the reaction is endothermic, while a negative ΔH° value for GO indicates that the reaction is exothermic. A negative ΔS° value for B and Z adsorbent species indicates a decrease in the randomness between solid and liquid, while a positive ΔS° value for GO indicates an increase in the randomness between solid and liquid.

Discussion and Conclusions

In this study, it was aimed to remove BrB, a dyestuff, as a pollutant species from existing environments by traditional adsorption method. In addition to being simple, fast and economical, the use of carbon-based nanomaterials as adsorbent species makes this study superior to traditional methods. Carbon-based nanomaterials are known as the material of the century, which has attracted great interest not only in pollution removal but also in many other application areas. For this purpose, GO, a carbon-based nanomaterial, was used as adsorbent species in addition to traditional adsorbent species such as B and Z in the removal of BrB by adsorption method. Parameters affecting adsorption such as pH, adsorbent amount, initial concentration of BrB, temperature, time were studied in various ranges. On the other hand, isotherm, kinetic and thermodynamic parameters were investigated. Considering the results obtained, it was observed that Langmuir isotherm was more favorable for all adsorbent types in terms of isotherm and pseudo-second order kinetic equation was observed in terms of kinetics. From the thermodynamic point of view, it was concluded that the reaction for GO was more tendency to be spontaneous. The reason why GO is more effective than other adsorbent species is that the functional groups on the surface of the adsorbent increase the surface area of the adsorbent. A significant increase in adsorption capacity was also observed due to the active functional groups on the adsorbent surface. Some of the literature studies on the removal of BrB by adsorption and the results of the current study are presented in Table 4. When the studies in this table are compared both among themselves and with our current study, it can be seen that the adsorption efficiency obtained for GO in this study (589 mg g^{-1}) is quite high. In addition, it is seen that the adsorption capacity value of carbon-based nanomaterials used as adsorbents in the studies referenced in Table 4.1 is higher than other adsorbents.

The results of this study on the removal of synthetically prepared BrB by adsorption method show that the method can be applied to real wastewater samples. Thus, wastewater containing organic and inorganic species that greatly threaten human and environmental health can be removed before being discharged directly into nature. Wastewater reuse has become an important necessity due to the insufficiency of existing water resources depending on the population growth. Nanomaterials are promising materials for wastewater recovery as in many other fields.

Table 4. Comparison of adsorption removal of BrPB with different adsorbents

Adsorbents	**q_m(mg g^{-1})**	
CNP	22,72	[18]
Magnetite Nanoparticles	400,50	[23]
CuS-NP-AC	106,38	[24]
Activated carbon obtained from Astragalus bisulcatus tree	51,21	[25]
Sorel's cement nanoparticles	4,88	[26]
Fe_2O_3–ZnO–$ZnFe_2O_4$/carbon nanocomposite	90,91	[27]
Polymer-clay composite	10,78	[28]
Thermally modified granular charcoal	101,62	[29]
Mesoporous hybrid gel derived from tetraethoxysilane and bis(trimethoxysilyl)hexane	27,60	[30]
Bentonit	15,7	Thisstudy
Zeolit	19,8	Thisstudy
Grafen oksit	589	Thisstudy

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Conflicts of Interest

The authors declare no conflict of interest.

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