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Natural Mineral and Biopolymers Based Adsorbent for Cationic Dyes Removal: Glutaraldehyde Crosslinked Alginate/Kaolin Bead

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Abstract

In this study, the removal of methylene blue (MB), malachite green (MG) and methyl violet (MV) from aqueous media by adsorption process using glutaraldehyde crosslinked alginate/kaolin hydrogel bead (g-Alg/Kao) was investigated. First of all, g-Alg/Kao was synthesized. g-Alg/Kao beads were investigated by FTIR analysis. Adsorption parameters such as solution pH value, adsorbent dosage, agitation time and initial dye concentration, which affect the removal of cationic dyes (MB, MG, MV) from aqueous solutions, were studied with this newly synthesized environmentally friendly composite adsorbent. Obtained experimental data were applied to Langmiur, Freundlich, Dubinin Radushkevich, Scatchard and Temkin isotherm models and related parameters were derived. The results revealed that the experimental data fit the Langmiur model better. According to Langmiur isotherm, the maximum adsorption capacity of MB, MG, MV was found to be 294.1, 122.0 and 357.1 mg/g, respectively. A batch contactor requires about 60 min contact time to achieve 84 % (for MB), 62% (for MG), 81% (for MV) removal percentages from aqueous solution. g-Alg/Kao show exceptional dye adsorption capability and high adsorption efficiency for MB, MG and MV removal from water. It was observed that the adsorption kinetics fit the pseudo-second-order model. Thermodynamic evaluation of adsorption showed that adsorption is endothermic, and adsorption is spontaneous. Recovery studies have shown that g-Alg/Kao composite has good adsorption/desorption performance.

1. Introduction

Today, environmental pollution is one of the problems affecting human health. Environmental pollution is a subject that has gained importance in our world. Damage to the environment by textile wastewater is a common problem. The wastewater of textile industries includes high levels of color and organic matter. These dyes cause significant pollution. Discharge of these wastewaters without treatment spoils the aesthetic appearance of the receiving water environment and causes destruction in aquatic life [1]. As dark colored waters prevent the passage of sunlight, slow down photosynthesis and reduce the amount of dissolved oxygen in the water, it is undesirable to discharge the wastewater in color. Wastewater, which can reach the human body with the receiving water environments, have carcinogenic and toxic effects. Therefore, when it is considered in terms of environment and human health, the treatment of wastewater is of great importance. For the removal of color from wastewater, alternative, cheap but effective methods have been sought instead of expensive systems in treatment methods [1-2]. Physical and chemical methods are generally used to remove the color of dyestuffs. However, these techniques have disadvantages such as not being economical in terms of facilities, equipment and materials and not being able to eliminate the environmental pollution problem. Many materials are being researched as an alternative to activated carbon, which is used in the adsorption

process, which is one of the methods used to remove dyes from wastewater and has a high cost. For this reason, studies on the search for low-cost adsorbents have increased in recent years. Materials such as apricot kernel shells [3], eggshell [4], walnut shell [5], tree and sea plant leaves [6], bagasse path [7], natural clays [8-9] can be used as adsorbent in dye removal. Among these low-cost adsorbents, clays are abundant in nature. Today, clays are widely used mainly in paper, rubber, cement, medical and agricultural pesticides, construction and especially in the ceramic industry. In addition, it has good adsorbing properties due to its high ion exchange potential. The adsorption ability of clays is due to the charge they have in the structure of their minerals. In addition, it is due to their porous structure and large surface area [10]. For these reasons, clays are widely used in the removal of dyestuffs from their aqueous solutions. The kaolin used in this study is a group of clay minerals within the clay minerals classification. Kaolin is a type of clay obtained from granite rocks. It has the molecular formula of $Al_2O_3.2SiO_2.2H_2O$ and its layered structure is formed by stacking successive $[Si_2O_5]^{2-}$ and $[Al_2(OH)_4]^{2+}$ layers [11]. The crystal structure of kaolin consists of two interconnected layers, an octahedron and a tetrahedron.

In the study, kaolin natural clay was added to the structure of biopolymers in the production of composite beads. Kaolin clays have different surface areas such as silanol and aluminol, which are pH dependent dependent adsorbents, as well as constant negative charged surfaces (formed as a result of isomorphic substitution). In the case of cationic dye studies, the increase in pH increases with increasing silanol and aluminol surfaces.

In recent years, biodegradable polymer-clay mixtures have been prepared and the properties of these polymers have been improved. For this purpose, clays such as bentonite, montmorillonite and sepiolite are more preferred. Studies on these issues have increased significantly today. As a biodegradable polymer, alginate is of great interest in scientific studies [12]. Alginate is the sodium salt of alginic acid, a natural polysaccharide, and its chemical formula is $C_6H_7O_6Na$. The alginate obtained from brown seaweed can easily dissolve in cold and hot water and, thanks to this feature, it can form heat-resistant gels. It is widely used due to its biocompatibility [12], biodegradability, non-toxicity, high gelling [13], viscosity and stabilizing properties [14], as well as being economical and abundant [15]. Alginate is used in various foods as a thickener, emulsion stabilizer, gelling agent and viscosity increaser in the food industry. In addition, alginate has many applications from the textile industry to medical applications, from food applications to dye removal [2,7,8,16].

In the application studies of hydrogels, the cross-linked form is generally preferred. Because cross-linking; It is a necessary process to ensure material integrity and to increase its mechanical strength to some extent. On the other hand, it is also necessary for controlling porosity, which is an important property for hydrogels. Artificial cross-linkers such as formaldehyde, glutaraldehyde, epoxy compounds and carboimide are widely used to modify the material, increase degradation resistance and stabilize it [17-19]. The crosslinking formation may include two alginate units, which may or may not belong to the same polymeric chain. Crosslinking using glutaraldehyde is an economical and simple crosslinking method.

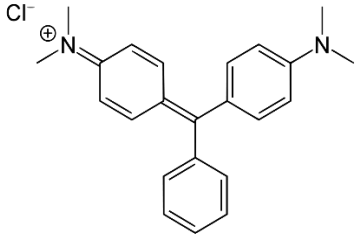
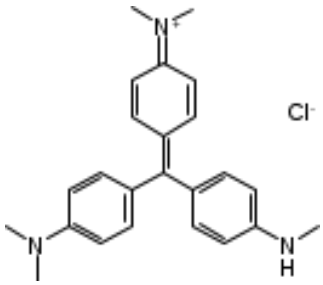
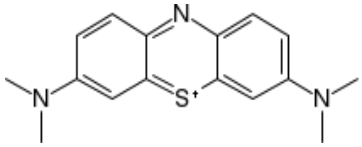
In this study, the use of glutaraldehyde crosslinked Alginate/Kaolin hydrogel bead was investigated in order to develop a suitable adsorbent for the removal of methylene blue, malachite green and methyl violet from aqueous solutions in a batch system. The new composite adsorban produced was characterized by SEM and FT-IR. In the studies conducted for these cationic dyestuffs, UV-Visible spectroscopy was used for quantitative determinations. In the study, in the batch system; the parameters of pH, adsorbent concentration, adsorbate concentration, contact time, temperature, adsorption-desorption cycle, amount of adsorbent was investigated.

2. Methodology

2.1 Materials

In studies, Sodium alginate powder (CAS No: 9005-38-3) Sigma-Aldrich, Kaolin was purchased from Bolus Alba (pH: 8.9-8.7, d: 2.76 g/cm^3, SiO_2 52.5 %, Al_2O_3 19.5 %, Fe_2O_3 10.5 %, CaO 5.5 %, MgO 3.0 %, Na_2O 0.25 %, K_2O 4.0 %, TiO_2 0.5 %), glutaraldehyde Sigma-Aldrich, NaOH HCl and $CaCl_2$ Merck brand were used. Methylene blue, malachite green, and methyl violet were purchased from Acros Organics (Table 1). All related chemicals used in the experiments were of analytical grade. In the preparation of the composite adsorbent, IKAMAG-RO15 model mechanical stirrer, Thermostated shaker of GFL 3033 model, a pH meter (Orion 900S2) with glass electrode was used. UV-visible spectrophotometer (Schmadzu UV-1700) was used for the determination of MB, MG, and MV. The FT-IR spectrum was recorded by a Bruker VERTEX 70 FT-IR spectrometer. Microstructure of the g-Alg/Kao was examined using of scanning electron microscope (SEM, Nova Nano SEM 200, FEI Company).

Table 1. Physicochemical properties of dyes (Malachite Green, Methyl Violet and Methylene Blue).

Commercial name	Structural formula	λ_{max}(nm)	Molecular Formula	M (g.mol-1)
Malachite Green oxalate		617	$C_{23}H_{25}N_2$ .1/2$C_2H_2O_4$.C_2HO_4	463.51
Methyl Violet 2B		579	$C_{24}H_{28}ClN_3$	393.96
Methylene Blue hydrate		664	$C_{16}H_{18}ClN_3S$. xH_2O	319.85

2.2 Preparation of Glutaraldehyde Crosslinked Alginate/Kaolin hydrogel beads

For the preparation of g-Alg/Kao, sodium alginate was first dissolved in 100 mL (5% w/v) distilled water. It was mixed on a magnetic stirrer for about 2 hours to obtain a homogeneous gel. On the other hand, 100 ml (5% w/v) kaolin aqueous suspension was prepared. Kaolin was thoroughly dispersed in distilled water at 450 rpm for 2 hours. Kaolin-water dispersion was added onto the prepared alginate gel and mixed in a magnetic stirrer for 5h until a homogeneous solution was formed. The sodium alginate-clay mixture was added to the 0.6 M $CaCl_2$ solution drop by drop with an injector, and the spheres were formed, and the formed spheres were mixed in a magnetic stirrer at 100 rpm for about 3 hours. The mixture was kept in $CaCl_2$ solution for about 1 night in a dark medium for overnight, then

the beads were filtered and washed with distilled water. To activate the prepared beads, composite adsorbent carrying new functional aldehyde groups was prepared by mixing with 10% (w/v) glutaraldehyde solution at 150 rpm for 3 hours. Then the beads cross-linked with glutaraldehyde were filtered, after washing with distilled water, hydrogel beads dried at ambient temperature and Glutaraldehyde Crosslinked Alginate/Kaolin hydrogel beads samples were obtained (Figure 1).

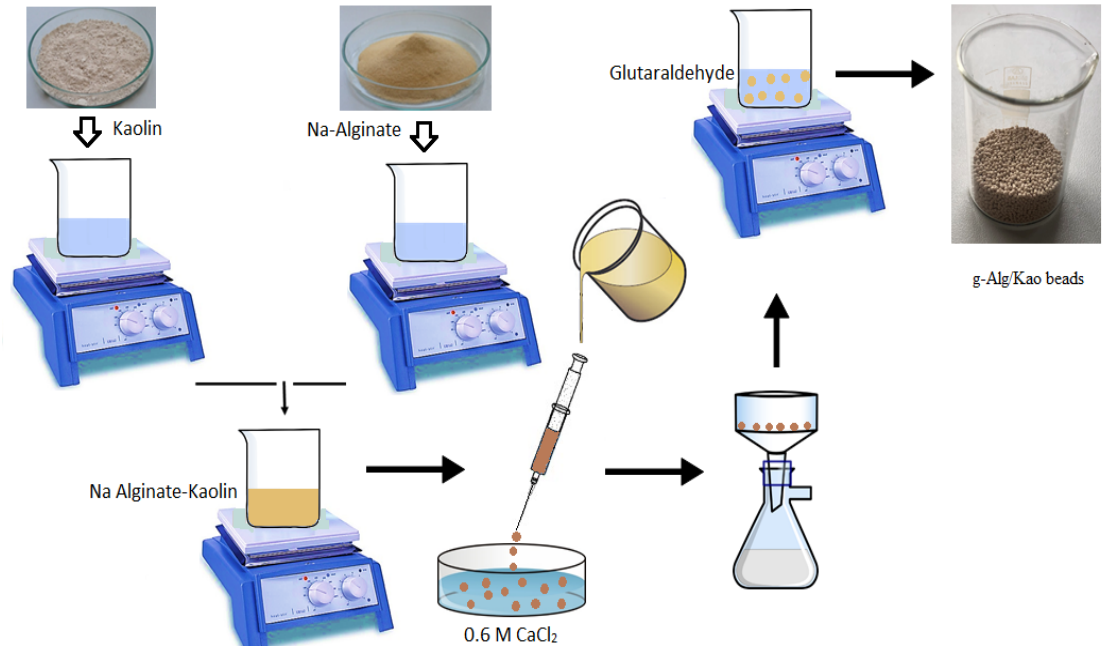


Figure 1. A schematic diagram presenting the preparation of g-Alg/Kao

2.2 Batch Adsorption

The dye solutions used in the study were obtained by diluting the stock solution prepared at a concentration of 1000 mg/L. Initial dye concentration (10-100 mg/L), contact time (5, 10, 20, 30, 60, 120 min) at different initial concentrations (25, 50 and 100 ppm) on g-Alg/Kao, adsorbent dosage (1-10 g/L), solution pH value (2-9) and temperature (20-40°C) are removed by studying efficiency was evaluated. The solution dye concentration after adsorption was analyzed for MB, MG and MV, at 664, 617 and 579 nm wavelengths in a UV-spectrophotometer, respectively. Isotherms, kinetics and thermodynamic studies were carried out. Adsorption capacity (qe) and dye removal (%) were calculated by Equations 1 and 2 below.

$$\% \text{ Adsorption} = (Co-Ce)/Co \times 100 \qquad \text{Eqn. 1}$$

$$\text{Adsorption Capacity (qe)} = (Co-Ce)/m \times V \qquad \text{Eqn. 2}$$

Where; qe; adsorption capacity (mg/g), Co; initial dye concentration (mg/L), Ce; Dye concentration remaining in solution after adsorption (mg/L), V; solution volume (L), m; adsorption amount is (g).

3. Results and Discussion

3.1 Characterization of The Beads

The FT-IR spectra of the g-Alg/Kao composite before and after adsorption are shown in Figure 2. When the spectrum of the g-Alg/Kao composite is examined, the Al-O peak at 674.96 cm^{-1} and the absorption bands of Si-O at 917.95 cm^{-1} are observed, which are characteristic peaks for kaolin [20]. -OH stresses at 3380.60 cm^{-1} at peaks in the FTIR spectrum of g-Alg/Kao, NH groups at 1070 cm^{-1},

asymmetric and symmetrical stresses at 1596.77 and 1428.99 cm^{-1} due to -COO-, –COC- stresses at 1022.09 cm^{-1} are characteristic bands of alginate [14,16,21]. The broad band at 3380.60 cm^{-1} presents vibration of -OH groups in the water molecules connected to the Si-O-Al surface by weak hydrogen bond in the kaolin structure of the used composite.

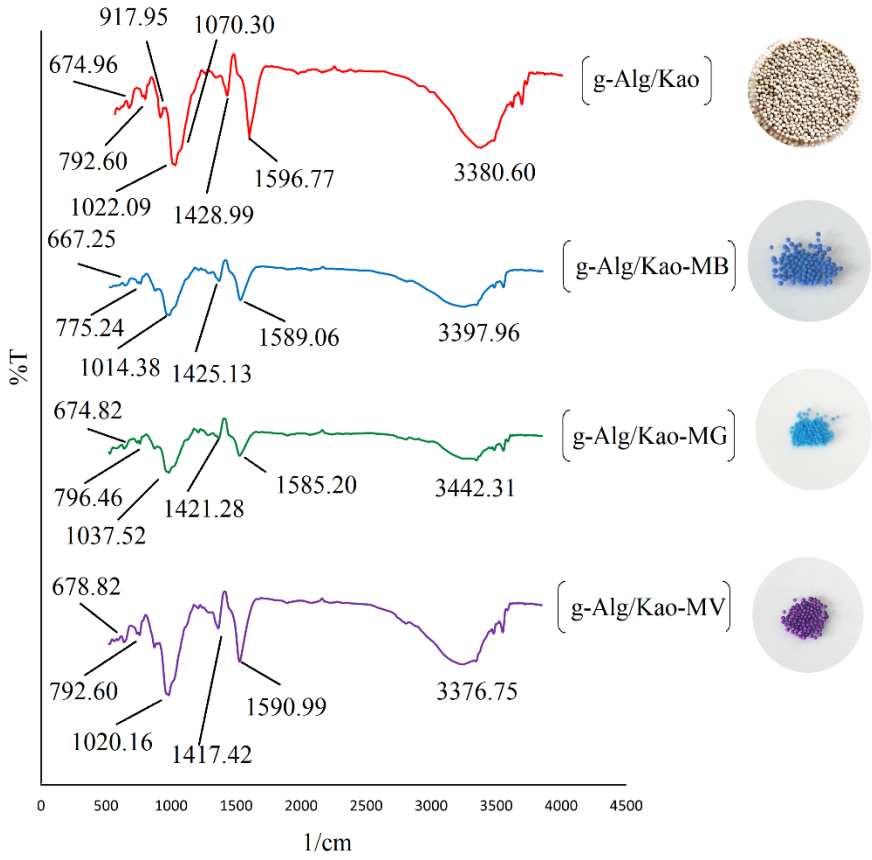


Figure 2. FTIR spectra of g-Alg/Kao before and after MB, MG, MV adsorption

Si-O vibration of Si-O-Si groups in kaolin was observed near 1022.09 cm^{-1} [22,23]. When the pre- and post-adsorption spectra of the g-Alg/Kao composite are compared, the location of the peaks does not change, but a decrease in peak intensities is observed. This is due to electrostatic interactions between MB, MG and MV and functional groups on the g-Alg/Kao composite surface. These results prove the adsorption of MB, MG and MV to the functional groups of the above-mentioned g-Alg/Kao composite. These changes; for MB prior to adsorption; It was observed that the peak in 1596.77 cm^{-1} to 1589.06 cm^{-1}, the peak in 1428.99 cm^{-1} to 1425.13 cm^{-1}, the peak in 1022.09 cm^{-1} to 1014.38 cm^{-1}, the peak in 917.95 cm^{-1} to 921.03 cm^{-1}, the peak in 792.60 cm^{-1} to 775.24 cm^{-1}, the peak in 674.96 cm^{-1} to 667.25 cm^{-1}, for MG; It was observed that the peak in 1596.77 cm^{-1} to 1585.20 cm^{-1}, the peak in 1428.99 cm^{-1} to 1421.28 cm^{-1}, the peak in 1022.09 cm^{-1} to 1037.52 cm^{-1}, the peak in 917.95 cm^{-1} to 916.02 cm^{-1}, the peak in 792.60 cm^{-1} to 796.46 cm^{-1}, the peak in 674.96 cm^{-1} to 674.82 cm^{-1}, for MV; It was observed that the peak in 1596.77 cm^{-1} to 1590.99 cm^{-1}, the peak in 1428.99 cm^{-1} to 1417.42 cm^{-1}, the peak in 1022.09 cm^{-1} to 1020.16 cm^{-1}, the peak in 917.95 cm^{-1} to 960.12 cm^{-1}, the peak in 792.60 cm^{-1} to 792.60 cm^{-1}, the peak in 674.96 cm^{-1} to 678.82 cm^{-1}, peak after adsorption and the decreased. Also, it is seen that the band around 3380.60 cm^{-1} in its spectrum shrinks after adsorption of all three dyes. The reason for this sharp decline is thought to be due to ionic interactions between the -

OH groups in the structure and the dyestuffs. Where the shift of the bands may indicate that these functional groups interact with the MB, MG and MV molecules.

3.2 Effect of Adsorbent Dosage

The amount of g-Alg/Kao to be added to the solution is one of the important factors affecting the efficiency of the amount of dyestuff to be adsorbed. If the amount of g-Alg/Kao to be used is low, the maximum adsorption efficiency that can be realized may decrease. If too much g-Alg/Kao is added to the solution, agglomerations may occur in the solution and adversely affect the adsorption efficiency [24]. In order to determine the effect of g-Alg/Kao amount, the experiments were carried out at 0.5, 1.0, 1.5, 2.0 and 2.5 g/L doses and the experimental results obtained are given in Figure 3. It was determined that the amount of dyestuff retained on the surface increased as the amount of g-Alg/Kao increased. When g-Alg/Kao is increased from 0.5 g/L to 1.0 g/L, dye removal for MB; from 47% to 81% for MG; It was observed that it increased from 28% to 54%, and from 45% to 80% for MV, then did not change much with the increase in dosage. However, when the amount of dyestuff per unit adsorbent is examined (qe), it is seen that dyestuff removal decreases with increasing g-Alg/Kao amount. This is due to the decrease in the contact surface of the dyestuff, due to the agglomeration of the particles as the amount of g-Alg/Kao increases. This decrease in adsorption density can be explained by the presence of unsaturated sorption sites throughout the sorption process [25]. For these reasons, it was determined that the most appropriate g-Alg/Kao dosage for the dyestuffs studied was 1 g/L. Such behavior is probably due to the decrease in the adsorbate/adsorbent ratio and consequently all the accessible adsorption sites are saturated, and the increase of adsorbent dosage does not allow higher removal of dye. Similar features were observed in literature. Liu et al. studied the effect of graphene oxide/alginate gel beads dose on the removal of MB dye and they found that the removal percentage increase with increasing the adsorbent dose and the optimum dosage was 1 g/L [26].

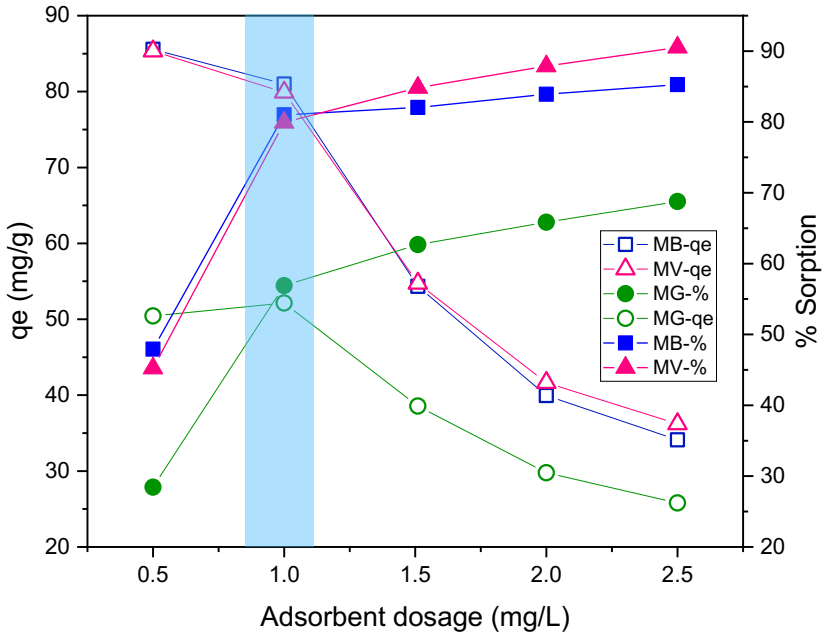


Figure 3. The effect of adsorbent dosage on the adsorption capacity and the percentage removal of MB, MG and MV by g-Alg/Kao.

3.3 Effect of pH

The pH value of the solution is an important control parameter in adsorption processes. The reason for this can be expressed as the change in the surface charge and therefore the adsorption capacity of the adsorbents. Adsorption capacities depending on pH for g-Alg/Kao are shown in Figure 4a. pHpzc is an important parameter to explain the adsorption of anions and cations at different pH values and to determine the optimum pH value for the pollutant. If the pH value of the adsorbent is above the pHpzc value, the adsorbent will be negatively charged, and if it is below the pHpzc value, the adsorbent will be positively charged [27]. Therefore, when the adsorbent surface is negatively charged, its anions will remain in the environment with the effect of electrostatic attraction, while its cation adsorption ability will increase. Likewise, when the adsorbent surface is positively charged, cation adsorption will tend to decrease. Figure 4b shows the results obtained during the pHpzc determination of kaolin and g-Alg/Kao. The point of zero charge (pHpzc) of g-Alg/Kao was found to be at pH 5.6. pHpzc is important to explain the adsorption mechanism. Adsorption of cationic dyes (MB, MG, MV) can be effective if pH > pHpzc. Using the concept of pHpzc, the surface of g-Alg/Kao will be predominant negatively charged when solution pH > 5.6, while predominant positively charged when pH < 5.6 [28]. The adsorption of cationic dyestuffs (MB, MG and MV) by g-Alg/Kao is more pronounced in the pH > pHpzc.

In the MB, MG and MV adsorption study using g-Alg/Kao, the effect of pH was investigated at pH: 3,4,5,6,7,9. In the cationic dye adsorption study conducted with g-Alg/Kao, the qt value increased with the increase in the pH value in the solution, but the qt values obtained between pH=6 and pH=10 values were almost equal. It was determined that qt values reached 73.09 mg/g for MB, 57.48 mg/g for MG, and 76.81 mg/g for MV when g-Alg/Kao was used as an adsorbent. The acidic pH values of the adsorbent are surrounded by H_3O^+ ions and the surface functional groups of the adsorbent are positively charged. H_3O^+ ions prevent the cationic dyes with the same load due to electrostatic pushing to approach the adsorbent surface. Therefore, the adsorption efficiency of the MB, MG and MV in the cationic form is low at the acidic pH values and increases as the pH increases. As can be seen from Figure 4b, a point is reached where the surface load is zero (pH range) with increasing pH. After this point, with the increase in pH value, g-Alg/Kao surfaces have a negative character and MB, MG and MV adsorption is increased.

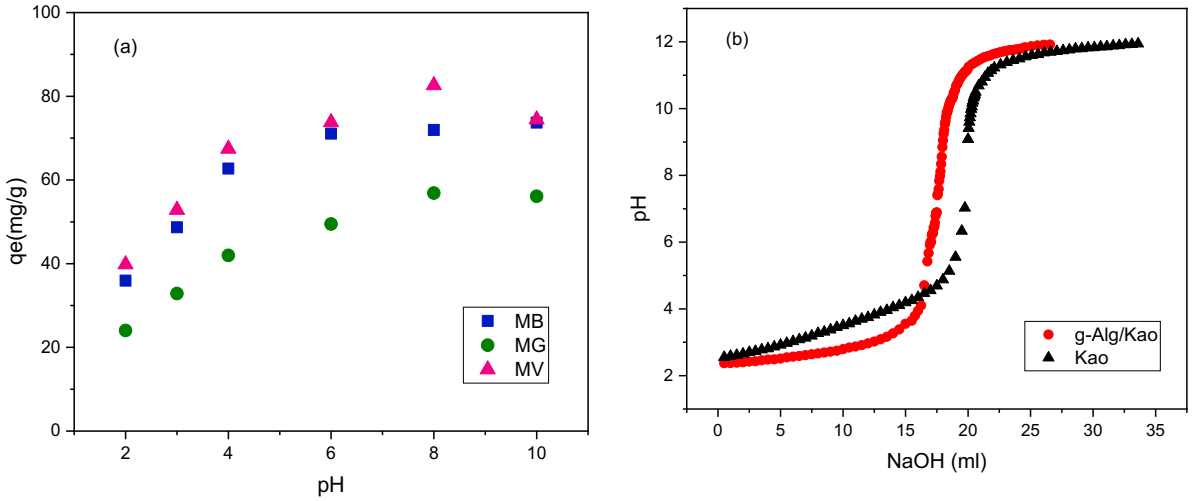


Figure 4. (a) The effect of pH on the adsorption of MB, MG and MV by g-Alg/Kao (b) pHpzc of Kao and g-Alg/Kao

According to the experimental results, the most suitable solution pH was determined to be around 6 in MB, MG, MV removal. The initial pH values of the solutions were found to be 6.2 for MB, 6.7 for MG and 6.4 for MV. Therefore, the initial pH values of the solutions were used during the experiments. Lower cationic dye adsorption at acidic pH values attributed to protonation of dye molecules and competing for active sites between excess H+ ions and cationic dye molecules. In accordance with the literature, higher pH resulted in higher adsorption in this study. For instance, Alver et al. [14] magnetic alginate/rice husk bio-composite for removal of methylene blue dye, since no significant change in adsorption capacity was achieved between pH 6–10, optimum conditions for adsorption are found to be pH 6. Djelad et al. [12] studied the removal of crystal violet dye from synthetic wastewater by using as alginate-whey biocomposite and reported that the maximum adsorption occurred at pH 6.

3.4 Effect of initial dye concentration

In order to determine the maximum adsorption capacity of synthesized g-Alg/Kao, adsorption studies of samples at different dye concentrations (25, 50, 75, 100, 200 and 400 ppm) were performed and absorbance values were measured in UV spectrophotometer. The effect of initial dye concentration on MB, MG, MV removal using g-Alg/Kao is shown in Figure 5. The removal efficiencies (qe) obtained in the adsorption of g-Alg/Kao and MB, MG, MV increased depending on the increasing dye concentration and reached a plateau after a certain value. Metin et al. studied the removal of cationic dyes by magnetic zeolite-alginate-polyanetholesulfonic acid gel beads adsorbent at different initial concentration of dye [29]. They found that the dye adsorption capacity increased with increasing the initial concentration of dyes.

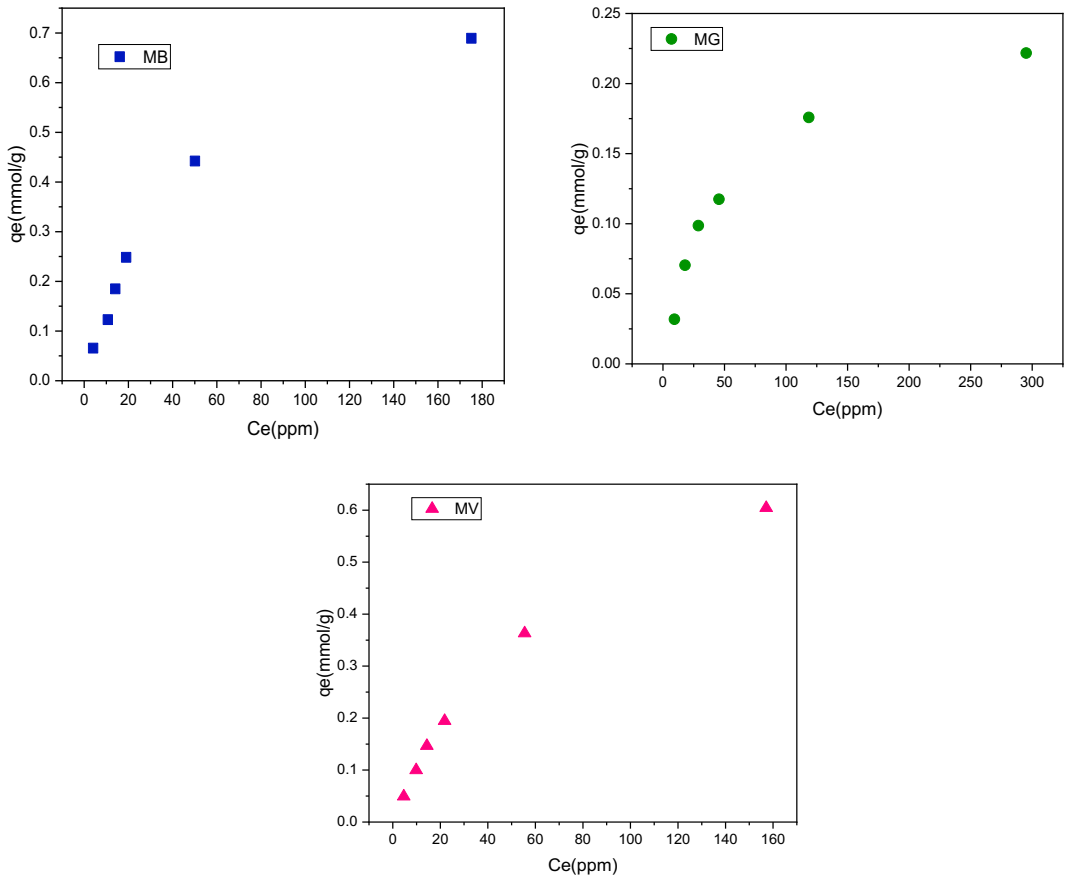


Figure 5. Adsorption isotherm g-Alg/Kao.

The initial dye concentration provides the necessary driving force on the mass transfer resistance of cationic dyes between the aqueous and solid phase [30]. Thus, for g-Alg/Kao, an increase in the initial dye concentration increases the adsorption by increasing the driving force [31]. On the other hand, as the binder areas on the g-Alg/Kao surface were filled by the dyestuff, the removal efficiency decreased with increasing initial concentration. At low initial concentrations, the dye interacts with the binding sites, resulting in a high adsorption rate. The reason for this is the decrease in suitable areas that can adsorb on the g-Alg/Kao surface with increasing MB, MG and MV concentrations in the solution [32, 33].

Isotherm equations in 3,4,5,6 and 7 were used for the calculated concentration values and Langmuir, Freundlich, D-R, Scatchard and Temkin isotherm curves, respectively (Figure 6). By using the equations of the drawn curves, the maximum adsorption capacities of the samples and the best adsorption isotherm model for the samples were determined. Equations 3-7; C_0 (mg/L) is the initial dye concentration in solution, C_e (mg/L) is the dye concentration at equilibrium, qe (mg/g) is the dye adsorption at equilibrium, q_0 (mg/g) is the maximum adsorption capacity, K_L (b) (L/mg) Langmuir constant, K_F (mg/g) Freundlich constant (related to Adsorption capacity), n Freundlich constant (related to Adsorption density), V (L) Solution volume, m (g) adsorbent mass taken. K_1 (L/mg) is the constant related to the heat of adsorption, K_2 is the dimensionless Temkin isotherm constant.

When the correlation coefficient values given in Table 2 are examined, it shows that the adsorption isotherm data are more suitable for the Langmuir isotherm model. The compatibility of the experimentally obtained isotherm data with the Langmuir isotherm model indicates that the adsorption of MB, MG and MV on g-Alg/Kao occurs in a single layer, the adsorbent surface is homogeneous, and the adsorption energy of all areas on the adsorbent surface is constant [39]. When the Langmuir isotherm parameters given in Table 2 are examined, it has been determined that the qe value, which gives the maximum adsorption capacity of the g-Alg/Kao and MV adsorption results, is higher than the MB and MG adsorption capacities. When Freundlich isotherm parameters are examined in the adsorption of MB, MG and MV with g-Alg/Kao samples, K_F (constant showing the relative adsorption capacity of the adsorbent) is the highest adsorption intensity (heterogeneity factor) of 1/n adsorbate (value between 0-1) and as it approaches 0, the heterogeneity level of the surface increases), the lowest 1/n value is seen in MV adsorption. This shows that the highest heterogeneous adsorption capacity is in MV adsorption. Estimated free energies from D-R model were found to be 8.45, 8.91 and 8.06 kj/mol for the MB, MG and MV, respectively. Free energies above 8 kJ/mol, adsorption process of chemical nature.

Using the Langmuir isotherm constant, the isotherm type can be classified according to the value of the dimensionless separation factor R_L constant, which explains the feasibility of the adsorption process; $R_L > 1$ unfavorable, $R_L = 1$ linear isotherm, $0 < R_L < 1$ favorable isotherm, $R_L = 0$ irreversible isotherm [40,41]. By using g-Alg/Kao, R_L values were calculated as 0.36, 0.36, 0.44 for the initial dyestuff concentrations of 25, 50 and 100 mg/L for MB, MG, MV removal, respectively. The fact that the calculated R_L values of MB, MG and MV for all studied concentrations vary between 0 and 1 indicates that the suitability condition is provided and that g-Alg/Kao is a suitable adsorbent for the removal of these cationic dyes.

Methylene Blue **Malachite Green** **Methyl Violet**

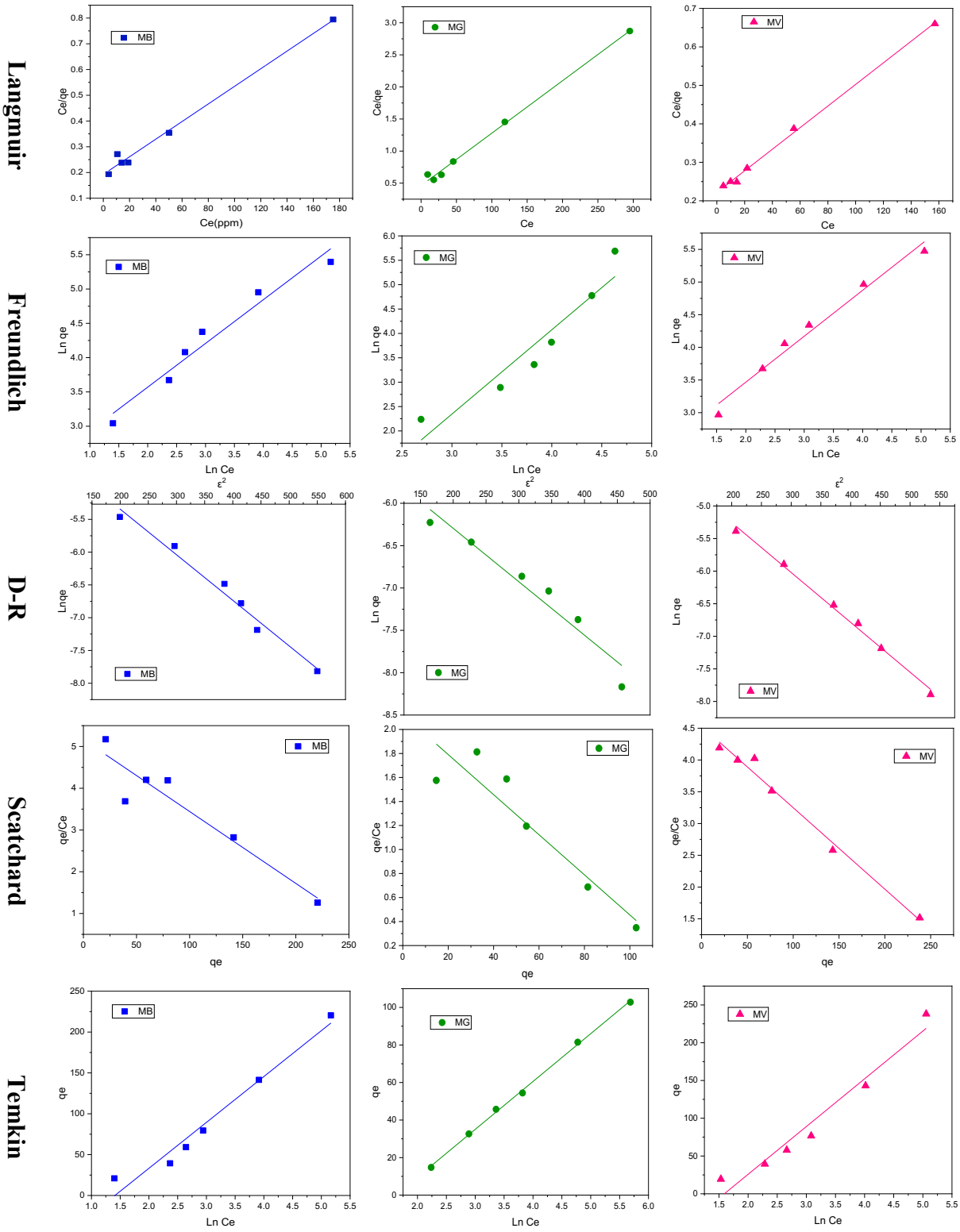


Figure 6. Langmuir, Freundlich, Dubinin-Radushkevich, Scatchard, and Temkin isotherms plot for the adsorption of MB, MG and MV onto g-Alg/Kao

Table 2. Adsorption isotherm parameters for removal of MG, MV and MB.

Model	Equation	Eqn	Dye	Parameters for dye	Ref.

Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{A_s} + \frac{1}{K_b A_s}$	(3)		**A_s**	**K_b**	**R^2**	**R_L**	[34]
			MB	294.1	0.018	0.991	0.36	
			MG	122.0	0.017	0.996	0.36	
			MV	357.1	0.013	0.998	0.44	
Freundlich	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$	(4)		**K_f**	**n**	**R^2**		[35]
			MB	9.9	1.57	0.958		
			MG	6.4	1.91	0.904		
			MV	7.8	1.42	0.979		
D-R	$\ln q_e = \ln q_m - \beta \varepsilon^2$	(5)		**X_m *10^{-2}**	**K**	**E**	**R^2**	[36]
			MB	1.90	0.007	8.45	0.978	
			MG	0.65	0.006	8.91	0.941	
			MV	2.41	0.008	8.06	0.995	
Temkin	$qe = B \ln K_T + B \ln Ce$	(6)		**B**	**K_t**	**R^2**		[37]
			MB	56.15	0.25	0.967		
			MG	25.50	0.20	0.999		
			MV	63.22	0.20	0.957		
Scathard	$qe / C_e = Q_s K_s - q_e K_s$	(7)		**Q_s**	**K_s**	**R^2**		[38]
			MB	300.3	0.017	0.897		
			MG	127.2	0.016	0.875		
			MV	353.9	0.013	0.986		

Table 3. Adsorption capacity of the other reported adsorbents for the removal of MB, MG and MV.

Adsorbent	Dye	qe (mg/g)	References
Graphene oxide/calcium alginate composites	MB	181.81	[42]
Mesoporous activated carbon-alginate	MB	230	[15]
Poly(vinyl alcohol)-sodium alginate-chitosan-montmorillonite nanosheets hydrogel beads	MB	137.2	[43]
Epichlorohydrin crosslinked chitosan/carbon–clay	MB	95.31	[2]
Carboxymethyl cellulose sodium/graphene oxide hydrogel microparticles	MB	58.24	[44]
tannic acid-poly(vinyl alcohol)/sodium alginate hydrogel beads	MB	147.06	[45]
magnetic sodium alginate modified zeolite	MB	181.85	[46]
Fe3O4/Activated charcoal/Alginate polymer beads	MB	2.079	[47]
Sodium alginate/NaOH treated SB charcoal beads	MG	57.5	[48]
Super paramagnetic sodium alginate-coated Fe3O4	MG	47.84	[49]
Magnetite supported alginate bead	MG	1.667	[50]
magnetic zeolite-polyanetholesulfonic acid/alginate gel	MG	164	[51]
Alginate/PAMAM – Halloysite	MG	113	[52]
Composite HNT-Fe3O4	MV	20.4	[53]
Alginate/acid activated bentonite beads	MV	145.80	[54]
acrylamide/graphene oxide bonded sodium alginate	MV	100.30	[29]
Grafted sodium alginate/ZnO/graphene oxide composite	MV	13.85	[55]
Biosilica/alginate nanobiocomposite	MV	21.32	[56]
Alginate-Whey composite beads	MV	220	[12]
g-Alg/Kao	MB	294.1	This study
g-Alg/Kao	MG	122.0	This study
g-Alg/Kao	MV	357.1	This study

In the light of the results obtained in the study, the MB, MG and MV removal studies in the literature and the adsorption studies on g-Alg/Kao adsorbent are compared and given in Table 3. It was seen that the result obtained in the study was quite high when compared with the literature. This shows

that in the removal of cationic dyes, both the use of biopolymers shows higher adsorption capacity and the use of clays, which are abundant in nature, increases the adsorption capacity of the material.

3.5 Effect of time

Adsorption graphs of MB, MG and MV at different initial concentrations (25, 50 and 100 ppm) on g-Alg/Kao at different times (5, 15, 30, 60, 120, 180 and 240 min) are given in Figure 7. In these graphs, it was observed that there was a rapid increase in the amount of MB, MV dyestuffs adsorbed in the first 15 minutes at three different concentrations when g-Alg/Kao was used. It was determined that the adsorption gradually came to equilibrium at the end of 15 minutes and reached equilibrium at the end of 60 minutes. On the other hand, it was determined that there was a rapid increase in MG adsorption in the first 30 minutes, and after 60 minutes, it gradually came to equilibrium and reached equilibrium at the end of 60 minutes. After that, 60 minutes was chosen as the optimum contact time since the removal efficiency did not change. This is due to the large number of empty areas on the g-Alg/Kao surface where the dye molecules can hold at the beginning of the adsorption. Most of the studies that used clays, alginate etc. as an adsorbent to remove various types of cationic dyes studied the effect of contact time and determined the time required to reach equilibrium. For example, Purnaningtyas et al. studied the effect of contact time on the removal of MB using Activated Carbon/Chitosan/Alginate Beads. They found that the highest removal rate of methylene blue (MB) and methyl violet 2B (MV 2B) dyes was achieved after 60 minutes for both dyes [57]. Afterwards, it was observed that the adsorption rate decreased due to the occupation of the adsorption areas by the dye molecules. The removal of MB, MG and MV from the aqueous solution was carried out in two steps. The fast first step in which the active areas on the adsorbent surface are empty (around the first 15 minutes), the second step where the rate of removal slows down as the number of active areas decreases (filled with dye).

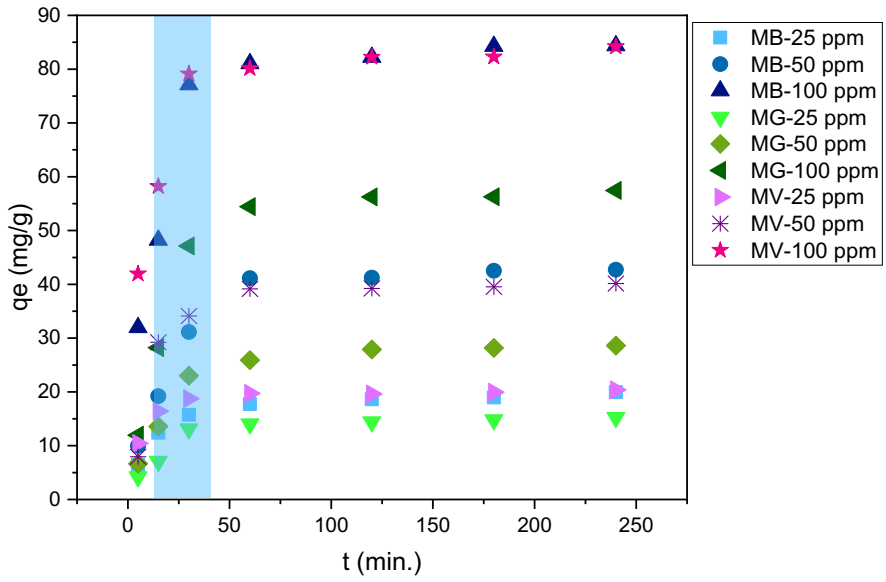


Figure 7. The effect of contact time on the adsorption of MB, MG and MV by g-Alg/Kao

3.4 Kinetic study

Kinetic studies allow controlling the kinetics of the adsorption process of MB, MG and MV on g-Alg/Kao. In order to study the MB, MG and MV kinetics on the synthesized g-Alg/Kao, adsorption studies of the samples were carried out at different concentrations at different times and the final

concentration values were measured in the UV spectrophotometer. First order kinetic model (pseudo-first order) and second order kinetic model (pseudo-second order) models were used to analyze the kinetics of MB, MG and MV adsorption on g-Alg/Kao (Figure 8).

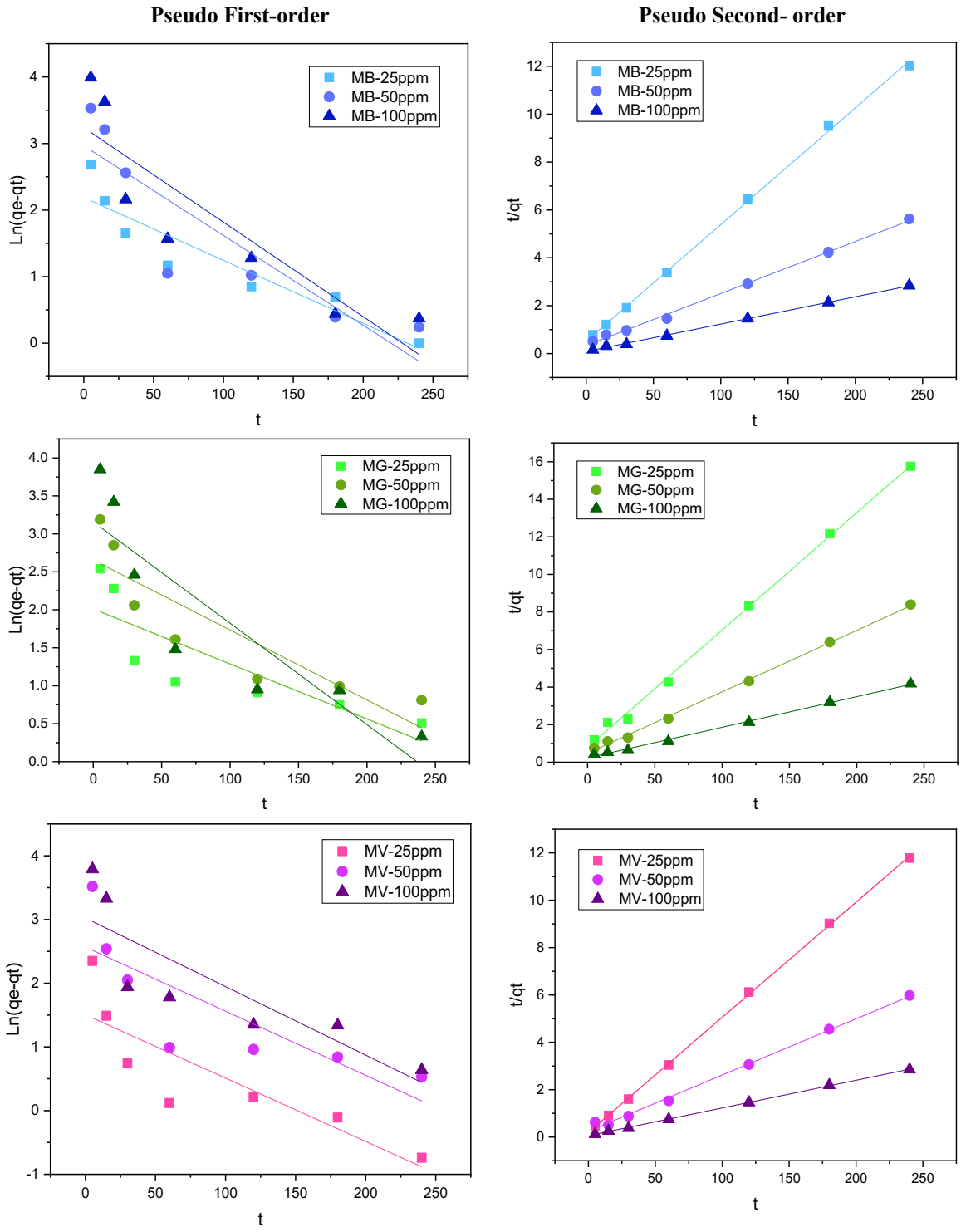


Figure 8. Kinetic models: pseudo-first-order kinetic model and pseudo-second-order kinetic model

The equations used to determine the adsorption kinetics are given in Table 4. Pseudo first order and Pseudo second order kinetic model curves given in Equations 8 and 9, respectively, are drawn. By using the equations of the drawn curves, the experimental kinetic data of the samples and the best kinetic model for the samples were determined.

$$In\ (q_e - q_t) = Inq_e - k_1 t \quad \text{Eqn. 8}$$

$$\frac{1}{q_t} = \frac{1}{k_2\ qe^2} + \frac{1}{q_e\, t} \quad \text{Eqn. 9}$$

In equations 4 and 6; q_e and q_t (mg.g-1) is the adsorption capacity at equilibrium and time t, respectively, k_1 (min -1) is the Pseudo-first-order rate constant for the kinetic model, k_2 (g.mg-1.min-1) is the pseudo-second-order rate constant for the kinetic model.

The correlation coefficient values in Table 4 were compared to determine which kinetic model the adsorption kinetics of MB, MG and MV were more compatible with. Accordingly, it is seen that the highest correlation coefficient values of all three dye data are in the pseudo-second order kinetic model. On the other hand, it is seen that the closest capacitance values to the experimental adsorption capacities are again in the pseudo-second order kinetic model. This shows that the adsorption kinetics of MB, MG, and MV on g-Alg/Kao are in good agreement with the pseudo-second-order kinetic model. The pseudo first-order kinetic model can be used for reversible reactions with the equilibrium established between solid and liquid phases. The pseudo-second-order kinetic model claims that chemical adsorption may be the rate-limiting step. Accordingly, it was thought that the MB, MG and MV adsorption method in the study could be chemical adsorption [58]. These obtained results agreed with the previous works conducted on adsorption of MB, MG and MV where the pseudo-second-order model described well the kinetics data [3, 15, 21, 29, 50].

Table 4. Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated and experimental qe values obtained at different initial MB, MG and MV concentrations.

		Pseudo First-order				Pseudo Second- order		
Dye	**C_o(ppm)**	***qe exp***	***k_1***	***qe***	***R^2***	***k_2***	***qe***	***R^2***
MB	25	20.95	0.0094	8.93	0.869	0.0047	20.49	0.999
MB	50	44.01	0.0135	19.39	0.800	0.0014	46.08	0.998
MB	100	85.83	0.0142	25.46	0.795	0.0015	87.72	0.999
MG	25	16.90	0.0073	7.49	0.706	0.0050	16.00	0.998
MG	50	30.87	0.0092	14.20	0.783	0.0023	30.58	0.998
MG	100	58.83	0.0133	23.53	0.799	0.0012	61.35	0.997
MV	25	20.85	0.0099	4.50	0.738	0.0122	20.58	0.999
MV	50	41.85	0.0101	13.02	0.680	0.0023	42.19	0.996
MV	100	86.08	0.0108	20.52	0.732	0.0024	85.47	0.999

3.4 Thermodynamics

Thermodynamic parameters (Gibbs free energy, enthalpy and entropy) were determined using Equation 13-15. Adsorption experiments were carried out at different temperatures (303, 313, 318 and 323 K). The graph drawn at the end of the adsorption experiments is shown in Figure 9. Values of Gibbs free energy represented by ΔG^o are -3674.4, -3511.7, -3349.1, -3186.4 kJ/mol for MB, -489.4, -320.0 -150.7, 18.7 kJ/mol for MG and -3629.6, -3974.5, -4319.4, -4664.2 kJ/mol for MV at 25, 35, 45, 55 0C, respectively. Negative values in Gibbs free energy indicate that adsorption tends to be spontaneous [59]. The decreasing value with increasing temperature in MB and MG shows that it tends to low temperature. The enthalpy (ΔH^o) value determined as -8525.3 and -5539.3 kJ/mol for MB, MG,

respectively, indicates that the exothermic event, while the value of 6653.1 kJ/mol for MV indicates that an endothermic event. The negative value of entropy (ΔS^o) calculated as -16.3, -16.9 J/molK for MB, MG, respectively, shows that the regularity of molecules increases during adsorption.

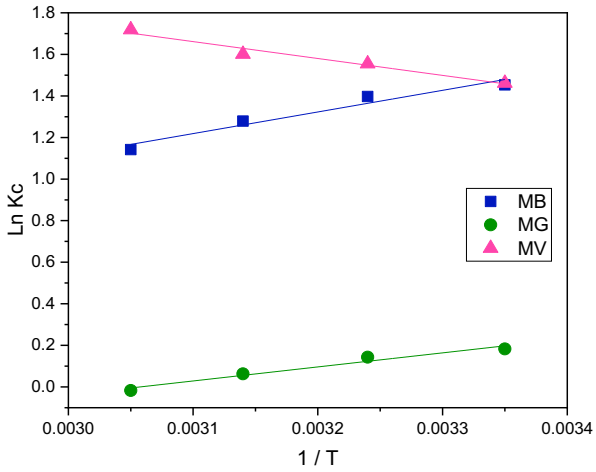


Figure 9. Effect of temperature on the adsorption of MB, MG and MV biosorption onto g-Alg/Kao.

Table 5. Thermodynamic parameters a for MB, MG and MV adsorption onto g-Alg/Kao

Dye	ΔS^o ($J\ K^{-1}mol^{-1}$)	ΔH^o J mol-1	ΔG^o (J mol-1) T=298.15K	T=308.15K	T=318.15K	T=328.15K	R^2
MB	-16.3	-8525.3	-3674.4	-3511.7	-3349.1	-3186.4	0.959
MG	-16.9	-5539.3	-489.4	-320.0	-150.7	18.7	0.972
MV	34.5	6653.1	-3629.6	-3974.5	-4319.4	-4664.2	0.971

3.4 Desorption Study

Reusability is among the factors to be considered in studies on absorbents. The reuse of the absorbent and the resulting reduced costs are of great importance in the design. This brings with it continuity in design under renewed conditions. Thus, since the variability will decrease, the efficiency expected from the absorbent will be maximized. This will make the process more useful, cheap and applicable. After adsorption, g-Alg/Kao was kept in 0.1 M HCl solution at 60°C with stirring for 24 hours. Then the composite beads were washed with distilled water and left to dry at 60°C. Under the adsorption condition specified in the experiment, the reproducibility was tried to be determined by subjecting the adsorption desorption processes repeated 5 times with g-Alg/Kao separately for MB, MG and MV. In Figure 10, the MV desorption capacity was higher than the others. According to the results obtained, it has been determined that as a result of each desorption process of g-Alg/Kao, there is an MV adsorption capacity of about 85%, so the reduction remains around 5%. Experimental results indicate that the prepared g-Alg/Kao showed good stability and a significant success in terms of effectiveness in reuses.

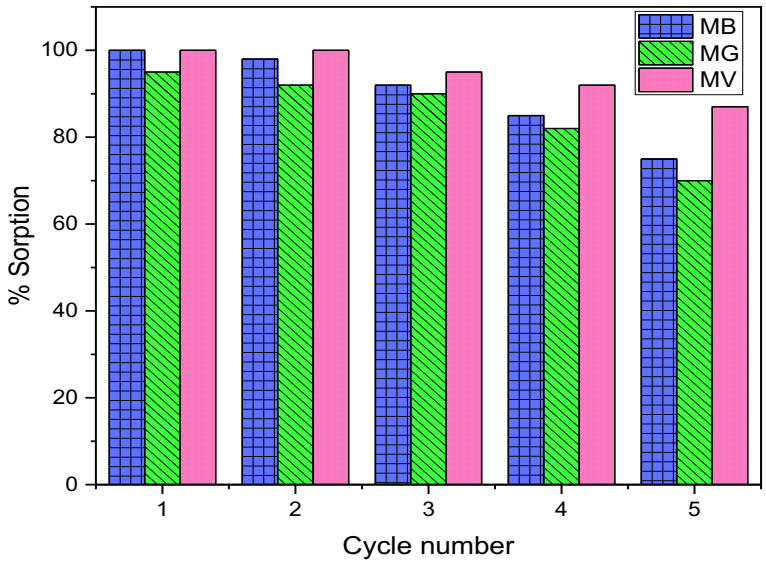


Figure 10. Desorption efficiency after recycle use.

Conclusion

In this study, Glutaraldehyde Crosslinked Alginate/Kaolin (g-Alg/Kao) hydrogel bead was prepared as adsorbent by using alginate as biopolymer and kaolin clay, which is abundant in nature and has low cost. In the experimental study, the effect of pH, initial dyestuff concentration, contact time and the effect of g-Alg/Kao amount on adsorption were investigated. When the graphs obtained for the cationic dye adsorption on g-Alg/Kao at different initial concentrations were examined, it was seen that the equilibrium time was 60 minutes. When examined from a kinetic point of view; It was observed that all three dyestuffs conformed to the pseudo-second-order kinetic model. When experimental data are applied to the adsorption isotherm, Langmuir, Freundlich, D-R, Scatchard and Temkin isotherms; In the adsorption study performed with MB, MG, MV, it was observed that they were compatible with the Langmuir isotherm, which was closest to 1 for R^2. Although the adsorption capacity and percent adsorption values did not change much in the pH (5-7) range, the highest adsorption efficiency was observed around pH 6. Therefore, the pH value at which the amount of substance remaining without adsorbing is the lowest is around 6. Considering the thermodynamic data, it was determined that the adsorption process with g-Alg/Kao for all three dyes MB, MG, MV was self-propelled, exothermic for MB and MG, and endothermic for MV. Considering the data obtained in the study, it is understood that the usability of basic dyes such as MB, MG, MV on g-Alg/Kao is high.

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest. *Compliance with Ethical Standards:* This article does not contain any studies involving human or animal subjects.

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