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Polymeric styrene–divinylbenzene resin Amberlyst-15: A novel, smart and alternative adsorbent for the removal of cationic methylene blue dye from aqueous solution

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ABSTRACT

In this study, the removal of methylene blue, which is frequently used in textile industry, from aqueous solution under appropriate adsorption conditions was investigated for the first time using Amberlyst-15, a polymeric styrene–divinylbenzene resin as adsorbent. Adsorption studies were carried out under different experimental conditions such as pH, contact time, initial dye concentration, adsorbent amount and temperature. The highest removal percentage in methylene blue removal studies with Amberlyst-15 was computed as 98.90 % for 100 ppm methylene blue using 1.0 g/L adsorbent. Adsorption isotherm data were analyzed using different isotherm models and isotherm constants were calculated. It was seen that the performed isotherm studies were compatible with the Langmuir model. The maximum adsorption capacity calculated by using the Langmuir isotherm equation was 178.57 mg/g for Amberlyst-15. Adsorption kinetic studies were evaluated with pseudo-first order, pseudo-second order and intraparticle diffusion model. The suitability of pseudo-second order kinetic model was determined for Amberlyst-15. In addition, thermodynamic parameters were investigated and FTIR analysis was performed to determine the functional groups responsible for adsorption. These results suggested that Amberlyst-15 polymeric resin is a promising candidate and new adsorbent for methylene blue and other dyes removal from wastewater. This study is to reveal that Amberlyst-15 can be used as an alternative and efficient sorbent in the removal of other dyes and pollutant species in wastewater via examining the suitability of Amberlyst-15 in the removal of methylene blue.

1. Introduction

Access to clean water, which plays a key role in protecting public health and is vital for human well-being, is a growing problem worldwide today. However, many people, especially in low-income and developing countries, face serious difficulties in accessing safe and clean drinking water sources [1,2]. Contaminants in water resources and other environmental mediums define to a wide spectrum of chemicals utilized in recently, including but not restricted to pesticides, insecticides, heavy metals, cosmetic products, dyes, personal care items, some fertilizers, and pharmaceuticals [3,4]. Among these pollutants, one of the most important and most common pollutant groups in wastewater is dyes. Five substantial industries such as textile, paper and pulp, dyeing, dye manufacturers, and tannery/paint are acknowledged to be accountable for the existence of dye residuals in the environment [5]. Dyes and their degradation products significantly are composed of complicated aromatic molecular structures and synthetic originations which are more resistant and inconvenient to biodegradation process. So, removing dyes from wastewater may be more difficult than other pollutants and may require more complex treatment processes [6]. Although the exact amount of paint and paint degradation products discharged into the environment by these branches of industry mentioned above is not known, it is obvious that this amount is quite high and poses a significant problem for human and environmental health in today [7].

The dyes and their metabolites go into food chains via bio-accumulation mechanism and cause potentially fatal damage to human and living things because of augmented dye concentration over the time. These dye molecules and ions can straightforwardly enter into the water systems and sources on account of wastewater of industrial and commercial applications, agricultural runoff, household. The release of dyes

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into the water sources gives rise to various environmental and health troubles. Most of the dyes currently in use have toxic, mutagenic, carcinogenic (bladder, kidney, liver) and teratogenic properties to human and living organisms. Also, these dyes can induce respiratory problems and allergic reactions in the eye, skin, mucous membrane irritation, and dermatitis [5,6]. Dyes provoke detriment to aquatic environment and organisms because of their heavy metal, aromatic, and chlorine ingredients [7]. Another of its most important harms is colored water negatively changes the photosynthetic activity in the aquatic environment because it prevents the transmission of sunlight because even effluents of dyes existence in small concentrations (< 1 ppm) are very highly discernible and recalcitrant [5,8–11]. Accordingly, the effective removal and treatment of the dyes from wastewater/water sources is greatly necessary for environmental security and public health [12]. To date, a variety of approaches namely chemical precipitation, sedimentation, flocculation, coagulation, ion exchange, membrane filtration, ultrafiltration, ozonation, photocatalysis, electrochemical remediation, bioremediation, electrocoagulation, photochemical degradation, adsorption [13,14] etc. have been implemented to treat wastewaters. The adsorption process is accepted to be a very efficacious, low-cost, and generally utilized technique among all existing pollutant removal processes [15]. This process in wastewater treatment implicates removals of pollutants employing based carbon materials such as active carbon and numerous obtainable potentially cheap adsorbent materials with the inclusion of biomass-based adsorbents [16].

Methylene blue is an aromatic heterocyclic basic dye with a molecular mass of 319.85 g mol^{-1}. Methylene blue is a well-known cationic thiazine dye with the molecular formula $C_{16}H_{18}N_3ClS$. Methylene blue is a highly water-soluble, positively charged compound that belongs to the polymethine dye class. According to the International Union of Pure and Applied Chemistry (IUPAC), its chemical name is [3,7-bis (dimethylamino) phenothiazine chloride tetra methylthionine chloride] and its color index (CI) is 52,015 [17]. The two-dimensional structure of methylene blue is shown in Fig. 1.

Recently years, polymeric resins have come out as encouraging candidates for the removal of various pollutants from environmental matrices because of their tunable surface features and high adsorption capacities [18]. In addition, different functional groups on the surface of polymeric resins can act selectively to achieve adsorption with the target molecule. Amberlyst-15, one of the oldest synthesized macroporous cation exchange resins and this resin was frequently employed as a heterogeneous catalyst for the synthesis of various organic molecules. Amberlyst-15 has a powerful acidic cation exchange resin, especially a divinylbenzene styrene sulfonic acid. This inimitable chemical structure ensures it with robust ion-exchange abilities, allowing Amberlyst-15 to be extremely effective in different chemical processes. Literature studies suggest a bidisperse pore size distribution for Amberlyst-15, containing micro and macro pores [19,20]. When the literature information is investigated, the number of studies on the use of Amberlyst-15 as an adsorbent in the removal of pollutants from wastewater is quite low. There are a very limited number of studies in which Amberlyst-15 is used as an adsorbent, especially in the adsorption removal of dyes, which are an important waste of the industry and are released in large quantities.

Apart from these mentioned studies, a few studies on metal removal from aqueous solutions with Amberlyst-15 have been published in recent years about adsorption of Cd (II) [21], and adsorption of Pb (II) and Cd (II) [22].

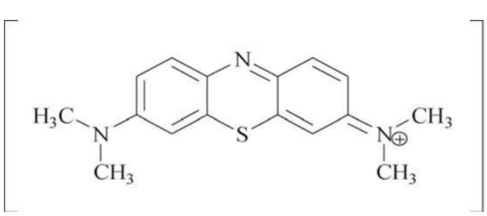

Fig. 1. Molecular structure of methylene blue.

When literature studies on the removal of dyes by adsorption method are examined, studies on the use of Amberlyst polymeric resins as adsorbents are very rare. The aim of the present study is to understand the potential of polymeric resin Amberlyst-15 adsorbent in the removal of methylene blue cationic dyes. When all the literature studies in which Amberlyst-15 is used as an adsorbent are examined, there is no research on utilizing Amberlyst-15 for removal of methylene blue from aqueous solution and waste waters. Studies in the literature show that Amberlyst-15 is a good ion exchange resin. Another main purpose of this study is to reveal that Amberlyst-15 can be used as an alternative and efficient sorbent in the removal of other dyes and pollutant species in wastewater via examining the suitability of Amberlyst-15 in the removal of methylene blue.

2. Experimental

2.1. Materials

The adsorbate molecule methylene blue (Sigma-Aldrich, CAS Number: 122965–43-9) and adsorbent Amberlyst-15 (CAS number: 39389–20-3) that were used in this study are Sigma brand. Other major chemicals sodium hydroxide and hydrochloric acid were supplied from Merck, Germany in analytical grade. Also, deionized water was made use of throughout the experimental stages.

2.2. Preparation of methylene blue solution

For the current investigation solution of adsorbate molecule (1000 ppm), that is methylene blue, was prepared via exactly weighed quantity of it was dissolved in distilled water. The volumetric flask in which the stock methylene blue solution is placed was then appropriately wrapped with aluminum foil and stored in a dark place to prohibit direct sunlight, which can give rise to discoloration. In the experimental studies, solutions of desired methylene blue concentrations were prepared by dilution of stock solution. Initial solution pH was controlled by adding hydrochloric acid and sodium hydroxide.

2.3. FTIR studies

The functional groups of the Amberlyst-15 were determined by utilizing FTIR spectroscopy (Perkin Elmer, Spectrum 100 model). The Amberlyst-15 sample was scanned over a wavelength range of 400–4000 cm^{-1} using with resolution of 4 cm^{-1} FTIR spectrophotometry with ATR technique.

2.4. Batch adsorption process of methylene blue

UV–Visible spectrophotometer (A T80 Model UV/VIS Spectrophotometer, PG Instruments) was used to determine the amounts of methylene blue in aqueous solutions before and after adsorption. In order to determine the maximum wavelength of methylene blue absorption in aqueous solution, a wavelength scan was performed in the wavelength range of 200 to 900 nm (Fig. 2) and the wavelength at which maximum absorbance was obtained was determined as 662 nm. This value was used throughout the entire experimental study.

Methylene blue removal studies were carried out at certain concentrations prepared by dilution from a 1000 ppm stock dye solution. First, the effect of pH and contact time on the adsorption of methylene blue was studied. For this purpose, the solution pH was adjusted between 2 and 11 and samples were taken at certain contact times using Amberlyst-15 as an adsorbent at each pH value. Percent removal values were calculated using **Eq. (1)** from the absorbance values before and after adsorption. Also, the amount of methylene blue adsorbed onto unit weight of Amberlyst-15, q_e (mg/g) was computed by utilizing **Eq. (2).**

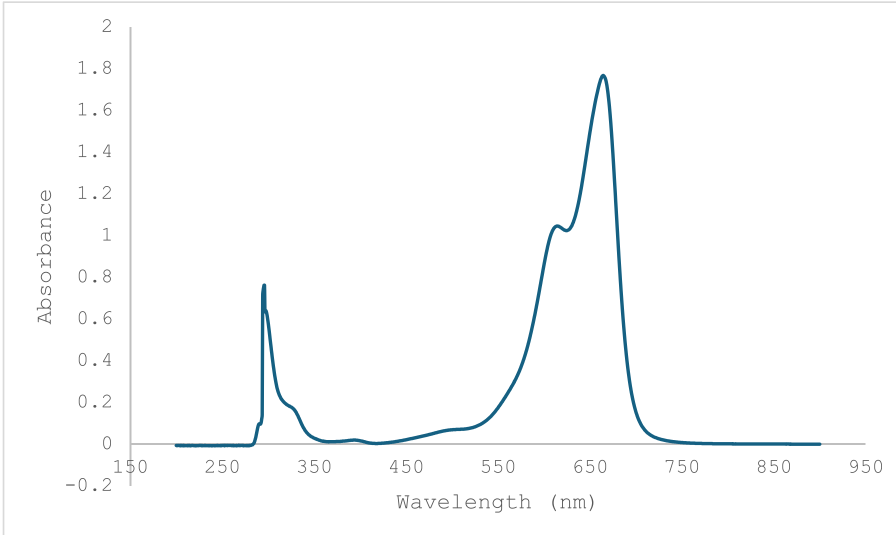

Fig. 2. UV–Vis spectrum for methylene blue (10 ppm).

After determining the optimum pH value and contact (equilibrium) time, the effect of the amount of Amberlyst-15 used as adsorbent on methylene blue removal was investigated. At this stage of the experimental study, adsorbent amounts varying between 0.0125 g and 0.1 g were added to 50 mL methylene blue solutions to perform the adsorption process. After determining the most appropriate adsorbent amount for adsorption studies, in order to investigate the effect of the initial concentration of methylene blue on removal, adsorption experiments were carried out in methylene blue solutions at concentrations between 50 and 250 ppm.

$$Removal(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

In these equations, C_0 (ppm) and Ce (ppm) correspond to the initial and the equilibrium concentrations of methylene blue dye, respectively. Also, m(g) is the mass of Amberlyst-15 and V (L) is the volume of methylene blue solution.

2.5. Adsorption isotherm and kinetics models

Within the scope of the study, isotherm studies were carried out to explain the mechanism of the adsorption process of Amberlyst-15 used as adsorbent in the removal of methylene blue. Isotherm models such as Freundlich, Langmuir, Temkin, Redlich-Peterson (R-P) and Dubinin-Radushkevich (D-R) were used. Adsorption isotherm studies of the removal of methylene blue by adsorption using Amberlyst-15 were investigated using the data of adsorption studies obtained with initial methylene blue concentrations of 50, 100, 150, 200 and 250 ppm at 298 K temperature and pH 9. In this study, kinetic studies of the adsorption of methylene blue by Amberlyst-15 were investigated according to pseudo first order, pseudo second order and intra particle diffusion models.

2.6. Thermodynamic investigations

Based on the obtained data, adsorption thermodynamics were investigated. In order to investigate the effect of temperature, removal studies were carried out at 293 K, 298 K, 308 K and 318 K. The adsorption thermodynamic parameters such as ΔG°, ΔH°, and ΔS° were computed according to the thermodynamic theory.

3. Results and Discussion

3.1. Effect of pH and contact time on methylene blue removal

pH value of the aqueous solution is one of the most prominent parameters influencing the adsorbent capacity in wastewater treatment process. The performance of adsorption process is dependent on the pH of solution, because alteration in pH causes to the change in the degree of ionization of the adsorptive material and the surface features of the adsorbent [23,24]. In general, as the solution pH value becomes more acidic, the percentage removal values of anionic dyes reach higher percentages, while the opposite is true for cationic dyes. So, low pH values are chosen for the removal of anionic dyes, while high pH values for cationic dyes [25]. Adsorption studies were performed at pH between 2–11 to research the influence of solution pH on adsorption capacity. The overall percentage removal (the average of 3 experimental measurements) by Amberlyst-15 for the 100 ppm methylene blue solution is given in Fig. 3.

According to experimental studies, methylene blue removal using Amberlyst-15 is seen to be over 70 % at all pH values. As can be seen from Fig. 3, the highest percentage removal was obtained at pH 9 (98.90 %) after 90 min of contact time. The lowest percentage removal value was obtained at pH 11 (71.44 %).

The possible adsorption mechanism proposed for the removal of methylene blue from aqueous solution using Amberlyst-15 is given in Fig. 4. Experimental studies using Amberlyst-15 show that methylene blue removal is high in basic solutions and lower in acidic solutions. This is related to the cationic structure of methylene blue. The pK_a value for methylene blue is 3.8. Therefore, the cationic form of methylene blue is more dominant in the solution at high pH values [26]. The increase in percentage removal values as pH increases in adsorption studies can be explained by the fact that the Amberlyst-15 surface is negatively charged in solutions with high pH values and the increase in the adsorption of methylene blue due to the electrostatic attraction force between the cationic methylene blue molecule and the negatively charged Amberlyst-15 surface. In solutions with low pH values, methylene blue adsorption has lower values due to the electrostatic repulsion force between the cationic methylene blue molecule and the cationic Amberlyst-15 surface due to the positive charge on the Amberlyst-15 surface [27]. In addition, the lower adsorption of methylene blue at low pH values is probably due to the presence of H^+ in the environment. In the acidic solution environment, there will be a competition between the positively charged methylene blue molecules and the positively

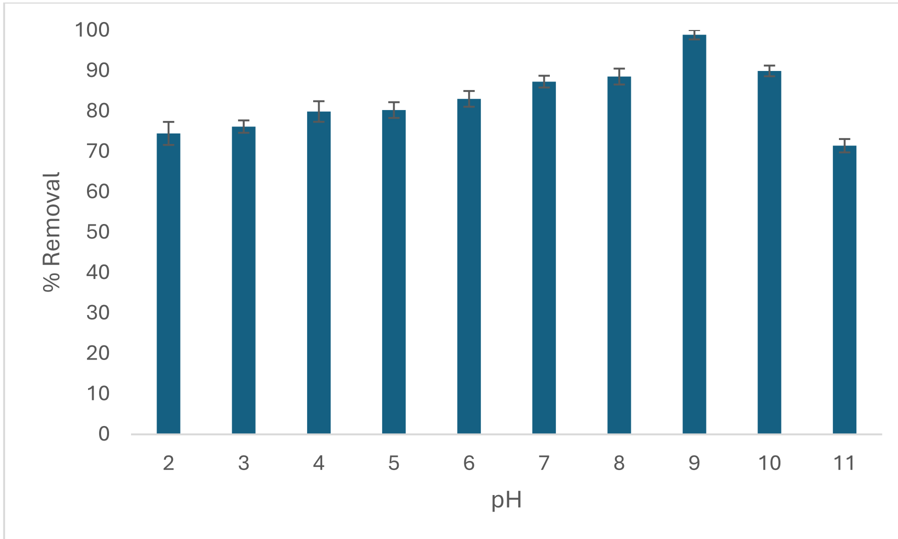

Fig. 3. Effect of solution pH on the removal of methylene blue by Amberlyst-15 (C_0:100 ppm, m:0.05 g, V:0.05 L, T:298 K, contact time:90 min, error bar – SD, n = 3).

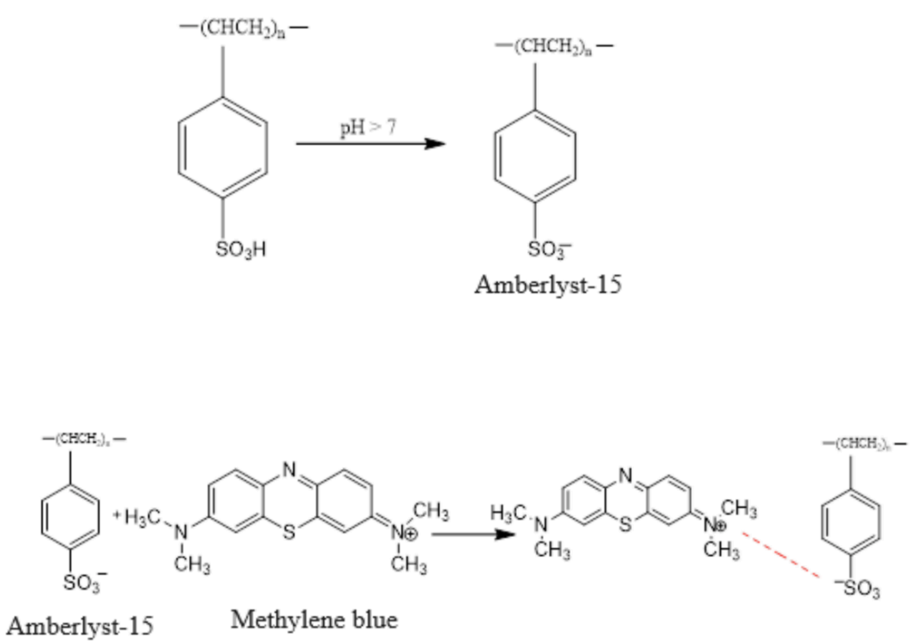

Fig. 4. Possible interaction mechanism of Amberlyst-15 with methylene blue.

charged H_3O^+ ions in terms of the adsorption process, and as a result, methylene blue adsorption will remain at lower values [28].

While examining the effect of solution pH on adsorption, the most suitable contact time for Amberlyst-15 was also investigated. In order to examine the effect of contact time (equilibrium) on the adsorption of methylene blue, samples were taken at different times (5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 min) and absorbance values were measured, and percentage removal values were computed. When the experimental results obtained were examined, the equilibrium time for methylene blue adsorption was determined as 90 min. It was observed that the percentage removal values of methylene blue did not change much at contact times longer than 90 min. In studies conducted with Amberlyst-15, the most suitable pH was determined as 9 and the contact time as 90 min and the experimental studies were continued.

3.2. Effect of Amberlyst-15 dosage on methylene blue removal

The investigation of the adsorbent dosage is crucial for prevention waste of the adsorbent material once the equilibrium phase has arrived [29]. The outcomes acquired from the influence of adsorbent dosage studies for removing methylene blue utilizing the Amberlyst-15 are given in Fig. 5.

In this study, the effect of Amberlyst-15 dosage (varying from 0.25 g/L to 2.0 g/L) on the percentage removal of the methylene blue at 100 ppm initial methylene blue concentration was investigated. Removal of methylene blue increased with increasing Amberlyst-15 dosage. When the amount of Amberlyst-15 was increased from 0.25 g/L to 2.00 g/L, the percentage removal of methylene blue increased from 62.19 % to 99.52 % after 90 min of contact time. The fact that the percentage removal values did not change significantly after 1.00 g/L Amberlyst-15 and the percentage removal value for methylene blue was quite high at

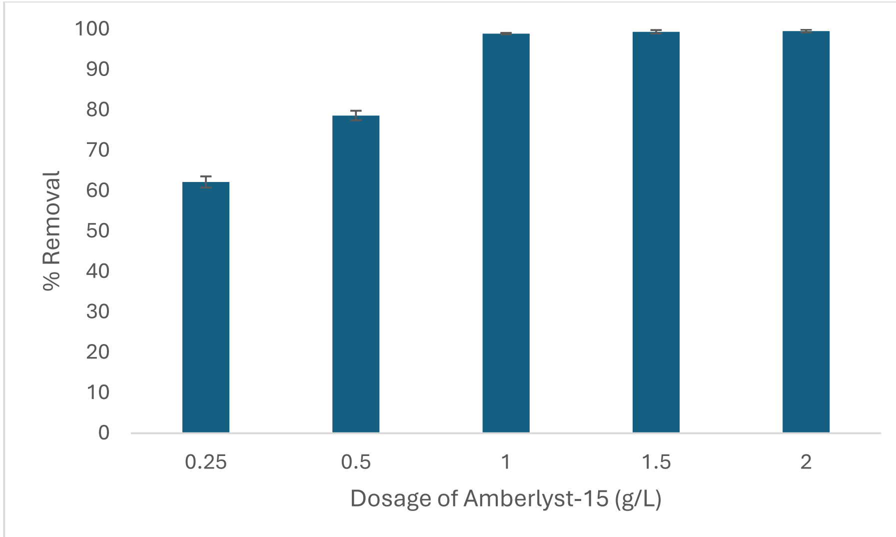

Fig. 5. Effect of adsorbent amount on the removal of methylene blue by Amberlyst-15 (pH: 9, C_0: 100 ppm, V: 0.05 L, T: 298 K, Contact time: 90 min, error bar – SD, n = 3).

98.90 % in this adsorbent amount shows that the optimum adsorbent amount as 1.00 g/L was sufficient for this study.

The obtained results showed that adsorbent dosage augments active sites ease of access. Because of limited numbers of active sites and lower adsorbent content, pollutant ions occupy a larger percentage of active sites, accelerating equilibrium. Nevertheless, with high adsorbent dosage, equilibrium gets longer to build, and more pollutant substances are successfully adsorbed owing to a lower probability of empty active sites fouling [13].

3.3. Effect of initial dye concentration on methylene blue removal

The effect of initial dye concentration inspects the relationship between the concentration of dye and the existing adsorption sites on the adsorbent's surface [30]. So, the initial concentration of the dye solution is an important experimental factor affecting the adsorption process. In the study examining the effect of dye concentration on the removal of methylene blue with Amberlyst-15, various methylene blue solutions were prepared with a pH of 9, (50; 100; 150; 200 and 250 ppm). A certain amount of Amberlyst-15 was added to each solution and stirred for 90 min on a magnetic stirrer. The results obtained are given in Fig. 6.

When Fig. 6 is examined, it is seen that the percentage removal values decrease gradually with increasing concentration of methylene blue. When the initial methylene blue concentration increases from 50 ppm to 250 ppm, the percentage removal values decrease from 99.13 % to 77.59 %. The decrease in percentage removal values with the increase in the initial concentration of methylene blue can be explained by the saturation of the active sites on the Amberlyst-15 surface and the inability of van der Waals repulsion forces to overcome the mass transport of methylene blue to the active sites responsible for adsorption on the Amberlyst-15 surface [5,31,32].

The influence of initial contaminant concentration is related to the contaminant concentration and also the binding sites existence on the surface of adsorbent. When the studies in the literature are examined, it is seen that the percentage of contaminant removal reduces with increasing initial contaminant concentration, which causes to a satiation

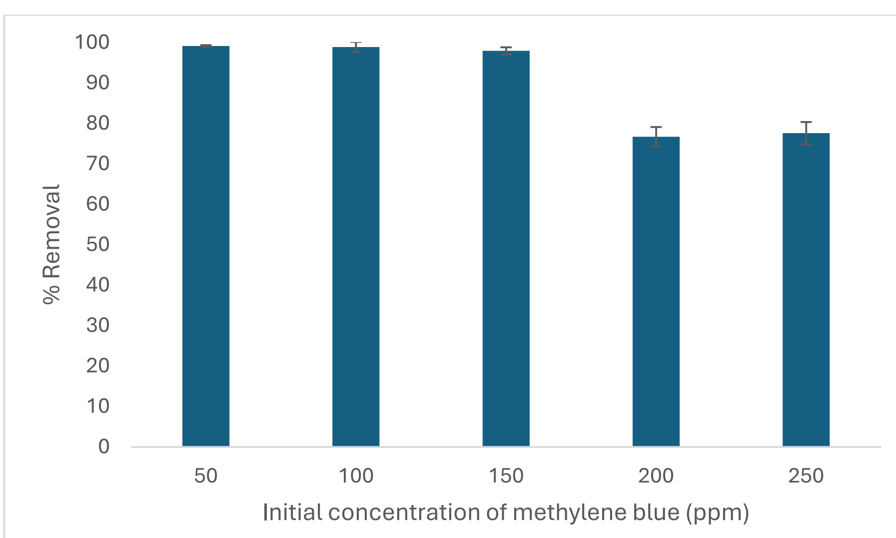

Fig. 6. Effect of dye concentration on the removal of methylene blue by Amberlyst-15 (pH: 9, m: 0.1 g, V: 0.05 L, T: 298 K, Contact time: 90 min, error bar – SD, n = 2).

of surface binding units responsible for adsorption. Nevertheless, enhancement of the initial contaminant concentration improves the adsorption capacity of adsorbent because of the high driving force of mass transfer in the initial high contaminant concentration [31,33].

3.4. Adsorption isotherm studies for methylene blue

The data obtained from these experimental studies examining the effect of the initial dye concentration were also used in isotherm studies to elucidate the adsorption mechanism. The adsorption isotherm investigations were conducted by fitting the adsorption data to Freundlich, Langmuir, Temkin, Dubinin-Radushkevich (D-R), and Redlich-Peterson (RP) isotherm models and isotherm constants were computed. The equations, correlation coefficients and isotherm terms obtained from these equations for above the isotherms examined in the studies on the removal of methylene blue by adsorption using Amberlyst-15 as adsorbent are given in Table 1 and Fig. 7 **(A), (B), (C), (D), and (E),** respectively**.**

According to the obtained data, when the correlation coefficients of Langmuir, Temkin and Freundlich isotherm models are compared, it is seen that the highest correlation coefficient (R^2) value belongs to the Langmuir isotherm. The correlation coefficient obtained from the Langmuir isotherm equation is 0.9759. Therefore, it can be said that the methylene blue adsorption performed with Amberlyst-15 is suitable for the Langmuir isotherm model. Using the Langmuir isotherm equation, the q_m value calculated from the slope value in the mathematical equation of the isotherm model and showing the maximum adsorption capacity is 178.57 mg/g. This value shows that the removal of methylene blue with Amberlyst-15 is extremely high. Using the intercept of the Langmuir isotherm graph, the K_L value was calculated as 0.777 L/mg. The results obtained from the Langmuir isotherm model show that methylene blue is bound to the Amberlyst-15 surface as a single layer and this binding occurs with physical forces. In addition, the compatibility of the adsorption process of methylene blue from aqueous solutions with Amberlyst-15 with the Langmuir isotherm model is indicative of the following hypotheses [34,35]. Every potential adsorption site on the adsorbent only binds one adsorbate ion. Adsorbate ions are adsorbed on openly described limiting binding locations. There is no relation between adjacent adsorbed ions because the adsorption binding sites are uniform and therefore the adsorption layer formed on the adsorbent surface is homogeneous and single-layered [36]. Langmuir model supposes that a monolayer is composed at the maximum adsorption that occurs on localized sites on the homogeneous surface to acquire the Langmuir isotherm linear form yielded by the following equation [37]. Also, the K_L value calculated from the Langmuir isotherm can be substituted into the equation $R_L = 1/(1 + K_L.C_0)$ to calculate the R_L value. The R_L value is called the dimensionless separation factor and is used to explain the suitability of the adsorbent. In the given equation, C_0 represents the initial dye concentration, and the K_L value represents the constant calculated from the Langmuir isotherm model. R_L values provide information about the type of isotherm. If the calculated R_L value; $R_L = 1$ indicates that the isotherm is linear, $R_L = 0$ indicates that the isotherm is irreversible, $0 < R_L < 1$ indicates that the isotherm is favorable and $R_L > 1$ indicates that the isotherm is unfavorable [38]. The R_L value calculated between 50 ppm and 250 ppm for Amberlyst 15 is between 0 and 1 (0.025–0.005 respectively) indicating that the adsorbent is favorable for adsorption studies.

Table 1
Isotherm equations and isotherm constants obtained for the adsorption of methylene blue onto the Amberlyst-15 surface.

Isotherm model	Mathematical equation	R^2	Isotherm parameters	
Langmuir	$\frac{Ce}{qe} = \frac{1}{q_m K_L} + \frac{1}{q_m} c_e$	0.9759	**K_L**	**q_m (mg/g)**
			0.777	178.570
Freundlich	$\ln q_e = \ln K_F + (1/n) \ln C_e$	0.7473	**K_F**	**1/n**
			82.278	0.211
Temkin	$q_e = blnA_T + blnC_e$	0.8203	**b**	**A_T**
			22.902	52.615
Dubinin-Radushkevich (D-R)	$\varepsilon = RTln\left(1+\frac{1}{C_e}\right) lnq_e = lnq_m - \beta\varepsilon^2$ $E = 1/\sqrt{(-2\beta)}$	0.9512	**β**	**q_m (mg/g)**
			-1.0 × 10^{-7}	162.179
Redlich-Peterson (RP)	$ln\frac{C_e}{q_e} = \beta lnC_e - lnA$	0.9765	**β**	**A**
			0.7893	82.26

A: Temkin isotherm constant, **b:** Temkin isotherm constant, **E:** Energy of adsorption, **K_F:** Freundlich isotherm constant, **K_L:** Langmuir isotherm constant, **n:** cooperative binding constant, **R:** ideal gas constant, **T:** Temperature, **q_m:** maximum adsorption capacity, ε: is the Polanyi potential, **β:** Redlich-Peterson constant.

Q_m value obtained from Langmuir equation was also comparable to the adsorption capacities of some other adsorbent materials for methylene blue (Table 2). Amberlyst-15 has a higher adsorption capacity compared to the other adsorbents obtained from some plant wastes and traditional adsorbents such as diatome and perlite. The easier preparation conditions and relatively high adsorption capacity suggest that Amberlyst-15 is a potential adsorbent material for dye removal from aqueous solutions.

The Dubinin-Radushkevich (D-R) isotherm model is used to determine whether the adsorption process is physical or chemical ion exchange [22]. The average free energy value (E), which provides information about whether the adsorption mechanism is physical or chemical, can be calculated using the mathematical equation given in Table 1. If the calculated E values are in the range of 8 kJ/mol ≤ E ≤ 16 kJ/mol, it is stated that the adsorption process occurs with a chemical ion exchange, and if E < is lower than 8 kJ/mol, the adsorption process is physically based [46]. The β value calculated from the Dubinin-Radushkevich equation for methylene blue adsorption on the Amberlyst 15 surface is -1.0×10^{-7}. When this value is substituted into the equation $E = 1/\sqrt{(-2\beta)}$, the E value for the adsorption process is 2.236 kJ/mol. Since the obtained E value is lower than 8 kJ/mol, it can be said that the adsorption process is physically based. Again, the q_m value is calculated from the cut-off point value of the obtained line equation. The q_m value for this experimental study was obtained as 162.179 mg/g.

3.5. Kinetic studies for methylene blue

Kinetic investigations can present knowledge about the native adsorption system (physical or chemical) and the force of held between the surface of adsorbent and adsorbate ions. In this context, different kinetic modeling methods such as pseudo first order, pseudo second order, and intra-particle diffusion kinetic models are applied, which are the most widely used and well explained in adsorption studies [47].

This kinetic model, which is based on the amount of adsorbed adsorbate, is the first-rate equation developed to characterize liquid–solid sorption kinetics and is also known as the "Lagergren Equation" [48,49].

If the integral of this equation is taken;

$$\ln(q_e - q_t) = \ln q_e - k_{1.t} \tag{3}$$

In the mathematical equations given above, the term k_1 represents the pseudo-first-order rate constant (1/min), q_t (mg/g) represent the amount of adsorbate adsorbed per unit adsorbent at any t time, respectively [50].

The pseudo-second-order kinetic model was derived by Ho and McKay. It is used to determine the adsorption capacity of the solid phase (adsorbent) and is also a useful kinetic model to describe the chemisorption mechanism [51].

$$\frac{t}{qt} = \frac{1}{qe^2 k_2} + \frac{t}{qe} \tag{4}$$

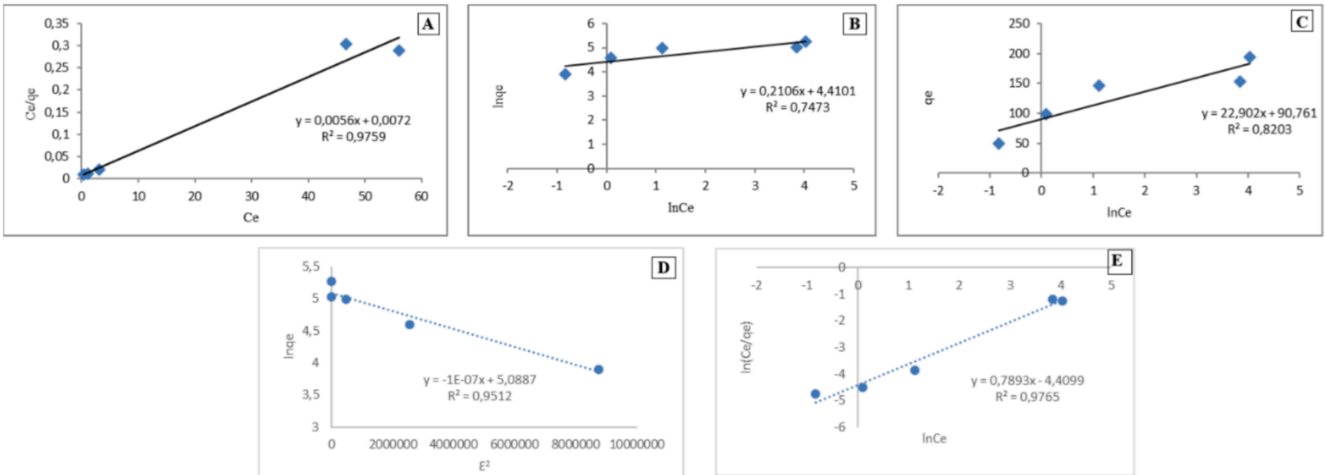

Fig. 7. Isotherm equations and graphs obtained for the adsorption of methylene blue onto the Amberlyst-15 surface (**A**: Langmuir, **B**: Freundlich, **C**: Temkin, **D**: Dubinin-Radushkevic, and **E**: Redlich-Peterson isotherm models).

Table 2
Comparison of maximum dye adsorption capacities for methylene blue by several adsorbents.

Adsorbent	q_m (mg/g)	Reference
Adsorbent obtained from Pineapple leaf	174.98	[39]
Adsorbent obtained from Coconut leaves	147.1	[40]
Commercial activated carbon	200.00	[41]
Perlite	162.30	[42]
Diatomite	198.00	[43]
Hydrochar from Shorea spp	37.8	[44]
Biochars obtained from Gigantochloa spp	86.6	[45]
Amberlyst-15	178.57	This study

In the mathematical equation given above, k_2 is the pseudo-second-order adsorption rate constant (g/mg min) [52].

If the diffusion mechanism cannot be explained clearly by the pseudo first and second order equations, the kinetic results are tried to be explained by the intraparticle diffusion model. This model was first derived by Weber and Moris in 1963. The equation of the intraparticle diffusion model is;

$$q_t = k_i.t^{1/2} + C \quad (5)$$

In this equation, C is a measure of the thickness of the boundary layer during the adsorption process. The higher the C value, the greater the effect of the boundary layer. k_i is the intraparticle diffusion constant (mg/g min$^{1/2}$) [53]. The graphs obtained for the kinetic models of the pseudo-first order, pseudo-second order, and intraparticle diffusion model for the adsorption of methylene blue with Amberlyst-15 are given

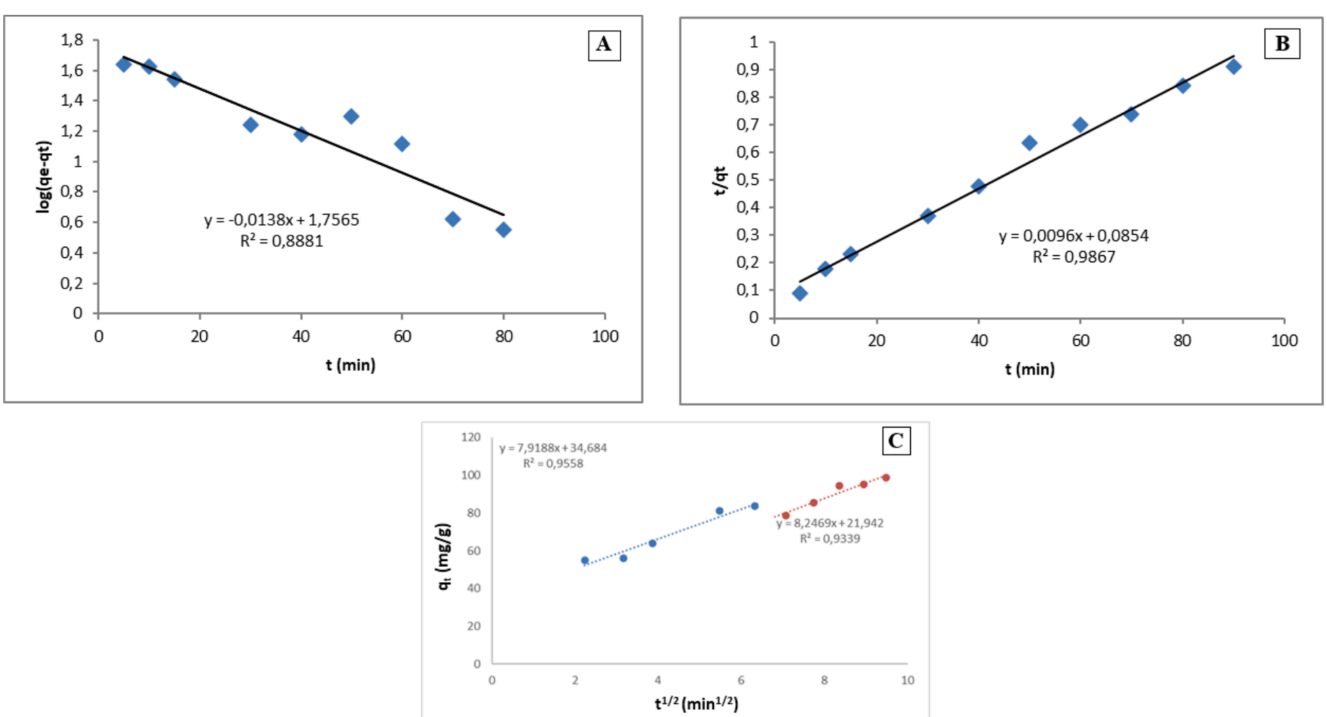

Fig. 8. Equations and graphs of the kinetic models obtained for the adsorption of methylene blue onto the Amberlyst-15 surface (**A:** Pseudo-first-order, **B:** Pseudo-second-order, and **C:** intraparticle diffusion model).

Table 3
Kinetic equations and constants obtained for the adsorption of methylene blue onto the Amberlyst-15 surface (C_0:100 ppm, pH:9).

Pseudo-first-order kinetic equation	R^2	k_1	Theoretical q_e (mg/g)	Experimental q_e (mg/g)
$y = -0.0138x + 1.7565$	0.8881	0.032	57.08	98.90
Pseudo-second-order kinetic equation	R^2	k_2	**Theoretical q_e (mg/g)**	**Experimental q_e (mg/g)**
$y = 0.0096x + 0.0854$	0.9867	1.079×10^{-3}	104.17	98.90
Intra-particle diffusion models	R^2	K_i	C	
$y = 7.9188x + 34.684$ $y = 8.2469x + 21.942$	0.9558 0.9339	7.919	34.684	

in Fig. 8A, 8B, and 8C, respectively.

Table 3 shows the values obtained from the calculations of the kinetic equations. Accordingly, the theoretical q_e values of the pseudo-first and second-order kinetic models were calculated as 57.08 mg/g and 104.17 mg/g, respectively. The experimental q_e value of the adsorption of methylene blue with Amberlyst-15 was found to be 98.90 mg/g. When the experimental and theoretical q_e values are compared, it is seen that the pseudo-second-order data are closer to each other. In this case, it can be said that the adsorption of methylene blue with Amberlyst-15 is compatible with the pseudo-second-order kinetic model.

3.6. Adsorption thermodynamics for methylene blue

To explain the mechanism of methylene blue adsorption on the Amberlyst-15, a set of novel experiments were performed at 293, 298, 308, and 318 K. Adsorption equilibrium constant (K_c) values were calculated and in order to perform thermodynamic calculations of methylene blue adsorption on Amberlyst-15 surface, lnK_c values were plotted against 1/T values and thermodynamic parameters were calculated with the help of the equation given below.

$$lnK_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (6)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

The adsorption thermodynamic parameters were computed according to the thermodynamic theory utilizing **Eqs (6) and (7)**, and the relationships for the ΔG°, ΔH°, and ΔS° are given in Table 4.

As can be seen from Table 4, the Gibbs free energy change (ΔG°) values calculated for the adsorption of methylene blue onto the Amberlyst-15 surface were found to be negative at all temperatures. The negative Gibbs free energy change values indicate that the adsorption of methylene blue onto the Amberlyst-15 surface is a spontaneous process (spontaneous) and is thermodynamically favorable. The ΔH° value calculated for the adsorption of methylene blue onto the Amberlyst-15 surface is 19.089 kJ/mol. The positive ΔH° value indicates that the adsorption process is endothermic (heat-receiving). The positive free entropy (ΔS°) value (0.0744 kJ/mol K) indicates an increase in the probability of randomness at the interface of the solid adsorbent surface and the solution containing the adsorbate during the adsorption process [54].

Table 4
Thermodynamic parameters of methylene blue adsorption onto Amberlyst-15.

T (K)	ΔG° (kJ/mol)	ΔS° (kJ/mol.K)	ΔH° (kJ/mol)
293	−2.71	0.0744	19.089
298	−3.08		
308	−3.83		
318	−4.57		

Other literature studies conducted with Amberlyst-15 also show similar results. Razzaq et al., studied the adsorption of Cd (II) using Amberlyst-15 as an adsorbent and they obtained a removal value of 99.95 % and a maximum adsorption capacity of 2.01 mmol/g after a contact time of 30 min at 323 K. As a result of their study, it was shown that the adsorption data were compatible with the pseudo-second-order kinetic model and the Langmuir isotherm [21]. Tunceli et al., investigated the adsorption kinetic, isotherms, and thermodynamic data for Pb (II) and Cd(II) ions in aqueous solutions by using Amberlyst-15 resin at different temperatures. Monolayer adsorption capacities of Amberlyst-15 for Pb(II) and Cd(II) according to the Langmuir isotherm model were calculated as 116 and 120 mg/g respectively at 318 K. Experimental results showed that kinetic models for adsorption of Pb(II) and Cd(II) on the Amberlyst-15 were matched with the pseudo-second-order, and the thermodynamic studies defined the adsorption process as exothermic, spontaneous, and chemical ion exchange [22].

3.7. FT-IR analysis

Fourier transform infrared spectroscopy (FTIR) enables the identification of functional groups in organic molecules and thus provides information about the possible adsorption mechanism.

In this study, Amberlyst-15 was used as an adsorbent for the first time in the adsorption-based removal process of methylene blue dye and it was observed that it removed methylene blue dye very successfully and effectively in the experimental studies. The physical appearance of Amberlyst-15 polymeric resin before and after methylene blue adsorption is shown in Fig. 9 below. As can be seen from the figure, methylene blue dye is clearly adsorbed on the Amberlyst-15 surface.

In experimental studies, the FTIR spectrum of methylene blue dye (Fig. 10) was first recorded and analyzed. When the FTIR spectrum obtained for methylene blue is examined, the stretching vibration of the –NH bond at 3358 cm^{-1} wavenumbers, the stretching vibrations of the C–H bond of the heterocycle at 3050 cm^{-1} and the bands belonging to the symmetric stretching of the C–H bond of the $-CH_2$ group at 2931 cm^{-1} are observed. The weak band observed at 2711 cm^{-1} is the stretching vibration of the C–H bonds in the $N(CH_3)_2$ groups, while the band observed at 1446 cm^{-1} is the asymmetric deformation vibration of these bonds. The strong band located at 1594 cm^{-1} represents the stretching vibration of the C=N double bond in the central ring, the bands located at 1546 and 1221 cm^{-1} represent the stretching vibration of the C-N bond, and the band observed at 1142 cm^{-1} represents the deformation vibration of the heterocyclic C-N bond. The bands observed at 1490 cm^{-1} and 1355 cm^{-1} are the stretching vibrations of the C=S group in the heterocyclic ring. One of the important bands in the FTIR spectrum given in Fig. 10 is the vibration band belonging to the C-S-C bonds located at 1068 cm^{-1} [17,55,56].

The IR spectra of Amberlyst-15 before and after methylene blue adsorption are given in Fig. 11. In the IR spectra of Amberlyst-15 before and after adsorption, the broad band observed at approximately 3388 cm^{-1} represents O–H groups, while the peak at 2928 cm^{-1} corresponds to C–H stretching vibrations and is the characteristic band indicating the presence of alkyl chains. Again, when the IR spectrum of Amberlyst-15 polymeric resin before methylene blue adsorption is examined; the peaks in the range of 1413–1686 and 666–902 cm^{-1} are observed as bands belonging to the out-of-plane bending vibrations of the benzene ring skeleton and the C single bond H groups in the substituted benzene styrene ring, respectively. The bands at 1124 and 1032 cm^{-1} belong to the symmetric and asymmetric stretching vibrations of single SO_3 – groups, respectively. When the IR spectra are examined after methylene blue adsorption, new and distinct bands are observed, especially at 1585, 1394, 1360 and 887.6 cm^{-1}. These bands are also clearly seen in the FTIR spectrum of methylene blue given in Fig. 10. The emergence of these bands belonging to methylene blue in the FTIR spectrum after

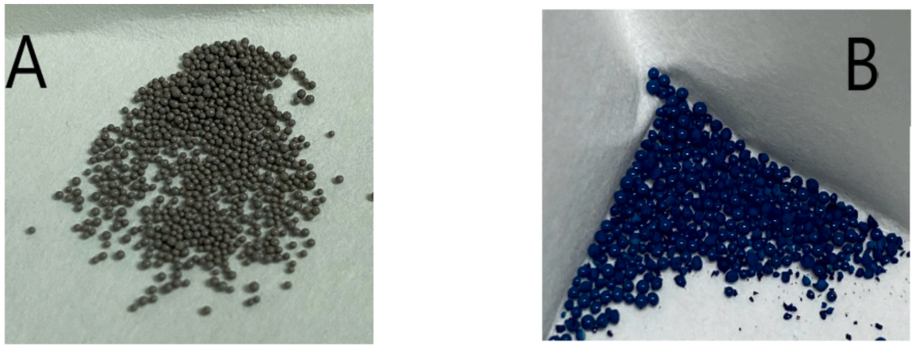

Fig. 9. Amberlyst 15 adsorbent; before (A) and after (B) adsorption of methylene blue.

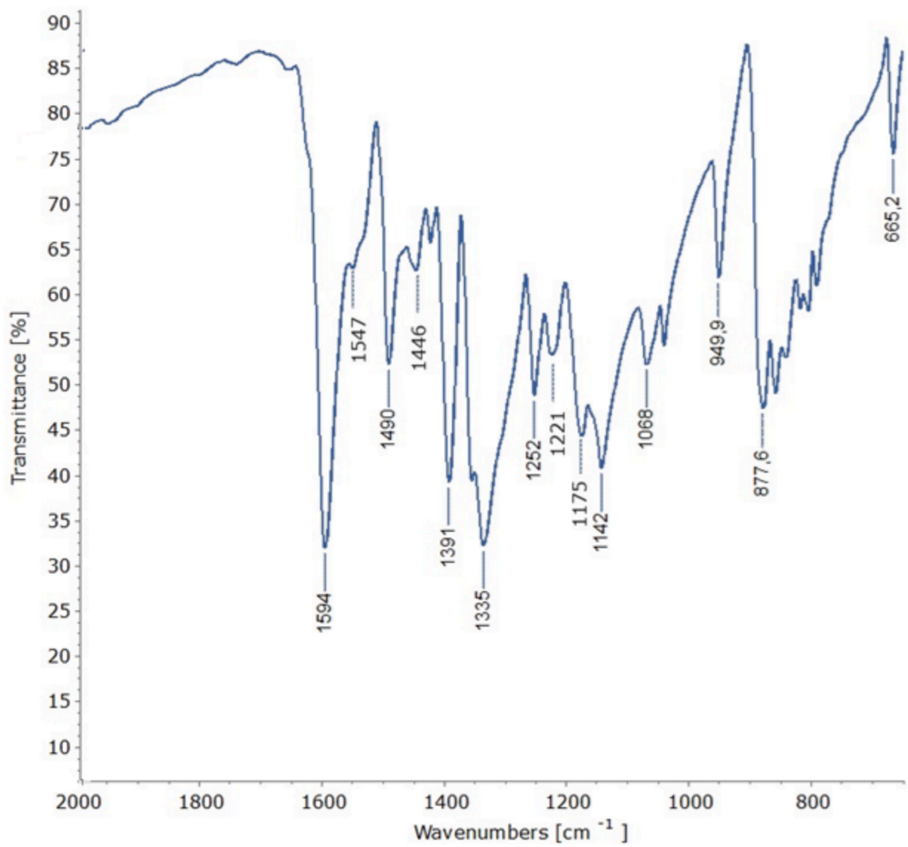

Fig. 10. FTIR spectrum of methylene blue dye.

adsorption indicates that methylene blue is adsorbed on the Amberlyst-15 surface. The changes observed in the FTIR spectrum seem to be compatible with the adsorption mechanism given in Fig. 4.

After the adsorption process, the shifting of specific peaks wavenumbers from their original locations (before adsorption) also alterations in peak intensity remarked the functional groups of adsorbent surface participation in the adsorption of the methylene blue molecule by electrostatic forces of attraction and/or by weak Van der Waals interplays [26].

4. Conclusions

In this study, the suitability of Amberlyst-15 polymeric resin as an adsorbent in the removal of methylene blue from wastewater was investigated. In the scope of experimental studies, the effects of temperature, pH, adsorbent amount, contact time and dye concentration changes on adsorption were investigated and the results were compared with the studies in the literature. Isotherm, kinetic and thermodynamic studies were performed to explain the adsorption mechanism. It can be said that methylene blue adsorption on Amberlyst-15 surface complies with Langmuir isotherm model. Data obtained from Langmuir isotherm model resulted in methylene blue adsorption on Amberlyst-15 surface as a single layer and physical forces were effective. According to Langmuir isotherm equation, q_m value was calculated as 178.57 mg/g and K_L value was calculated as 0.777 L/mg. According to the results, maximum adsorption capacity of methylene blue on Amberlyst-15 surface is 178.57 mg/g. In the methylene blue adsorption studies carried out with Amberlyst-15, it was observed that the experimental q_e obtained with the pseudo-second-order kinetic model and the theoretical q_e were close to each other. In the thermodynamic studies of methylene blue removal with Amberlyst-15, negative ΔG° indicates that the adsorption occurs spontaneously, while positive ΔH° indicates that energy is received from

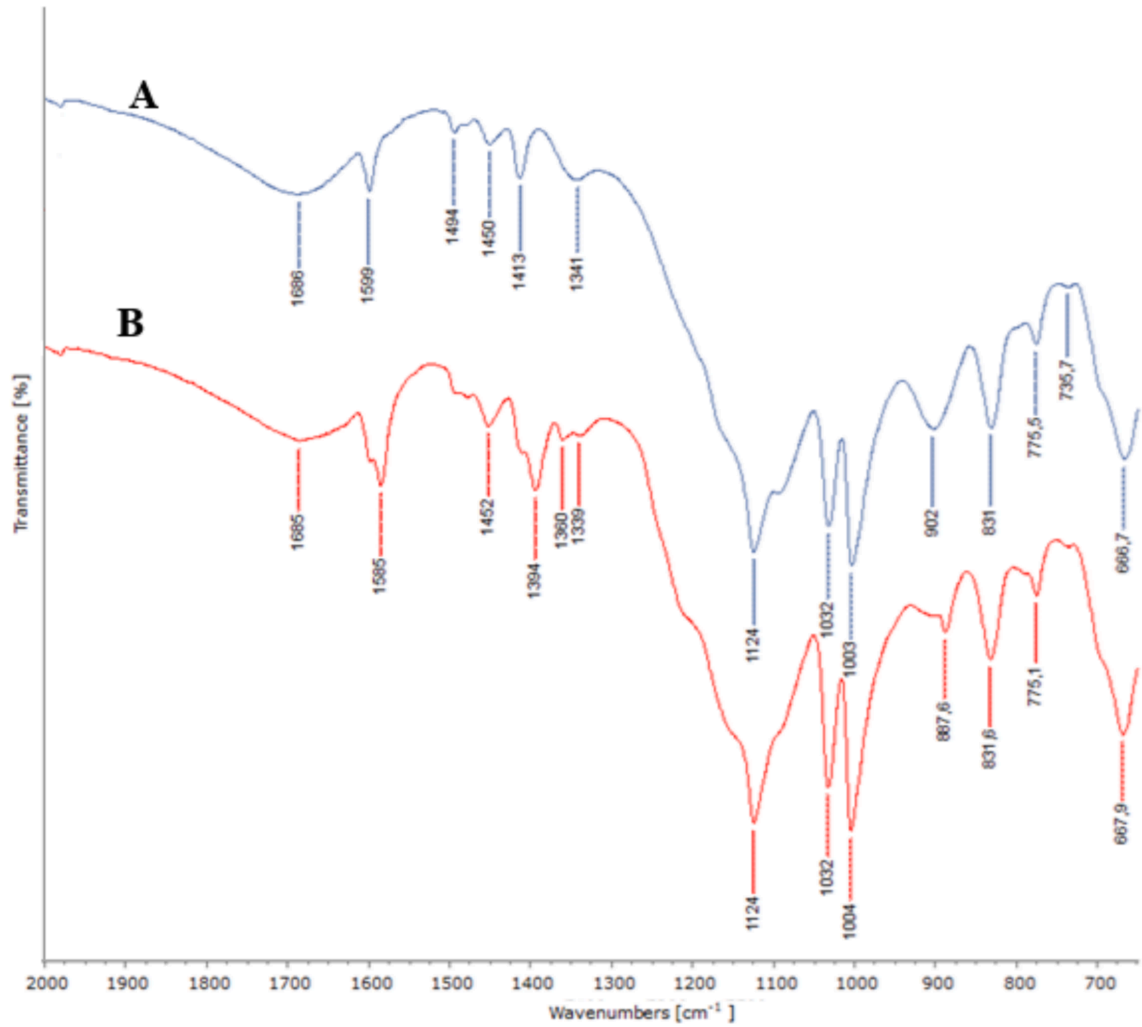

Fig. 11. FTIR spectra of Amberlyst-15 before (A) and after (B) methylene blue dye adsorption.

outside during adsorption.

CRediT authorship contribution statement

Ayse Sarısoylu Nart: Software, Resources, Formal analysis, Data curation. **Hülya Silah:** Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Any data that is generated within the report will be available, if required, from the corresponding author.

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