Application of Polyacrylamide for Methylene Blue Removal from Aqueous Solutions

Hassan Zavvar Mousavi*, Aisan Khaligh, Mahdi Behzad and Jalal Rahchamani

Department of Chemistry, Semnan University, Semnan, Iran

Abstract: In this study the removal of methylene blue (MB) dye from aqueous solutions by polyacrylamide (PAA) as a potential adsorbent was reported. PAA was characterized using SEM and FTIR measurements. Batch adsorption experiments were performed as a function of the solution pH, contact time, solute concentration and temperature. Evaluation of the obtained data with isotherm studies indicated that the adsorption process was matched well with the Langmuir model. The maximum capacity of adsorbent for MB was 111.1 mg g^{-1}. Kinetic studies were carried out on various kinetic models and the pseudo-second order kinetic model was fitted very well with experimental data. Moreover, the thermodynamic parameters indicated that the adsorption reaction was endothermic and spontaneous process.

Keywords: Polyacrylamide, Removal, Methylene blue, Isotherm, Kinetic.

1. INTRODUCTION

Dye-contaminated wastewater, its treatment and disposal is a serious environmental problem which is faced by the textile, dye synthesis, printing, paper, rubber, cosmetic, food and related industries [1, 2]. Over 10,000 dyes with an annual production of 7×10^5 tons worldwide have been reported to be commercially available [3]. Dyes are usually synthetic materials. They have complex aromatic molecular structures. Most of them are stable and are not easily biodegraded. Dyes are usually harmful materials and most of the organic dyes and their products have a mutagenic or carcinogenic effect on human beings. As a result, greater attention must be paid to their treatment before their discharge [2].

Methylene blue (MB) is a thiazine cationic dye. It has found wide applications in several industries such as cottons or wools dyeing and paper coloring [4]. Though MB is not a strongly hazardous material but it is potentially able to have some harmful effects. It is reported that the exposure to MB may cause mental confusion, increased heart rate, vomiting and several other problems for humans [4-6]. Owing to these harmful effects on humans, the removal of MB from industrial effluents has become one of the major environmental concerns.

Many physical, chemical, and even biological processes have been investigated for the removal of dyes from aquatic environments, including oxidation and sonochemical degradation [7], photocatalytic degradation [8], coagulation [9], photochemical and sonochemical combined processes [10], photocatalytic and electrochemical combined treatment [11], electrocoagulation [12], photo-Fenton processes [13], ozonation [14] and adsorption [15-18]. Among these approaches, adsorption is generally preferred due to its sludge free clean operation, high efficiency, ease of handling, low cost and availability of different adsorbents. Several adsorbents have been studied for their potential ability of adsorbing dyes from aqueous effluents, including rice husk [19], durian peel [20], rattan sawdust [21], modified chitosan [22], perlite [23], peanut husk [24], montmorillonite [25] and compost [26].

The development of new adsorbent for the removal of heavy metal ions, dyes and other toxic materials is the subject of great interest nowadays. These materials are supposed to have superior properties such as high adsorption capacities, fast adsorption rates and higher mechanical strength for water and wastewater treatment. Recently, the use of synthetic polymeric materials as new class of adsorbents with fair adsorption capacities is so considered [17, 27-30]. In this regard, Polyacrylamide (PAA) is one of the most widely used polymers. PAA has large numbers of amide side groups. It can be defined as water-swollen, three-dimensional networks which can absorb a large amount of water compared to other water absorbing materials. It has found wide applications in many fields, e.g. municipal water treatment, mineral processing and drag reduction [17, 31, 32].

In the present study, PAA was used to remove MB form aqueous solutions. The adsorption kinetics and thermodynamics, contact time, initial concentration of MB, temperature and pH effects were investigated in batch mode. The analyses of equilibrium data have been done using different adsorption isotherms.

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*Address correspondence to this author at the Department of Chemistry, Semnan University, Semnan, Iran; Tel: +98- 231-3354057; Fax: +98-231-3354110; E-mail: hzmousavi@semnan.ac.ir

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2. EXPERIMENTATION

2.1. Materials

All chemicals were purchased from commercial sources and were used without further purification. Polyacrylamide was obtained from, Guangzhou Chemical Reagent Factory, Guangzhou, China. Stock solution of MB ($C_{16}H_{18}N_3SCl.\ 3H_2O$, λ_{max}= 668 nm) was prepared by dissolving accurately weighted amount of dye in distilled water to the concentration of 1 g/L. The experimental solutions were obtained by diluting the dye stock solution with distilled water to the needed initial concentrations.

2.2. Preparation of Adsorbent

PAA was immersed in distilled water for 3 h. The swollen gels were taken out at regular time intervals and were then wiped superficially with a filter paper, weighed and replaced in the same solution to ensure the state of equilibrium swelling.

2.3. Batch Studies

Removal experiments were performed using batch technique to obtain the adsorption rate and equilibrium data. A suspension containing 0.02 g of PAA was mixed by stirring (125 rpm) with a 200 ml aqueous solution of MB at a known initial concentration in an Erlenmeyer flask which was immersed in a bath in thermostated water keeping constant working temperature. The pH values of the solutions were adjusted by adding negligible amounts of NaOH or HNO_3 solutions. An aliquot of the solution was withdrawn at the pre-determined time intervals, and was centrifuged at 4000 rpm for 10 min, then filtered through a What-man filter paper. The residual concentration of dye was subsequently determined in the filtrate using UV–Visible spectrophotometer at the wavelength of maximum absorbance. The adsorption tests were continued until the equilibrium concentration was reached. Effects of pH (2–10), contact time (25–240 min), kinetic experiments (50-300 mg/L initial MB concentration), adsorption isotherm (50-300 mg/L initial MB concentration) and thermodynamic studies (298–318 K) on adsorption were studied. All the experimental data were the averages of triplicate determinations.

For the experiments of adsorption kinetics, mentioned procedure with 200 ml aqueous solution of MB at different initial concentrations (50–300 mg/L) was performed. The amount of MB adsorbed onto adsorbent was calculated using the following expression:

$$q_t = \frac{(C_i - C_t)}{w} \times V \tag{1}$$

where q_t is the mass of adsorbed MB per unit mass of adsorbent (mg g^{-1}); C_i and C_t are the initial and actual concentration (mg L^{-1}) of MB at time t, respectively; V is the volume of the treated solution (mL); w is the mass of adsorbent (g).

2.4. Characterization Methods

The FTIR spectrum of polymeric adsorbent was recorded on a Shimadzu FTIR (model 8000 Series, Japan) spectrophotometer using KBr pellets. The microstructure of the PAA was examined using Hitachi (model: JSM-5600 imaging mode) scanning electron microscope (SEM). The absorption spectrum of the dye was recorded on a Shimadzu UV-Vis (model 1601, Japan) spectrophotometer. A Metrohm pH meter (model E-632) with a glass combination electrode was used for pH measurements.

3. RESULTS AND DISCUSSION

3.1. Absorbent Characterization

Scanning electron microscopy (SEM) was used to investigate the morphology of the PAA (Figure **1**). As it could be seen from the SEM image, the PAA has very few small pores on the surface. The surface roughness could be considered as a factor providing an increase in the surface area.

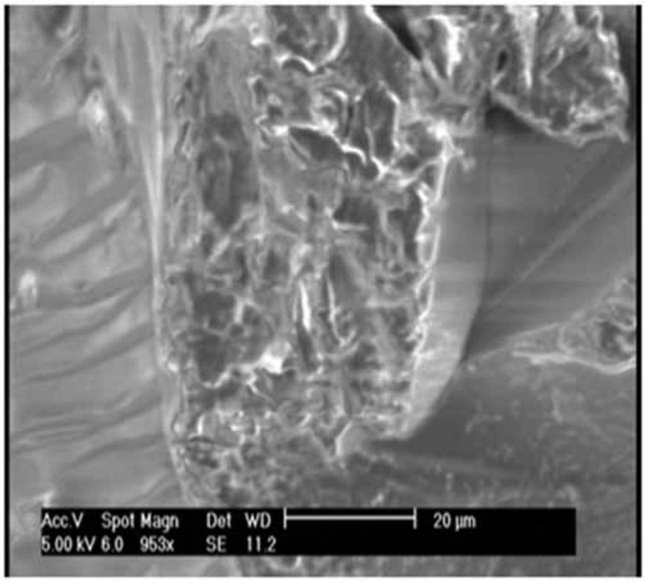

Figure 1: SEM image of polyacrylamide.

The FTIR spectrum of PAA is displayed in Figure **2**. The most significant feature of the spectrum is the appearance of two bands at around 3400 and 1690 cm^{-1} which are assigned to NH_2 and C=O groups stretching vibration, respectively. Furthermore, the signals at around 3000 cm^{-1} are also assignable to the stretching vibrations of aliphatic C-Hs. Since the FTIR frequencies of MB overlap with the FTIR frequencies of PAA, no further insight is obtained from the FTIR spectroscopy after the adsorption.

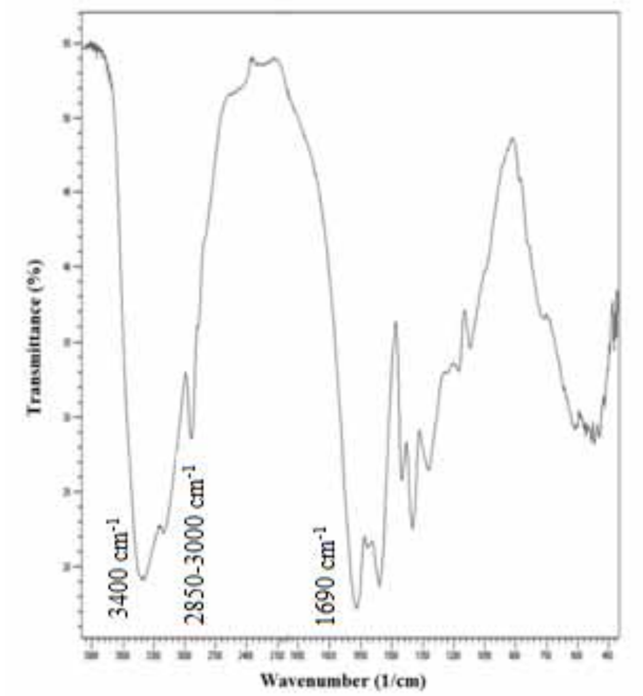

Figure 2: FTIR spectrum of polyacrylamide.

3.2. Effect of pH

pH plays a significant role in affecting the extent of adsorption, particularly when the adsorbent and adsorbate, both are charged species [28]. In the current study the adsorbate MB is a cationic dye while the adsorbent PAA contains ionizable amine groups along polymer chains. The effect of pH on the adsorption of MB by PAA was studied over the pH range of 2–10 with 100 mg/L initial concentration of MB. As could be seen from Figure **3**, the adsorption is low at lower pH values. But as the pH increases, a significant increase in the adsorption is observed. Our results showed that the optimized pH range for the removal of MB was between 8 and 10.

MB is a dye which dissociates in water solution followed by a cationic hydrolysis in the next steps. The adsorption process happens mainly because of electrostatic attractions with amide groups in the adsorbent. However, at lower pHs more protons will protonate NH_2 groups of PAA to form NH_3^+. ,−NH-3-+.So they would be unable to adsorb dye molecules and poor adsorption may only be due to H-bonding interactions between N and S atoms of MB molecules and H atoms from NH_2 groups of polymeric adsorbent. Therefore, at higher pHs The available NH_2 groups will interact with dye molecule and adsorption will occur. Similar results have also been reported [17, 27, 32, 33].

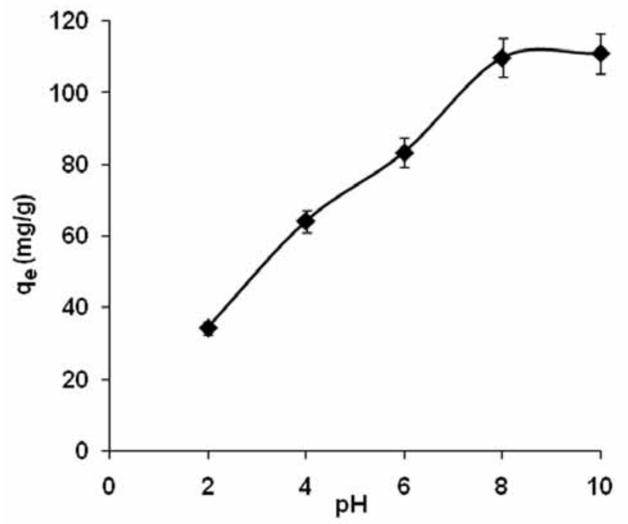

Figure 3: Effect of initial pH on MB adsorption by PAA (initial MB concentration 100 mg/L; 0.1 g/L of PAA, agitation speed 125 rpm; contact time 120 min; temperature 298 K).

3.3. Effects of Contact Time

Equilibrium time is another important parameter to dyes wastewater treatment process. The effect of the contact time on the adsorption capacity of PAA for MB with known initial concentrations, the dosage of 0.1 g/L, and pH of 8 were described in Figure **4**. It is clear that the adsorption rate of MB increased with time and adsorption equilibrium was obtained after stirring for 120 min with initial MB concentrations of 50-300 mg L^{-1}. Not much benefit was obtained from stirring longer than 120 min; therefore, the adsorption time was fixed at 120 min in the subsequent adsorption experiments. The initial rate of MB adsorption was fast. This could be explained by the fact that large numbers of adsorption sites of the PAA were available at the beginning but afterwards, slower adsorption rates were seen which were obviously due to the saturation of active sites. The initial concentrations of MB were also important. As the initial concentrations increased from 50 to 300 mg L^{-1}, the amount of adsorbed MB also increased up to 1200 mg g^{-1}. The increase in the driving force of the concentration gradient could have resulted in the overcome to the mass transfer resistance of the MB molecules between the aqueous phases and the solid phases with the increase in the initial concentration.

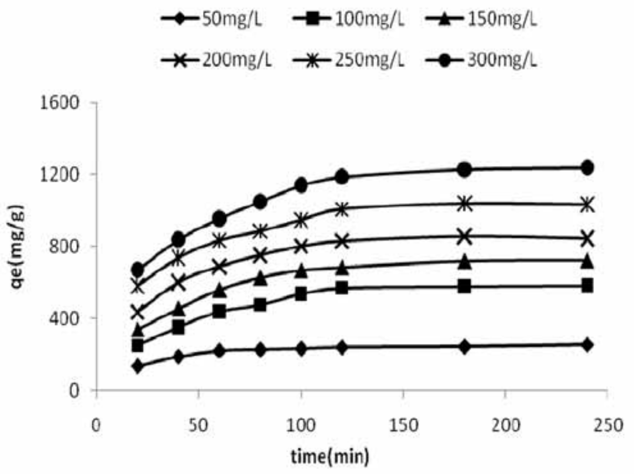

Figure 4: Effect of contact time on MB adsorption by PAA (initial MB concentration 5-300 mg/L; 0.1 g/L of PAA; pH= 8; agitation speed125 rpm; temperature 298 K).

3.4. Effect of Temperature

To investigate the temperature effect on the adsorption of MB, the equilibrium adsorption studies were carried out at 298, 308 and 318 K. Obviously, the adsorption of MB on PAA increased with the rise in temperature from 298 K to 318 K (Figure **5**), which suggested that the removal process was endothermic. This might be as a result of the increase in the mobility of the dye with increasing temperature [34]. An increasing number of molecules may also obtain sufficient energy to undertake the interaction with active sites of the surface. Furthermore, higher temperatures may produce a swelling effect within the internal structure of the PAA which enables larger dyes to further penetrate [35, 36].

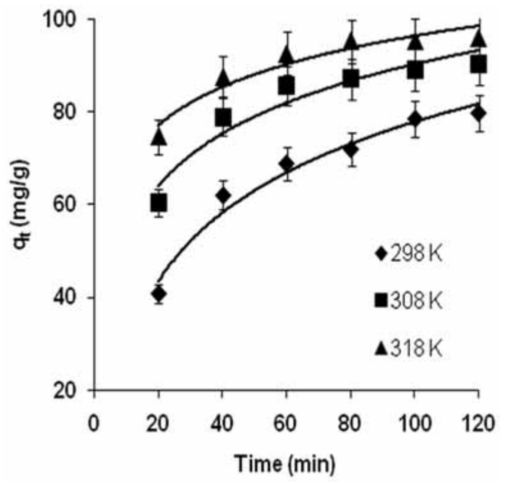

Figure 5: Effect of Temperature on MB adsorption by PAA (initial MB concentration 100 mg/L; 0.1 g/L of PAA; pH= 8; agitation speed125 rpm; contact time 120 min).

3.5. Adsorption Isotherms Studies

Adsorption isotherms play an important role in the analysis and design of the adsorption systems. In the present study, the experimental equilibrium adsorption data were tested using Langmuir, Freundlich and Tempkin isotherm models.

Langmuir adsorption isotherm is valid in the case of monolayer adsorption onto the surface with a finite number of identical sites. The Linear Langmuir equation is given below [37]:

$$\frac{C_e}{q_e} = \frac{1}{K_L\, q_{max}} + \frac{C_e}{q_{max}} \tag{2}$$

Where q_e is the amount of MB adsorbed at equilibrium (mg g^{-1}), q_{max} the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg g^{-1}), C_e the equilibrium concentration of MB in solution (mg L^{-1}), and K_L is the Langmuir constant (L mg^{-1}), related to the free energy of adsorption. Linear plots of C_e/q_e versus C_e were employed to determine the values of q_{max} and K_L (Figure **6**). The data obtained with the correlation coefficients (R^2) were listed in Table **1.**

The Langmuir equation can be re-expressed in term of a dimensionless factor, R_L, which predicts whether an adsorption system is favorable or unfavorable. R_L is defined as follows [38]:

$$R_L = \frac{1}{1+K_L C_0} \tag{3}$$

C_0 (mg L^{-1}) is the highest initial solute concentration and K_L is the Langmuir constant (L mg^{-1}). R_L values between 0 and 1 indicate favorable adsorption. The R_L value in the present study has been found to be 0.2, which is an indication of the favorable adsorption of MB dye on the adsorbent.

The Freundlich isotherm model is an empirical equation which is applicable to describe heterogeneous systems. This is characterized by a factor named as the heterogeneity factor 1/n. Freundlich isotherm is used for the description of multilayer adsorption with interaction between adsorbed molecules. The linear Freundlich equation is expressed as follows [39]:

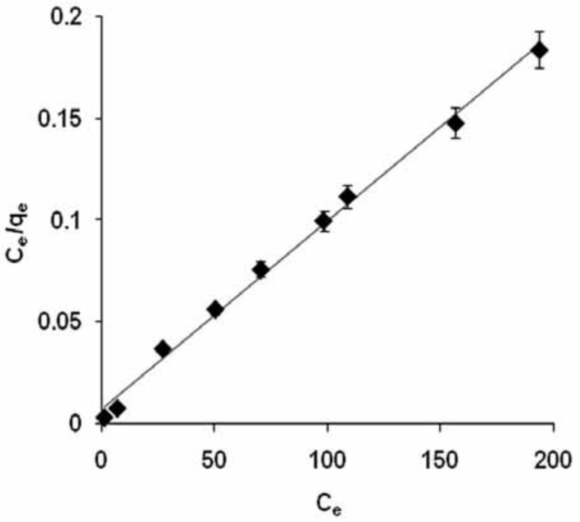

Figure 6: Langmuir plots for MB adsorption on PAA (initial MB concentration 50-300 mg/L; 0.1 g/L of PAA; pH= 8; temperature 298 K).

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{4}$$

Where K_F and n are Freundlich isotherm constants which are related to adsorption capacity (mg^{1-n} L^n g^{-1}) and adsorption intensity, respectively. A plot of $\ln(q_e)$, q-e. versus $\ln(C_e)$ enables the constant K_F and n to be determined. It is clear from Table **1** that the values of n were greater than 1, while n > 1 represent favorable adsorption condition [40].

There are two important assumptions in Tempkin isotherm model: (i) some indirect adsorbate/adsorbate interactions decreases the adsorption energy linearly as a result of the surface coverage and (ii) a uniform distribution of binding energies characterizes the adsorption, up to some maximum binding energy [41, 42]. The linear form of Tempkin isotherm model is given as:

$$q_e = B_T \ln K_T + B_T \ln C_e \tag{5}$$

Where K_T is the equilibrium binding constant related to the maximum binding energy (L mg^{-1}). The B_T is constant related to the heat of adsorption (kJ mol^{-1}). The determination of the isotherm constants B_T and K_T could be achieved from the slope and the intercept of the plot of q_e versus $\ln C_e$, respectively.

The data obtained with the correlation coefficients (R^2) for all the adsorption isotherms were presented in Table **1**. Comparison of the linear isotherm plots shows that the Langmuir model yielded a much better fit than the other studied models. This indicates the homogeneous nature of PAA surface which means that

Table 1: Isotherm Parameters for MB Adsorption on PAA at 298 K

Langmuir isotherm			Freundlich isotherm			Tempkin isotherm		
q_{max}	K_L	R^2	K_F	n	R^2	K_T	B_T	R^2
111.1	0.112	0.999	457	6.71	0.988	59.5	107.5	0.955

Table 2: Comparison of Adsorption Capacities of Various Adsorbents for the Removal of MB

Adsorbent	q_{max} (mg g^{-1})	Reference
Algal biomass	171	43
Fibrous clay	85.0	44
Orange peel	17.6	45
Spent activated clay	78	46
Shaddock peel	305.8	47
Activated carbon	412	1
Coir pith carbon	5.8	48
Spent cottonseed hull	185.2	49
Poly(vinyl acetate)	2.612	50
Poly(acrylamide-co-maleic acid)	2.2	51
Polyacrylamide grafted attapulgite	9.27	52
Polyacrylamide	111.1	Present study

each dye molecule/PAA adsorption has equal adsorption activation energy. Therefore uptake of MB preferably follows the monolayer adsorption process.

A comparison of the maximum adsorption capacities of different adsorbents for MB dye removal was also reported in Table **2**. It is clear from this table that the adsorption capacity of PAA used in the present study is significant. Therefore, PAA is considered to be excellent and potential adsorbent for dyes removal from aqueous solutions.

3.6. Kinetic Studies

The dynamics of the adsorption process in terms of the order and the rate constant can be evaluated using the kinetic adsorption data. The kinetics of MB adsorption on PAA was analyzed using pseudo-first-order, pseudo-second-order and intra-particle diffusion models. The correlation coefficient (R^2, close or equal to 1) is used to evaluate the suitability of different models. The linearized-integral forms of studied kinetic models are expressed as [53, 54, 55]:

$$\ln\left(q_1 - q_t\right) = \ln q_1 - k_1 t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \tag{7}$$

$$q_t = k_i\, t^{1/2} + C$$
(8)

Where q_1 (or q_2) and ,q-t.q_t (mg g^{-1}) are the values of amount adsorbed per unit mass of sorbent at equilibrium and at any time t. k_1 (L min^{-1}) is the pseudo-first-order adsorption rate coefficient. k_2 (g/mg min) is the pseudo-second-order constant. The values of k_2 at different initial dye concentrations were calculated from the slopes of the respective linear plots of t/q_t vs. t (Figure **7**). k_i (mg/g min$^{1/2}$) is the diffusion rate coefficient and C is the intercept and relate to the thickness of the boundary layer. The parameter values for each model were obtained from the respective fitting curve resulting from the linear form of pseudo-first order, pseudo-second order and intra-particle diffusion kinetic equations. The results were listed in Table **3** along with the correlation coefficient. It can be seen that pseudo-second-order kinetic model provides a good correlation (R^2, close to 1) for the adsorption of MB dye at all initial dye concentrations. What is more, the q_2 values, calculated by pseudo-second-order model, represent a fine agreement with the detected values in experiment. This clearly indicates that the pseudo-second order model, an indication of the chemisorptions mechanism, is able to describe properly the kinetic behavior of MB adsorption on PAA.

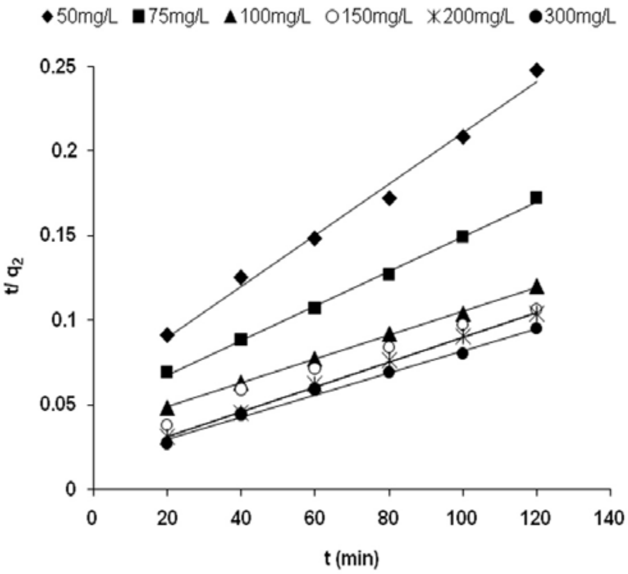

Figure 7: Pseudo-second-order kinetics plots for MB adsorption on PAA (initial MB concentration 50-300 mg/L; 0.1 g/L of PAA; pH= 8; temperature 298 K).

3.7. Thermodynamic Studies

Thermodynamic studies are used to decipher any reaction in a better way. In the present study also, the variation in the extent of adsorption with respect to temperature has been explained based on thermodynamic parameters viz. Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0). Thermodynamic parameters were obtained at different temperatures (298-318 K) according to the following formulas:

$$K_C = \frac{q_e}{C_e} \tag{9}$$

$$\Delta G^0 = -RT \ln K_C \tag{10}$$

$$\mathrm{Ln}\, K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{11}$$

Where K_C is the equilibrium constant, R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). ΔH^0 and ΔS^0 were obtained from slope and intercept of the plot of Ln K_C versus 1/T. The values of the thermodynamic parameters were recorded in Table **4**. Positive ΔH^0 values at different temperatures showed the endothermic nature of

Table 3: Kinetic Parameters for MB Adsorption on PAA at 298 K

		Pseudo first-order model			**Pseudo second-order model**			**Intra-particle diffusion model**	
C_0 (mg/L)	**q_e(exp.) (mg/g)**	**q_1(cal.) (mg g^{-1})**	**K_1**	**R^2**	**q_2(cal.) (mg g^{-1})**	**K_2**	**R^2**	**k_i**	**R^2**
50	482	1267	0.055	0.939	662	3.82×10^{-5}	0.998	44.01	0.938
75	695	841	0.029	0.993	970	2.27×10^{-5}	0.998	70.43	0.973
100	998	1233	0.029	0.958	1408	1.47×10^{-5}	0.999	92.76	0.974
150	1127	1054	0.021	0.983	1369	3.08×10^{-4}	0.999	110.6	0.983
200	1150	920	0.027	0.986	1370	3.20×10^{-5}	0.999	115.4	0.971
300	1255	1815	0.041	0.881	1538	2.56×10^{-5}	0.992	123.3	0.967

Table 4: Thermodynamic Parameters for MB Adsorption on PAA at Different Temperatures

ΔH^0 (kJ/mol)	**ΔS^0 (kJ/mol K)**	**ΔG^0 (kJ/mol)**		
69.57	263	298 K	308 K	318 K
		-9.14	-12.75	-14.15

adsorption process, which was supported by the increasing adsorption of MB dye with the increase in temperature. While negative values of ΔG^0 indicated that the adsorption of MB was spontaneous process under the conditions applied. Positive values of ΔS^0 were indicative of increased randomness at the adsorbent–adsorbate interface.

The pseudo-second-order rate constant of dye adsorption is expressed as a function of temperature by the Arrhenius type relationship:

$$\ln K_2 = \ln A - \frac{E_a}{RT} \tag{12}$$

Where E_a is the Arrhenius activation energy of sorption, representing the minimum energy that reactants must have for the reaction to proceed; A the Arrhenius factor; R the gas constant; T is the solution temperature. When $\ln k_2$ is plotted versus 1/T, a straight line with slope $-E_a/R$ is obtained. The chemisorption or physisorption mechanisms are often an important indicator to describe the type of interaction between dye molecule and adsorbent. The physisorption processes usually have energies in the range of 4–40 kJ/mol, while higher activation energies (40–400 kJ/mol) suggest chemisorption [56]. The value of E_a in this study was 61.9 kJ/mol which indicates that MB adsorption on PAA is chemical in nature

4. CONCLUSION

The present study indicated that PAA was an effective adsorbent for the removal of MB from aqueous solutions. The batch study parameters, pH of solution, contact time and temperature, were found to be effective on the adsorption efficiency of MB dye. The kinetics and isotherm experiment data could be well described with the pseudo-second-order model and the Langmuir isotherm model, respectively. The maximum adsorption capacity of 111.1 mg g^{-1} was also obtained for MB at optimum conditions of pH 8, temperature 298 K and contact time of 120 min with 0.1 g/L of PAA. Base on thermodynamic studies, the adsorption reaction was spontaneous and endothermic in nature and the main strength of adsorption was the chemical adsorption.

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