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Removal of methylene blue by modified polyacrylonitrile from aqueous solution

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ABSTRACT

Chelating resins based on polyacrylonitrile (PAN) and monoethanolamine (MEA) were prepared with three volume percent of monoethanolamine. The resins (PAN-MEA) have been studied by FT-IR. The prepared resin (PAN-MEA I) were applied to remove of methylene blue from aqueous solution. The effects of adsorbent dose, initial pH, temperature, initial methylene blue concentration and contact time were investigated. Adsorption increased with increasing dye concentration, initial pH, and temperature. The maximum adsorption capacity of 158.954.3 mg g^{-1} of Methylene blue was achieved. Pseudo first-order, pseudo-second-order and intraparticle diffusion models were considered to evaluate the rate parameters. The adsorption followed pseudo-second-order kinetic model with correlation coefficients greater than 0.999. Experimental data were analyzed by model equations such as Langmuir, Freundlich and Temkin isotherms. It was found that Langmuir isotherm model was the best fitted with the adsorption data. Thermodynamic parameters of $\Delta G°$, $\Delta H°$ and $\Delta S°$ indicated the adsorption process was spontaneous and endothermic.

KEYWORDS

Polyacrylonitrile;
Monoethanolamine;
Adsorption;
Methylene blue;
Thermodynamic parameter.

INTRODUCTION

Synthetic dyes are one of the main pollutant groups of water and wastewater. Dye contamination in wastewater causes problems in several ways: the presence of dyes in water, even in very low quantities, is highly visible and undesirable; color interferes with penetration of sunlight into waters; retards photosynthesis; inhibits the growth of aquatic biota and interferes with gas solubility in water bodies. It follows that dyes need to be removed before the effluents are discharged into environment. However, this has always been a major problem because of the difficulty of treating such wastewaters by conventional methods[1,2].

Chelating resins with complex ligands containing sulphur, nitrogen, and oxygen atoms have excellent sorption capacity for dyes due to the strong affinity between sulphur, nitrogen, and oxygen atoms with dyes. There are many different methods for treating industrial wastewaters and current methods include precipitation, coagulation/flotation, sedimentation, adsorption, membrane processes, electrochemical techniques, ion exchange, biological processes and chemical reactions[3-5]. Amongst these, adsorption process has been developed as a major option for separation and purification of dyes from different dilute aqueous solutions.

The objective of this paper is synthesis and the evaluation of PAN-MEA as adsorbents of methylene blue. Characterization of the synthesized adsorbent was studied by Fourier-transform infrared spectroscopy (FT-IR). The effects of the pH, contact time, initial concentration of methylene blue, amount of adsorbent and temperature on the adsorption capacity of the PAN-MEA for MB were studied. Also, the thermodynamics and kinetic parameters of the MB adsorption onto PAN-MEA have been investigated.

EXPERIMENTAL

Materials

Polyacrylonitrile powder was provided by Polyacryl Co. (Isfahan, Iran) with a molecular weight of 60000 g mol^{-1} (10% Methacrylate, based on elemental analysis data). Monoethanolamine (MEA) was purchased from Merck and used without purification. A cationic dye, Methylene blue was provided by Fluka and used as received. The FT-IR spectra (500–4000 cm^{-1}) was obtained from ABB, MB3000 (Canada) spectrometer by using KBr pellets and scanning electron microscope ZEISS DSM 960 (Germany).

Chemical modification of PAN with MEA (PAN-MEA)

Functionalization of PAN was conducted by MEA according to Todorov et al. procedure (Figure 1)[6]. PAN (5.3 g, 0.1 mol) and MEA (48.9(PAN-MEA I), 24.1(PAN-MEA II) and 18 (PAN-MEA III) mL) were mixed in a three-necked flask (250 mL) equipped with stirrer, condenser, and thermometer. The reaction mixture was stirred in the heating bath (120°C). The initial dispersion was gradually transformed into a gel and then dissolved. The resulting clear, viscous solution indicates completion of the reaction, taking place within 60 min. The reaction product was cooled to room temperature, diluted with ethanol to the appearance of a light brown solution. The mixture was poured into the five-fold excess of acetone for the precipitation of the product. The precipitation was washed with Soxhlet using acetone. The light yellow powder was dried in vacuum at 60°C.

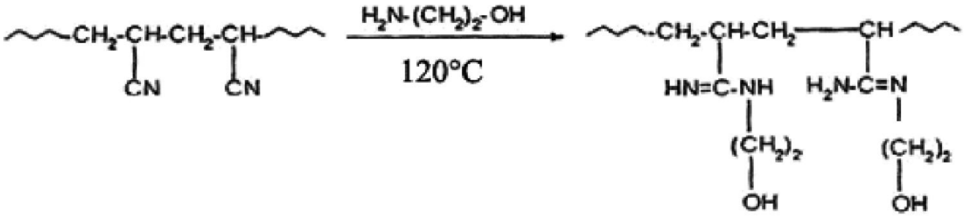

Figure 1 : Scheme of PAN–MEA synthesized.

Adsorption experiments

The 100-mL samples containing known concentration of dye and PAN-MEA were added to Erlenmeyer flasks. The flasks were stirred with a rate of 300 rpm in a water bath (Pars Azma, Iran). The pH of the dye solutions was adjusted in the range of 4-6 with 0.1 N HCl or 0.1 N NaOH by using a WTW pH 3110 SET 2 pH-meter (Germany) with a combined pH electrode. The remaining methylene blue was determined spectrophotometically (PG Instruments T70 Plus, United Kingdom) at λmax=664 nm using a calibration curve.

The amounts of dye adsorbed on PAN-MEA at any time, t, were calculated from the dye concentrations in solutions before and after adsorption. At any time, the amount of dye adsorbed (mg g^{-1}) (q_t), by PAN-MEA were calculated through Eq. (1):

$$q_t = V(C_0 - C_t)/W \qquad (1)$$

where q_t is the amount dye adsorbed into PAN-MEA at any time (mg g^{-1}), C_0 and C_t are the concentration of dye before adsorption and after contact time (mg L^{-1}), respectively; V is the volume of dye solution (L), and W is the mass of PAN-MEA sample used (g)[7,8].

In order to determine the best kinetic model which fits the adsorption experimental data, the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were examined. The linear forms of these models can be described by Eqs. (2-4):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3)$$

$$q_t = k_i t^{1/2} + C \qquad (4)$$

where q_e is the amount of the adsorbed pollutant at equilibrium per unit mass of the adsorbent (mg g^{-1}), k_1 (min^{-1}), k_2 (g mg^{-1} min^{-1}) and k_i (mg g^{-1} min$^{-1/2}$) are the rate constants of the adsorption in pseudo-first-order (Eq. (2)), pseudo-second-order (Eq. (3)) and intraparticle diffusion models (Eq. (4)), respectively[9-11].

RESULTS AND DISCUSSION

PAN-MEA was prepared by a simple reaction between PAN and MEA at 120ºC for 1 h (Figure 1).Figure 2 shows the FT-IR spectra of the raw PAN and prepared PAN-MEA resins. The FT-IR spectrum of the raw PAN (Figure 2a) shows the peaks at 3528 cm^{-1} (OH stretching), 2242 cm^{-1} (Ca'N stretching), 2931 cm^{-1} (CH stretching in CH, CH_2 and CH_3 groups), 1456 cm^{-1} (CH bending), and 1735 cm^{-1} (C=O stretching) which are the confirmation of the original powder as a copolymer of acrylonitrile (AN) and methylacrylate (MA). After the reaction of PAN with MEA, the spectrum of the obtained amine containing PAN shows many significant changes. In PAN-MEA I, the peak at 2245 cm^{-1} disappears completely (Figure 2b). In addition, the new bonds observed at 1651, 1556, 1597 and 1381 cm^{-1} for the PAN-MEA can be assigned to the C=O (or C=N) groups in amide, the N–H group in amine or amide and the C–N group in amide, respectively [12]. These results confirmed the introduction of monoethanolamine groups in the polyacrylonitrile structure (Figure 1). TABLE 1 shows detail of FT-IR adsorption signals for PAN-MEA resins and its MB adsorption.

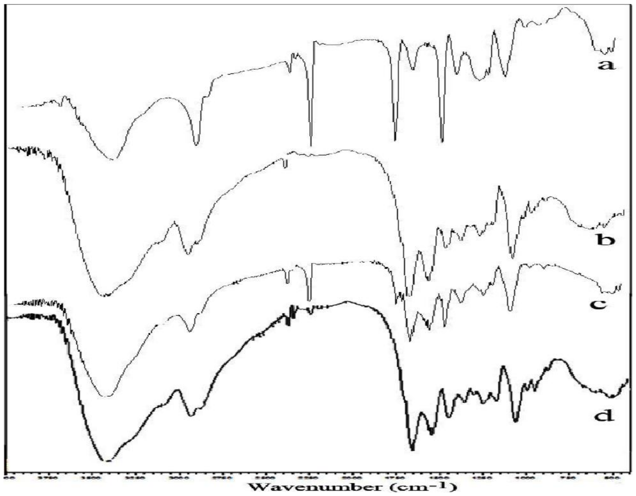

Figure 2 : FT-IR spectra of a) PAN, b) PAN-MEA I, c) PAN-MEA II, (d) PAN- MEA III.

TABLE 1 : FT-IR adsorption signals (cm^{-1}) for PAN-MEA resins and its methylene blue sorption.

	NH_2, NH (Stretching)	C-H (stretching)	C=N (Stretching)	C=O or C=N	N-H (Bending)	C-H (Bending)
PAN	-	2931	2245	1635	-	-
PAN-MEA I	3406	2931	-	1654	1543	1060
PAN-MEA II	3425	2939	2245	1654	1539	1068
PAN-MEA III	3410	2932	2241	1654	1543	1060
PAN-MEA I MB	3425	2924	-	1651	1543	1018
PAN-MEA II MB	3425	2931	2245	1658	1542	1072
PAN-MEA III MB	3425	2924	2245	1658	1543	1064

Adsorption behavior of PAN-MEA

In the high concentration of MEA, the modification of PAN done well and the adsorption ability of resin were increased, so here we considered adsorption behavior of MB onto PAN-MEA I.

Effect of pH

The amount of MB adsorbed onto PAN-MEA I as a function of pH was shown in Figure 3. As shown in Figure 3, the high uptake capacity was achieved at high pH values. The observed lower uptake in an acidic medium may be attributed to the partial protonation of the active groups and the competition of H^+ with MB for adsorption sites on the PAN-MEA I.

Effect of contact time and initial concentration of MB

The effect of initial MB concentration and contact time on the adsorption rate of MB onto resins is shown in Figure 4. The amount of dye adsorbed at anytime increases from 15.04 to 52.3 mg g^{-1} by increasing the initial MB concentration from 20 to 60 mg L^{-1}. Therefore, adsorption increases with increasing initial dye concentration. The results show that uptake of MB is rapid for the first 20min reaching equilibrium within about 30 min.

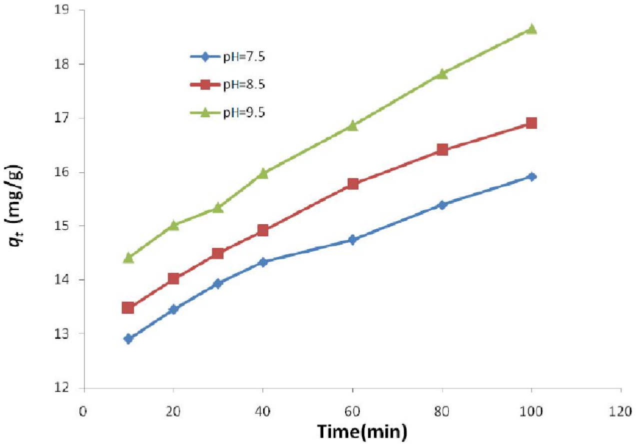

Figure 3 : Effect of contact time and initial pH on the removal rate of MB onto PAN-MEA I from aqueous solutions (T=25 °C, $[MB]_o$=50mg L^{-1}, resin=0.1 g).

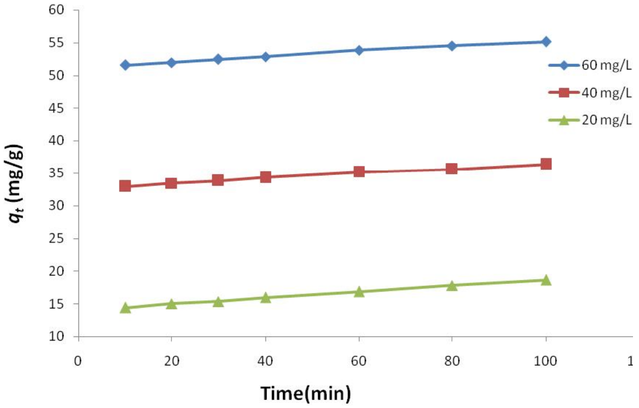

Figure 4 : Effect of contact time and initial concentration of MB onto PAN-MEA I from aqueous solutions (T=25 °C, pH= 9.5).

Effect of adsorbent dosage

Adsorbent dose is a significant parameter in the determination of adsorption capacity. In order to study the effect of adsorbent mass on the adsorption of MB, a series of adsorption experiments was carried out with different adsorbent dosages at initial dye concentration of 50 mg L^{-1}. Figure 5 shows the effect of adsorbent dose on the removal of MB. Along with the increase of adsorbent dosage from 0.1 to 0.3 g, the MB sorption capacity decreased from 15.15 to 3.04 mg g^{-1}. This may be attributed to the aggregation of adsorbent particles at high dosage, which reduces the total surface area of the adsorbent and results in an increase in the diffusion path length. Also Increasing the dosage of PAN-MEA and keeping the dye concentration constant makes a large number of sites available for a fixed concentration of sorbate, hence the reduction in the value of q_t[13].

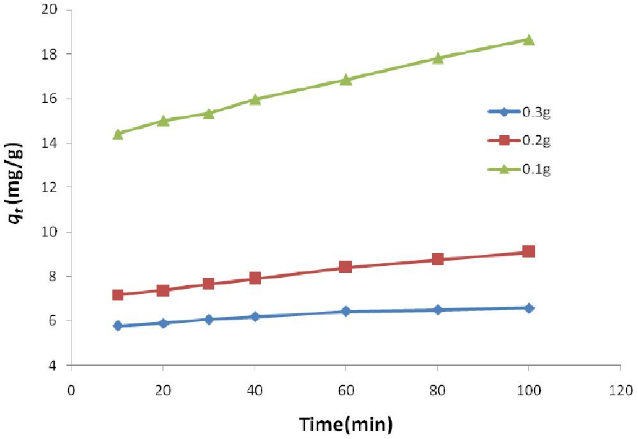

Figure 5 : Effect of adsorbent dose on adsorption of MB onto PAN-MEA I (T=25 °C, $[MB]_o$=50mg g^{-1}, pH=9.5).

Effect of temperature

To study the effect of temperature on the adsorption of MB adsorption by PAN-MEA I, the experiments were performed at temperatures of 25, 40, and 55 °C. Figure 6, shows the influence of temperature on the adsorption of MB onto PAN-MEA I. As it was observed, the equilibrium adsorption capacity of methylene blue onto PAN-MEA I was found to increase with increasing temperature, especially in higher equilibrium concentration, or lower adsorbent dose because of high driving force of adsorption. This fact indicates that the mobility of MB increased with the temperature. The adsorbent shows the endothermic nature of adsorption.

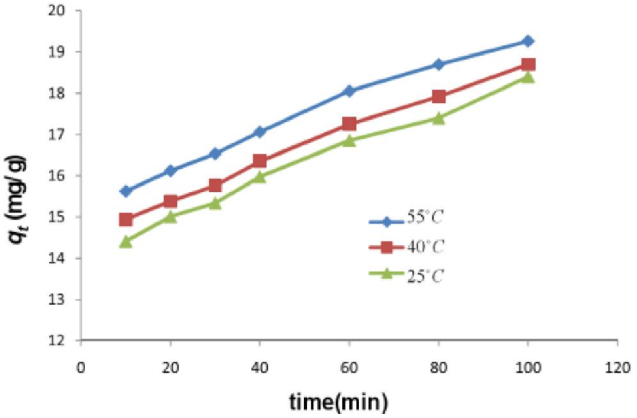

Figure 6 : Effect of contact time and temperature on the removal efficiency of MB onto PAN-MEA I from aqueous solutions ($[MB]_o$= 50 mg L^{-1}, pH= 9.5, resin=0.1 g).

Kinetics of adsorption process

From the study of the kinetics of adsorption results are shown in TABLE 2. The pseudo-second order model well described the experimental data (R^2>0.99). Similar results have been observed in the adsorption of methylene blue onto HNTs[14]. In contrast the pseudo-first order model and the intraparticle diffusion models do not describe the adsorption of MB. Figure 7 shown the pseudo-second order curves of PAN-MEA I with MB in the various temperature.

TABLE 2 : Adsorption kinetic parameters of MB onto PAN-MEA I.

Sample	PAN-MEA I		
Temperature (°C)	25	40	55
Pseudo-first-order			
k_1, min^{-1}	0.0067	0.0043	0.0024
R^2	0.989	0.985	0.991
Pseudo-second-order			
k_2, mg g^{-1} min^{-1}	0.045	0.035	0.026
$q_{e,\,cal}$ (mg g^{-1})	16.5	18.4	19.4
$q_{e,Exp}$ (mg g^{-1})	15.9	17.1	17.9
R^2	0.999	0.999	0.999
Intraparticle diffusion			
k_i, mg g^{-1} min$^{1/2}$	0.627	0.562	0.555
C	12.6	12.9	13.6
R^2	0.983	0.986	0.987

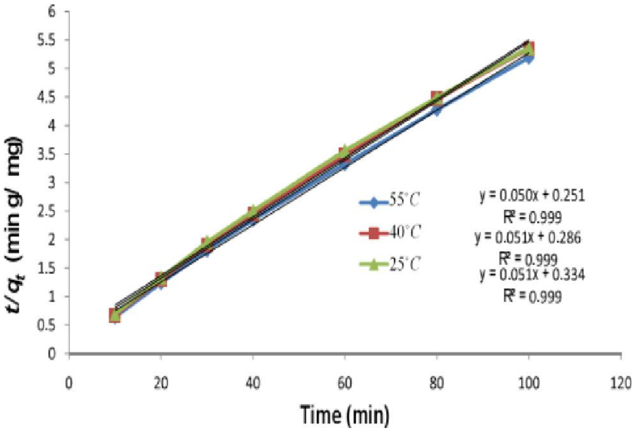

Figure 7 : Pseudo-second-order plots for the adsorption of MB onto PAN-MEA I at various temperatures ($[MB]_o$=50mg L^{-1}, resin=0.1 g, pH=9.5).

Activation parameters

From three of the pseudo-second-order rate constants, k_2 (here K_{sm}), each at a different temperature, and using the Arrhenius equation (Eq. (5)), it is possible to gain some insight into the type of adsorption.

$$\ln k_{sm} = \ln A - E_a/RT \qquad (5)$$

Here E_a is the activation energy (J mol^{-1}), k_{sm} the pseudo-second-order rate constant for adsorption (g mol^{-1} s^{-1}), A the temperature-independent Arrhenius factor (g mol^{-1} s^{-1}), R the gas constant (8.314 J K^{-1} mol^{-1}), and T the solution temperature (K). The slope of the plot of $\ln k_{sm}$ vs. T^{-1} can then be used to evaluate E_a. Low activation energies (5–40 kJ mol^{-1}) are characteristic of physical adsorption, while higher ones (40–800 kJ mol^{-1}) suggest chemisorption[15]. The present results give E_a = ~ +9.45 kJ mol^{-1} for the adsorption of MB onto PAN-MEA I, indicating that the adsorption has a low potential barrier and corresponds therefore to physisorption (Figure 8).

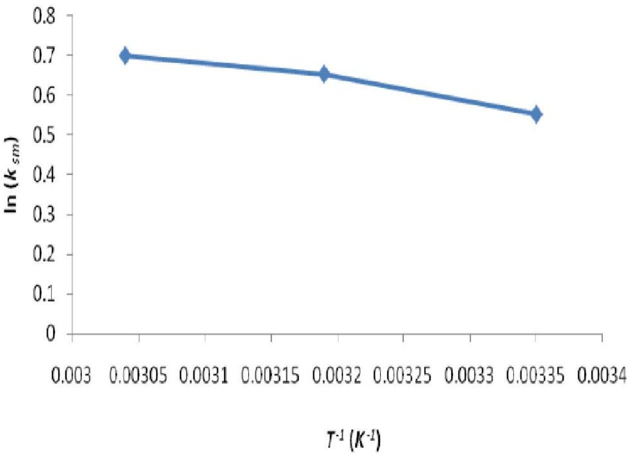

Figure 8 : plot of $\ln k_{sm}$ vs. T^{-1}: estimation of the activation energy, E_a, for the adsorption of MB onto PAN-MEA I.

Adsorption isotherms

The adsorption equilibrium isotherm is important for describing how the adsorbate molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state. It is expressed by relating the amount of adsorbate taken up per gram of adsorbent, q_e (mg g^{-1}), to the equilibrium solution concentration, C_e (mg L^{-1}), at a fixed temperature. The analysis of the isotherm data by seeing how well they can be accommodated by different models is a crucial step in establishing a model that can be successfully used for design purposes. Adsorption equilibrium is a dynamic concept achieved when the rate at which molecules adsorb onto a surface is equal to the rate at which they desorbed. At equilibrium, no change can be observed in the concentration of the solute on the solid surface or in the bulk solution, a situation characteristic of the entire system, including solute, adsorbent, solvent, temperature, pH, and so on[16].

The quantity of dye that could be taken up by an adsorbent is a function of both the concentration of the dye and the temperature. The amount of dye adsorbed is determined as a function of the concentration at a constant temperature, which could be explained by adsorption isotherms. In this study, three isotherms Langmuir (Eq. (6))[17], Freundlich (Eq. (7))[18] and Temkin (Eq. (8))[19] were tested.

$$\frac{C_e}{q_e}=\frac{1}{K_L}+\frac{a_L}{K_L}C_e \tag{6}$$

$$\log q_e=\log K_F+\frac{1}{n}\log C_e \tag{7}$$

$$q_e=B_1\ln K_T+B_1\ln C_e \tag{8}$$

Here q_e is the solid phase equilibrium concentration, i.e., the amount of MB adsorbed per unit weight of the PAN-MEA I (mg g^{-1}); C_e is the liquid phase equilibrium concentration (mg L^{-1}), K_L and a_L are Langmuir constants found from the intercept and slope of the straight line of the plot C_e/q_e versus C_e. The a_L constant is related to the free energy or net enthalpy of adsorption (L mg^{-1}) ($a_L \alpha e^{-\Delta H/RT}$)[20], and K_L is the equilibrium constant of Langmuir (L g^{-1}). K_F is a Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}) and $1/n$ is the adsorption intensity. $B_1 = RT/b$, K_T is the equilibrium binding constant (Lmg^{-1}) and B_1 is the heat of adsorption.

The isotherm constants for all the isotherms studied were calculated from the linear form of each model and the correlation coefficients are given in TABLE 3. Based on the high values of R^2 (more than 0.99), the experimental equilibrium data was fitted to Langmuir and Freundlich isotherms. Figure 9 shows the Langmuir plot for the adsorption of MB onto PAN-MEA I at 25, 40, and 55 ºC, as reproduced by the linearized Langmuir equation. However the Langmuir isotherm gave a better fit than the Freundlich isotherm for MB adsorbed on PAN-MEA I. This suggests that monolayer adsorption of malachite green takes place on the homogeneous surface of PAN-MEA I.

Adsorption thermodynamics

The thermodynamic parameters are crucial for a better comprehension of the effect of temperature on adsorption. Since the K_L Langmuir constant is essentially an equilibrium constant, the variation of K_L with temperature (TABLE 3) can be used to estimate the enthalpy change accompanying adsorption, ΔH^o, i.e., the standard enthalpy change of adsorption at a fixed surface coverage[21]. The thermodynamic parameters ΔH^o, ΔS^o, and ΔG^o associated with the adsorption process can be determined by using the following equations:

$$\Delta G° = -RT\ln K_L \tag{9}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{10}$$

Where K_L is Langmuir constant when concentration terms are expressed in L mol^{-1}, R (8.314 J mol^{-1} K^{-1}) is the universal gas constant and T (K) is the temperature. The $\Delta H°$ and $\Delta S°$ values can be calculated from the slope and intercept of the plot of $\Delta G°$ versus T. The free energy changes ($\Delta G°$) are negative, indicating the

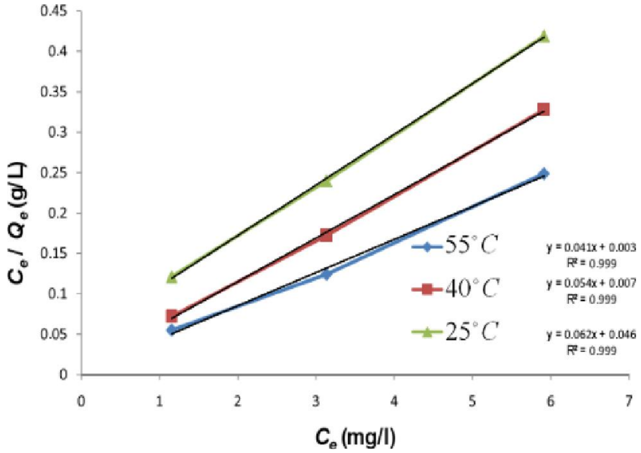

Figure 9 : Langmuir plot of adsorption of MB onto PAN-MEA I at various temperatures (PH=9.5, resin=0.1 g).

TABLE 3 : The adsorption parameters of Langmuir, Freundlich and Temkin models for PAN-MEA I at different temperatures.

PAN-MEA I									
	Langmuir			Freundlich			Temkin		
Temperature (°C)	K_L	a_L	R^2	$1/n$	K_F	R^2	B_1	K_T	R^2
25	135	3.177	0.999	0.048	1.43	0.971	17.8	4.8	0.996
40	123	2.876	0.999	0.053	1.39	0.981	-	-	-
55	108	2.694	0.999	0.067	1.30	0.989	-	-	-

spontaneity and feasibility of these processes. The decrease in ΔG° value with increasing temperature reveals that adsorption of MB onto PAN-MEA I become more favorable at higher temperature.

The positive value of ΔH° further confirms that the adsorption processes are endothermic in nature. The positive value of ΔS° infers increase of randomness at solid–solution interface during the adsorption of MB on the active sites of PAN-MEA I[22]. Moreover, positive value of ΔS° reflects affinity of the adsorbent for MB.

CONCLUSIONS

In the present study, the removal of MB from aqueous solutions was investigated by utilizing modified polyacrylonitrile. This resin has been demonstrated to be highly effective for the removal of dye from aqueous solutions. The equilibrium data have been analyzed using Langmuir, Freundlich and Temkin isotherms. The characteristic parameters for each isotherm and pertinent correlation coefficients have been determined. The Langmuir isotherm was demonstrated to provide the best correlation for the adsorption of MB onto PAN-MEA I. The adsorption of MB onto PAN-MEA I obeyed pseudo-second-order kinetics with activation energy +9.45 kJ mol^{-1}, this is consistent with the description of the process as physisorption. The Methylene blue adsorbed PAN-MEA I aggregated and deposited completely within 30 min.

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