Sorptive Removal of Methylene Blue from Aqueous Solutions by Polymer/Activated Charcoal Composites

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ABSTRACT: In this study, a new sorbent, a poly(acrylamide-*co*-itaconic acid) [P(AAm-*co*-IA)]/activated charcoal (AC) composite, was prepared by the aqueous polymerization of acrylamide and itaconic acid in the presence of AC with *N*,*N*′-methylene bisacrylamide as a crosslinker and potassium persulfate as an initiator. The P(AAm-*co*-IA)/AC composite sorbent showed a fair capacity to adsorb the cationic dye methylene blue. The maximum sorption capacity, as studied at 23, 37, and 50°C and determined with the Langmuir isotherm model, was found to be 909.0, 312.5, and 192.3 mg/g, respectively. For an initial concentration of 5 mg/L, the kinetic uptake data were studied with various kinetic models. The pseudo-second-order equation was found to fairly fit the uptake data with a regression value of 0.999. The dye uptake increased with the pH of the sorbate solution, and the optimum pH was found to be in the range of 7–10. Intraparticle diffusion was also observed to take place, and the coefficient of intraparticle diffusion was evaluated to be 26.51×10^{-2} mg g^{-1} $min^{-1/2}$. The various thermodynamic parameters were also determined to predict the nature of the uptake process. The sorption process was found to be spontaneous, as indicated by a negative standard free energy change. The negative standard enthalpy change suggested an exothermic nature for the uptake. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2525–2532, 2011

Key words: adsorption; composites; UV-visible spectroscopy

INTRODUCTION

The disposal of dye effluents such as dyestuff, textiles, paints and varnishes, ink, pulp, and paper from various industries is of great concern because of their toxic and harmful effects on human health. Over 100,000 commercially available dyes exist, and more than 7×10^5 tons is produced annually, with a considerable fraction being discharged in aqueous effluents.[1] By diminishing the transparency of water, dyes such as methylene blue (MB) modify the penetration of solar radiation, thereby affecting the photosynthetic activity[2] and affecting aquatic life and food webs[3]; they may also be carcinogenic and mutagenic.[4] Consequently, many treatment processes have been applied for the removal of dyes from wastewater. These processes include photocatalytic degradation,[5] biodegradation,[6] electrochemical degradation,[7] photo-Fenton processes,[8] and adsorption.[9]

Out of these processes, adsorption with suitable adsorbent materials has emerged as the most promising technique for the effective removal of dyes such as MB. The various sorbent materials used for removing MB include spent tea leaves,[10] bentonite clay,[11] activated desert plants,[12] montmorillonite,[13] zeolites,[14] and activated charcoal (AC).[15,16] Among them, AC is the most widely used adsorbent with great success because of its salient features, such as low production costs, an extensive surface area, well-developed micropore reproducibility, and a high adsorption capacity.[17] However, despite so many advantageous features, the aggregation of powdered charcoal under various experimental conditions and the chocking of charcoal in fixed column experiments hamper its large-scale applications as an adsorbent. Most recently, synthetic polymeric sorbents have also attracted the attention of environmental chemists because of their high uptake capacity and dispersive nature. For example, Paulino et al.[18] used a superabsorbent hydrogel composed of gum Arabic, polyacrylate, and polyacrylamide for the removal of MB and reported a maximum sorption capacity (Q_o) of 58 mg/g. Similarly, hydrogel beads, composed of sodium alginate and polyaspartate, were employed recently for the removal of MB from aqueous solutions.[19] However, the higher preparation cost of synthetic polymers has really been a limiting factor for the large-scale use of these polymeric sorbents, although they possess a fair dispersive tendency in the sorption system, unlike activated powdered charcoal.

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Therefore, these observations have led us to think that the use of polymer/charcoal composites could be the best solution for minimizing the agglomerating tendency of charcoal powder and also for reducing the preparation cost of synthetic polymers. Therefore, in this work we have developed a novel poly(acrylamide-*co*-itaconic acid) [P(AAm-*co*-IA)]/AC composite material as an effective sorbent for the removal of MB. In a preliminary study, we found that with an initial MB concentration of 10 mg/L, the equilibrium MB uptake (mg/g) for P(AAm-*co*-IA)/AC, charcoal powder, and a P(AAm-*co*-IA)/AC composite was 18.8, 19.4, and 18.0, respectively; this indicated that the polyacrylamide/AC composite exhibited nearly the same sorption capacity with additional advantages such as a fair dispersive ability and lower preparation costs.

EXPERIMENTAL

Materials

The monomers acrylamide (AAm) and itaconic acid (IA), the crosslinker *N*,*N*′-methylene bisacrylamide, the catalyst tetraethylmethylenediamine (TEMED), and the initiator potassium persulfate were obtained from E. Merck (Mumbai, India). AC and MB (formula weight (FW) = 373.9, maximum wavelength = 670 nm) were purchased from Hi Media Chemicals (Mumbai, India) and were used as received. The monomer AAm was recrystallized in methanol to remove the inhibitor. Double-distilled water was used throughout the studies.

Preparation of the P(AAm-*co*-IA)/AC composites

The polymer/activated carbon composites were prepared by the free-radical-induced aqueous polymerization of AAm and IA in the presence of uniformly dispersed fine AC. In brief, the monomers AAm (105.514 m*M*) and IA (3.843 m*M*) and the crosslinker *N*,*N*′-methylene bisacrylamide (1.784 m*M*) were dissolved in distilled water for a total volume of 35 mL. To this, 0.3 g of AC was added. Finally, the reaction was initiated by the addition of 0.647 m*M* potassium persulfate and 1800 μL of the catalyst TEMED under vigorous shaking. After the whole reaction mixture gelled, it was put into an electric oven (Tempstar, India) at 60°C to ensure complete polymerization. The resulting P(AAm-*co*-IA)/AC composite was washed thoroughly in distilled water to remove the unreacted salts and then dried at 50°C in a dust-free chamber. The dried mass was ground and passed through standard sieves to obtain sorbent particles with the average geometrical mean diameter of 185 μm. The composite sorbent particles were stored in a dry place for further use.

MB uptake studies

Batch sorption experiments were carried out in a thermostated rotary shaker (Rivotek, Jalandhar, India) with 125-mL Erlenmeyer flasks containing 50-mL aqueous MB solutions and 0.05 g of the sorbent under constant stirring at 50 rpm. At predetermined time intervals, sorbate solutions were taken out, filtered, and then analyzed for the MB concentration at 670 nm with an ultraviolet–visible spectrophotometer (8400S, Shimadzu, Japan). The concentrations of the MB solutions were determined with a standard calibration curve obtained with MB solutions of known concentrations. The dye uptake was determined with the following expression:

$$Q = (C_o - C_e)V/W \tag{1}$$

where Q is the dye uptake (mg/g); C_o and C_e are the initial and final dye concentrations (mg/L), respectively; V is the volume of the sorbate solution (L); and W is the sorbent dose (g).

Analysis of the data

Each data point was taken as the average of three measurements with a standard deviation of 2.0%; when the relative error exceeded 2.0%, the data were discarded, and a new experiment was conducted until the relative error fell within the acceptable range. The values of the kinetic and isotherm parameters were determined by a nonlinear regression analysis with Origin (version 7.5).

RESULTS AND DISCUSSION

Preparation of the P(AAm-*co*-IA)/AC composites

The polymer/charcoal composite sorbent was prepared by free-radical-induced aqueous polymerization in the presence of uniformly dispersed powdered AC. To prevent the carbon particle from settling down during the gelation process, the appropriate quantity of the catalyst TEMED was added to catalyze the gelation process. It was observed that the addition of 1800 μL of TEMED (see the Experimental section) caused the gelation process to complete in nearly 2–3 s, an amount of time quite insufficient for powdered charcoal particles to settle down.

In other words, AC particles remained fairly suspended during the course of the polymerization reaction. After the gelation was over, the reaction mixture was kept in an oven at 60°C for 1 h to ensure complete gelation. In this way, due care was taken to obtain an almost uniform distribution of AC particles within the polymer matrix. To test the homogeneity of the composite material, the freshly

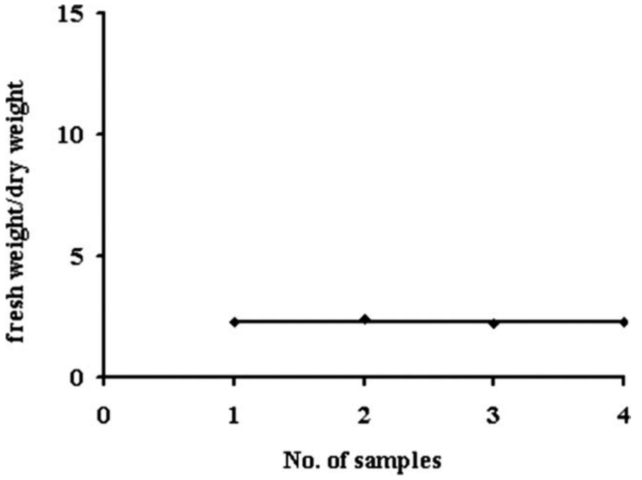

Figure 1 Homogeneity test for the P(AAm-*co*-IA)/AC composite sorbent.

prepared gelled mass was divided into a number of parts, and the ratio of fresh mass to dry mass for each part was determined.[20] A plot of the ratio of fresh mass to dried mass and the number of parts yielded a straight horizontal line, as shown in Figure 1, thus showing that the ratio was the same for each part. This indicated that the TEMED-catalyzed gelation of AAm and IA in the presence of uniformly dispersed powdered AC particles resulted in the formation of a homogeneous composite sorbent. Table I depicts various physical parameters of the prepared P(AAm-*co*-IA)/AC composite obtained with various formulas presented in our previous work.[20]

Effect of pH on the MB uptake

The dependence of the uptake of MB on the pH of the sorbate solution is depicted in Figure 2. The results reveal that dye uptake is minimal at pH 2.0, increases with an increase in the pH of the sorption medium, and attains its maximum at pH 7.0. With a further increase in the pH up to10.0, the adsorption remains almost constant. The observed findings may be explained as follows. Initially, when the pH of the sorption system is quite low (i.e., pH 2.0), the —COOH groups present along the macromolecular chains of P(AAm-*co*-IA) remain un-ionized, and therefore the binding of cationic drug molecules is not favored. In addition, the un-ionized carboxylic groups also produce additional crosslinks within the gel particle, thus imparting to it an almost compact structure and discouraging the entrance of the solute into the sorbent particles. However, as AC particle are also present within the gel, they provide favorable adsorption sites for dye molecules. In this way, the MB uptake is mainly due to AC present within the composite sorbent particles. Now, as the pH of the sorbate is increased, the carboxylic groups present along the polymeric chains begin to ionize to yield $—COO^-$ groups, which act as strong binding sites for positively charged dye molecules. In addition, the repulsion among similarly charged $—COO^-$ groups causes the macromolecular chains to relax or unfold, thus resulting in a swelling of gel/AC composite particles. This also enhances the diffusion of MB molecules into the composite particles,[21] thus favoring dye uptake. In addition, AC particles also contribute to dye uptake by providing binding sites. Therefore, as the pH of the solution continues to increase, more and more MB molecules are sorbed into composite particles. Finally, maximum uptake is observed near pH 7.0 when nearly all —COOH groups present within the composite particles have ionized. When the pH is further increased beyond 7.0, the uptake remains almost constant. In this way, pH 7.0 may be considered the optimum pH for easy processability of the dye uptake. Similar types of results were also reported by Anirudhan et al.,[22] who reported the adsorption of MB onto humic acid immobilized polymer/bentonite composites.

TABLE I
Physical Parameters of the Adsorbent

Parameter	Value
Particle size (μm)	185
True density[a]	1.0
Tapped density[a]	0.55
Porosity (%)[a]	55
Apparent density[a]	0.45

[a] Obtained with methods reported by Bajpai and Tankhiwale.[20]

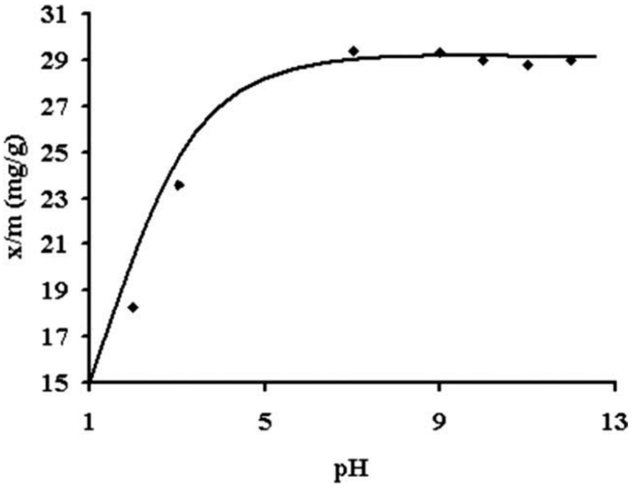

Figure 2 Effect of the pH of the sorption system on the dye uptake (mg/g; [MB] = 10 mg/L, temperature = 23 ± 2°C). x/m is the amount of dye adsorbed in mg/g of sorbent.

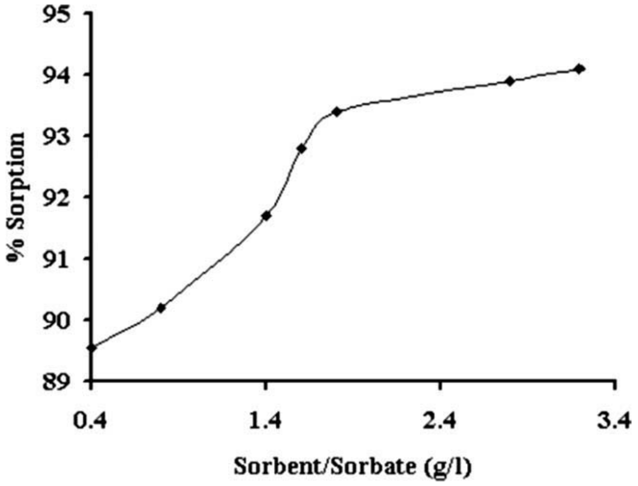

Figure 3 Effect of the sorbent–sorbate ratio (g/L) on the percentage dye uptake ([MB] = 10 mg/L, temperature = 23 ± 2°C).

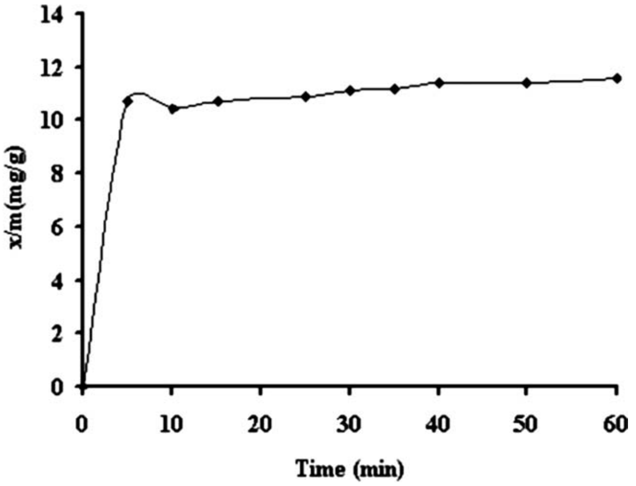

Figure 4 Dynamic uptake of MB by the composite sorbent as a function of time at pH 6.8 (self; [MB] = 50 mg/L, temperature = 23 ± 2°C).

Effect of the solid/liquid ratio on the MB uptake

Figure 3 shows the effect of the solid/liquid ratio (0.4–4.0 g/L) on 10 mg/L MB adsorption at 25°C and at pH 7.0. It is clear that the uptake of the dye increases slowly with an increase in the solid/liquid ratio and attains an almost constant value of 93.4% as the ratio exceeds 1.8. Therefore, a solid/liquid ratio of 2.0 (i.e., 0.1 g of sorbent in 50 mL of a sorbate solution) was selected as the optimum solid/liquid ratio for further investigations.

Adsorption kinetics

A kinetic study of MB uptake was carried out through the agitation of 0.1 g of composite sorbent particles in 50 mL of a dye solution with an initial concentration of 50 mg/L under constant stirring at 23°C. The results, as shown in Figure 4, reveal that dye uptake is very fast in the beginning and attains equilibrium in nearly 45 min. The largest amount of dye (>90%) was removed within the first 5 min of contact. This may simply be attributed to the fact that that polymer/AC composite particles have a fairly high swelling capacity, and consequently, their networks are sufficiently expanded to allow faster diffusion of sorbate molecules into the swollen sorbent particles. This expanded network of the sorbent favors the interactions of the cationic MB molecules with highly preferable anionic $\mathrm{-COO^-}$ sorption sites present within the polymer network. In addition, AC particles, present within the swollen polymer matrix, also provide active sites for dye uptake. In fact, such a rapid sorption phenomenon is advantageous in process applications.[23]

The main issue when one is searching for an appropriate sorption mechanism is the selection of a mathematical model that not only fits the experimental data with fair accuracy but also complies with a reasonable sorption mechanism.[24] Generally, the sorption process by porous sorbents involves several steps: (1) bulk diffusion, (2) external mass transfer (boundary layer or film diffusion) between the external surface of the sorbent particles and the surrounding fluid phase, (3) intraparticle transport within the particles, and (4) reaction kinetics at phase boundaries. On the basis of a majority of the studies of the uptake of dye by sorbent particles, it has been concluded that dye sorption is usually controlled by two mechanisms: external and internal diffusion.[25] In this study, the kinetic dye uptake data were analyzed with the pseudo-first-order, pseudo-second-order, and Elovich kinetic models.

The pseudo-first-order kinetic model, as given by Lagergren and Sven,[26] considers the rate of

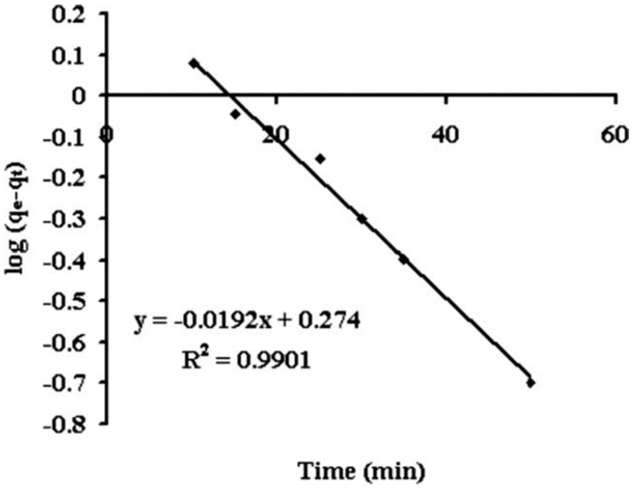

Figure 5 Pseudo-first-order plot for the uptake of MB into the composite sorbent.

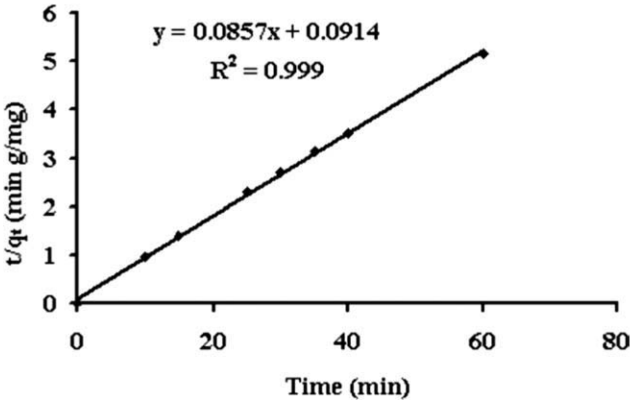

Figure 6 Pseudo-second-order plot for the dye uptake.

occupation of sorption sites to be proportional to the number of unoccupied sites:

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

where k_1 is the rate constant of the pseudo-first-order sorption (min^{-1}) and q_t and q_e are the amounts of sorbate sorbed at time t and at equilibrium (mg/g), respectively. A straight line obtained between $\ln(q_e - q_t)$ and t is indicative of the applicability of the pseudo-first-order model. In addition, a pseudo-second-order equation, developed by Ho and Mckay,[27] can be expressed as follows:

$$t/q_t = 1/k_{2ad} \cdot q_e^2 + t/q_e \quad (3)$$

where k_{2ad} is the pseudo-second-order rate constant. A linear plot of t/q_t versus t suggests the suitability of this model for our kinetic uptake data.[28] Finally, the simple Elovich model can be expressed as follows:

$$q_t = \alpha + \beta \ln t \quad (4)$$

where α is initial rate in mg g^{-1} min^{-1} and β is related to extent of surface coverage. A plot of q_t versus ln t should give a linear relationship for the applicability of this kinetic model.

The experimental data, displayed in Figure 4, were applied to the pseudo-first-order, pseudo-second-order, and Elovich equations, thus yielding the linear plots shown in Figures 5–7 with respective regression values of 0.991, 0.999, and 0.979, respectively. Hence, the suitability of these models follows this order: pseudo-second-order model > pseudo-first-order model > simple Elovich model.

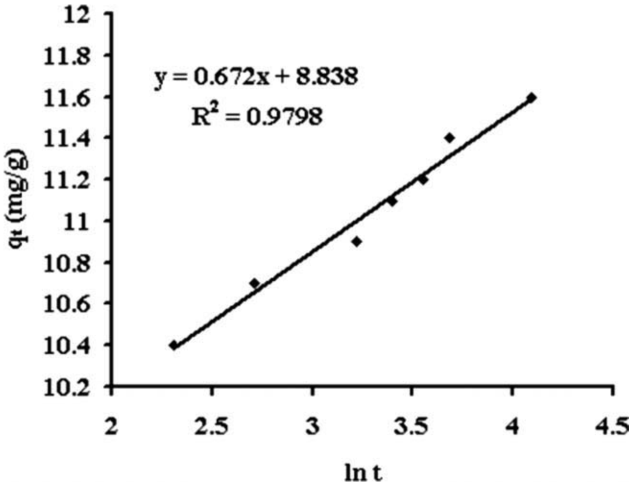

Figure 7 Simple Elovich plot for the uptake of MB into the composite sorbent.

Table II describes various kinetic parameters related to these models; they were determined from intercepts and slopes obtained with eqs. (2)–(4). The value of q_e obtained with the pseudo-second-order model (11.60) was closest to the experimental value (11.66), thus establishing the superiority of this model with respect to the others.

As these kinetic models were not able to identify the diffusion mechanism, the intraparticle diffusion model was also tested.[13] It is an empirically determined functional relationship common to most sorption processes in which the sorbate uptake varies proportionally with $t^{1/2}$ rather than t. According to this model

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

where k_i is the intraparticle diffusion coefficient and c is thickness of boundary layer. If the uptake process occurs through an intraparticle diffusional mechanism, then a straight line passing through the origin is obtained. In this study, the q_t–$t^{1/2}$ plot, as shown in Figure 8, shows a double straight line nature: the initial and final stages. The initial linear portion indicates boundary layer diffusion, whereas

TABLE II
Depiction of the Kinetic Parameters Obtained with Different Kinetic Models

Pseudo-first-order model		Pseudo-second-order model		Simple Elovich model		
$k_1 \times 10^3$ (min^{-1})	R^2	$k_2 \times 10^3$ (g mg^{-1} min^{-1})	R^2	α (mg g^{-1} min^{-1})	β	R^2
44.1	0.990	80.35	0.999	8.838	0.672	0.909

Initial MB concentration = 5 mg/L; temperature = 23°C; k_2 is pseudo second order rate constant.

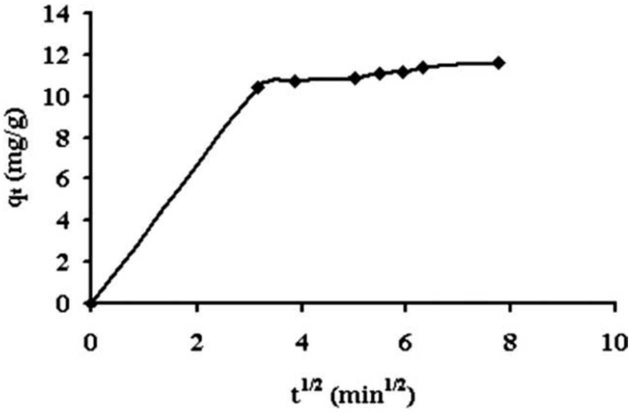

Figure 8 q_t versus $t^{1/2}$ for the determination of k_i.

the final linear portion indicates that the removal process is dominated by intraparticle diffusion in this part of the uptake process.[9] k_i, determined from the slope of the final linear part, was found to be 26.51×10^{-2} mg g^{-1} min$^{-1/2}$. Here it is also worth mentioning that the initial linear part represents instantaneous or external surface sorption, which is appreciably faster than the latter part of the uptake process. Such behavior of sorbent–sorbate systems is quite common and has been reported frequently.[10]

Equilibrium sorption studies

Equilibrium uptake studies for any removal process are of immense importance, especially for recommending the process for large-scale application. In this study, the equilibrium sorption studies were carried out at three temperatures (23, 37, and 50°C) with initial dye solution concentrations in the range of 5–60 mg/L. The results were analyzed with the Langmuir,[29] Freundlich,[30] and Temkin isotherm models.[31] However, the Freundlich and Temkin isotherm models did not have fairly high regression values (<0.86) and hence were rejected.

The linearized Langmuir isotherm, as suggested by Ho,[32] can be presented as follows:

$$\frac{1}{q_e} = \frac{1}{C_e}\left[\frac{1}{bQ_o}\right] + \frac{1}{Q_o} \tag{6}$$

where C_e is the equilibrium concentration (mg/g), q_e is the amount sorbed at equilibrium (mg/g), Q_o is the maximum sorption capacity and represents a practical sorption limitation when the sorbent surface is fully covered with monolayer sorbate molecules, and b is the Langmuir constant (L/mg). The Langmuir isotherms, obtained at three different temperatures, are depicted in Figure 9. The values of Q_o and b, determined from intercepts and slopes of linear plots, are given in Table III. It is clear that Q_o decreases with an increase in temperature, thus indicating the exothermic nature of the uptake process. The observed finding may be explained by the fact

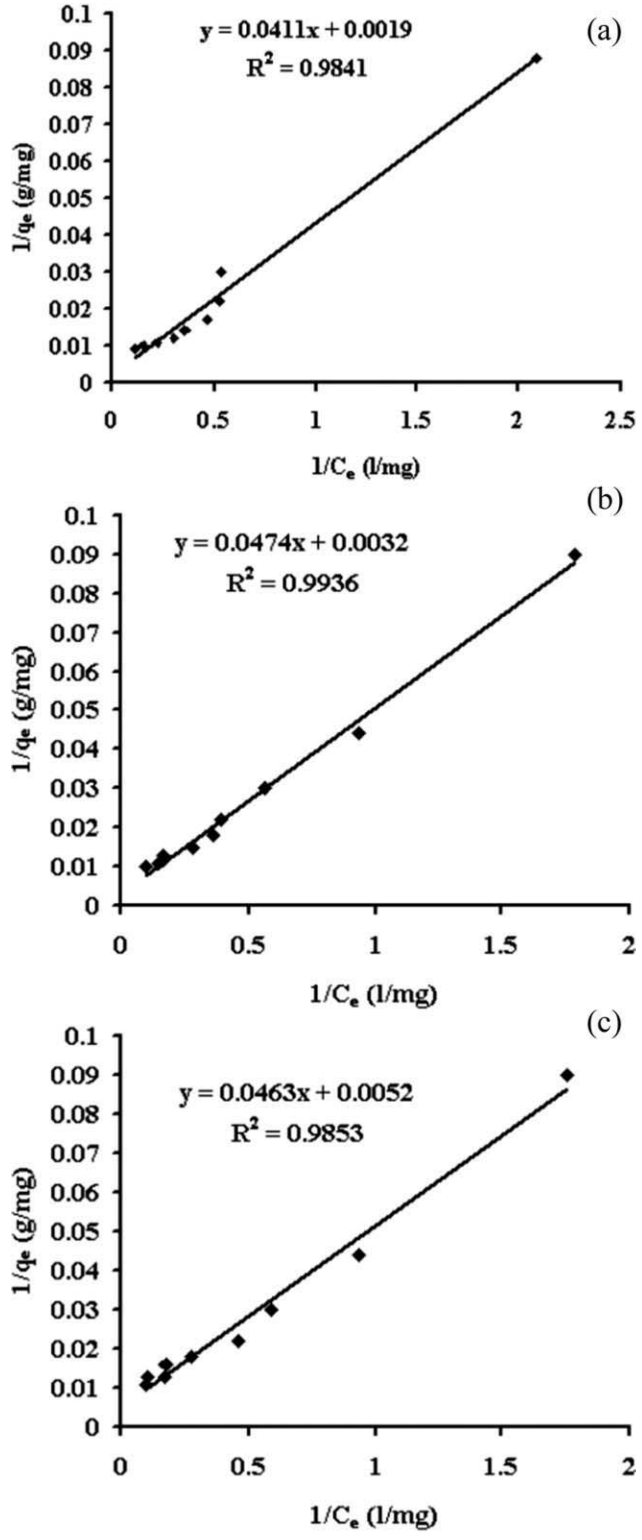

Figure 9 Langmuir isotherms for the equilibrium dye uptake by the composite sorbent at (a) 23, (b) 37, and (c) 50°C.

TABLE III
b and R_L Values Obtained for the Equilibrium Uptake of MB onto the Composite Sorbent at Different Temperatures

Temperature (K)	Parameters for the Langmuir isotherm		
	Q_o (mg/g)	b (L/mg)	R_L
296	909.0	0.026	0.884–0.390
310	312.5	0.067	0.749–0.199
323	192.3	0.112	0.641–0.151

that the uptake of cationic dye molecules is mainly due to their electrostatic binding with negatively charged —COO$^-$ groups present within the polymer/composite sorbent particles. Because of an increase in temperature, the kinetic energy of sorbate molecules is increased, and this weakens the force of attraction between cationic MB molecules and anionic binding sites. Moreover, the increase in temperature also disfavors the binding of the sorbate onto residual valencies of activated carbon particles via van der Waals forces of attraction. Therefore, am increase in temperature causes a decrease in dye uptake. However, these results are the opposite of those obtained by Almeida et al.,[13] who observed an increase in MB uptake onto montmorillonite clay with temperature.

Finally, the essential characteristics of Langmuir isotherms, related to the isotherm shape, can be expressed in terms of a dimensionless constant separation factor, which is also called the equilibrium parameter (R_L):[33]

$$R_L = \frac{1}{1 + bC_o} \tag{7}$$

The values of R_L indicate that the isotherm type is (1) unfavorable ($R_L > 1$), (2) linear ($R_L = 1$), (3) favorable ($0 < R_L < 1$), or (4) irreversible ($R_L = 0$).[34] The degree of favorability is generally related to the irreversibility of the system, providing a qualitative arrangement of the sorbate–sorbent system. The values of R_L, depicted in Table III, indicate that the adsorption process is favorable at these three temperatures. It is also clear from these values that they tend toward unity rather than toward zero, thus representing the reversibility.

Evaluation of the thermodynamic parameters

The thermodynamic considerations of an adsorption process are essential for determining whether the process is spontaneous or not. The standard free energy change (ΔG^o) is an indication of the spontaneity during the sorption process and hence is an important parameter. If ΔG^o is negative, then the sorption process must be spontaneous in nature. The values of ΔG^o were determined with the following expression:[35]

$$\Delta G^o = -\,RT \ln K_c \tag{8}$$

where R is gas constant, T is temperature in Kelvin, and K_c is the equilibrium constant:

$$K_c = C_{ad}/C_e \tag{9}$$

where C_{ad} is the equilibrium concentration of the dye in the sorbent (mg/L) and C_e is the equilibrium concentration of the dye in solution (mg/L).

For an MB aqueous solution with an initial concentration of 60 mg/L, the values of K_c were found to be 21.30, 2.50, and 1.29 at 23, 37, and 50°C, respectively. Finally, ΔG^o values were calculated with eq. (8) and were found to be −7.5, −2.4, and −0.7 kJ/mol at 23, 37, and 50°C, respectively. The negative values indicate that the sorption of MB into the sorbent is spontaneous in nature. Moreover, the increase in the numerical values of $-\Delta G^o$ with the temperature rising indicates that a lower temperature favors the sorption of MB.

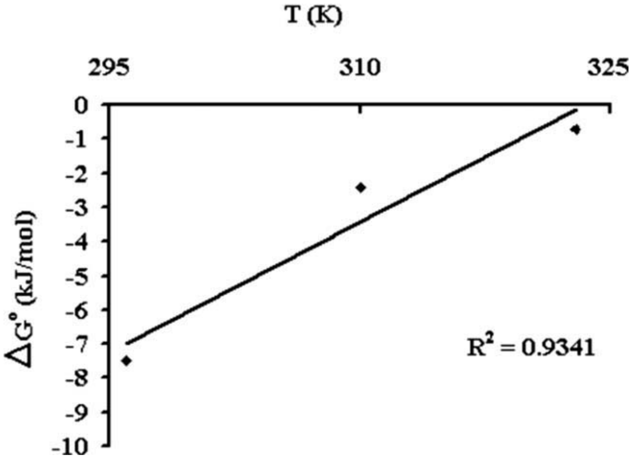

Figure 10 ΔG^o versus T for the determination of ΔS^o and ΔH^o.

TABLE IV
Various Thermodynamic Parameters Obtained at Three Temperatures for the Uptake of MB by the Composite Sorbent

Temperature (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J mol^{-1} K^{-1})
296	−7.5		
310	−2.4	−81.9	−253.3
323	−0.7		

TABLE V
Data Showing the Equilibrium Sorption Capacity for MB onto Various Sorbents

Sorbent	Q_o (mg/g)	Reference
P(AAm-*co*-IA)/AC composite	526.3	This study
Natural zeolite	29.1	14
Activated desert plant	23.0	12
Powdered activated carbon	91.0	15
Wheat bran	3.1	9
Bentonite	175.0	11
Activated carbon fiber	100.0	37
Coffee husks	90.0	38
Fallen phoenix tree leaves	83.8	39
Spent tea leaves	300.0	10
Superadsorbent hydrogel	58.8	18

To determine values of the standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o), the following relation was used:

$$\Delta G^o = \Delta H^o - T\Delta S^o \ (10) \qquad (10)$$

A plot of ΔG^o versus T, shown in Figure 10, is fairly linear with an R^2 value of 0.9341. From the slope and intercept of the linear plot, ΔS^o and ΔH^o were found to be -253.3 J mol^{-1} K^{-1} and -81.96 kJ/mol, respectively. The negative value of ΔH^o is indicative of the exothermic nature of the sorption process. The negative ΔS^o value suggests a decrease in the sorbate concentration at the solid–solution interface, therefore indicating an increase in the sorbate concentration in the solid phase. This is the normal result of the physical adsorption phenomenon that takes place through electrostatic interactions, as mentioned earlier.[36] The values of all thermodynamic parameters are given in Table IV.

CONCLUSIONS

From this study, it can be concluded that the P(AAm-*co*-IA)/AC composite sorbent demonstrates effective removal of MB, favoring higher adsorption at lower temperatures. The dye uptake process is quite rapid and is best interpreted by the pseudo-second-order kinetic model. The equilibrium sorption data are best interpreted by the Langmuir isotherm model

The suitability of this composite sorbent is also established by the fact that it demonstrates a fair Q_o value in comparison with other sorbent materials (see Table V). Therefore, the polymer/AC composite material has great potential to be used on a large scale for effective dye removal.

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