Journal of Advanced Scientific Research

Available online through http://www.sciensage.info/jasr

ISSN
0976-9595
Research Article

APPLICATION OF POLY-3 (METHYL THIOPHENE)-SAWDUST NANO COMPOSITE FOR REMOVAL OF ANIONIC CARMOISINE DYE FROM AQUEOUS SOLUTIONS

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ABSTRACT

In this study the adsorption behavior of sawdust (SD) coated with poly-3 (methyl thiophene) as a synthetic adsorbent (P3MTh/SD) for separation of carmoisine (an anionic dye) from water solutions was investigated. The morphology of sorbents was studied by scanning electron microscopy (SEM). Various experiments have been carried out using batch adsorption technique to study the effects of the main parameters such as contact time, initial dye concentration, pH, dye solution temperature on the adsorption process. The results showed that the adsorption attained to equilibrium in 60 min. Isotherm study conformed well to Freundlich equation and the monolayer sorption capacity obtained from the Langmuir model was 2.77 and 21.64 mg/g for SD and P3MTh/SD, respectively. The kinetic studies indicated that the adsorption of carmoisine on both sorbents follows pseudo-second order kinetic. From thermodynamic studies, it was observed that the adsorption was spontaneous and endothermic. P3MTh/SD was found to be very effective adsorbent in wastewater treatment for removal of carmoisine dye.

Keywords: Poly-3 methyl thiophene, Sawdust, Carmoisine, Adsorption, Isotherm, Kinetics

1. INTRODUCTION

Dyes and their products are considered as one of the most important class of environmental pollutants due to their stability to photodegradation, biodegradation and oxidizing agents and also their toxic effects on living organisms. Nowadays the color uptake as an important aspect of wastewater treatment becomes more critical than before. Among the various chemical, physical and biological treatment processes have been applied for dye removal, adsorption of dye at the solid/liquid interface has been extensively studied in recent years in terms of initial cost, simplicity of design, environment-friendly and ease of operation [1]. Activated carbon has been the most favored sorbent in adsorption process due to its adsorption capacity, adequate pore size distributions, and relatively high mechanical strength. But the high cost and difficulty of regeneration has restricted its use and engendered a considerable amount of work being done to develop cheap and effective adsorbents [2] like, slag, fly ash and agricultural waste residues [3,4].

Agricultural wastes such as wood sawdust have been found to be potential low-cost and easily available sorbents for dye removal [5-8]. These materials contain lignin, cellulose and hemicellulose groups that facilitate binding dyes. According to our experiments in laboratory, the adsorption behavior of sawdust and many other biosorbents toward anionic dyes are not suitable. Therefore chemical pretreatment of sawdust is necessary to enhance the efficiency of sawdust adsorption.
Recently it has been found that modification of sawdust with conducting polymers such as polypyrrole and polyaniline have been found to be very effective for dye and heavy metal ions removal from aqueous solutions [7, 9-10]. However, up to now little reports have been published about the removal of dye solutions by polythiophene derivates as an adsorbent. Our investigations have shown this conducting polymer can be used as an efficient adsorbent for removal of various dyes from aqueous solution in terms of its specific polar chemical structure, high surface area and strong tendency for intermolecular interactions with organic dye molecules.

In the current study, the sawdust was treated with poly-3(methylthiophene), known as P3MTh/SD and applied for removal of carmoisine, a typical monoazo dye (Fig.1). Carmoisine is a synthetic red food dye from the azo dye group which is still used in coloring food, paints, inks, plastics, cosmetics and medications despite of its carcinogenic effects.

The parameters studied in batch mode include the influence of initial dye concentrations, contact time, solution pH and solution temperature. The data obtained in different conditions was applied to access isotherm, kinetics and thermodynamic variables and then compared with those obtained from untreated sawdust which was used under the same operational adsorption conditions.

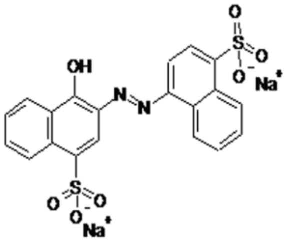

Fig.1. Chemical structure of carmoisine dye molecule

2. MATERIAL AND METHODS

2.1. Chemicals and Equipments

Wood sawdust sample (SD) was obtained from a local carpentry workshop (Iran). All other chemicals and reagents were procured from Merck, Germany. A solution of 200 mg/L carmoisine (disodium 4 hydroxy-3-Naphtylene-1-Sulfonate), $C_{27}H_{31}N_2O_7S_2Na$, (MW= 582/67g/mol) was prepared in distilled water as stock solution. Carmoisine shows an intense absorption peak in the visible region at 500 nm.
This wavelength corresponds to the maximum absorption peak of the carmoisine monomer. The pH adjustments were carried out using dilute NaOH and HCl solutions. A single beam Perkin-Elmer UV-Vis spectrophotometer was used for measuring the absorption. A Metrohm pH meter (model 827) with a combined double junction glass electrode was used for pH measurements. The surface morphologies of the adsorbents were examined using the scanning electron microscopy (SEM) by an XL30 (Philips Co., Netherlands) apparatus operated at a 17 kV accelerating potential.

2.2. Coating of sawdust by poly (3-methylthiophene)

The preparation of sawdust coated with poly-3 (methyl thiophene) known as P3MTh/SD was done after some modification of the procedure as described before [10]. For this purpose 2.0 g of sawdust was packed into a glass column and was conditioned with 6 mL of chloroform. The column was then immersed in 2.0 mL of 3-methyl thiophene monomer solution which was prepared in 20.0 mL chloroform ($CHCl_3$). The outlet solution was passed through the sawdust for several times under 1mL/min of flow rate. After elution the excess monomer, 50.0 mL of oxidant solution (0.8M $FeCl_3$ in mixture of methanol and chloroform) was added and the reaction was allowed to continue for 12h at room temperature. During the polymerization (Fig.2), the solution yielded a greenish black precipitate. The precipitate was then washed with deionized water and was dried in oven at 35-40 °C.

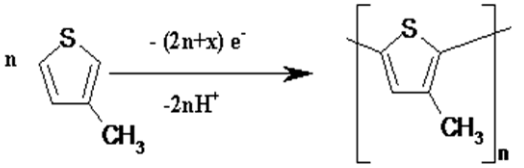

Fig.2. The overall polymerization reaction of 3-methylthiophene

2.3. Adsorption isotherm, kinetics and thermodynamic study using batch system

In order to better understand the adsorption process, the equilibrium experiments at first were carried out in batch mode by contacting 0.5 g of SD and P3MTh/SD with 100 mL of carmoisine solution of different initial dye concentrations, 40–120 mg/L at pH=2 for one hour.

At the next step, two sorption kinetic equations were used to examine the mechanism of adsorption process such as mass transfer and chemical reaction [11]. In each experiment, 0.5 g of SD and P3MTh/SD were mixed with 100 ml of 50 mg/L carmoisine. The initial pH of the solution was adjusted to 2.0 ± 0.1. The solution was then stirred on a shaker at 25 °C±1°C for various time intervals (5-60 minutes). The left out dye concentration in the solution was determined by measuring the absorbance at 500 nm and using a calibration curve. Before measurement of the dye concentration, the mixture was centrifuged (Hettich universal II) under 3500 rpm for 5 minutes. The amount of carmoisine adsorbed on both sorbents (q_v in mg/g) and efficiency of dye removed (%Sorption) were calculated by using the following expressions [5, 12]:

$$\%Sorption=\frac{C_0-C_t}{C_0}\times 100 \tag{1}$$

$$q_v=\frac{\left(C_0-C_t\right)}{M}\times V \tag{2}$$

Where C_0 is initial dye concentration (mg/L), C_t is the left out dye concentration in bulk solution at time t (mg/L), V is the volume of dye solution (L), and M is adsorbent mass (g).
The amount of adsorption at equilibrium, q_e (mg/g), was calculated by replace the C_t with C_e (liquid-phase concentration of dye at equilibrium, mg/L). Thermodynamic experiments were carried out by contacting 0.5 g of each sorbent (SD and P3MTh/SD) with 100 ml of 50 mg/L carmoisine solution at different temperatures, 298, 308, 323 and 343K and shaking at a constant speed of 50 rpm in a shaking water bath (Grant Operation C100196) for 1h to ensure the equilibrium is obtained. The samples were then centrifuged and analyzed for remaining dye.

3. RESULTS AND DISCUSSION

3.1. Morphological structure

The surface morphology of an adsorbent can be extensively characterized using scanning electron microscopy [13]. The SEM image of the sawdust (Fig.3.a) was observed to be smooth and fibrous. Its layered structure had made a good condition for adsorption of pollutants.

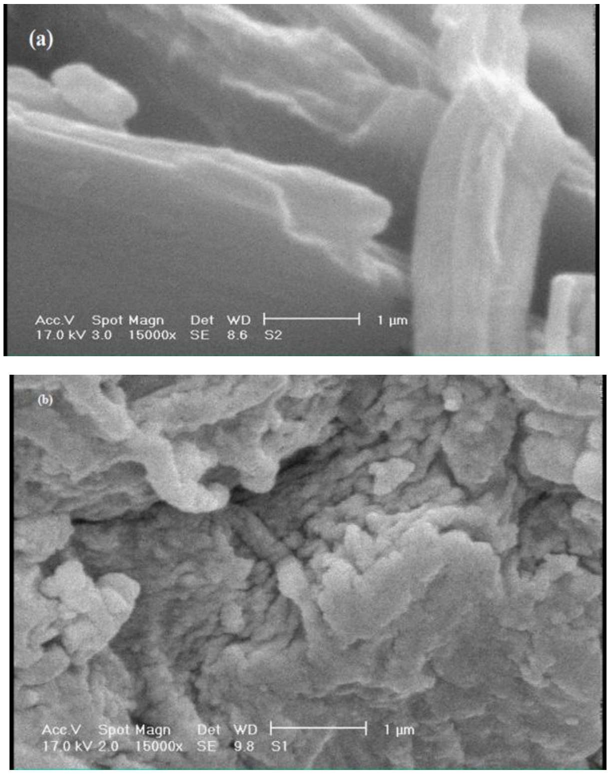

Fig. 3. Scanning electron micrographs of (a) SD and (b) P3MTh/SD

P3MTh/SD consists of nano particles with various sizes. The porous characteristics of the adsorbent would do positive effect on adsorption. The treatment of SD by P3MTh led to an increase of porosity volume and large surface area for dye interaction and a great capacity for dye holding. According to Fig.3.b the pores reduce the mass transfer resistance and facilitate the diffusion of dye molecules.

3.2. Effect of pH on dye adsorption

The experiments were carried out at 100 mL of 50 mg/L initial dye concentration with 0.5 g adsorbent mass at 298K and various pH values (2-10) for 1 h. As shown in Table.1 the uptakes were much higher in acidic solution than those in neutral and alkaline conditions. This is attributed to the increasing electropositive charge of the adsorbent which favored the adsorption of dye anions due to the electrostatic attraction [14].

Table.1. The effect of initial pH dye solution on sorption efficiency

pH	2	4	6	8	10
% Sorption (SD)	22.6	9.4	4.5	4.1	3.5
% Sorption (P3MTh/SD)	80.3	50.1	30.7	13.6	8.8

High efficient removal of carmoisine by polymeric adsorbent is due to its high porosity, great surface area and intrinsic positive charge of P3MTh as a type of n-doping polymer in which the anionic dopant (Cl^-) is exchanged by anionic dye. As the data show (Table.1) the sorption efficiency of P3MTh/SD is 3.5 times more than untreated SD in optimum pH= 2.

3.3. Effect of initial concentration

The influence of initial concentration of carmoisine on the sorption efficiency and adsorption capacity of SD and P3MTh/SD are shown in Table.2 and Fig. 4 respectively. For a fixed mass of adsorbent, the amount of dye can be adsorbed is constant. Because the surface active sites on the sorbent are finite. So the higher the concentration of the dye, the smaller the sorption percentage (%Sorption) is obtained (Table.2). On the other hand the sorption capacity of adsorbents (q_v) increased with increase in dye concentration (Fig.4). The increase in initial dye concentration is introduced as a driving force of the concentration gradient which facilitates the dye movement molecules from bulk to the surface of sorbent [15].

Table.2. The effect of initial dye concentration on sorption efficiency

Initial dye concentration (mg/L)	40	60	80	100	120
% Sorption (SD)	25.7	18.6	14.6	12.2	10.6
% Sorption (P3MTh/SD)	83.8	78.4	75.4	71.7	69.4

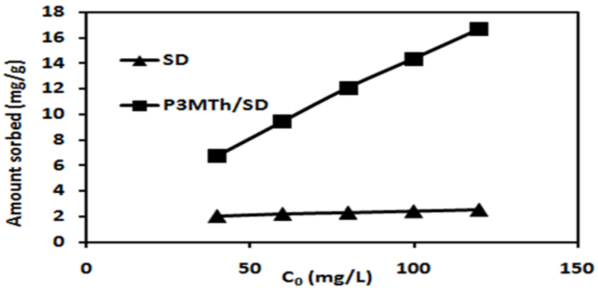

Fig.4. The effect of initial dye concentration on sorption capacity of SD and P3MTh/SD

The results indicate the great increase in sorption capacity of polymer coated sawdust compared to uncoated sawdust.

3.4. Adsorption Isotherms

The adsorption isotherm indicates the distribution of adsorption molecules between the liquid phase and the solid phase at constant temperature and equilibrium state. To study the adsorption isotherm, the experimental data were interpreted using two equilibrium models: the Freundlich and the Langmuir equations.

3.5. Langmuir isotherm

Langmuir model suggests a mono layer sorption, uniform energies of adsorption onto the surface, without interaction between the sorbed molecules [16]. The linear form of Langmuir is expressed as:

$$\frac{1}{q_e} = \frac{1}{KC_e q_m} + \frac{1}{q_m} \qquad (3)$$

where q_e is the amount of dye sorbed (mg/g), C_e is the equilibrium concentration (mg/L), q_m is the maxmum adsorption capacity for a complete monolayer (mg/g), and K is the sorption equilibrium constant related to energy of adsorption (L/mg). A plot of $1/q_e$ versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/(KC_e q_m)$. The essential characteristics of the Langmuir equation can be represented in terms of a dimensionless separation factor, R_L, which is introduced by the following equation [17]:

$$R_L = \frac{1}{1 + KC_i} \qquad (4)$$

Where, C_i is the maximum initial concentration of adsorbate (mg/L). The value of R_L indicates the type of the isotherm whether it is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The values of R_L in the present investigation were found to be 0.083 and 0.1106 for SD and P3MTh/SD respectively.

3.6. Freundlich isotherm

The Freundlich model is often applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The linear for of Freundlich isotherm is represented by [18]:

$$\log q_e = \log K + \frac{1}{n} \log C_e \qquad (5)$$

Where, q_e is the equilibrium dye concentration on the adsorbent (mg/L); C_e, the equilibrium dye concentration in solution (mg/L); K, the Freundlich constant (mg/g (L/mg)1/n) which represents the adsorption capacity and n is the heterogeneity factor. Value of n > 1 represents the adsorption process is favorable. A plot of log q_e versus log C_e indicates a straight line of slope 1/n and an intercept of log K. The values of Langmuir and Freundlich parameters with the non linear correlation coefficients (R^2) are listed in Table.3.

Table.3. Isotherm parameters obtained from adsorption of carmoisine dye onto SD and P3MTh/SD

Adsorbent	Langmuir parameters				Freundlich parameters		
	q_m (mg/g)	K_L (L/mg)	R_L	R^2	K	n	R^2
SD	2.80	0.092	0.083	0.9157	1.19	6.20	0.9951
P3MTh/SD	21.60	0.067	0.1106	0.983	2.49	1.90	0.9989

In the case of SD, the equilibrium sorption data were very best represented by the Freundlich isotherm. The R^2 value for Langmuir isotherm (0.9157) is obviously lower than Freundlich isotherm (0.9951). The value of Freundlich exponent n (6.20) is the range of n > 1, indicating a favorable adsorption and multilayer coverage process of sorption. But in the case of P3MTh/SD there is no considerable difference between R^2 values obtained for Langmuir (0.983) and Freundlich isotherm (0.9989). From this table, it is concluded that the adsorption of carmoisine on to the polymeric sorbent matched to both isotherm models. A comparison of maximum monolayer adsorption capacity of carmoisine onto two adsorbents indicates P3MTh/SD has a relatively large adsorption capacity of 21.60 mg/g which shows about 8 times more than SD (2.8).

3.7. Effect of contact time

The adsorption data of carmoisine versus contact time are listed in Table.4. As our data showed, for 100 mL carmoisine solution with initial concentration of 50 mg/L the contact time needed to reach equilibrium was less than 1 h. However, the experimental data were measured at 1 h to be sure that no significant change in the adsorption took place after this time. Moreover the sorption process is considerably fast and more than 60% of dye solution was adsorbed by polymeric sorbent in the first 5 minutes.

Table.4. The effect of contact time on sorption of carmoisine dye

Contact Time (min)	5	10	20	30	40	50	60
% Sorption (SD)	10.8	13.2	16.4	18.8	20.2	21.7	22.6
%Sorption (P3MTh/SD)	61.5	68.7	70.1	75.5	77.6	79.2	80.3

It is observed that the dye uptake increases with time and the trend is relatively sharp and then attains to maximum at equilibrium time. This is due to the large number of active binding sites for adsorption during the initial stage and gradual occupancy of them after a lapse of time which makes the sorption becomes less efficient in the later stages [6].

3.8. Kinetics Study

3.8.1 Pseudo-first-order model

The Lagergren rate equation or Pseudo-first-order kinetics is widely used for the sorption of a solute from a liquid solution. The linear form of the equation is expressed as [19]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (6)$$

Where q_t and q_e (mg/g) are the amount of carmoisine adsorbed at equilibrium and at time t (min) respectively and k_1 (1/min) is the pseudo-first-order rate constant. After integration by applying the initial conditions q_t=0 at t=0 and q_t=q_t at t=t equation becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (7)$$

The adsorption rate constant (k_1) were calculated from the plot of log (q_e −q_t) against t (Fig.5). The plot indicates that Lagergren's model is not fit to the carmoisine adsorption on both adsorbents.

3.8.2 Pseudo-second order model

The kinetics was also described as a pseudo-second-order process. The differential equation is the following [20]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (8)$$

Where k_2 is the equilibrium rate constant of pseudo second-order adsorption (g/mg·min). By integrating the equation, applying the boundary conditions and rearrangement, the linear form can be obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}t \qquad (9)$$

The slopes and intercepts of plots t/q_t versus t were calculated to access the pseudo second-order rate constants q_e and k_2.

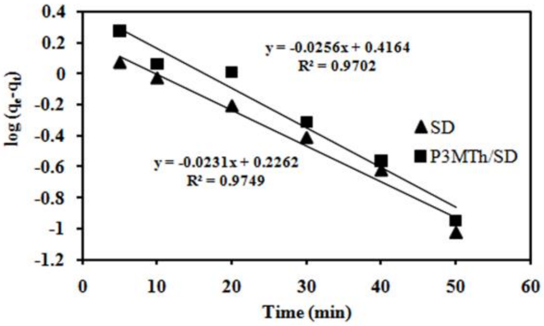

Fig.5. Pseudo-first-order kinetic model for the adsorption of Carmoisine on SD and P3MTh/SD

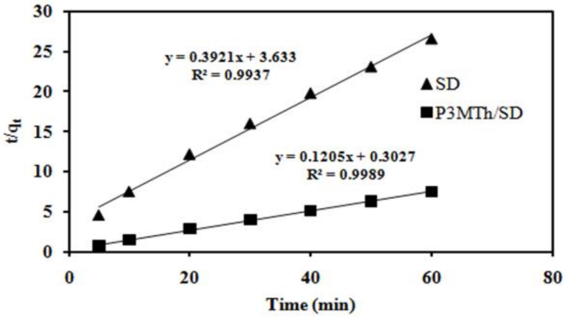

Fig.6. Pseudo-second-order kinetic model for the adsorption of Carmoisine on SD and P3MTh/SD

The calculated kinetic parameters of SD and P3MTh/SD and the corresponding linear regression correlation coefficients R^2 are given in Table.5. As shown in Fig.6 and Table.5, the high value of regression coefficient (R^2) and good agreement between experimental q_e and calculated q_e from the pseudo second-order kinetic model, clearly confirm that the carmoisine dye sorption on both sorbents is mainly happened via chemisorption process.

3.9. Effect of temperature on adsorption of carmoisine dye

The effect of temperature on the adsorption process of carmoisine on SD and P3MTh/SD was investigated at four temperatures: 298, 308, 323 and 343 K. As it is depicted in Fig.7, the sorption efficiency had a little increase by raising the temperature. This is due to the fact that in high temperature, the diffusion rate of the dye molecules and their kinetic energy increases through the external boundary layer and internal sites of the sorbent [21, 22].

Table.5. Comparison of the different kinetic model parameters at 25 °C

Sorbent	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			
	q_{e1} (mg/g)	k_1 (1/min)	R^2	q_{e2} (mg/g)	k_2 (g/mg min)	q_{e2} (exp) (mg/g)	R^2
SD	4.42	0.053	0.9749	2.54	0.042	2.26	0.9937
P3MTh/SD	2.40	0.059	0.9702	8.30	0.048	8.03	0.9989

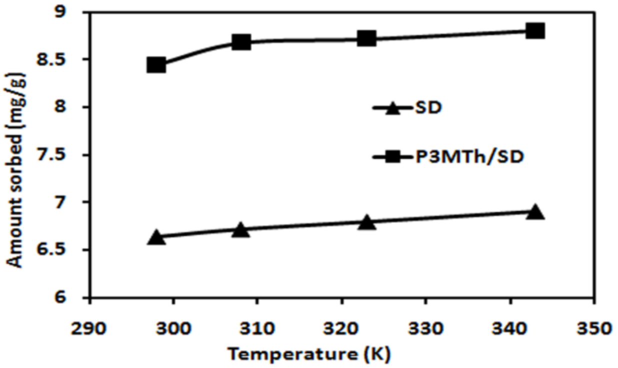

Fig.7. The effect of temperature on sorption capacity

The adsorption of carmoisine on to SD and P3MTh/SD is not temperature-dependant and the synthesized sorbent is an efficient option even in room temperature.

3.10. Thermodynamic study

The data obtained at different temperatures can be used to evaluate the thermodynamic parameters. The standard Gibbs free energy change (ΔG^0) is the fundamental parameter of spontaneity of a process and can be expressed as [23, 24]:

$$\Delta G^0 = -RT\ln K_C \qquad (10)$$

where K_c is the adsorption distribution coefficient, R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). The standard enthalpy change (ΔH^0) and the standard entropy change (ΔS^0) were computed from the following equation:

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad , \quad K_c = \frac{C_{Ad}}{C_e} \qquad (11)$$

A plot of ln K_c versus 1/T should be straight line. The slope and intercept of the plot gives the values of ΔH^0 and ΔS^0 while ΔG^0 was calculated using Eq. (10). The values associated with the thermodynamic parameters are listed in Table.6.

Negative values of ΔG^0 in all temperatures indicate the feasibility of the process and spontaneous nature of the adsorption with a high performance of carmoisine for P3MTh/SD while the positive ΔG^0 values for untreated SD shows the non-spontaneous adsorption process and more needed activation energy. Positive values of ΔH^0 indicate the endothermic nature of the process. In spite of SD, the positive value of ΔS^0 for P3MTh/SD confirms the favorable condition for adsorption and also the preference of the polymeric sorbent for removal of anionic dyes from aqueous solutions.

Table.6. Thermodynamic parameters for sorption of carmoisine on SD and P3MTh/SD

Adsorbent	*T* (K)	K_c	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol.K)
SD	298	0.29	3.05	2.27	-2.58
	308	0.30	3.07		
	323	0.32	3.09		
	343	0.33	3.17		
P3MTh/SD	298	4.08	-3.48	2.90	21.34
	308	4.29	-3.73		
	323	4.50	-4.40		
	343	4.76	-4.45		

4. CONCLUSION

Sawdust coated with poly (3-methyl thiophene) was found as an efficient adsorbent for anionic dye removal. The amount of dye uptake increased with increase in initial dye concentration, contact time and also in acidic pH dye solution. Adsorption isotherm data were well described by both Langmuir and Freundlich models for adsorbent with polymeric matrices and the reaction reached equilibrium during 1 h of contact time. The kinetic data revealed that the pseudo second-order kinetic model provided the best correlation of the experimental data for rapid carmoisine uptake onto SD and P3MTh/SD, suggesting a chemisorption mechanism. Negative values of ΔG^0 indicate the spontaneous nature of adsorption and because of the positive values of ΔH^0 for both sorbents, the sorption process was assumed to be endothermic. Findings presented in this study showed that chemical modification of sawdust by poly (3-methylthiophene) optimized the dye uptake capacity and the proposed adsorbent can be used as a promising candidate for anionic dye removal efficiently.

5. ACKNOWLEDGMENT

The authors wish to acknowledge the financial support provided by the Postgraduate Studies of University of Guilan, Iran.

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