Application of Polypyrrole Coated onto Wood Sawdust for the Removal of Carmoisine Dye from Aqueous Solutions

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ABSTRACT: In this research, the removal of carmoisine dye from aqueous solutions using polypyrrole coated onto sawdust (PPy/SD) has been investigated. The sorption experiments were performed using both batch and column systems. The effects of some important parameters such as pH, initial concentration, sorbent dosage, exposure time, and temperature on uptake of carmoisine dye were investigated. Based on the data obtained in batch system, it was found that maximum adsorption is occurred under acidic conditions. Complete removal was observed when a dye solution with the initial concentration of 100 mg L⁻¹ was treated by 1.0 g of the used adsorbent (PPy/SD) at pH value of 4 and room temperature. However, higher

INTRODUCTION

Removal of hazardous dyes from wastewaters using economic means has become a real challenge to global scientists. Carmoisine dye as shown by Scheme 1 is a synthetic acid azo dye containing both NN and CC chromophore groups (pyrazolone dye). This acid dye is a water soluble used mostly in the form of sodium salts of the sulfonic or carboxylic acids ($C_{20}H_{12}N_2Na_2O_7S_2$), melting point > 300°C; used in coloring food, paints, inks, plastics, cosmetics, and medications (Wikipedia; http://wapedia. mobi/en/Azorubine). For many years, it was used as coloring material for edibles like jams and preservatives; however, most of the developed countries finally prohibited its use in edibles due to the presence of *b*-napthylamine, a well-known carcinogen, in it.^{1,2} Azo dyes generally have been known to be carcinogenic for over 60 years and cause many serious dangers for human being.^{3–6} It has also been well established that carmoisine A and its metabolites inhibit true and pseudo-cholinesterase

sorption was observed at elevated temperature. According to the kinetics study, it was found that the experimental data fitted very well the pseudo-second-order kinetic model ($k_2 = 0.184$ g mg⁻¹ min⁻¹). It was found that polypyrrole chemically coated on SD is an efficient system for the removal of carmoisine dye from aqueous solutions. Desorption of the dye-loaded column was also possible by using dilute NaOH solution with high efficiency (~ 80%). © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 804–812, 2011

Key words: carmoisine; polypyrrole; sawdust; sorption; kinetics; desorption

enzyme activity in human erythrocytes and plasma.⁷ It is also identified as an electron-deficient xenobiotic compound, less susceptible to oxidative catabolism by bacteria.^{8–10} Consequently, carmoisine tends to persist under aerobic environmental conditions.

Conventional methods like nanofilteration, ozonation, solar-assisted photocatalytic degradation, precipitation, dynamic column-solid phase extraction system, capillary electrophoresis, C18 cartridge or various combinations of these techniques with chromatographic methods, and electrochemical methods are used for the removal of toxic dyes from wastewater.^{11–18} These techniques have the disadvantage of requiring expensive equipment and expert operators. However, most of these methods suffer from one or more limitations. Among all the available physical or chemical methods of water treatment, only the adsorption technique is measured as most efficient and adaptable in practice.¹

Conducting polymers such as polypyrrole, polyaniline, and polythiophene have been the focus of numerous theoretical and experimental investigations in the last two decades due to their interesting and unique electrical conductivity and electroactivity.¹⁹ Their structural versatility is attracting researchers for their multiple applications such as in rechargeable batteries, light-emitting diodes, super capacitors, sensors, solar cells, actuators, and separation.^{20–24}

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Scheme 1 Chemical structure of carmoisine.

Previously reported applications of conducting polymers are mostly based on their electrical conductivity and unique electroactivity.²⁵⁻²⁷ Almost of the previously reported applications of conducting electroactive polymers need using an electrochemical cell or applied current or potential. However, we have recently found that these new polymeric materials due to their specific polar chemical structure and strong tendency for intermolecular interactions with organic dye molecules can be used as an efficient adsorbent for the removal of cationic or basic dyes from aqueous solutions using simple operational conditions without any need to a special instrument.^{28,29} So, in the current investigation, we are reporting that the introduced polymeric adsorbents in this work can also be used for the removal or adsorption of acidic or anionic dyes from aqueous wastes effectively too. It has been well documented that low-cost agricultural byproducts the same as biomaterials can also be used for the removal of cationic dye but fail to adsorb anionic dyes with modification because of their chemical structure and functional groups. However, we have found that thin films of polypyrrole coated onto sawdust (PPy/ SD) can be used effectively for the removal of anionic or acidic dyes from aqueous solutions such as textile wastewaters.

EXPERIMENTAL

Materials and equipments

All chemicals used were analytical reagents grade and prepared in deionized water. Pyrrole was obtained from Merck and distilled before use. SD was obtained from a local carpentry workshop. A solution of carmoisine with the concentration of 200 mg L⁻¹ was prepared in deionized water and used as stock solution. Absorbance measurements were carried out on a single-beam Perkin–Elmer UV–vis spectrophotometer with a 1-cm cell. A Metrohm pH meter (model 827) with a combined double junction glass electrode, calibrated against two standard buffer solutions at pH 4.0 and 7.0, was used for determining pH. The surface morphologies of polymer samples were studied using scanning electron microscopy (SEM; Model VEGA).

Determination of carmoisine

The measurement of carmoisine was carried out in aqueous media spectrophotometrically (λ_{max}) 508 nm at pH 4.2).² Quantitative analysis of this dye was carried out using a calibration graph obtained for standard carmoisine solution in deionized water in the concentration range from 0.0 to 20.0 mg L^{-1} . The calibration curve shows that Beer's law is obeyed in this concentration range. pH adjustments were carried out using dilute NaOH and HCl solutions. All the experiments were carried out at least in triplicate. The results were average of these measurements. The linear regression analysis was carried out for the treatment of the data. The relative standard deviation (RSD) was less than 1.0%, and the detection limit value, based on the three times the standard deviation of the blank, was 0.03 mg L^{-1} .

Preparation of SD coated by polypyrrole adsorbent (PPy/SD)

Polymerization of pyrrole was carried out in aqueous solution. Polymer was synthesized directly on the surface of the sawdust (SD), which has previously soaked in monomer solutions by slow addition of chemical oxidant (FeCl₃) at room temperature.³⁰ The polymer was collected using vacuum filtration technique. The precipitate was then washed with copious amounts of deionized water and methanol, and the polymer was allowed to dry for 2 days at room temperature and at temperature about 50°C (in an oven) for 1 h. To have reproducible data, the polymer particles were sieved (35–50 mesh size) before use. The surface morphologies of the polymer coated on SD before and after dye treatment were characterized with SEM [Fig. 1(a,b)].

Sorption experiments

In batch experiment, fixed amounts of sorbent were treated with carmoisine dye solution containing various initial concentrations (0.0–200.0 mg L⁻¹ for PPy/SD) at room temperature. During each experiment, the solutions were agitated moderately using a mechanical shaker. In column experiments, a glass column with dimensions of 1.0-cm diameter and 15-cm length was used. About 1.0 g adsorbent (SD or PPy/SD) was packed in the column (5 cm height), and then the carmoisine solution with an initial concentration of 50 mg L⁻¹ was passed through the column with constant flow rate (3.0 mL min⁻¹) at room



Figure 1 SEM images: (a) PPy/SD (before dye treatment) and (b) PPy/SD (after dye treatment).

temperature. The outlet solution was analyzed for unadsorbed carmoisine dye after equal time intervals (collecting of each 10 mL). The dye-sorption percentage was calculated using the following relationships:

$$\% \text{ Sorption} = \frac{C_o - C_e}{C_0} \times 100 \tag{1}$$

$$\frac{x}{m} = \frac{C_o - C_e}{m} \times V \tag{2}$$

where C_0 and C_e are initial and equilibrium concentrations of carmoisine (mg L⁻¹), respectively, *V* is the volume (L) of dye test solution, and x/m stands for milligram of dye sorbed per gram of adsorbent. Alternatively, regeneration of the used adsorbent was examined. Desorption efficiency was measured using the following equations:

$$\% \text{ Desorption} = \frac{m*}{m_o} \times 100$$
 (3)

$$m^* = C_e \times V'$$
 and $m_o = (C_o - C_e) \times V$ (4)

where m_o (mg) of the sorbed dye onto the adsorbent, m^* (mg) of the released dye in the regenerated solution, and V' is the volume of washing solution (L). C_o and C_e are the initial (inlet) and equilibrium (outlet) concentrations (mg L⁻¹) of dye, respectively.

RESULTS AND DISCUSSION

Sorption of carmoisine ion by PPy/SD and SD (batch system)

Effect of pH

For this investigation, fixed amounts of the selected sorbents (1.0 g) were treated separately with 25 mL of carmoisine dye solution with the initial concentration of 100 mg L^{-1} at various equilibrium pH values from 2 to 11. The results obtained are shown in Figure 2. According to the results, the sorption of carmoisine dye by PPy/SD was more efficient at pH range of 2-5. However, with increasing the pH of solution, the removal efficiency was decreased. Higher dye removal under acidic media can be due to the protonation of the adsorbent surface and electrostatic interactions between the adsorbent and anionic dye molecules (carmoisine), which facilitate the diffusion process. Although, at alkaline conditions, removal of carmoisine dye was decreased greatly. The decrease of dye removal at high pH values can be due to the competitive effect (repulsions) of OH⁻ ions with the anionic dye molecules for adsorption. Therefore, our further studies in this research were carried out at pH of 4.

Effect of initial concentration

For this investigation, aliquots of fixed amounts of adsorbent (1.0 g PPy/SD) were treated with 25 mL



Figure 2 Effect of pH on carmoisine sorption onto SD (\blacktriangle) and PPy/SD (\bigcirc).

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Figure 3 Effect of initial carmoisine concentration on its sorption onto SD (\blacktriangle) and PPy/SD (\bigcirc).

of carmoisine dye solutions (from 50 to 200 mg L^{-1}) for duration of 1 h. The exposures were accompanied by moderately shaking. The obtained data have been shown in Figure 3.

It was noted that uncoated SD does not adsorb carmoisine dye from aqueous solutions effectively. In contrast, PPy/SD can remove carmoisine dye very effectively. Removal of carmoisine dye using PPy/SD seems to be occurred mostly via anion exchange [shown by eq. (5)] and intermolecular interactions. Anion exchange properties of PPy-conducting polymers, doped with small size dopants such as Cl⁻, have already been reported.^{26,27}

$$\begin{split} 2PPy^+/Cl^- \;(polym) + Dye^{2^-} \;(sol) &\rightarrow ((PPy^+)_2/\\ Dye^{2^-} \;(polym) + 2Cl^- \;(sol) \eqno(5) \end{split}$$

Adsorption isotherms

The equilibrium adsorption isotherms are of fundamental importance in the design of any adsorption system. In this study, Langmuir and Freundlich isotherms were used for the treatments of the equilibrium adsorption data.^{31,32} The Langmuir adsorption isotherm is the best-known linear model for monolayer adsorption and most frequently used to determine the adsorption parameters. Langmuir model is represented by the following equations:

$$\frac{X}{m} = \frac{X_m b C_e}{1 + b C_e}$$
(Nonlinear form) (6)

$$\frac{m}{x} = \frac{1}{x_m} + \frac{1}{x_m b C_e} \quad \text{(Linearized form)} \tag{7}$$

where x/m is the amount of dye adsorbed (mg g⁻¹), represents the adsorptive capacity of the adsorbent for the equilibrium effluent concentration, x_m is the maximum amount sorbed (mg g⁻¹), *b* is a Lang-

muir's constant signifying energy of sorption (L; mg⁻¹), and C_e is equilibrium concentration of carmoisine dye in the aqueous phase (mg L⁻¹). The Langmuir equation [eqs. (6) and (7)] makes several assumptions, such as monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies. Another widely used equation in adsorption processes is the Freundlich equation. The Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. The Freundlich model is represented by the following equations:

$$q_e = \frac{x}{m} = KC_e^{(1/n)} \quad \text{(Nonlinear form)} \tag{8}$$

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad \text{(Linearized form)} \tag{9}$$

where x/m (or q_e) is equilibrium adsorption capacity (mg g⁻¹), C_e is the equilibrium or residual concentration (mg L⁻¹) of carmoisine dye in solution, and K and 1/n are empirical Freundlich constants indicating sorption capacity of adsorbent and intensity of adsorption (mg g⁻¹), respectively, which are determined from the log q_e versus log C_e .

The Freundlich isotherm can be efficient on multilayer, assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. The plot of m/xagainst $1/C_e$ in Figure 4(a) gave straight lines for all the concentrations, and the high correlation coefficient obtained for PPy/SD ($R^2 = 0.983$) implies that the adsorption for adsorbent well fitted to Langmuir isotherm. The essential characteristics of Langmuir isotherms may be expressed by a dimensionless constant, named parameter of equilibrium, R_L . The dimensionless separation factor R_L tells the favorability and the shape of the adsorption isotherms by applying the following equation.¹⁸

$$R_L = 1/(1 + bC_o)$$
(10)

where *b* signifies the Langmuir constant (*L*; mg⁻¹) and C_o is the initial concentration of the adsorbate (mg L⁻¹). $R_L > 1$ means unfavorable isotherm, $R_L =$ 1 means linear isotherm, $R_L = 0$ –1 means favorable isotherm, and $R_L = 0$ means irreversible isotherm. In this study, the R_L values were found to be 0.002– 0.009 (for PPy/SD) for concentration ranges of 50– 200 mg L⁻¹ carmoisine dye (Table I). The R_L values obtained are less than unity, confirming that adsorption process is favored in both the cases and applicability of Langmuir isotherm also. The Freundlich isotherm (linear form) obtained for the adsorbent employed in this research is shown in Figure 4(b). It



Figure 4 (a) Langmuir isotherm for the sorption of carmoisine by PPy/SD. (b) Freundlich isotherm for the sorption of carmoisine by PPy/SD.

could be concluded that the adsorption isotherm of carmoisine using PPy/SD gave a better fit to the Langmuir model (Table I).

Effect of sorbent dosage

In this experiment, different weights of PPy/SD (0.10–1.0 g) were treated with 25-mL carmoisine dye solutions with constant concentration of 100 mg L^{-1} .

 TABLE I

 The Langmuir and Freundlich Parameters Obtained

 from the Related Sorption Isotherms of Carmoisine

 Dye onto PPy/SD

| C_o | q_e | $1/C_e$ | m/x | $\log q_e$ | $\text{Log } C_e$ | R_L | п | Κ | b |
|-------------------------|------------------------------|------------------------------|------------------------------|------------------------------|----------------------------------|----------------------------------|------|------|------|
| 50 100 150 200 | 1.24 2.48 3.39 4.50 | 5.00 2.63 0.19 0.10 | 0.81 0.49 0.29 0.22 | 0.09 0.39 0.53 0.65 | $-0.69 \\ -0.42 \\ 0.85 \\ 0.99$ | 0.009 0.004 0.003 0.002 | 3.77 | 2.27 | 2.05 |





Figure 5 Effect of PPy dosage on carmoisine sorption onto PPy/SD.

As the results indicate (Fig. 5), with increasing of the sorbent dosage, removal percentage of the dye is increased gradually. Such a trend is mainly due to the increase of sorptive surface area and availability of the more adsorption sites. Therefore, 1.0 g of PPy/SD was chosen as optimum dosage for carmoisine removal for the next experiments.

Effect of exposure time

For performing of this experiment, 1.0 g of sorbent (PPy/SD) samples was treated with 25 mL of 100 mg L^{-1} carmoisine dye for different contact times (10–60 min) accompanied by shaking at room temperature. The results of adsorption obtained from the analysis of unadsorbed carmoisine in solution are shown in Figure 6. As the results indicate, removal of carmoisine using PPy/SD adsorbent occurs quickly and is not very time-dependent process. As the data show, the complete removal of carmoisine by PPy/SD was happened within 40 min.



Figure 6 Effect of contact time on carmoisine sorption onto PPy/SD.

| TABLE II Effect of Temperature on the Removal Percentage of Carmoisine Dye onto PPy/SD | | | | | | | | |
|--|------|------|------|------|------|--|--|--|
| T (K) | 298 | 308 | 318 | 328 | 338 | | | |
| Removal (%) | 85.5 | 95.5 | 97.6 | 99.0 | 99.9 | | | |

Effect of temperature

In this section of experiment, 0.6 g of PPy/SD was treated with 25 mL of 100 mg L⁻¹ carmoisine for 1 h accompanied by stirring at different temperature (298–338 K). The constancy of the temperature was maintained with an accuracy of $\pm 1.0^{\circ}$ C. The results are summarized in Table II. As the data obtained show, removal of dye increased with increasing temperature.

Effect of salt on dye removal

For this investigation, aliquots amount of PPy/SD (1.0 g) were treated with constant concentration of dye solutions (100 mg L⁻¹) in the presence of different salts at various concentrations (0.05–0.50*M*) for duration of 1 h. The results are summarized in Table III. As the data show, the dye removal performance was not affected much. However, some decrease was observed when higher concentration of the salt was used. In the case of sodium sulfite, the decrease in removal was more than the other used salts. The small decrease in dye removal in the presence of the salts can be probably due to the competition between the anions of the salt and the dye anion for adsorption onto the PPy/SD.

Desorption studies (column system)

In this study, 1.0 g of sorbent (PPy/SD and SD) was first treated with 25 mL of Carmoisine ion with concentration 50 mg L⁻¹. The exhausted column was then treated with 0.01*M*, 0.05*M*, and 0.1*M* NaOH solution for regeneration. As the obtained data show (Table IV), increasing concentration of NaOH, recovery percentage was increased. Higher concentration of base was avoided, because SD is not very stable in highly acidic (or basic) solutions. Desorption per-

TABLE III Effect of Different Salts on Dye Removal Percentage

| Salt | Conc. of salt (M) | % Removal | Salt | Conc. of salt (M) | % Removal |
|---------------------------------|------------------------|----------------------|---------------------------------|------------------------|----------------------|
| NaCl | 0.05 0.10 0.50 | 98.7 97.2 93.8 | Na ₂ SO ₃ | 0.05 0.10 0.50 | 93.8 87.2 80.8 |
| Na ₂ SO ₄ | $0.05 \\ 0.10 \\ 0.50$ | 98.2 96.3 92.1 | CH ₃ COONa | $0.05 \\ 0.10 \\ 0.50$ | 97.5 95.1 91.6 |

TABLE IV Effect of Different Concentration of NaOH on Desorption Percentage of Carmoisine

| | NaOH | I Solution concent | tration |
|-----------|-------|--------------------|--------------|
| Adsorbent | 0.01M | 0.05M | 0.1 <i>M</i> |
| PPy/SD | 37.5% | 59.2% | 80.1% |

centage was calculated using eq. (3). It was found that more than 80% of the adsorbed dye can be eluted from PPy/SD column when a solution of 0.10M NaOH was used as regenerant or washing solution. However, it seems that it will be possible to improve desorption efficiency, using more concentrated NaOH solution, but due to poor chemical stability of the substrate (SD) or the polymer under strong alkaline conditions, using higher concentration of NaOH for complete regeneration of the exhausted column was avoided. When the regenerated column was reused for a new extraction under the same above-mentioned conditions, it was observed that about 93% of the dye was removed. This indicates that some decrease is occurred in removal performance. However, the loss of sorption percentage was not considerable at least for three cycles (<10%).

Breakthrough curve (column system)

When working sorption experiments with columns, the breakthrough curves are very useful. A plot of effluent solute concentration versus time usually yields as S-shaped curve, at which the solute concentration reaches its maximum allowable value referred to as a breakthrough curve. The point where the effluent solute concentration reaches 95% of its influent value is usually called the point of column exhaustion. For performing this experiment, 1.0 g of PPy/SD and SD packed in a glass column, and then carmoisine solution with concentration of 50 mg L^{-1} passed through the column with constant flow rate (3.0 mL min⁻¹). Each time, 10 mL was poured into the column. The outlet solution was then analyzed for unsorbed carmoisine ion to obtain the breakthrough curve. The breakthrough curves obtained for the examined sorbents used for sorption of carmoisine in a column system are shown in Figure 7.

As it is evident from the results obtained in this experiment, the break point for PPy/SD is observed after treatment of about 170 mL of 50 mg L^{-1} carmoisine-polluted solution. As it is depicted from the breakthrough analysis (Fig. 7), saturation of the adsorbent (PPy/SD) occurred after passing of about 500-mL dye solution under the used experimental conditions. However, the breakthrough curve obtained for SD is very sharp, and the break point



Figure 7 Breakthrough curves for adsorption of carmoisine dye by SD (\blacktriangle), PPy/SD (\blacklozenge).

and column exhaustion occurred very quickly. As the results show that PPy/SD seems to be much more effective sorbent compared to SD for the removal of carmoisine ion in column or flow systems.

Kinetics of the dye removal

To investigate the mechanism of sorption, two kinetic models were tested including the pseudo-first-order and pseudo-second-order models.³³ The pseudo-first-order kinetic model has been extensively used to analyze dyes adsorption kinetic. For the further investigation of kinetics data, the pseudo-second-order model was used. The linear forms of the both kinetic models are shown below:

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$
 (11)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(12)

where q_t and q_e are the amount adsorbed at time tand at equilibrium (mg g⁻¹), respectively. k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the equilibrium rate constants of pseudo-first-order and pseudosecond-order adsorption, respectively. The calculated values of above equation illustrated graphical in Figure 8(a,b) and parameters obtained from these charts are presented in Table V. It was found that the rate constant (k_1) decreased with an increase in temperature. But the rate constant (k_2) increased with an increase in temperature. It was also observed that correlation coefficients for pseudo-first order were lower than pseudo-second order for all temperatures. Furthermore, difference between experimental and calculated q_e shows no applicability of the pseudo-first-order model in predicting the kinetics of the carmoisine adsorption onto the PPy/SD.

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However, the linear plots of t/q_t versus t show good agreement between experimental and calculated q_e values at two examined temperatures (Table V). The correlation coefficients for the second-order kinetics model (r_2^2) are greater than 0.999, indicating the applicability of this kinetics equation and the second-order nature of the adsorption process of carmoisine onto PPy/SD.

Thermodynamic parameters

To study the effect of thermodynamic parameters, such as the change in Gibb's free energy (ΔG°), the change in entropy (ΔS°) and the change in enthalpy (ΔH°) were also investigated and calculated for adsorbent using following relations³⁴:

$$\Delta G^{\circ} = -RT \ln K_C \tag{13}$$

$$K_c = \frac{C_{\rm Ad}}{C_e} \tag{14}$$



Figure 8 (a) The pseudo-second-order linear plots of t/q_t versus t, T = 298 K (\bigcirc) and T = 308 K (\blacksquare). (b) The pseudo-first-order linear plots of ln $(q_e - q_t)$ versus t, T = 298 K (\bigcirc) and T = 308 K (\blacksquare).

| | Adsorption Kinetic Parameters of Carmoisine onto PPy/SD | | | | | | | |
|--------------|---|--------|-----------|---------|---------------------|-------|-----------|---------|
| <i>T</i> (K) | Pseudo-first order | | | | Pseudo-second order | | | |
| | q_e^{a} | k_1 | q_e^{b} | r_1^2 | q_e^{a} | k_2 | q_e^{b} | r_2^2 |
| 298 | 0.768 | -0.089 | 2.49 | 0.992 | 2.61 | 0.184 | 2.49 | 0.999 |
| 308 | 0.508 | -0.138 | 2.47 | 0.923 | 2.51 | 0.567 | 2.47 | 0.999 |

TABLE V

^a Calculated.

^b Experimental.

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \left(\frac{1}{T}\right) \tag{15}$$

where K_C is the equilibrium constant, C_{Ad} is the amount of dye adsorbed on solid at equilibrium (mg L^{-1}), C_e is the equilibrium concentration of dye in the solution (mg L^{-1}), R is the gas constant (8.314 J $mol^{-1} K^{-1}$), and T is the temperature in kelvin. The values of ΔH° and ΔS° can be obtained from the slope and intercept of Van't Hoff plot of in $\ln K_C$ versus 1/T. The use of Van't Hoff plot is an indirect, but accurate method to calculate thermodynamic adsorption parameters at solid-solution interfaces.³⁴ The calculated values of thermodynamic parameters are presented in Table VI.

The positive value of ΔH° as shown in Table VI indicates endothermic nature of adsorption. The positive value of entropy changes (ΔS°) shows increased randomness of the adsorption process. The negative values of ΔG° for the adsorption on PPy/SD due to from a spontaneous process, whereby no energy input from outside of the system required. However, the values of ΔG° increased with increased temperature suggesting that adsorption of carmoisine on PPy/SD becomes more favorable at higher temperature.

CONCLUSIONS

SD was found on a very cheap, economical, and environmentally friendly substrate for the coating of conducting electroactive polymers such as polypyrrole as an effective adsorbent for the removal of carmoisine dye from aqueous solutions. Uncoated SD was found to be an ineffective adsorbent for the removal of carmoisine dye, because the sorption was very low (\sim 20–25%). It was found that PPy/SD is

TABLE VI Thermodynamic Parameters for the Adsorption of Carmoisine onto PPv/SD

| | | | | | _ | |
|-----------------|-----------------|----------------------------|---------------------------------|------------------|--------|--------|
| | Δ | ΔH° (J/mol) | ΔS° (J/mol.K) | | | |
| 298 K -4.410 | 308 K -7.810 | 318 K -9.444 | 328 K -12.701 | 338 K -21.985 | 112.65 | 389.17 |

more effective and efficient for uptake of carmoisine dye under acidic conditions (pH = 2-5). Desorption study showed that the adsorbed carmoisine dye can be washed out by dilute solution of NaOH with high performance. Based on the kinetic studies, sorption process follows from pseudo-second-order model, and the value of k_2 was increased when the solution temperature was increased. The thermodynamic study showed that the sorption of carmoisine dye by PPy/SD is an endothermic process, and the change in Gibb's free energy was negative, which confirms the more spontaneity of the adsorption at elevated temperature.

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