# Equilibrium Adsorption Studies on Removal of Diclofenac Sodium from Aqueous Solution Using Sawdust– Polyaniline (SD–PAn) Composites

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**ABSTRACT:** In this work, equilibrium adsorption studies were carried out for the removal of antiinflamatory drug diclofenac sodium (DS) from aqueous solutions using saw-dust–polyaniline(SD-PAn) composite as a potential sorbent at 20, 30, and 40°C. The composite sorbent was characterized by FTIR and SEM analysis. The particles exhibited porous and rough surface. The equilibrium uptake data was interpreted by the Langmuir, the Freundlic, the Temkin, and the Dubinin–Redushkevich (D-R) isotherm models. The maximum adsorption capacity was found to decrease with

increase in temperature, thus indicating exothermic nature of the adsorption process. The thermodynamic parameters were evaluated using Langmuir, Flory–Huggins, Frumkin, and modified-Frumkin models. The negative values of  $\Delta G_{\rm ads}^0$  and  $\Delta H^0$  indicated spontaneous and exothermic nature of the adsorption process, respectively. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1382–1390, 2012

Key words: adsorption; isotherm; thermodynamic parameters; drug

# INTRODUCTION

In recent years, there has been growing concern about the occurrence of pharmaceuticals in the aquatic system.<sup>1</sup> These include antibiotics, hormone drugs, antiinflammatory drugs, insecticides, antiseptics, nutrition promoters, etc. Antiinflammatory drugs are a group of pharmacologically active substances that are used to relieve pains. Nonsteroidal antiinflammatory drugs (NSAID) are drugs with analgesic, antipyretic and, in higher doses, antiinflammatory effects.<sup>2</sup> The drug diclofenac sodium is the accepted name of 2-[(2, 6-dichlorophenyl) amino] benzene acetic acid sodium salt (see Fig. 1) with a  $pK_a$  of 4.0.<sup>3</sup> This is a NSAI drug and is used in the treatment of rheumatic disorder.

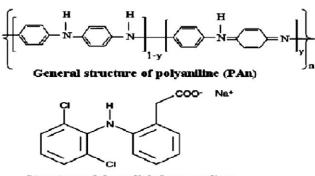
Several research works have demonstrated the presence of this kind of pharmaceutical in wastewater treatment plant effluents, rivers, lakes, and occasionally in groundwater.<sup>4</sup> In recent past, several methods have been tested for the removal of these pharmaceuticals from water. These include sedimentation,<sup>5</sup> biodegradation,<sup>6</sup> phototransformation,<sup>7</sup> chlorination,<sup>8</sup> ozonation,<sup>9</sup> and adsorption.<sup>10</sup> Of these, adsorption has proven to be an effective one due to the facts such as applicability over a wide range of sorbate concentrations, inexpensive instrumentation setup, involvement of many parameters to control the rate of adsorption like pH, temperature, porosity and particle size of sorbent, agitation speed, etc. That is why this technique has been widely adopted for removal of pharmaceutical drugs<sup>11–15</sup> from wastewater.

Activated carbon has been widely used to remove pharmaceuticals from water and wastewater.<sup>16</sup> It has high adsorption efficiency. However the major drawback for wastewater treatment utilization comes from economic considerations; the commercially available activated carbons are expensive,<sup>15</sup> thus rendering their infeasibility for large scale operations. Therefore there has been a constant search for costeffective adsorbents to remove pharmaceuticals and other organic contaminants from wastewater.

we hereby report an investigation of adsorption of Diclofenac Sodium onto Sawdust/Polyaniline composite sorbent. Polyaniline is a well known conducting/electro active polymer and in acid doped state (PAn/HCl) it can be used as an anion exchanger and is capable of adsorbing anionic drug like Diclofenac Sodium through ion-exchange mechanism.<sup>17</sup> However, to make the adsorbent PAn more effective and inexpensive, it is desirable to make its composite with a cheap material like sawdust which is an agricultural by-product and is a porous material. Therefore, sawdust/polyaniline composite adsorbent is expected to

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Structure of drug diclofenac sodium

Figure 1 Structure of polyaniline and drug diclofenac sodium.

possess fair porosity which should enhance the adsorption capacity of this novel adsorbent.

#### **EXPERIMENTAL**

## Materials

All chemicals used were analytical reagents (AR grade). Aniline (Merck, Mumbai, India) was vacuum distilled before polymerization. The adsorbent sawdust (SD), robusta(sal) used in the study was obtained from a local saw mill and was equilibrated in water for 10 days to remove the coloring ingredients. The drug Diclofenac Sodium (SD; Molecular weight 318.14, Molecular formula-NH<sub>10</sub>Cl<sub>2</sub>C<sub>14</sub>O<sub>2</sub>Na, Batch No.-NP-9001; Fig. 1) was supplied by Cadila Pharmaceuticals Limited, India and was in liquid form intended to be used as IM. In addition the composition was: 1 mL containing 25 mg Diclofenac Sodium, 4% v/v Benzyl alcohol as preservative and water as solvent. Sodium hydroxide, potassium persulfate, hydrochloric acid, formic acid, and other salts were purchased from Central Drug House, Mumbai, India. The double distilled water was used throughout the study.

## Preparation of polyaniline

Polyaniline was prepared by oxidative polymerization of monomer aniline. The detailed procedure for preparation of polyaniline(PAn) is as follows; 5.0 g (0.054 mol) of freshly distilled aniline was dissolved in 250 mL of 1*M* HCl. The mixture was cooled to below 5°C by using an ice bath. A 250 mL of a precooled 0.3*M* K<sub>4</sub>S<sub>2</sub>O<sub>8</sub> solution, prepared in 1*M* HCl was added slowly under vigorous stirring to monomer solution over a period of 30 min. Because the reaction is highly exothermic ( $\Delta H = -372$  kJ mol<sup>-1</sup>), the reaction vessel was placed in an ice bath cooling system during addition of oxidant. After the complete addition of oxidant, the reaction mixture was left stirring for about two hours at low temperature (i.e., 5°C) and left unstirred overnight at room temperature. The precipitated polymer (dark blue powder) was filtered and washed with distilled water and dilute HCl solution until the washing liquid was colorless. To remove oligomers and other nonpolymeric impurities the precipitate was washed thoroughly with methanol and distilled water. The polymer was dried at 50–60°C in an oven, powdered in a mortar and stored for processing. Based on the weight of the monomer used and the product polymer formed, the polymerization yield was found to be nearly 90%.

#### Preparation of SD/Pan composite adsorbent

To dissolve polyaniline in formic acid for coating and composite formation, the polymer was first treated with 0.5M NaOH solution for 2 h. Then, it was washed with distilled water and dried in an oven at 60°C. About 0.5 g of base-treated PAn, emeraldine base (EB), was dissolved in 50 mL of formic acid. The polymer solution was filtered to remove any nondissolvable solids. For preparation of polyaniline coated sawdust (SD/PAn), 5 g of sawdust was mixed with 50 mL of EB in formic acid (1% w/v) in a beaker (100 cm<sup>3</sup>) and stirred for two hours at room temperature and left for another 2 h without stirring. The excess of the solvent was evaporated by heating the SD/PAn at  $\sim 60^{\circ}$ C in an electric oven. The product obtained was dark green in color (see Fig. 2). Although SD/PAn can also be prepared via direct synthesis of polymer on the surface of sawdust; however, coating by the cast method was found to give more uniform and homogeneous coating.

# Characterization methods

The Fourier Transform Infrared (FTIR) Spectroscopy analysis was carried out with himadzu FTIR Spectrophotometer (8400S, Shimadzu, Japan) using KBr pelleting method. The physicochemical parameters of composite adsorbent were determined using



**Figure 2** Optical photograph of sawdust/polyaniline composite sorbent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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*n*-heptane as a nonsolvent by the method described elsewhere.<sup>18</sup> To investigate the surface morphology, SEM images were recorded by using a LEO 435 VP scanning electron Microscope (LEO Electron Microscopy, Cambridge, England) operating at 15 kV.

# Adsorption experiment

Batch adsorption experiments were carried out by agitating a definite quantity of adsorbent (i.e., 20 mg) with 20 mL of drug solution of desired concentration in an Erlenmeyer flask of 100 mL capacity, under constant stirring speed in a thermostated flask shaker (Rivotek, India) for a period of 2 h. After the adsorption was over, the solution was centrifuged and the supernatant was analyzed spectrophotometrically (Systronics 2201- UV- spectrophotometer) at 302 nm. The amount of drug adsorbed in mg per gram of adsorbent (i.e.,  $q_e = (\frac{x}{m})_e$ ) was calculated using following expression

$$q_e = \left(\frac{x}{m}\right)_e = \frac{(C_o - C_e) \times V}{W} \tag{1}$$

where  $C_o$  (mg L<sup>-1</sup>) and  $C_e$  (mg L<sup>-1</sup>) are the initial and equilibrium concentrations of drug in aqueous solutions, respectively; *V* is volume (in liter) taken for the adsorption experiment, and *W* is the amount (in gram) of adsorbent. All the experiments were carried out in triplicate and average values are reported in the data.

#### Adsorption isotherms

Analysis of equilibrium data is important for developing an equation that can be used to compare different adsorbents under different operational conditions and to design and optimize an operating procedure. To examine the relationship between adsorption and adsorbate concentration at equilibrium, various adsorption isotherm models are widely applied for fitting the data.

In the present investigation the Langmuir, the Freundlich, and the Temkin isotherm models were used to describe the equilibrium between the drug molecules adsorbed onto the adsorbent and those present in the drug solution.

The Langmuir model essentially describes the monolayer type of adsorption. It is usually expressed as follows<sup>19</sup>:

$$q_e = \frac{Q_0 \ K_L \ C_e}{1 + K_L \ C_e} \tag{2}$$

where  $K_L$  represents Langmuir equilibrium adsorption constant (L mg<sup>-1</sup> or mmol<sup>-1</sup>) and  $Q_o$  (mg g<sup>-1</sup>) is the Langmuir maximum sorption capacity.

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The linearized form of eq. (2) is given as

$$\frac{1}{q_e} = \frac{1}{Q_0 K_L} \cdot \frac{1}{C_e} + \frac{1}{Q_0}$$
(3)

A plot of  $\frac{1}{q_e}$  against  $\frac{1}{C_e}$  gives a straight line with a slope of  $\frac{1}{Q_o K_L}$  and an intercept of  $\frac{1}{Q_o}$ . Using slope and intercept values, constants  $K_L$  and  $Q_o$  were evaluated.

The Freundlich isotherm model<sup>20</sup> is also an empirical equation like the Langmuir model. It is used to estimate the adsorption intensity of the adsorbent towards the adsorbate and in the logarithmic form it is given as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where *n* represents the Freundlich constant (dimensionless), and it is related to adsorption intensity.  $K_F$  (mg g<sup>-1</sup> (L mg<sup>-1</sup>)<sup>1/n</sup>) is the Freundlich adsorption constant related to the adsorption capacity.<sup>21</sup>

A plot of  $q_e$ versus log  $C_e$  gives a straight line with (1/n) as a slope and log  $K_F$  as the intercept. Both  $K_F$  and n determine the curvature and the steepness of the isotherm.<sup>21</sup>Finally Temkin isotherm<sup>22</sup> in the logarithmic form, is given as

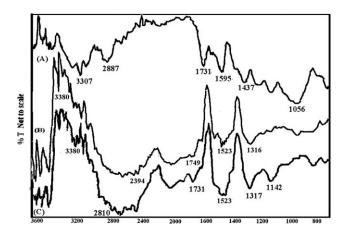
$$q_e = B \ln k_T + B \ln C_e \tag{5}$$

A plot of  $q_e$  versus ln  $C_e$  enables the determination of the isotherm constants B and  $k_T$  from the slope and the intercept respectively.  $k_T$  is the equilibrium binding constant corresponding to the maximum binding energy and constant B is related to the heat of adsorption.<sup>23</sup>

#### **RESULTS AND DISCUSSION**

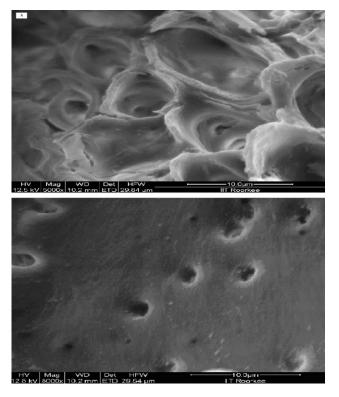
#### FTIR spectral analysis

The FTIR spectrum of plain sawdust, polyaniline, and SD/PAn composite are shown in Figure 3(A–C). In the spectrum of sawdust the adsorption peak, appearing around 3614 cm<sup>-1</sup> indicates existence of free and intermolecular bonded -OH groups. A broad band, at 3440-3460 cm<sup>-1</sup> is attributed to sum of contributions from water and -OH exchangeable groups (phenolic and alcoholic).<sup>24</sup> The band appearing at 2880-2900 cm<sup>-1</sup> corresponds to CH stretching from -CH<sub>2</sub> group. Likewise, band present at around 1731  $cm^{-1}$  could be assigned to -C=O stretching attributed to lignin aromatic groups. The presence of band around 1600 cm<sup>-1</sup> may be due to amide (N–H) group in sawdust. Moreover, peak at 1437 cm<sup>-1</sup> corresponds to -OH deformation. Finally, additional peaks at 532 and 451 cm<sup>-1</sup> can be assigned to bending modes of aromatic compounds.<sup>25</sup>

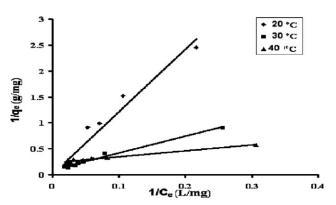


**Figure 3** FTIR spectra of (A) sawdust, (B) polyaniline, and (C) SD/PAn composite.

The FTIR spectrum of PAn and SD/PAn composite are also shown in Figure 3(B,C). In the spectrum of SD/PAn composite adsorbent some additional peaks appear which confirm formation of polyaniline. A peak, obtained at 2800 cm<sup>-1</sup> is due to symmetrical >CH<sub>2</sub> stretching of alkanes. A prominent peak appears at 3380 cm<sup>-1</sup> which corresponds to *N*—H stretching of secondary amine. The characteristic peak due to presence of quinoid ring C–N stretching vibration of aromatic secondary amine appears at 1523 and 1317 cm<sup>-1</sup>, respectively.<sup>26</sup>



**Figure 4** Scanning electron micrograph image of (A) Plain SD  $\times$ 5000 magnification and (B) SD/PAn sorbent  $\times$ 5000 magnification.



**Figure 5** The Langmuir isotherm plots for drug uptake by SD/PAn adsorbent at different temperatures.

#### Surface morphology

The formation of polyaniline within the SD matrix may result in change in surface morphology of the composite sorbent. To investigate this we recorded SEM images of plain SD and SD/PAn composite materials with  $5000 \times$  magnification. The result as shown in Figure 4(A,B) respectively, indicates that the SD particles have quite rough surface and there are irregular shaped pores present. However, the SEM image of composite as shown in Figure 4(B) indicates that the surface is fairly smooth as compared to plain SD but still pore can be observed.

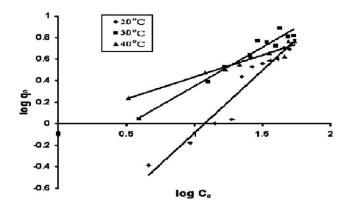
## Adsorption isotherm

The Langmuir, the Freundlich, and the Temkin isotherms were obtained for drug uptake of SD/PAn composite sorbent at 20, 30, and 40°C using the isotherm eqs. (3), (4), and (5), respectively. The results are shown in Figures 5-7 respectively, which are linear plots. Based on regression values, obtained, the order of fitness of these isotherm models was Langmuir > Freundlic > Temkin. The slopes and intercepts of these linear plots were used to calculate various parameters related to these isotherm models. All the parameters are shown in Table I. It can be seen that maximum sorption capacity  $Q_{o}$ , decreases from 89.28 to 4.41 mg  $g^{-1}$  with the increase in temperature from 20 to 40°C. This indicates that the sorption process is exothermic in nature. The observed finding may be explained as follows: The composite sorbent has exchangeable Cl- counter ions in doped state which undergo ion-exchange process with drug anions as per following reaction:

 $SD/PA^+Cl^- + drug^- \rightarrow SD/PA^+drug^- + Cl^-$ 

When temperature of adsorbate solution is increased, the electrostatic binding between SD/ PAn<sup>+</sup> and drug anion molecules becomes weak due to enhanced kinetic energy of adsorbate molecules.

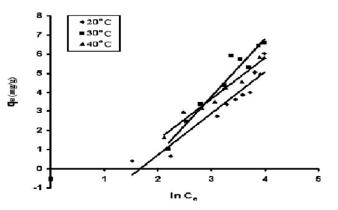
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**Figure 6** The Freundlic isotherm plots for adsorption of drug DS onto SD/PAn composite adsorbent at different temperatures.

This results in lower uptake by composite sorbent. However, it is noteworthy that increased temperature usually results in generation of new active sites, faster diffusion of adsorbate molecules as reported by some authors.<sup>11</sup> It appears that these effects are not pronounced in the present study. Similar results have also been reported by Sevim et al.27 and Ertugay and Bayhan<sup>28</sup> for adsorption of cationic cobalt porphyrazine and copper (ll) onto sepiolite and mushroom biomass respectively. Here it is also to bo noted that above proposed mechanism indicates release of Cl<sup>-</sup> ions from the copolymeric adsorbent. Toconfirm this, the supernatant was tested for the presence of chloride ions by adding a few drops of 0.1M AgNO<sub>3</sub> into the solution. The transformation of solution from a clear to highly turbid state indicated the formation of chloride ions in the sorption system.

To determine whether the adsorption process is favorable or unfavorable for Langmuir type of adsorption, a dimensionless constant separation factor  $R_L$  was used. The value of  $R_L$  was calculated using following expression<sup>29</sup>



**Figure 7** The Temkin isotherm plots for drug uptake by SD/PAn adsorbent at different temperatures.

$$R_L = \frac{1}{1 + b \ C_0} \tag{6}$$

where  $C_o$  is the initial concentration (mg L<sup>-1</sup>); and *b* is the Langmuir constant. If the value of  $R_L < 1$ , it indicates a favorable adsorption and if  $R_L > 1$  then, an unfavorable adsorption is observed. In the current study, the  $R_L$  values for the initial concentration range of 5–60 mg L<sup>-1</sup> were found to be 0.99–0.94, 0.98–0.85, and 0.91–0.46 at 20, 30, and 40°C, respectively, thus indicating favorable adsorption (see Fig. 8).

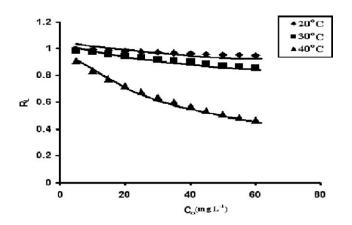
Finally,  $q_e$  versus  $C_e$  plots were also obtained using the various isotherm models and compared with the experimental data obtained at 30°C. The results, as shown in Figure 9, also support our finding that Langmuir isotherm model is best fitted on the equilibrium uptake data.

Dubinin and Redushkewich<sup>30</sup> proposed a well-linked equation for the analysis of isotherm to determine if the adsorption occurred by a physical or chemical process. The D-R isotherm is more general than the Langmuir model because it does not assume a homogeneous surface, a constant adsorption potential or absence of steric

S. no.	Isotherm model	Parameters	Temperature (°C)		
			20	30	40
1.	Langmuir isotherm model	$Q_o (mg g-)$	89.28	10.98	4.416
	0	$egin{array}{llllllllllllllllllllllllllllllllllll$	$9.16 \times 10^{-4}$	$2.8 \times 10^{-3}$	$1.9 \times 10^{-2}$
		$R^2$	0.961	0.985	0.943
2.	Freundlic isotherm model	п	1.171	0.726	0.41
		$\frac{K_F}{R^2}$ (mg g <sup>-1</sup> ) (L mg <sup>-1</sup> ) <sup>1/n</sup>	0.0557	0.4197	1.049
		$R^2$	0.944	0.958	0.943
3.	Temkin Isotherm Model	$A_T$	0.189	0.175	0.274
		$B_T$	1.121	0.828	1.215
		$B_T R^2$	0.94	0.949	0.966
4.	Dubinin-Radushkewick isotherm model	E (kJ mol <sup>-1</sup> )	7.14	9.37	12.315
		$C_m$	$1.5 \times 10^{-3}$	$3.6 \times 10^{-4}$	$9 \times 10^{-5}$
		$C_m$ $R^2$	0.9676	0.9611	0.9423

 TABLE I

 Parameters for Various Isotherms Obtained Using Equilibrium Sorption Data



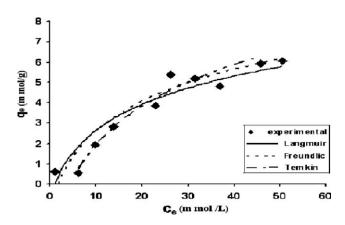
**Figure 8** Varial of RL values with initial concentrations of drug solution at different temperatures.

hindrance between adsorbed and incoming molecules. This isotherm equation is given as

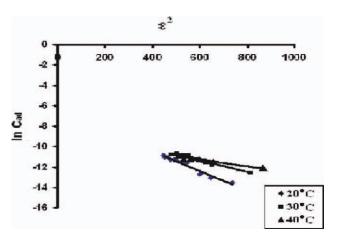
$$\ln q_{\rm e} = \ln q_{\rm max} - \beta \, \varepsilon^2 \tag{7}$$

where  $q_e$  is the amount of drug adsorbed (moles  $g^{-1}$ ) and  $q_{max}$  is the maximum amount that can be adsorbed under optimized experimental conditions;  $\beta$  is a constant with dimension of energy, and polyanyi potential  $\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$ , where *R* is the gas constant in kJ mol<sup>-1</sup> K<sup>-4</sup>, *T* is the absolute temperature in K, and  $C_e$  is the equilibrium concentration (mol L<sup>-1</sup>) of drug solution. The equilibrium uptake data, obtained at various temperatures, was used to plot ln  $q_e$  versus  $\varepsilon^2$  as shown in Figure 10. The slope and intercept of linear plots obtained were used to evaluate  $q_{max}$  and  $\beta$ , respectively. Finally the mean sorption energy *E* was calculated by putting values of  $\beta$  in the following expression:

$$E = \frac{1}{\sqrt{-2B}} \tag{8}$$



**Figure 9** Comparison of experimental and predicted adsorption isotherms of DS onto SD/PAn adsorbent according to all analyzed models.



**Figure 10** D-R isotherm plots for adsorption of drug DS onto SD/PAn adsorbent at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which is the free energy of transfer of one mole of solute from infinity to surface of the adsorbent.

The values of *E* ranging from 1 to 8 kJ mol<sup>-1</sup> indicates that adsorption process is physical while *E* values between 8 and 16 kJ mol<sup>-1</sup> suggest that adsorption is being controlled by ion-exchange and E > 16 kJ mol<sup>-1</sup> signifies an adsorption being governed by particle diffusion mechanism.<sup>31</sup> In the present study, for the temperature range of 20–30°C, the *E* values were found to be in the range of 7.14–9.37 kJ mol<sup>-1</sup>. This indicates that adsorption is physical in nature and is operative through ion-exchange mechanism.

#### Thermodynamic parameters

Thermodynamic parameters such as  $\Delta G_{ads}^{o}$ ,  $\Delta H_{or}$  and  $\Delta S_{o}$  reveal significant information about the insight of an adsorption process like its spontaneous nature, its exothermocity or endothermocity, and changes in randomness of the adsorption system etc.

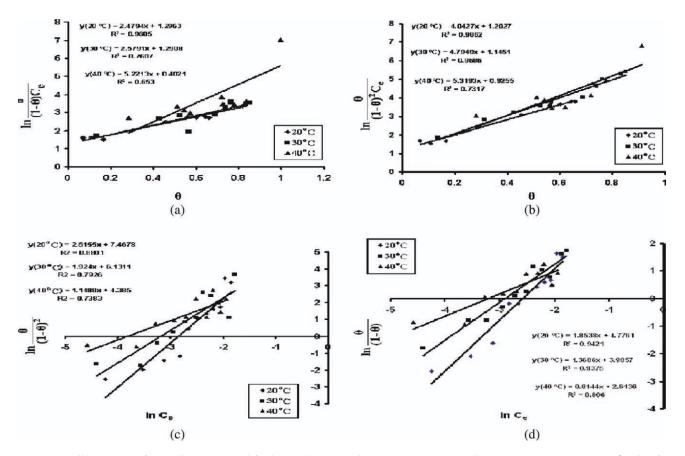
A general adsorption isotherm for adsorption at solid-liquid interface taking into account the effect of size ratio (*n*) and lateral interaction coefficient ( $\alpha$ ) between the adsorbed molecules, has the following form<sup>32</sup>;

$$\frac{\theta \cdot e^{-2\alpha\theta}}{\left(1-\theta\right)^n} = K \ C_e \tag{9}$$

$$K = \frac{e^{(-\Delta G_{\rm ads}/RT)}}{55.5} \tag{10}$$

is the absorbability of the adsorbate molecules at infinite low coverage,  $C_e$  is the equilibrium concentration in mol L<sup>-1</sup>,  $\theta$  is the degree of surface coverage, R is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), T is the temperature in K. The surface coverage  $\theta$  can be calculated as  $\theta = \frac{q_e}{q_{e(\text{max})}}$  where  $q_{e\text{max}}$  is the maximum

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**Figure 11** Illustration of Frumkin (A), modified Frumkin (B), Flory-Huggins (C), and Langmuir (D) equations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

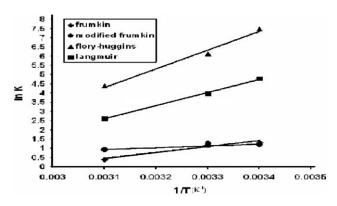
adsorption as shown in  $q_e$  versus  $C_e$  profile and  $q_e$  is the amount adsorbed at equilibrium corresponding to equilibrium concentration  $C_e$ .

The calculation of  $\Delta G_{ads}^{o}$  was made using the four models, namely: the Frumkin,<sup>33</sup> the modified Frumkin,<sup>34</sup> the Flory–Huggins,<sup>35</sup> and the Langmuir.<sup>19</sup>

The logarithmic form of eq. (11) is

$$\ln \theta - \ln (1 - \theta)^n C_e = 2\alpha \theta + \ln K \tag{11}$$

The *n* and  $\alpha$  value pairs for Frumkin, modified Frumkin, Flory-Huggins, and Langmuir isotherm



**Figure 12** ln*k* versus 1/T plots for evaluation of  $\Delta G^0_{ads.}$ 

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models are 1,1; 2,1; 2,0; and 1,0 respectively. On substituting these values in eq. (11), the following linearized forms of these isotherm models are obtained, respectively

$$\ln \frac{\theta}{C_e(1-\theta)} = 2\theta + \ln K \tag{12}$$

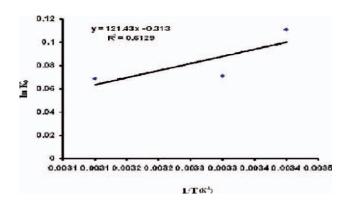
$$\ln \frac{\theta}{C_e (1-\theta)^2} = 2\theta + \ln K \tag{13}$$

$$\ln \frac{\theta}{(1-\theta)} = \ln C_e + \ln K \tag{14}$$

and

$$\ln \frac{\theta}{\left(1-\theta\right)^2} = \ln C_e + \ln K \tag{15}$$

Figure 11 show linear plots obtained between  $\ln \frac{\theta}{(1-\theta)C_e}$  and  $\theta$ ,  $\ln \frac{\theta}{(1-\theta)^2C_e}$  and  $\theta$ ,  $\ln \frac{\theta}{(1-\theta)^2}$  and  $\ln C_e$ , and  $\ln \frac{\theta}{(1-\theta)}$  and  $\ln C_e$  respectively, for aforementioned isotherm models. The intercepts obtained for these plots yielded values of  $\ln k$  at different temperatures corresponding to each model at 20, 30, and  $40^{\circ}$ C.



**Figure 13**  $\ln k_o$  versus 1/T plot for evaluation of  $\Delta H^0$  and  $\Delta S^0$ . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To calculate  $\Delta G^{o}_{ads'}$  logarithmic form of eq. (10) was used

$$\ln k = -\frac{\Delta G_{\text{ads}}}{R} \cdot \frac{1}{T} - \ln 55.5 \tag{16}$$

Figure 12(A–D) show lnk versus 1/T plots for the Frumkin, the modified Frumkin, the Flory–Huggins, and the Langmuir isotherm models, respectively. Except the Frumkin model ( $R^2 = 0.8964$ ), the other three models showed fair regression values of 0.9812, 0.9873, and 0.9987, respectively. The  $\Delta G_{ads}^{o}$  values, obtained using slopes of linear plots were found to be -26.505, -7.882, -83.63, and -59.52 kJ mol<sup>-1</sup>, respectively. The negative values of  $\Delta G_{ads}^{o}$  were indicative of the spontaneous nature of the adsorption process.

To calculate  $\Delta H^o$  and  $\Delta S^o$ , thermodynamic distribution coefficient,  $K_o$  was obtained by the method used by Anirudhan and Sreedhar<sup>24</sup> which involves plotting  $\ln \frac{q_e}{C_e}$  versus  $q_e$  and then extrapolating it to zero $q_e$ . The values of antilog of intercept thus yielded thermodynamic distribution coefficient  $K_o$  at different temperatures. From the variation of  $\ln K_o$  with temperature, the standard enthalpy ( $\Delta H^o$ ) and entropy ( $\Delta S^o$ ) changes were computed using the following equation

$$\ln K_o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R} \cdot \frac{1}{T}$$
(17)

The plot of  $\ln K_o$  versus 1/T was linear (see Fig. 13). The values of  $\Delta H^o$  and  $\Delta S^o$ , as calculated from the slope and intercept of the linear plot were found to be -1.006 kJ mol<sup>-1</sup> and -0.313 kJ mol<sup>-1</sup> K<sup>-1</sup> respectively. The negative  $\Delta H^o$  value is indicative of exothermic nature of the process which is also supported by our observations that maximum sorption capacity  $Q_o$  decreases with temperature, as discussed in previous section. The negative value of  $\Delta S^o$  indicates the stability of the sorption process with no

structural change at solid–liquid interface. Similar observations have also been reported by Aman et al.<sup>36</sup>

#### CONCLUSIONS

From this study it may be concluded that polyaniline/sawdust composite sorbent has potential to remove drug Diclofenac Sodium from aqueous solution. The equilibrium uptake data was best interpreted in terms of Langmuir isotherm model for which the maximum adsorption capacity  $Q_o$  was found to decrease from 89.28 to 4.41 mg g<sup>-1</sup> as the temperature was increased from 20 to 40°C. So the adsorption process was exothermic in nature. The average value of mean sorption energy *E*, as evaluated using D-R isotherm model, was around 7.14– 9.37 kJ mol<sup>-1</sup> this indicating that adsorption occurred through ion-exchange mechanism.

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