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Adsorption of aniline, phenol, 4-chlorophenol and 4-nitrophenol onto granular activated carbon: isotherm, thermodynamics and relationship with solvatochromic parameters[#]

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ABSTRACT

In the present paper, equilibrium adsorption isotherm data generated in the temperature range of 288-318 K are reported for the adsorption of Aniline (AN), Phenol (P), 4-chlorophenol (CP) and 4-nitrophenol (NP) from aqueous solution onto granular activated carbon (GAC). Adsorption of these adsorbates onto GAC was found to be favourably influenced by an increase in temperature. Redlich–Peterson model represented the equilibrium data very well for AN and NP. However, Tempkin model was the best for P and CP. The high negative value of change in Gibb's free energy (ΔG0) indicated the feasible and spontaneous adsorption of AN, P, CP and NP adsorption onto GAC. Adsorption process was found to be endothermic for all the adsorbates. The dispersion force between the π-electrons of GAC and the π-electrons in AN, P, CP and NP molecules is the main adsorption mechanism. The adsorption behavior of AN, P, CP and NP strongly depends upon the intrinsic molar volume (VI), thus, steric effect has strong influence on observed adsorption coefficients values. This study also shows that hydrogen bonding between the adsorbates and the GAC plays an important role in the adsorption behavior.

Keywords: *Adsorption; Granular Activated Carbon; Aniline; Phenol; 4-chlorophenol; 4- nitrophenol; Isotherms; Thermodynamics.*

1. INTRODUCTION

With the increasing concern for public health and environmental quality, the stringent limits on the acceptable environmental levels of organic pollutants have been established. A common problem faced by most of the industries is the disposal of large volume of wastewater containing organic compounds. Phenol (P) and its derivatives and associated compounds are very important organic intermediates, used in the manufacture of many products in such units as drugs, rubber, pesticides, varnishes and also, dyestuffs, chemicals, petrochemicals, paper, wood, metallurgy and coking plants [1-5]. Phenols are extremely toxic to living species [6-7]. Phenols and aniline are mutagenic and also carcinogenic [8-9]. Total phenol concentration in the wastewater of a typical Indian refinery processing and resin manufacture is ~135 mg/l and 12–300 mg/l, respectively [10-11]. Phenols constitute the 11th of the 126 chemicals, which have been designated as priority pollutants by Environmental Protection Agency (EPA) USEPA and European Union has also classified several phenols as priority contaminants [12-13]. The World Health Organisation (WHO) has set limit of phenol concentration in potable water as 0.001 mg/l [14]. Phenolic compounds impart objectionable taste and odor to drinking water at concentrations as low as 0.005 mg/l.

Various treatment methods such as adsorption [15-22], photodegradation [23], coagulation and flocculation [24], chemical oxidation [25-28], biological process [3-4, 29- 30], etc. have been studied for the removal of phenols from wastewater. Conventional methods for the removal or destruction of AN from wastewaters include solvent extraction, biodegradation [31-32], catalytic oxidation [33], membrane separation [34-36], ultrasonic degradation [37], supercritical water oxidation [38], and electrochemical oxidation [39]. Adsorptive removal of Aniline [40-42] and phenolics [19, 21, 43-47] from wastewaters has been reported. The adsorption of P and substituted phenols from aqueous solution on activated carbons has been intensively investigated for several decades [9, 18, 48-50]. Of all the methods proposed for the removal of phenols and associated compounds, the adsorption appears to offer the best prospects for overall treatment, especially for the effluents with moderate and low concentrations. Because of a good capacity for adsorption of organic matter, granular and powder activated carbon (GAC and PAC) are the most widely used adsorbents for the adsorptive removal [51-53].

The present paper reports the experimental data and the modeling of the equilibrium temperature on the equilibrium adsorption has also been investigated. Thermodynamics of adsorption of AN, P, CP and NP from synthetic wastewater onto GAC. The effect of adsorption process have been studied and the change in Gibbs free energy (ΔG_0) and the enthalpy (ΔH_0), and isosteric heat of adsorption have also been determined.

2. EXPERIMENTAL SECTION

Materials. All the chemicals used in the study were of analytical reagent grade. AN was procured from Qualigens Fine Chemicals, Mumbai. P was procured from Ranbaxy Fine Chemicals, New Delhi. CP ($\text{4-ClC}_6\text{H}_5\text{OH}$), NP ($\text{4-NO}_2\text{C}_6\text{H}_5\text{OH}$), NaOH, and HCl were obtained from S.D. Fine Chemicals, Mumbai. Stock solutions of the AN, P, CP and NP were made by dissolving an exact amount of the respective compound in double distilled water (DDW). The GAC supplied by S.D. Fine-Chemicals limited, (Mumbai, India) was manufactured from coconut shells.

Methods: The physico-chemical characterization of GAC was performed using standard procedures and the results are given elsewhere [17]. The initial and residual concentration of AN, P, CP and NP were determined by finding out the absorbance of the respective solutions at 230, 269, 279 and 317 nm, respectively, using UV/vis spectrophotometer (Lambada 35; PerkinElmer, MA 02451, USA). Detailed procedure for batch adsorption study was given elsewhere [17].

Adsorption equilibrium study. Equilibrium adsorption studies are required for the design of an adsorption system. For use of these studies in the design and optimization of the process, it is necessary to correlate the equilibrium sorption data. These are several equilibrium isotherm [19] have discussed the theory associated with the most commonly used isotherm models.

We have used four equilibrium isotherm equations, namely Freundlich [54], Langmuir [55], Redlich-Peterson (R-P) [56] and Temkin [57] to test their efficacy in representing the equilibrium sorption data at different temperatures. Sum of square of errors (SSE) was used as a criterion for finding out the most appropriate model to represent the experimental data. The SSE is given as:

$$SSE = \sum_{i=1}^{n} (q_{e,\exp} - q_{e,cal})_i^2 \qquad (3)$$

Where, qe,exp and qe,cal are the experimental and calculated equilibrium adsorbate uptake, respectively; and n is the number of data points.

Adsorption thermodynamics. ΔG0 , ΔH0 , ΔS0 and temperature. The equilibrium adsorption constant (KD) can be related to as follows:

$$\ln K_D = \frac{-\Delta G_0}{RT} = \frac{\Delta S_0}{RT} - \frac{\Delta H_0}{R}\frac{1}{T} \qquad (4)$$

Where, T is the absolute temperature (K), R is the universal gas constant (8.314×10−3 kJ/mol K) and KD (=qe / Ce) is the single point or linear sorption distribution coefficient. Thus, ΔH0 which is the enthalpy change (kJ/mol) can be determined from the slope of the linear Van't Hoff plot, i.e. ln K D versus (1/T). This ΔH 0 corresponds to the isosteric heat of adsorption (ΔH st ,0) with zero surface coverage (i.e. qe =0) [58]. K D at qe =0 can be obtained from the intercept of the ln qe Ce versus qe plot [18]. Apparent isosteric heat of adsorption (ΔHst,a) at constant surface coverage (qe) is calculated using the Clausius-Clapeyron equation [59]:

$$\Delta H_{st,a} = R \left. \frac{d \ln C_e}{d(1/T)} \right|_{q_e} \qquad (5)$$

3. RESULTS SECTION

3.1. Equilibrium adsorption. The results for the equilibrium adsorption of AN, P, CP and NP onto GAC are presented in Fig.1 (a-d). In order to show the low concentration region more clearly, only results for 20<C0 <1000 mg/l are shown in the figure. The isotherms express the equilibrium adsorptive uptake, qe (mmol/g) by GAC as a function of the equilibrium concentration in solution, Ce (mmol/l). The isotherms for various compounds- AN, P, CP and NP are quite different from each other. Smaller adsorption is manifested in the low concentration range, while an almost linear increase in qe is observed in the higher concentration range.

3.1.1. Effect of temperature. Fig.1 (a-d) shows the plots of adsorption isotherms, qe versus Ce, for AN, P, CP and NP-GAC systems at three temperatures, namely 288, 303 and 318 K. It is found that the adsorption of all the solutes increases with an increase in temperature. The adsorptive uptake, qe rises sharply at a low Ce value and then gradually with an increase in Ce. When the temperature of the adsorption system was increased from 288 K to 318 K. qe increased: from 1.29 to 2.15 mmol/g (for AN), 1.40 to 1.51 mmol/g (for P), 1.4 to 1.8 mmol/g (for CP) and 1.21 to 1.35 mmol/g (for NP). It may be seen that the effect of temperature is most pronounced for AN, where ~ 67% increase in equilibrium uptake qe has been observed. An increase in temperature increases the chemical potential of the organic molecules to penetrate through the surface pores of GAC. Also, the mobility of the adsorbate increases with an increase in temperature. These together results in the enhancement in the adsorptive capacity of the GAC at higher temperatures. An increase in the P adsorption capacity of the carbonaceous adsorbents with an increase in temperature has also been reported by other investigators [19, 60-61].

The investigators have ascribed different reasons for the endothermic nature of adsorption of phenolics onto activated carbons. A rise in adsorption temperature weakens the hydrogen bonds formed among water molecules and between water molecules and the solute or the adsorbent [62] and enhances the pore diffusion [19, 63-64]. Therefore, an increase in temperature favors dehydration of the adsorbate molecules, which makes them more planar and gives them a larger dipolar moment. An increase in planarity provides the solute molecules greater access to the pores of the GAC, while increase in dipolar moment results in enhanced adsorbent–adsorbate interactions. As a result, the adsorption found to be endothermic because of the endothermicity of the dehydration adsorbates molecules. Therefore, the sorptive uptake increases with an increase in temperature.

3.2. Adsorption isotherm modeling. The Langmuir, Freundlich, Tempkin and R-P isotherm parameters along with coefficient of determination (R^2) and SSE values for the fit of the equilibrium sorption data of various solutes onto GAC at various temperatures are given in Tables 2 and 3. The R^2 values alone are not sufficient in determining the best isotherm model to represent the experimental data because they are generally found to be > 0.91 for all the four models. The SSE values are found to be smaller for Redlich-Peterson model for AN and NP, while Temkin model gives smaller values for P and CP in comparison to other models. Therefore, it can be concluded that Temkin model is the best among the four models for representing the adsorption isotherm data of the P and CP on GAC, while Redlich-Peterson model is the best among the four models for representing the adsorption isotherm data of the AN- and NP-GAC system.

The q_{max} value of the Langmuir model is the most important parameter because this measures the solute adsorption capacity of GAC. The q_{max} values are given in Tables 2 and 3. A comparison of isotherm parameters and isotherm plots shows that the adsorption of P is greater than that of AN at 288 and 303 K while AN adsorption gets enhanced gets more adsorbed at 318 K. Higher adsorption of P at lower temperature may be due to lower intrinsic molar volume (V_I) of P (5.36 $cm^3 mol^{-1}$) than that of An (5.67 $cm^3 mol^{-1}$). The solubility of AN (34 g l^{-1}) is lower than that of P (83 g l^{-1}). At lower temperature, adsorption behavior does not seem to be affected by solubility factor. However, at higher temperature higher adsorption of AN is found which may be alluded to its lower solubility.

Comparison of q_{max} values (mmol g^{-1}) for different solutes are found shows the q_{max} values in the following order: P>CP>NP. This trend may be attributed to the lower values of V_I for P (5.36 $cm^3 mol^{-1}$) than that of CP (6.25 $cm^3 mol^{-1}$) and NP (6.85 $cm^3 mol^{-1}$) and to the size exclusion (steric) effect. Larger molecular size of NP and CP cause them to occupy more area on the GAC surface resulting in lower q_{max} values in mmol g^{-1} units [65-66]. However, the q_{max} values in mg g^{-1} follow the trend NP>CP>P. This trend is similar to that of K_D (adsorption coefficient). The reasons are discussed in details in later sections.

The main contributions to adsorption of organics onto GAC are π-π dispersion [67], hydrogen-boding interactions [68] and donor-acceptor interactions [69]. Isothermal experiments were conducted at the optimum pH values of 7, 6, 5.75 and 6 for the maximum adsorptive uptake of AN, P, CP and NP, respectively. At any solution pH, organic acids and organic bases will be either in their non-dissociated form or in dissociated form, depending on their dissociation constant values (pKa). For pH< pKa, organic bases (like AN) become cationic (dissociation) species because of protonation, whereas organic acids (like P) remain in non-dissociated form. For pH > pKa, organic bases are predominantly in non-dissociated neutral form whereas organic acids form anionic (dissociated) species [30]. The pKa value of AN, P, CP and NP are 4.63, 9.95, 9.38 and 7.15, respectively. Considering the dissociation reactions of all the solutes as given in Table 4, it is found that all the solutes are in neutral form at any temperature and that the electrostatic attraction/repulsion between adsorbates and the adsorbent is ruled out.

The GAC surface is considered to be highly polarizable and amphoteric in nature. It attracts π-acceptors to the electron rich graphene surface area near edges and π-donors to the electron-deficient central regions [70]. Generally, π- π interactions depend on the size and shape of the aromatic system and the substitution unit [71-72]. A number of studies have shown that both electron withdrawing (e.g., $-NO_2$ and –Cl) and electron-donating (e.g., $-NH_2$ and –OH) substituents on benzene can increase the adsorption of aromatic organic compounds onto GAC. The electronic effects of substituents on benzene type adsorbates are usually examined with substituent constants developed by Hammett from reaction studies 73-74]. The values of σ for –Cl and $-NO_2$ groups for substitution phenolic compounds are 0.23 and 1.25, respectively (Table 5). Thus, it seems that the substitution of P by more electron-withdrawing $-NO_2$ group results in an increase in its adsorption onto GAC.

Table 6 shows the values of K_D as determined by procedure adopted by [18] for all solute-GAC systems. K_D represents the partition coefficient of adsorbate between the solution and the adsorbed phases at infinite dilution [75]. A close look at the K_D values shows that it follows the trend as NP>CP>P>AN at all temperatures.

Variation of K_D with σ and dipole moment (D) for P, CP and NP is shown in Fig. 2. A high correlation between K_D and σ and D is observed. It may, thus, be inferred that the substitution of more electron-withdrawing group onto phenol increases its K_D values. Also, the adsorbate having higher D value gets easily adsorbed onto GAC.

3.3. Correlation of adsorption coefficients with solvatochromic parameters. Solvatochromic parameters like intrinsic molar volume (V_I), the polarity/polarizability parameter (π), the hydrogen-bonding donor parameter (α_s) and hydrogen-boding acceptor parameter (β_m) can be used to predict K_D values. The linear solvation energy relationships (LSER) models based on solvatochromic parameters are generally used to predict the K_D values of adsorption of various compounds onto GAC.

The values of solvatochromic parameters of AN, P, CP and NP are listed in Table 1, whereas the K_D values of adsorption of these compounds onto GAC at 288, 303 and 318 K are listed in Table 6. Significant linear relationship was observed between K_D and β_m or α_s or V_I (Table 7 and Fig. 3). However, no relationship was observed between K_D values and π parameter (Fig. 3 and Table 7). Among the four solvatochromic parameters, β_m (R^2=0.760-0.876) and V_I (R^2=0.758-.873) showed high linear correlation with K_D at all temperatures. A significant relationship (R^2=0.573-0.620) was also observed between K_D and α_s**.** Considering the fact that R^2 values greater than 0.876 were not obtained using LSER with respect to individual parameters, quadratic solvation energy relationships (QSER) were also fitted to the data. However, even QSER relationship did not improve the correlation. Therefore, the LSER model only has been used.

Regression equations of the form of Eq. (6) given by [76-77] could be used to predict the behavior of adsorption of various adsorbates onto GAC.

$$K_D = a_0 + a_1 V_I + a_2 \beta + a_3 \alpha + a_4 \pi \qquad (6)$$

Where, a_0 , a_1 , a_2 , a_3 and a_4 are the regression coefficients. These coefficients evaluate the contributions of the corresponding solvent effects on K_D. The following regression relationships were deduced after the fitting of the data at 288, 303 and 318 K, respectively.

288 K: $K_D = -54.08 + 0.117 V_I - 0.7\beta - 23.58\alpha$ $R^2=1$ (7)

303 K: $K_D = 342.37 - 0.759 V_I + 13.77\beta + 173.20\alpha$ $R^2=0.999$ (8)

318 K: $K_D = 223.7 - 0.45 V_I + 10.37\beta + 117.99\alpha$ $R^2=1$ (9)

Assuming the a_0 in Eq. (6) to be a function of temperature (of Arrhenius equation form), the following modified equation was used to predict the adsorption behavior at all temperatures:

$$K_D = K_{D0}\exp(-A/T) + a_1 V_I + a_2\beta + a_3\alpha + a_4\pi \quad (10)$$

Where, K_{D0} and A is a constant and T is the absolute temperature (K). The statistical confidence of regression relationships at a given significance value was determined by F -test: $F = R^2(N-k-l)/\left(k(1-R^2)\right)$ where, N and k are the number of experimental K_D values and the solvatochromic indexes, respectively and R is the correlation coefficient and R^2 is the coefficient of determination [78].

The fitting of the Eq. (10) as shown in Fig. 4 was first carried out with all the parameters and later on by neglecting the π parameter. R^2 values showed insignificant difference when π parameter was also considered. Thus, it was be concluded that π parameter has negligible effect in the adsorption behavior and could be neglected in the correlation.

The final regression equation which considered the effect of temperature but neglected the effect of π is given as:

$$K_D = 76.82\exp(-211/T) - 0.3633 V_I - 7.624\beta + 85.65\alpha;$$

$$R^2=0.787; \qquad F(12,5)=10.8 \qquad (11)$$

Eq. (11) is statistically significant at 95% confidence interval because $F(12,5)=10.8 > F_{0.05}(12,5)=4.68$.

This study shows that adsorption behavior of AN, P, CP and NP strongly depended upon the V_I, thus, steric effect has strong influence on observed K_D values. This study also shows that the hydrogen bonding between the adsorbates and the GAC plays an important role in the adsorption behavior. It seems that the adsorbate and GAC act as both hydrogen bonding acceptor or donor, however, higher correlations for β_m show that adsorbates act more as hydrogen bonding acceptor and GAC surface acts as hydrogen bonding donor.

3.3. Adsorption thermodynamics. Fig. 5 shows the Van't Hoff's plot for AN, P, CP and NP adsorption onto GAC from which ΔH_0 and ΔS_0 values have been estimated (Table 6). ΔG_0 values were negative indicating that the adsorption process led to a decrease in ΔG_0 and that the adsorption process is feasible and spontaneous [19,79].

Generally, the ΔG_0 value is in the range of -20 to 0 kJ mol^{-1} for physisorption and in the range of −80 to −400 kJ mol^{-1} for chemisorption [80]. Most of the ΔG_0 values obtained at 288 and 303 K for all the adsorbates lie between -20 and 0 kJ mol^{-1} whereas ΔG_0 values obtained at 318 K are in the range of -20 to -25 kJ mol^{-1}. It may, thus, be inferred that the adsorption of AN, P, CP and NP is physical in nature, although, chemisorption becomes significant at higher temperatures. The absolute ΔG_0 values for all the four adsorbates increase with an increase in temperature, which elucidates the increasing tendency of adsorption spontaneity and further confirms the chemical character of the adsorption at higher temperatures.

The positive values of ΔH_0 (48.48, 43.50, 26.73 and 52.13 for AN, P, CP and NP, respectively) indicate the endothermic nature of the adsorption process. In physiosorption, the bond between adsorbent and adsorbate is Van-der walls interaction and ΔH_0 is typically in the range of 5-10 kJ mol^{-1} for liquid phase adsorption. In case of chemisorption, a chemical bond is formed between adsorbate molecules and the surface; and the chemisorption energy is, generally, in the range of 30-70 kJ mol^{-1}[81]. The adsorption for AN, P, CP and NP onto GAC, is thus both by physical adsorption and chemical transition [82].

The ΔH_0 of AN is greater than P, CP and NP, indicating that the interaction of the GAC with AN is a little stronger. The enthalpy of adsorption of organic molecules from aqueous solution onto activated carbon is usually within the range of 8–65 kJ mol^{-1}[83]. The values obtained in the present study are in the same range.

The positive value of ΔS_0 (214.69, 200.02, 152.52 and 243.98 J mol^{-1} K^{-1} for AN, P, CP and NP, respectively) suggests increased randomness at the solid/solution interface with some structural changes in the adsorbates and the GAC. It also indicates an affinity of the GAC towards the adsorbates [19]. The positive ΔS_0 value also corresponds to an increase in the degree of freedom of the adsorbed species [84].

3.4. Isosteric heat of adsorption. Apparent isosteric heat of adsorption ($\Delta H_{st,a}$) at constant surface coverage (qe=0.4, 0.8, 1.2, 1.6 and 2 mmol g^{-1} for AN; 0.3, 0.6, 0.9, 1.2 and 1.5 mmol g^{-1}; and qe=0.25, 0.5, 0.75, 1, 1.25 mmol g^{-1} for CP and NP) was calculated using the Clausius-Clapeyron equation [59].

The equilibrium concentration (Ce) at a constant adsorbate uptake, qe was obtained from the adsorption isotherm data at different temperatures. ($\Delta H_{st,a}$ was calculated from the slope of the lnCe versus (1/T) plot for varying qe. The isosteres corresponding to different equilibrium adsorption uptake of AN, P, CP and NP by GAC are shown in Fig. 6. The linear regression correlation coefficients of the isosters and the corresponding isosteric enthalpies for all the adsorbates are presented in Table 6. The results suggest that Eq. (5) represents the experimental data very well. The variation of $\Delta H_{st,a}$ of the six adsorbate–adsorbent systems with the surface loading is presented in Fig. 7. The $\Delta H_{st,a}$ is high at very low coverage but decreases steadily with an increase in qe. This indicates that the GAC has energetically heterogeneous surface.

The dependence of heat of adsorption with surface coverage is usually observed to display the adsorbent–adsorbate interaction followed by the adsorbate–adsorbate interaction. The adsorbent–adsorbate interaction takes place initially at lower qe values resulting in high heats of adsorption. On the other hand, adsorbate–adsorbate interaction occurs with an increase in the surface coverage. The variation in $\Delta H_{st,a}$ with surface loading can also be attributed to the possibility of having lateral interactions between adsorbed AN, P, CP and NP.

Li et al.[85] reported negative values of $\Delta H_{st,a}$ for adsorption of four phenolic (phenol, *p*-cresol, *p*-chlorophenol, and *p*-nitrophenol) compounds onto Amberlite XAD-4. However, Srivastava et al. [19] reported that the $\Delta H_{st,a}$ values for phenol adsorption onto bagasse fly ash and laboratory- and commercial-grade activated carbons were endothermic in nature. This trend matches with the trend reported in the present study.

Table 1. Physic-chemical properties and solvatochromic parameters.

Parameters	AN	P	CP	NP	References
Molecular weight (MW) (g mol^{-1})	**93.13**	**94.11**	**128.56**	**139.11**	**[86]**
Water solubility (g l^{-1}) at 25 ^{0}C (C_s)	**34**	**83**	**27**	**12.4**	**[86]**
pK_a	**4.63**	**9.95**	**9.38**	**7.15**	**[30, 75, 87]**
Octanol/ water partition coefficient at 25 ^{0}C ($\log K_{ow}$)	**0.94**	**1.46**	**2.39**	**1.91**	**[30, 88]**
Projected area (nm^2) (A_m)	**0.47**	**0.437**	**0.482**	**0.519**	**[41, 51, 89]**
Dipole moment (Debye) (D)	**1.17**	**1.233**	**1.477(**	**5.44**	**[90-92]**
Polarity /Polarizability parameter (π)	**0.73**	**0.72**	**0.72**	**1.01**	**[30,74,75]**
Intrinsic molar volume (cm^3/mol) (V_I)	**0.567**	**0.536**	**0.625**	**0.685**	**[30,74,75]**
hydrogen-bonding donor parameter (α_s)	**0.16**	**0.61**	**0.67**	**0.93**	**[30,74,75]**
hydrogen-bonding acceptor parameter (β_m)	**0.5**	**0.33**	**0.72**	**1.01**	**[30,74,75]**

Table 2. Isotherm parameters for the adsorption of AN and P onto GAC at different temperature (t=24 h, m =10 g l^{-1}). AN and P adsorption onto GAC at different temperatures.

AN-GAC						**P-GAC**				
Freundlich										
	K_F	$1/n$	R^2			K_F	$1/n$	R^2		
288	**1.11**	**0.569**	**0.829**	**0.1540**		**1.350**	**0.617**	**0.914**	**0.1211**	
303	**1.58**	**0.603**	**0.868**	**0.1272**		**1.436**	**0.537**	**0.933**	**0.0838**	
318	**2.22**	**0.4821**	**0.992**	**0.0280**		**1.499**	**0.467**	**0.961**	**0.0539**	
Langmuir										
Temp. (K)	q_m **(mmol g^{-1})**	K_L **(l mmol^{-1})**	R^2	**SSE**		q_m **(mmol g^{-1})**	K_L **(l mmol^{-1})**	R^2	**SSE**	
288	**1.29**	**3.51**	**0.854**	**0.1338**		**1.49**	**3.2757**	**0.974**	**0.0757**	
303	**1.48**	**4.44**	**0.901**	**0.0965**		**1.50**	**4.5539**	**0.964**	**0.0425**	
318	**2.15**	**5.58**	**0.984**	**0.0479**		**1.51**	**5.9323**	**0.966**	**0.0457**	
Tempkin										
Temp. (K)	K_T **(l mmol^{-1})**	B_T **(mmol g^{-1})**	R^2	**SSE**		K_T **(l mmol^{-1})**	B_T	R^2	**SSE**	
288	**32.31**	**0.300**	**0.889**	**0.0986**		**26.35**	**0.3892**	**0.994**	**0.0073**	
303	**49.15**	**0.318**	**0.923**	**0.072**		**63.05**	**0.2939**	**0.971**	**0.0362**	
313	**400.17**	**0.262**	**0.890**	**0.3012**		**120.27**	**0.2605**	**0.986**	**0.0165**	
R-P										
Temp. (K)	K_R **(l g^{-1})**	a_R **(l mmol^{-1})**	β	R^2	**SSE**	K_R **(l/g)**	a_R **(l mmol^{-1})**	β	R^2	**SSE**
288	**4.53**	**3.51**	**0.999**	**0.854**	**0.1338**	**4.17**	**2.261**	**0.999**	**0.958**	**0.0616**
303	**6.55**	**4.43**	**0.999**	**0.901**	**0.0965**	**6.94**	**4.660**	**0.999**	**0.965**	**0.0425**
318	**29.29**	**12.92**	**0.649**	**0.991**	**0.0245**	**13.38**	**9.478**	**0.869**	**0.974**	**0.0336**

Freundlich: $q_e = K_F C_e^{1/n}$ **; Langmuir:** $q_e = \dfrac{q_m K_L C_e}{1+K_L C_e}$ **;**

Temkin: $q_e = B_T \ln\left(C_e K_T\right)$**; R-P:** $q_e = \dfrac{K_R C_e}{1+a_R C_e^{\beta}}$

Table 3. Isotherm parameters for the adsorption of CP and NP onto GAC at different temperature (t=24 h, m =10 g l^{-1}). CP and NP adsorption onto GAC at different temperatures.

CP-GAC						**NP-GAC**				
Freundlich										
Temp. (K)	K_F **((mmol g^{-1})/ (mmol l^{-1})$^{1/n}$))**	$1/n$	R^2	**SSE**		K_F **((mmol g^{-1})/ (mmol l^{-1})$^{1/n}$)**	$1/n$	R^2	**SSE**	
288	**4.96**	**0.817**	**0.931**	**0.0459**		**1.51**	**0.73**	**0.983**	**0.0082**	
303	**3.39**	**0.620**	**0.828**	**0.1101**		**1.83**	**0.62**	**0.999**	**0.0004**	
318	**2.49**	**0.443**	**0.868**	**0.089**		**2.36**	**0.54**	**0.980**	**0.0142**	
Langmuir										
Temp. (K)	q_m **(mmol g^{-1})**	K_L **(l/ mmol)**	R^2	**SSE**		q_m **(mmol g^{-1})**	K_L **(l $mmol^{-1}$)**	R^2	**SSE**	
288	**1.15**	**14.46**	**0.994**	**0.0747**		**1.21**	**3.48**	**0.986**	**0.0067**	
303	**1.35**	**15.97**	**0.893**	**0.0768**		**1.24**	**5.73**	**0.996**	**0.0032**	
318	**1.38**	**25.84**	**0.876**	**0.0742**		**1.35**	**11.17**	**0.986**	**0.0114**	
Tempkin										
Temp. (K)	K_T **(l $mmol^{-1}$)**	B_T **(mmol g^{-1})**	R^2	**SSE**		K_T **(l $mmol^{-1}$)**	B_T	R^2	**SSE**	
288	**81.94**	**0.3721**	**0.9912**	**0.0052**		**67.07**	**0.20**	**0.974**	**0.012**	
303	**124.44**	**0.3498**	**0.9407**	**0.0368**		**493.66**	**0.12**	**0.894**	**0.0495**	
313	**313.84**	**0.2725**	**0.9412**	**0.0388**		**579.60**	**0.16**	**0.960**	**0.0205**	
R-P										
Temp. (K)	K_R **(l g^{-1})**	a_R **(l $mmol^{-1}$)**	β	R^2	**SSE**	K_R **(l g^{-1})**	a_R **(l $mmol^{-1}$)**	β	R^2	**SSE**
288	**11.37**	**4.75**	**0.999**	**0.9604**	**0.0325**	**4.13**	**2.63**	**0.829**	**0.986**	**0.0056**
303	**20.40**	**13.90**	**0.999**	**0.8930**	**0.0754**	**65.33**	**35.76**	**0.405**	**0.998**	**0.0004**
318	**42.46**	**36.10**	**0.999**	**0.9177**	**0.0626**	**34.45**	**20.04**	**0.696**	**0.992**	**0.0036**

Table 4. Dissociation constants of AN, P, CP and NP compounds.

Compound	**Dissociation reactions**	pK_a	**Reference**
AN	$C_6H_5NH_3^+ + H_2O \approx C_6H_5NH_2 + H_3O^+$	**4.63**	**-**
P	$C_6H_5OH + H_2O \approx C_6H_5O^- + H_3O^+$	**9.95**	**Yu et al. (2004)**
CP	$C_6H_4ClOH + H_2O \approx C_6H_4ClO^- + H_3O^+$	**9.38**	**Yu et al. (2004)**
NP	$C_6H_4(NO_2)OH + H_2O \approx C_6H_4(NO_2)O^- + H_3O^+$	**7.15**	**-**

Table 5. Hammett constant for phenol and its substitution compound (Vasudevan, and Stone, 1996; Dean, 1999).

Group	**Hammett constant (σ)**
OH	**0**
-Cl	**0.23**
$-NO_2$	**1.25**

Table 6. Thermodynamic parameters of the adsorption of AN, P, CP and NP onto GAC.

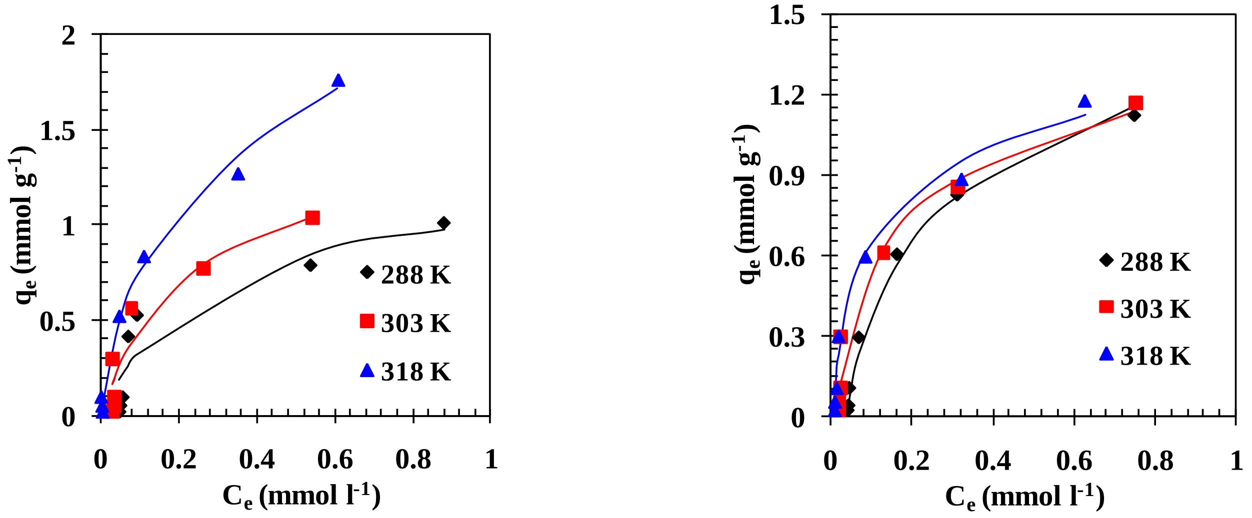
Temp. (K)	K_D **(l g^{-1})**	ΔG_0 **(kJ mol^{-1})**	ΔH_0 **(kJ mol^{-})**	ΔS_0 **(J mol^{-1} K^{-1})**	K_D **(l/g)**	ΔG_0 **(kJ mol^{-1})**	ΔH_0 **(kJ mol^{-1})**	ΔS_0 **(J mol^{-1} K^{-1})**
	AN-GAC				**P-GAC**			
288	**0.295**	**-13.62**	**48.48**	**214.69**	**0.365**	**-14.13**	**43.50**	**200.02**
303	**0.585**	**-16.05**			**0.894**	**-17.12**		
318	**2.01**	**-20.11**			**2.023**	**-20.13**		
	CP-GAC				**NP-GAC**			
288	**1.53**	**-17.56**	**26.73**	**152.52**	**1.523**	**-17.55**	**52.13**	**243.98**
303	**1.68**	**-18.71**			**9.917**	**-23.19**		
318	**4.45**	**-22.22**			**11.54**	**-24.74**		

Table 7. Correlation of adsorption coefficients with solvatochromic parameters.

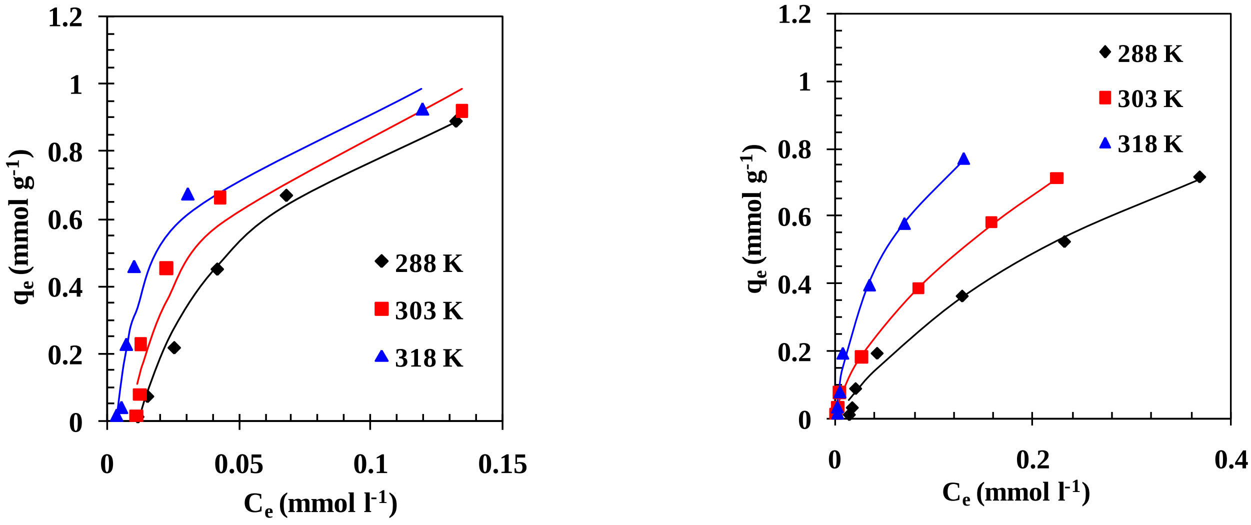
Temp. (K)	Linear equation	R^2	Quadratic equation	R^2
Hydrogen-bonding acceptor parameter (β_m)				
288	$K_D=1.664\beta_m-0.057$	0.593	$K_D=-1.8943\beta_m^2+4.613\beta_m-1.1255$	0.786
303	$K_D=10.54\beta_m-2.978$	0.573	$K_D=36.08\beta_m^2-35.478\beta_m+8.8603$	0.994
318	$K_D=11.08\beta_m-1.561$	0.620	$K_D=27.035\beta_m^2-22.198\beta_m+6.388$	1.000
Hydrogen-bonding donor parameter (α_s)				
288	$K_D=2.052\alpha_s-0.385$	0.761	$K_D=1.2119\alpha_s^2+0.3938\alpha_s+0.1764$	0.613
303	$K_D=13.3\alpha_s-5.242$	0.769	$K_D=36.852\alpha_s^2-28.09\alpha_s+4.1445$	0.999
318	$K_D=14.35\alpha_s-4.179$	0.876	$K_D=34.57\alpha_s^2-25.158\alpha_s+5.1203$	0.986
Intrinsic molar volume (cm^3/mol) (V_I)				
288	$K_D=63.98V_I-33.29$	0.873	$K_D=-0.4863\times10^{-4}V_I^2+0.069V_I-22.764$	0.842
303	$K_D=58.95V_I-32.29$	0.758	$K_D=8.0117\times10^{-4}V_I^2-0.92V_I+264.28$	0.991
318	$K_D=9.43V_I-4.76$	0.805	$K_D=5.9503\times10^{-4}V_I^2-0.66V_I+186.67$	0.999
Polarity /Polarizability parameter (π)				
288	$K_D=0.915\pi-0.338$	0.012	$K_D=-141.2\pi^2+179.02\pi-55.057$	0.949
303	$K_D=15.56\pi-6.574$	0.085	$K_D=-418.33\pi^2+543.24\pi-170.87$	0.283
318	$K_D=16.25\pi-5.461$	0.091	$K_D=-549.21\pi^2+709.01\pi-220.93$	0.425

Table 8. Isosteric enthalpy of AN, P, CP and NP onto GAC.

	$\Delta H_{st,a}$ (kJ mol^{-1})	R^2		$\Delta H_{st,a}$ (kJ mol^{-1})	R^2
q_e (mmol g^{-1})	**AN-GAC**		q_e (mmol g^{-1})	**P-GAC**	
0.4	58.45	0.8835	0.3	25.47	0.9969
0.8	53.73	0.9181	0.6	16.36	0.9976
1.2	48.99	0.9532	0.9	11.02	0.9984
1.6	44.27	0.9839	1.2	7.24	0.9994
2	39.53	0.9998	1.5	4.30	1.0000
q_e (mmol g^{-1})	**CP-GAC**		q_e (mmol g^{-1})	**NP-GAC**	
0.25	27.71	0.9568	0.25	42.98	0.9854
0.5	21.55	0.9762	0.5	34.47	0.9819
0.75	15.38	0.9970	0.75	29.49	0.9787
1	9.21	0.9679	1	25.97	0.9755
1.25	3.04	0.3443	1.25	23.22	0.9721

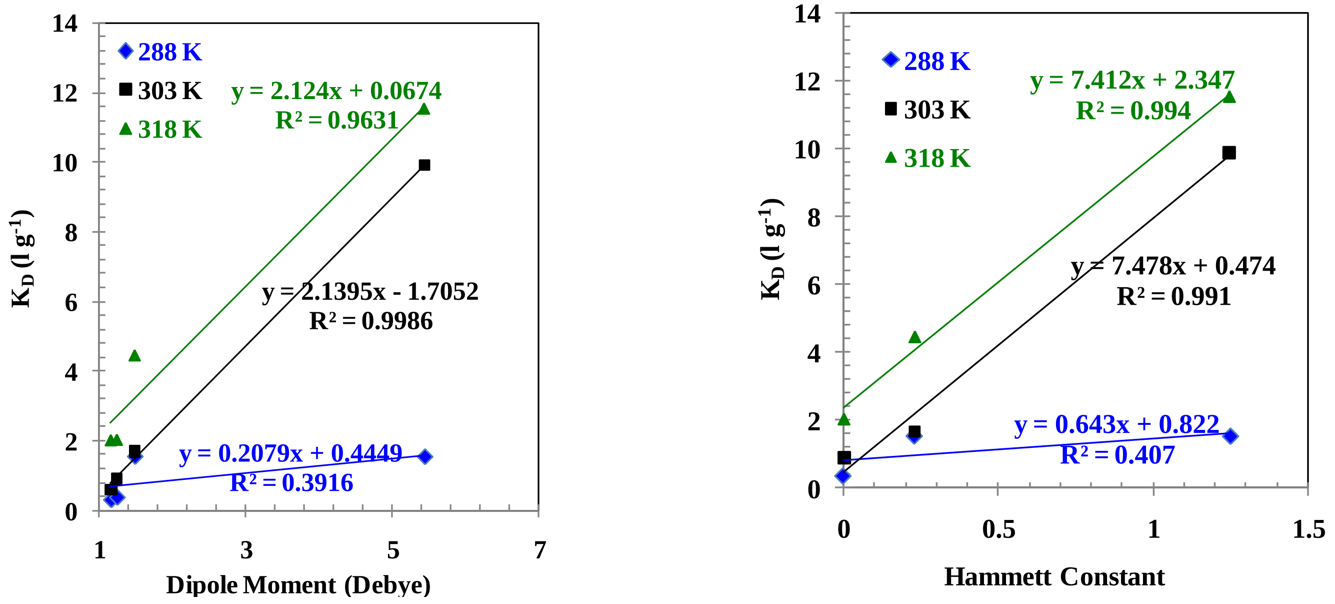


(a) AN-GAC **(b) P-GAC**



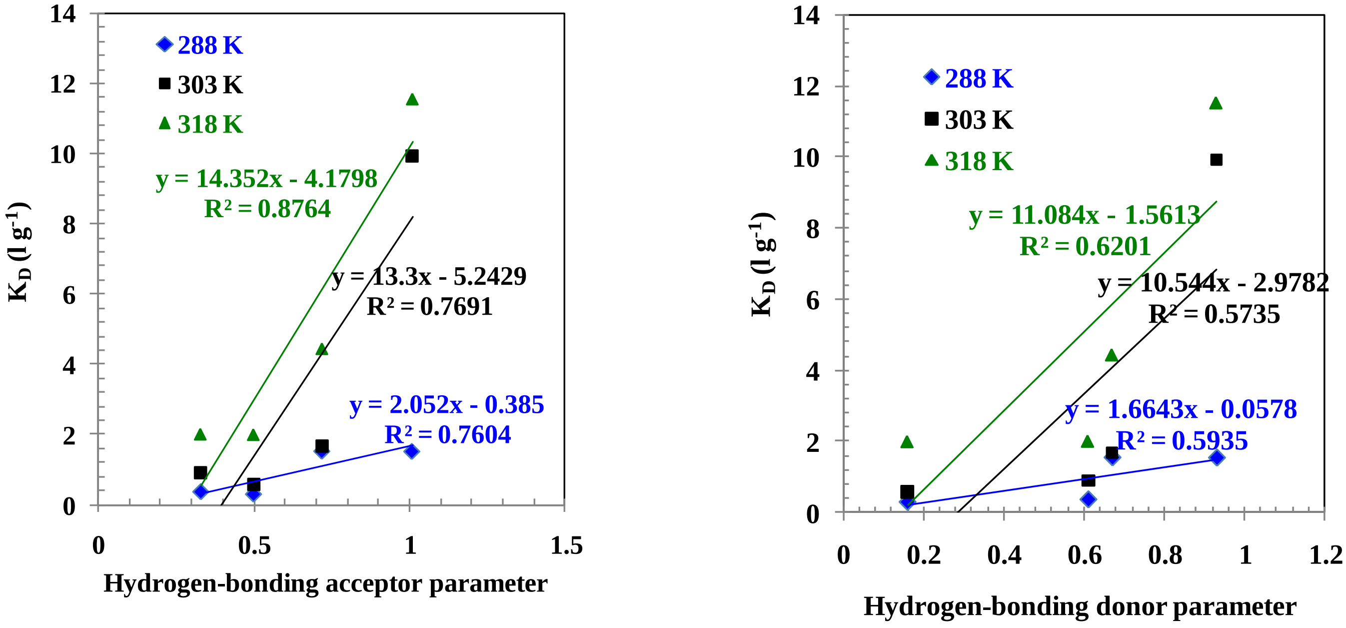
(c) CP-GAC **(d) NP-GAC**

Figure 1. Equilibrium adsorption isotherms at different temperature. (a) AN-GAC system, lines fitted by R-P model; (b) P-GAC system, lines fitted by Tempkin model; (c) CP-GAC system, lines fitted by Tempkin model; and; (d) NP-GAC system, lines fitted by R-P model.

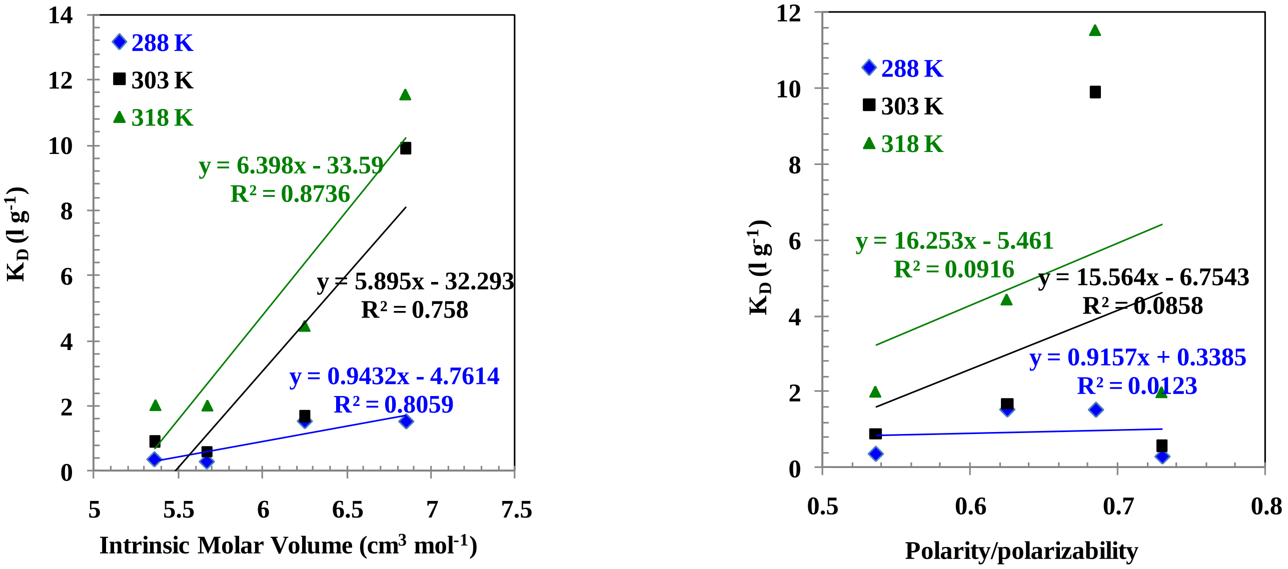


(a) Dipole Moment **(b) Hammett Constant**

Figure 2. Variation of adsorption coefficients with dipole moment and Hammett constant.



(a) Hydrogen-bonding acceptor parameter **(b) Hydrogen-bonding donor parameter**



(c) Intrinsic Molar Volume (cm^3 mol^{-1}) **(d) Polarity/polarizability**

Figure 3. Effect of solvatochromic parameters on adsorption coefficients at different temperatures.

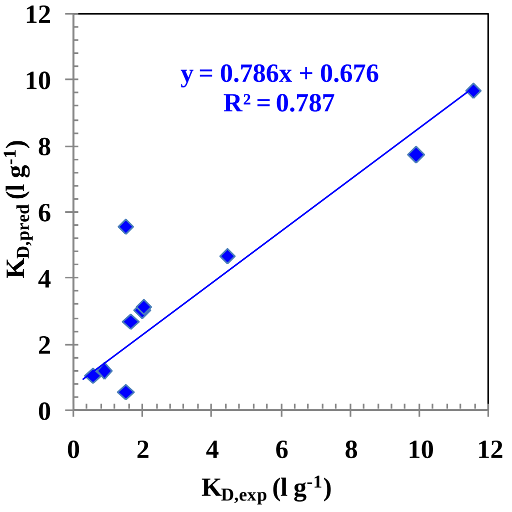


Figure 4. Correlation between experimental and predicted K_D values given by Eq. (11).

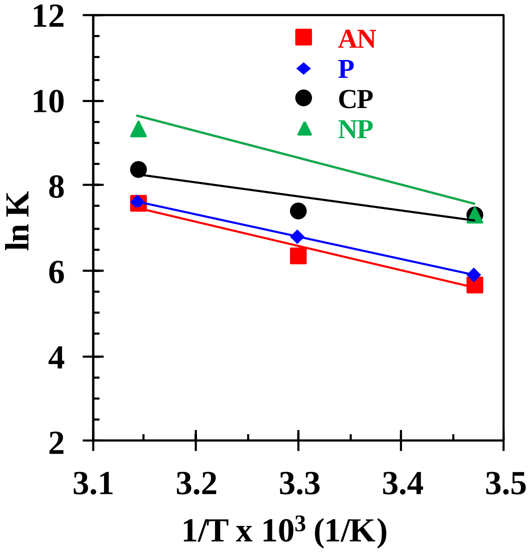
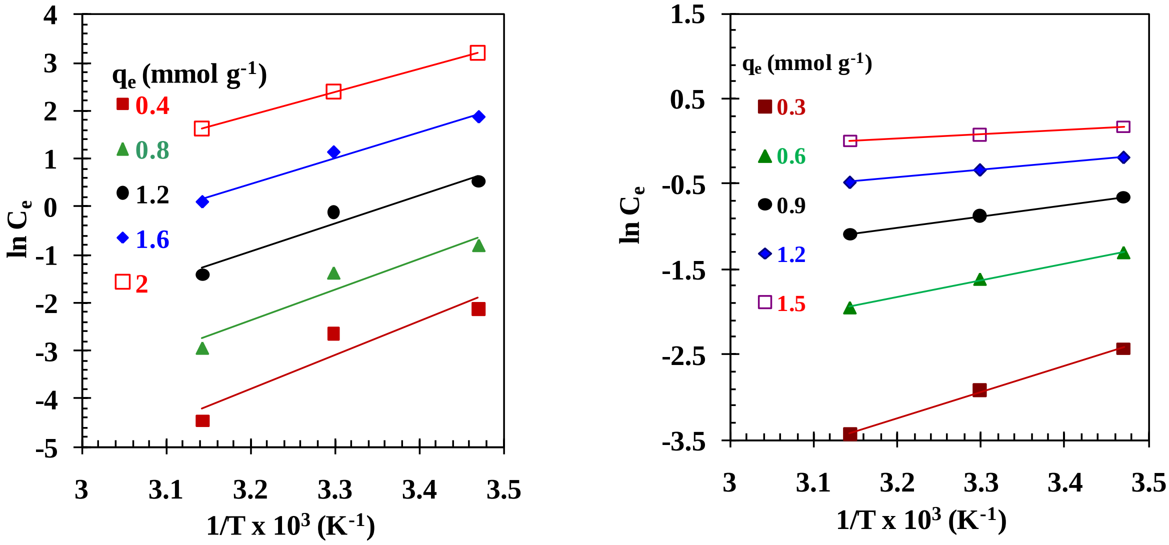
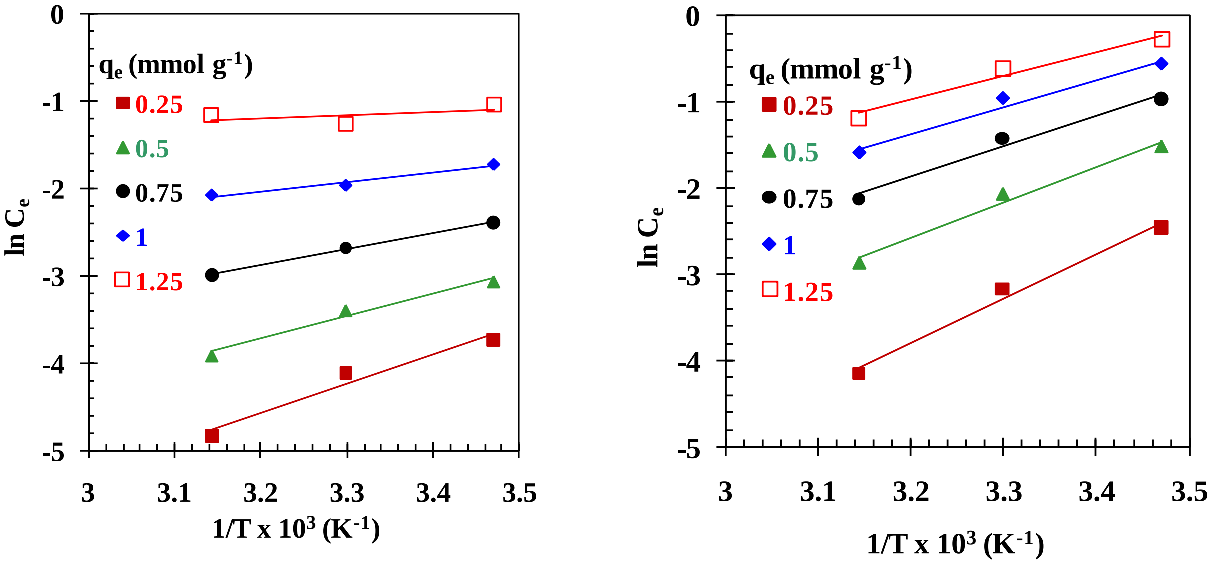


Figure 5. Van't Hoff Plot of adsorption equilibrium constant K for AN, P, CP and NP.



(a) AN-GAC

(b) P-GAC



(a) CP-GAC

(b) NP-GAC

Figure 6. Adsorption isosters for determining isosteric heat of adsorption for AN, P, CP and NP adsorption onto GAC.

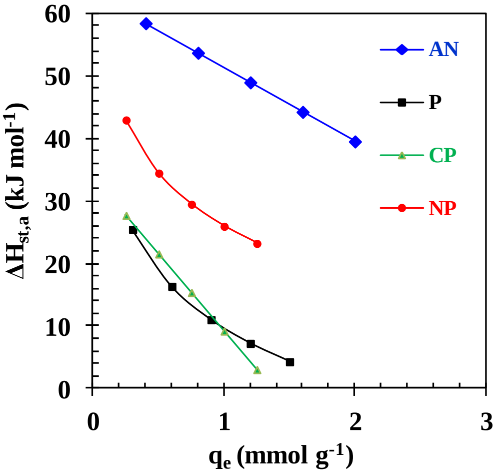


Figure 7. Variation of $\Delta H_{st,a}$ with respect to surface loading for AN, P, CP and NP adsorption onto GAC.

4. CONCLUSIONS

In the presented study, Redlich-Peterson model represented the equilibrium data very well for AN and NP. However, Temkin model was the best for P and CP. Adsorption of AN, P, CP, and NP onto GAC was found to be endothermic in nature. The negative value of ΔG_0 indicated the feasible and spontaneous adsorption of AN, P, CP and NP adsorption onto GAC. Solvatochromic parameters like intrinsic molar volume (V_I), the polarity/polarizability parameter (π), the hydrogen-bonding donor parameter (α_s) and hydrogen-boding acceptor parameter (β_m) were used to predict adsorption coefficient (K_D) values. The linear solvation energy relationships (LSER) models based on solvatochromic parameters were used to predict the adsorption coefficient (K_D) values. This study shows that the V_I and hydrogen bonding plays an important roles in the adsorption behavior of AN, P, CP and NP onto GAC.

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