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Determination of Thermodynamic Parameters of Phenol Adsorption onto Sewage Sludge based Adsorbent by different Methods

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Abstract

The aim of this study is the determination of thermodynamic parameters of the adsorption of phenol onto sewage sludge based adsorbent (SSBA) by different methods. Thermodynamic parameters are calculated from three equilibrium constants (K_c) that were derived from the isotherm constants of Langmuir (K_L), the distribution coefficient (K_d) and Freundlich isotherm exponent (n). For this, removal of phenol from aqueous solutions by adsorption under batch equilibrium experimental conditions at 293, 303 and 328 K was investigated. All values obtained for ΔG° are negatives this indicated that the adsorption process of phenol on the SSBA is spontaneous and thermodynamically feasible process.

We also note that as the temperature increases, the absolute value of ΔG° decreases, it shows that the adsorption is more spontaneous at low temperatures. All values of the standard enthalpy ΔH° are negative and less than 35 kJ.mol^{-1} which confirm that the process is an exothermic physisorption. The negative values of the standard entropy ΔS° clearly show that the arrangement of phenol molecules is more preferred on the surface of the adsorbent.

Keywords: Thermodynamic parameters, phenol, adsorption, sewage sludge.

Introduction

Adsorption is an important technique used for the removal of low concentrations of organic or inorganic pollutants from large volumes of potable water, process effluents, wastewater and aqueous solutions[8]. Thermodynamics studies play an important role in thoroughly understanding the types and mechanisms of the adsorption process under variations of the solution temperature[14]. Generally, the sorption of chemical compounds (gas or liquid) on the surface of solid can be described by an equilibrium between the adsorption reaction and the inverse reaction of desorption. Like any other chemical reaction, the Gibbs free energy change of adsorption (ΔG) is the difference between the free energy of the products minus the free energies of the reagents. At the beginning of the adsorption reaction, ΔG is negative, but at the equilibrium, ΔG becomes zero because the free energy of adsorption is the same in both phases (solid and fluid). In fact, thermodynamic parameters of adsorption such as the standard Gibbs free energy (ΔG°), the standard enthalpy (ΔH°) and the standard entropy (ΔS°) are evaluated at equilibrium. The value of ΔG° can be determined according to the equilibrium thermodynamic constant (K_c) which is a key toward correct estimates of all thermodynamic parameters [6].

In recent years, researchers are paying more attention to the estimation of thermodynamic parameters in liquid-phase adsorption and especially in the correct calculation of the free energy change[3], thermodynamic equilibrium constant [1,11] and the unit problem in thermodynamic calculation[16].

In this context, the aim of this study is to compare the values of thermodynamic parameters calculated from three thermodynamic equilibrium constants (K_c) that were derived from the isotherm constants of Langmuir (K_L), the distribution coefficient (K_d) and Freundlich isotherm exponent (n). Based on the estimated thermodynamic parameters adsorption mechanisms of phenol onto sewage sludge based adsorbent (SSBA) were also discussed.

Material and Methods

Sewage sludge based adsorbent was prepared by a chemical activation using sulphuric acid H_2SO_4. Procedure of activation is reported in our previous work[3]. The experimental solutions of phenol of various initial concentrations (C_0) were prepared by diluting the stock solution of 1 g.L^{-1} to the desired concentrations. Adsorption was carried out at three different temperatures 20, 30 and 55 °C respectively and under atmospheric pressure in batch conditions. Adsorption was performed by introducing 100 mg of sewage sludge based adsorbent (SSBA) into brown dark bottles, containing 20 mL of phenol solution with initial concentrations of 40–200 mg.L^{-1}. The mixture was stirred with a magnetic agitation at 300 rpm until equilibrium was reached.

Then, the separation was effectuated by centrifugation at 3000 rpm during 15 min and the suspension was analyzed by UV–Vis spectrophotometer, Shimadzu, model UV-160 at wave length of 270 nm to determine the residual concentration of phenol. In our previous work[4], we have

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shown that at pH<pKa, phenol adsorption onto SSBA is pH independent, for this reason all experiments were performed at free solution pH.

Results and Discussion

Effect of temperature: Adsorption data are generally described by adsorption isotherms such as the Langmuir and Freundlich isotherms[9]. These isotherms relate the amount of solute adsorbed at equilibrium per mass of adsorbent (called also adsorption capacity) q_e ($mg.g^{-1}$). The adsorbate concentration at equilibrium (called also residual concentration) C_e ($mg.L^{-1}$). The effect of temperature was evaluated in the case of phenol adsorption on the SSBA for three different temperatures (293, 303 and 328 K). Figure 1 shows that the phenol adsorption capacity decreases with the increase of the temperature of the system, indicating that the adsorption process of phenol on the SSBA is exothermic.

This conclusion is confirmed by the calculation of the standard enthalpy of adsorption $\Delta H°$. The results obtained show that the phenol is better adsorbed at room temperature (20°C) which is adequate in the case of the treatment of domestic wastewater effluents where the water temperature is below 20°C.

Thermodynamic parameters: The standard Gibbs free energy change $\Delta G°$ plays an important role in understanding about the spontaneous occurrence of adsorption process at a given temperature; $\Delta G°$ can be calculated by the following relationship:

$$\Delta G° = -RT \ln (K_c/K_c°) \quad (1)$$

where R is the universal gas constant ($8.314\ J.mol^{-1}.K^{-1}$), T is the absolute temperature in Kelvins, K_c is the equilibrium constant and $K_c°$ is the equilibrium constant at the standard or reference state.

In the equation 1, K_c and $K_c°$ must have the same dimensions and the same units and if we chose arbitrary, the value of the equilibrium constant at the reference state $K_c°$ is equal to unity ($K_c° = 1$). Then the equation becomes:

$$\Delta G° = -RT \ln (K_c) \quad (2)$$

From the equation (2), it is clear that the magnitude and sign of $\Delta G°$ depend directly on the value of K_c. For $K_c>1$, the value of $\Delta G°$ is negative and the adsorption process occurs favourably and spontaneously, for $K_c<1$, the value of $\Delta G°$ is positive and the adsorption process is non-feasible and non-spontaneous. The nature of the adsorption process is also affected by the standard enthalpy change ($\Delta H°$) which provides information about the energy release during adsorption process (exothermic process or endothermic process). The standard entropy change ($\Delta S°$) indicates that if the randomness increases, the value is positive. If it decreases, the value is negative. The relation of $\Delta G°$ with $\Delta H°$ and $\Delta S°$ is generally expressed as:

$$\Delta G° = \Delta H° - T\Delta S° \quad (3)$$

According to equation (3), $\Delta G°$ will always be negative at any given temperature of a system with negative values of $\Delta H°$ and positive values of $\Delta S°$. Thus, knowledge of the signs of various thermodynamic parameters is highly important in determining the spontaneity of a given process.

The knowledge of the value of the thermodynamic equilibrium constant K_c at least for three different temperatures can easily calculate the value of $\Delta G°$ for each temperature. The determination of $\Delta H°$ and $\Delta S°$ can be performed graphically by the plot of Van't Hoff diagram as in equation (4):

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (4)$$

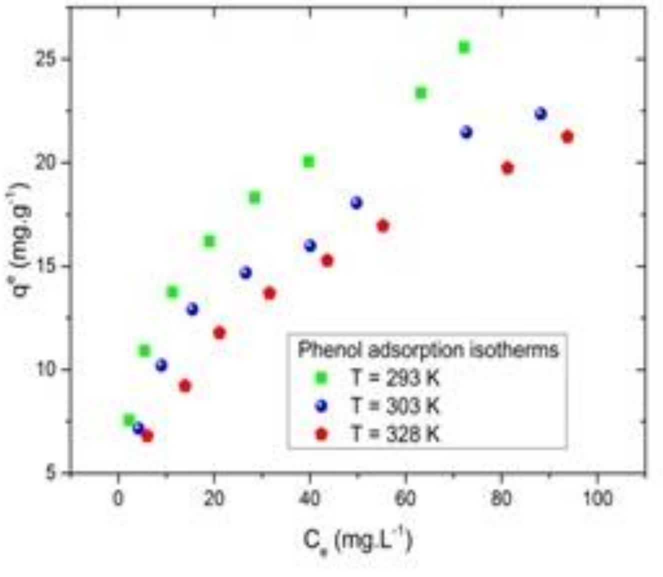

Fig. 1: Effect of temperature on the adsorption capacity of phenol onto SSBA

Although the approach for the determination of thermodynamic parameters is fairly easy, the major problem lies with the determination of the thermodynamic equilibrium constant K_c.

In this work, three different methods for the calculation of thermodynamic equilibrium constant K_c are shown as well as the results obtained by each method in the case of the adsorption of phenol on the SSBA. At the end, a comparison between the results of different methods is made essentially on the basis of the evaluation of the absolute error in the calculation of different parameters.

Method 1: Determination of K_c from the constant K_L of Langmuir isotherm

In this method [13], the thermodynamic equilibrium constant K_c is assumed to be equal to the equilibrium constant K_L of Langmuir isotherm ($L.mol^{-1}$). The value of K_L at the reference state is taken equal to 1 $L.mol^{-1}$ so that equation (2) becomes:

$$\Delta G° = -RT \ln K_L \quad (5)$$

Method 2: Determination of K_c from the distribution coefficient K_d

In this method,[5] the equilibrium constant K_c is assumed to be equal to the distribution coefficient K_d.

$$K_d = q_e/C_e \quad (6)$$

where q_e is the adsorption capacity at the equilibrium in ($mg.g^{-1}$), C_e is the residual concentration of phenol in ($mg.L^{-1}$) and K_d is the distribution coefficient of the adsorption in ($L.g^{-1}$). The value of K_d at the reference state is taken equal to 1 $L.g^{-1}$ so that equation (2) becomes:

$$\Delta G° = -RT \ln K_d \quad (7)$$

Method 3: Determination of K_c from the exponent n of the Freundlich isotherm

In this method[2], the exponent n in the Freundlich isotherm is used for the calculation of the thermodynamic equilibrium constant K_c. n is a dimensionless constant usually used to evaluate the intensity of the adsorption.

$$n = \ln K_c \quad (8)$$

And equation (2) becomes:

$$\Delta G° = -RT(n) \quad (9)$$

The determination of ΔH° and ΔS° can be performed graphically by the approach described above using the plot of Van't Hoff diagram as in eq. 5. ΔH° and ΔS° were obtained from the slope and intercept of Van't Hoff plots[4] of ($\ln K_c$) versus (1/T) where $\ln K_c = \ln K_L$ for the first method, $\ln K_c = \ln K_d$ for the second method and $\ln K_c = n$ for the third method. The Van't Hoff plots are shown in figures 2, 3 and 4 for the first, the second and the third method respectively.

Table 1 shows the calculated values of the thermodynamic parameters for the adsorption of phenol to sewage sludge based adsorbent SSBA.

From table 1, the results obtained for the three thermodynamic parameters ΔG°, ΔH° and ΔS° are different but have the same order of magnitude except for the parameter ΔG° obtained by the first method where the values are considerably higher.

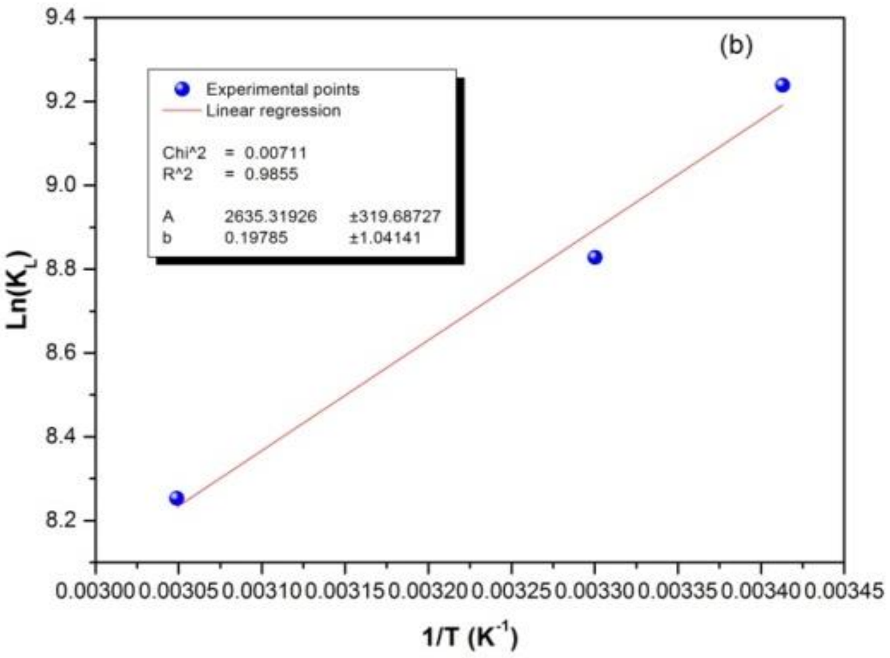

Fig. 2: Van't Hoff diagram of method 1 (K_L constant of Langmuir isotherm)

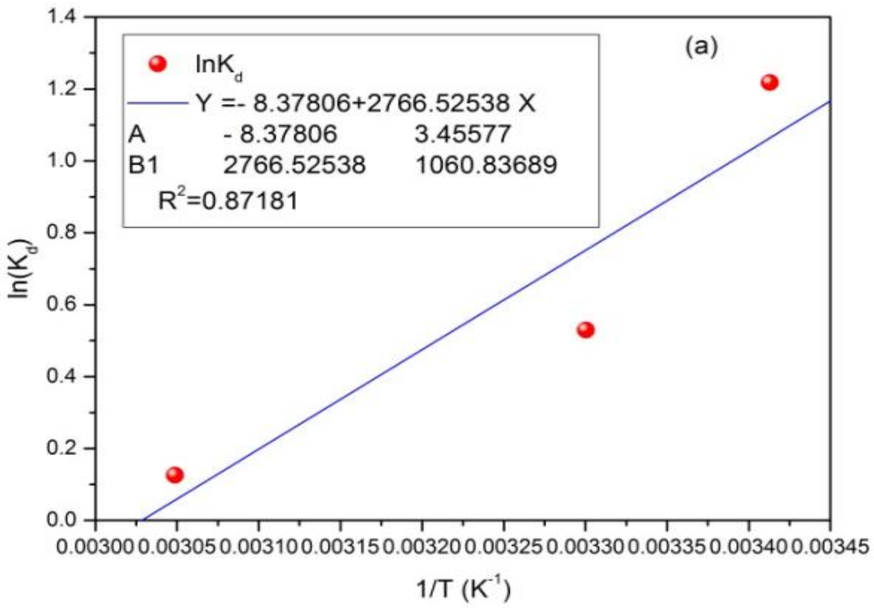

Fig. 3: Van't Hoff diagram of method 2 (distribution coefficient K_d at C_0=40 mg.L^{-1})

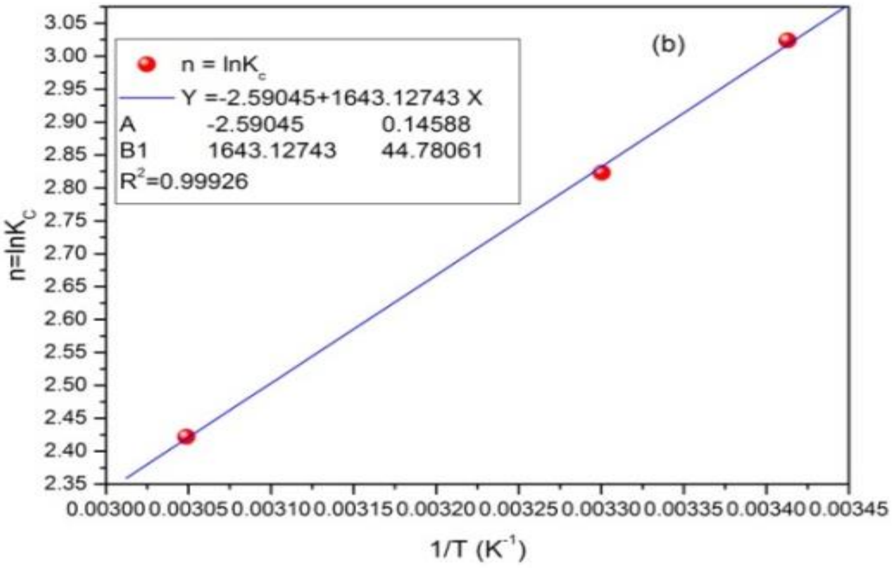

Fig. 4: Van't Hoff diagram of method 3 (Exponent n of Freundlich isotherm)

Table 1
Thermodynamic parameters for the adsorption of phenol onto SSBA by three methods

Thermodynamic parameters	**Temperature (K)**		
	293	**303**	**328**
K_L (L.mol^{-1})	10286	6823	3840
K_d (L.g^{-1})	3.381	1.698	1.134
n	3.024±0.094	2.823±0.143	2.422±0.054
ΔG° (kJ.mol^{-1}) Method 1	-22.505±2.550	-22.239±1.561	-22.506±0.961
ΔG° (kJ.mol^{-1}) Method 2	-8.235	-4.277	-3.091
ΔG° (kJ.mol^{-1}) Method 3	-7.366±0.229	-7.111±0.360	-6.605±0.147
Method used	Method 1	Method 2	Method 3
ΔH° (kJ.mol-1)	-21.910±2.658	-23.001±8.820	-13.661±0.372
ΔS° (J.mol-1.K-1)	0.933±8.646	-69.655±28.733	-21.533±1.214

The estimation of the absolute error made during the calculation of the various parameters is acceptable except in the case of the calculation of ΔS° by the first method where the error is greater than the result, so this result of ΔS° will not be taken into consideration.

Also, it can be seen that the thermodynamic parameters determined by the third method have a lower absolute error. This observation can be explained by the fact that the equilibrium data of phenol adsorption onto SSBA are well represented by the Freundlich isotherm and not by Langmuir isotherm[10].

The ΔG° values obtained are all negative, showing that the process of adsorption of phenol on the SSBA is a spontaneous and thermodynamically possible process. It is also noted that as the temperature increases more, the absolute value of ΔG° decreases, this shows that the adsorption is more spontaneous at low temperature. In general[12], the range of free energy values ΔG° for physisorption is between -20 and 0 $kJ.mol^{-1}$ while for chemisorption is between -80 and -400 $kJ.mol^{-1}$. The ΔG° values obtained by the three methods range from -22.50 $kJ.mol^{-1}$ to -3.09 $kJ.mol^{-1}$, indicating that the adsorption of the phenol on the SSBA is a physisorption.

The negative values of the standard enthalpy ΔH° confirm that the adsorption of phenol on the SSBA is an exothermic process. Concerning the nature of the adsorption, the values of ΔH° obtained are between -23 $kJ.mol^{-1}$ and -13.66 $kJ.mol^{-1}$.

According to Murzin et al[8], for chemisorption the value of ΔH° is between 30 and 70 $kJ.mol^{-1}$ for the molecules and between 100 and 400 $kJ.mol^{-1}$ for the atoms and the value of ΔH° for a physisorption is less than 35 $kJ.mol^{-1}$. This shows that the process of phenol adsorption on SSBA is physical in nature.

On the other hand and according to the heat of adsorption of the different forces[15], the phenol adsorption mechanisms on SSBA are mainly attributed to phenol binding by hydrogen bonding to the adsorbent and to dipolar attractions between phenol and water molecules. The negative value of the standard entropy ΔS° shows clearly that the arrangement of phenol molecules is more orderly on the surface of the adsorbent.

Conclusion

Thermodynamic study of phenol adsorption onto SSBA is carried out according to three different methods. The obtained values of thermodynamic parameters are different but have the same order of magnitude and present a certain coherence about adsorption mechanisms. Thermodynamic parameters estimated by the determination of the thermodynamic equilibrium constant K_c from the exponent n of the Freundlich isotherm (method 3) has the lowest absolute error. The values obtained for ΔG°, ΔH° and ΔS° suggest that the adsorption is physical and that the process is spontaneous and exothermic in nature.

According to the value of ΔH° which is less than 35 $kJ.mol^{-1}$, we can say that the mechanisms of adsorption of phenol on the SSBA are mainly attributed to the binding of phenol by hydrogen bonding with the adsorbent and dipolar attractions between the molecules of phenol and water.

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