

HETEROGENEITY ANALYSIS BASED ON LIQUID-PHASE ADSORPTION OF CHLOROPHENOLS ON ACTIVATED CARBON AND POLYMER RESINS

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Energy distribution function is the fundamental information that describes heterogeneous characteristics of porous solid adsorbents. This study focuses on the analysis of surface energy heterogeneity from the liquid-phase adsorption of chlorophenols (2-CP and 2,4-DCP) on three different adsorbents (F-400, XAD-1600, and XAD-7). The Langmuir-Freundlich isotherm equation was used to estimate the monolayer adsorption capacity of adsorbents studied. The adsorption energy distribution functions were calculated by using the generalized nonlinear regularization method (GENEREG) which is a linear Fredholm integral equation of first kind. Analysis of energy distribution functions of porous sorbents provided significant comparative information of their heterogeneity. Compared to polymeric sorbents, F-400 with relative large surface area and small pore size showed a wide range of adsorption energy. It was also found that the surface energy heterogeneity highly depends on the heterogeneity parameter of isotherm and the structural differences of adsorbates.

INTRODUCTION

Chlorophenols are very useful compounds in various industries such as herbicide, paint, solvent, petrochemical refinery, coal conversion, pharmaceutical, pulp, paper, and chlorination of wastewater. The proper removal or destruction of these materials is of great importance in environmental concern. Among the proposed methods such as biological treatment, solvent extraction, catalytic oxidation, adsorption is a well-established and powerful technique for the removal of effluent pollutants. Activated carbon, activated carbon fiber, and non-ionic polymer resins have been widely used for this purpose. In general, adsorption of organic compounds generally occurs through a variety of physicochemical mechanisms and forces such as van der Waals, dipole-dipole interactions, ion exchange, and covalent bonding. Also, the nature of bonding mechanisms as well as the extent and strength of adsorption depend on the surface chemistry of porous adsorbents and the chemical characteristics of adsorbates including polarity, functional groups, and solubility. Many studies on the adsorption equilibrium, kinetics, and column dynamics have been investigated so far.¹⁻⁵

In order to understand, analyze, and design the adsorption-based process, reliable information of adsorbent is very important. especially, the surface energy heterogeneity is the fundamental and informative data to understand the adsorption properties. Although many studies have been widely focused on the surface energy distribution of gas-solid adsorption, little has been investigated on the adsorption energy distribution of liquid-solid system. Therefore, the ultimate goal of this study is to evaluate the surface energy heterogeneity based on the liquid-phase adsorption equilibrium of two chlorophenols onto three different adsorbents (F-400, XAD-1600, and XAD-7). The adsorption equilibrium isotherms were measured by using

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the static method and the well-known Langmuir-Freundlich isotherm was employed to estimate the value of the monolayer capacity. Adsorption energy distribution functions were calculated based on a generalized nonlinear regularization method (GENEREG).

EXPERIMENTAL

Adsorbates and Adsorbents

The polymeric adsorbents used in this study are XAD-7 and XAD-1600. XAD-7 is hydrophilic and a porous aliphatic matrix resin consisting of cross-linked polymethacrylates. XAD-1600 is hydrophobic and a spherical polystyrene resin cross-linked with divinylbenzene. They were supplied by Rohm and Haas Co. (USA). Coconut-based activated carbon, F400, was purchased from CARGON Co. (USA). The water content of fully swollen resin particles was determined from the weight loss of the samples that occurred while drying in a vacuum oven at 383.15 K for 72 h. The arithmetic average particle diameter was determined by sorting wet resin particles with the aid of an optical microscope. Nitrogen adsorption-desorption was measured on an ASAP 2010 volumetric adsorption apparatus (Micrometrics) at 77.4 K. The surface area was calculated by using the BET method. The pore diameter was obtained from the BJH pore size distribution method. The physical properties of XAD-7, XAD-1600, and F400 are given in Table 1.

Table 1
Physical properties of adsorbents.

Adsorbent	Unit	F-400	XAD-7	XAD-1600
Chemical structure	-	Coal	Aliphatic, methylacrylate	Aromatic styrene-divinylbenzene
Hydrophobicity	-	-	Hydrophilic	Hydrophilic
Particle size	μm	840	430-690	350-450
Particle density	m^3/kg	815	760	459
Particle porosity	-	0.56	0.43	0.55
Moisture holding capacity	%	-	67	69
Surface area	m^2/g	1012	450	840
Average pore diameter	\AA	27	51	63
Specific gravity	-	-	1.05	1.04

Two chlorophenols of 2-chlorophenol (2-CP) and 2,4-dichlorophenol (2,4-DCP) were used for model compounds. They were purchased from Junsei Co. (Japan). The important properties of 2-CP and 2,4-DCP are shown in Table 2. These materials were used without further purification.

Table 2
Properties of adsorbates used in adsorption studies.

	2-CP	2,4-DCP
Formula	$\text{C}_6\text{H}_5\text{ClOH}$	$\text{C}_6\text{H}_3\text{OCl}_2\text{OH}$
Molecular Weight	128.56	163.01
Melting Point	43	45
Boiling Point	217	210
Log(Kow)	2.17	3.23
pK	8.55	7.85
Solubility in water(g/100ml)	2.85	0.45
Specific gravity	1.31	1.38

Equilibrium Experiment

Prior to perform the experiments, the polymeric adsorbents were leached with isopropyl alcohol for 24 h to wet internal pores. Adsorbent particles were loaded in a 0.02 m ID glass column, and a ten-bed volume of sodium hydroxide (0.1N) and HCl (0.1N) were passed through the column successively at a flow rate of $1.0 \times 10^{-4} \text{ m}^3/\text{min}$ in order to remove the impurities. Finally, a twenty bed-volume of distilled and deionized water was passed through at the same flow rate to rinse off HCl. The experiments were carried out by contacting a given amount of adsorbent with adsorbate solution of 1–8 mol/m^3 in an incubator shaking at a constant temperature (298.15 K). The dry base weight of the adsorbent was measured after drying hrs in a vacuum oven at 383.15 K for 48. After the equilibrium was reached, the excess 2-CP and 2,4-DCP lefts in solutions were analyzed by using UV spectrometry (Varian, model DMS 100s). The adsorption capacity of activated carbon and the polymeric adsorbents was determined according to

$$q = \frac{V(C_0 - C)}{w} \quad (1)$$

where C_0 and C are the initial and equilibrium liquid-phase concentrations, respectively, V is the volume of solution, and w is the weight of dry adsorbents.

RESULTS AND DISCUSSION

Adsorption Equilibrium Isotherm

Adsorption equilibrium isotherm data is very important and essential information for characterizing, analyzing and understanding an adsorption system. In general, adsorption capacity is closely related with the properties of adsorbate and adsorbent such as molecular size, solubility, functionality, and polarity. Previous studies have shown that the adsorption capacity of phenolic compounds on activated carbon highly depends on the surface functional groups connected with dispersive and electrostatic interactions.⁶⁻⁸ In the case of polymeric adsorbents, the dispersive force between the adsorbate and the polymer resin is main factor to adsorb the organic molecules. The adsorption equilibrium data of 2-CP and 2,4-DCP on two polymer resins (XAD-7 and XAD-1600) and activated carbon (F-400) at 298.15 K are presented in Fig. 1. It was found that the adsorption capacity of two chlorophenols on a given sorbent with respect to a mass basis was $F-400 > XAD-1600 > XAD-7$. In addition, adsorption capacity of 2,4-DCP having relatively high $\log K_{ow}$ (*i.e.*, high hydrophobicity) on all sorbents was greater than that of 2-CP. It implies that the adsorption capacity of activated carbon and nonionic polymeric sorbents is closely connected with the hydrophobicity of adsorbate. These results are similar to that of the previous reports.⁹

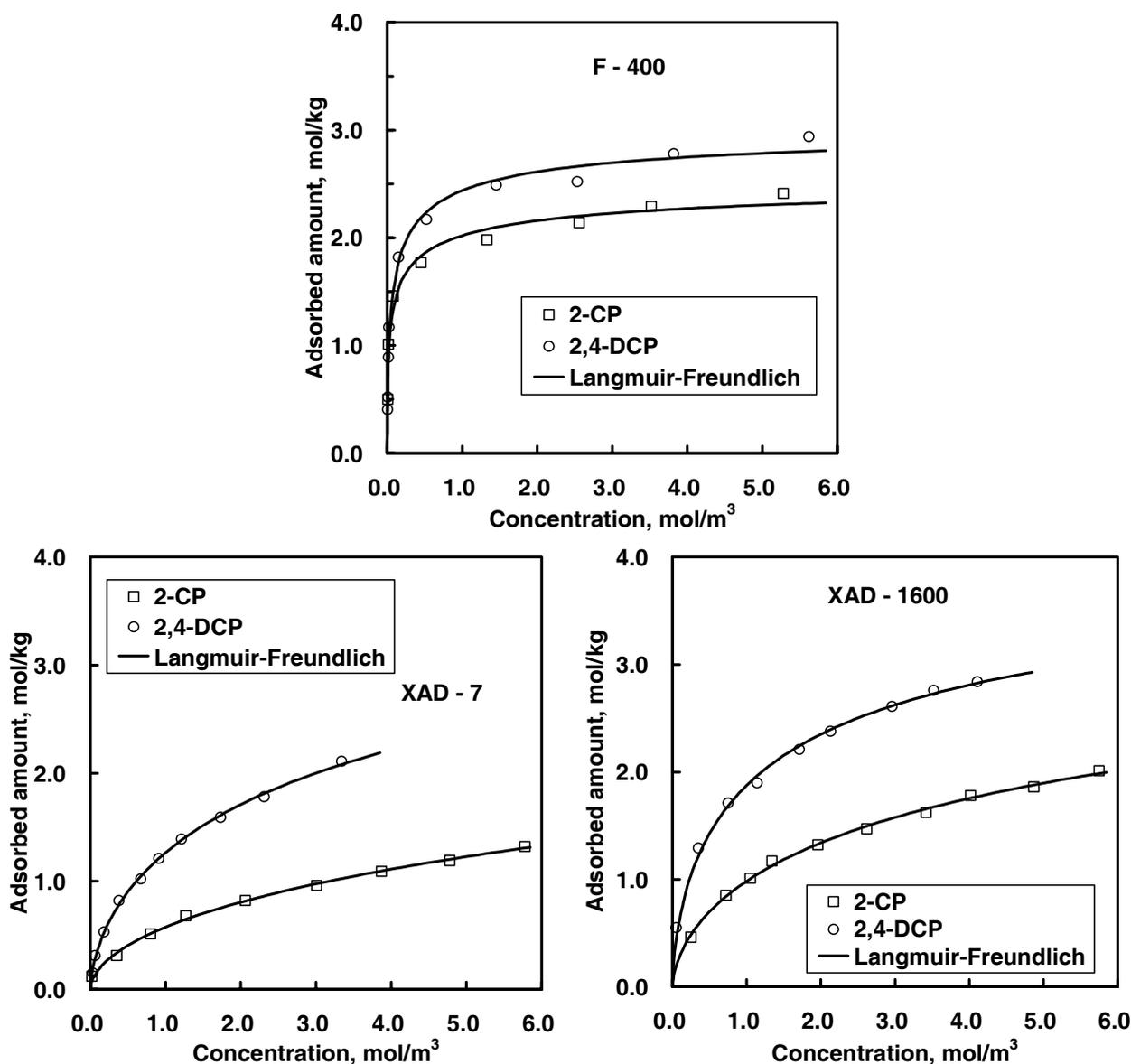


Fig. 1 – Adsorption equilibrium isotherms of 2-CP and 2,4-DCP on different adsorbents at 298.15K

For the proper selection of adsorption isotherm equation is very important to analyze the heterogeneous adsorption systems. In general, Langmuir isotherm has been extensively used to determine the monolayer amount in aqueous adsorption systems. However, Podkoscielny *et al.* (2003) have reported Langmuir-Freundlich isotherm equation could be more reasonable for estimating the monolayer capacity of liquid sorption and correlating experimental adsorption data. Therefore, in the present study, Langmuir-Freundlich equation seems to be proper for approximating the most adsorption systems having quasi-Gaussian energy distribution to describe the adsorption isotherm data and surface heterogeneity.⁶ The Langmuir-Freundlich equation is as follows:

$$\theta = \frac{n}{n_0} = \frac{(Kc)^m}{1 + (Kc)^m} \quad (2)$$

where θ is the fractional coverage, n is the adsorbed amount, n_0 is the monolayer adsorption capacity, K is the equilibrium constant, c is the solute equilibrium concentration, and m is the system heterogeneity parameter. When the heterogeneity parameter, m , approaches unity, this equation reduces to the famous Langmuir isotherm (i.e., homogeneous adsorption).

To determine the optimum adsorption equation parameters, in the present work, Nelder-Mead simplex method was used using pattern search algorithm. Here, the object function is based on the square of residuals (SOR), which is the magnitude of the determined value that is closely related to the accuracy of fit and the number of experimental points.¹⁰ The SOR is expressed as follows:

$$SOR = \frac{1}{2} \sum (N_{exp} - N_{cal})^2 \quad (3)$$

where N_{cal} and N_{exp} are the calculated and experimental amounts adsorbed, respectively. The determined adsorption isotherm equation parameters and SOR values of selective systems are listed in the Table 3.

Table 3
Adsorption isotherm parameters of two chlorophenols on different adsorbents at 298.15 K.

Sorbate	Sorbent	Parameters			SOR
		n_0	K	m	
2-CP	F-400	2.651	13.162	0.452	0.054
	XAD-7	6.268	0.015	0.547	0.002
	XAD-1600	4.206	0.145	0.614	0.003
2,4-DCP	F-400	3.108	11.193	0.535	0.059
	XAD-7	4.941	0.179	0.621	0.002
	XAD-1600	4.340	0.650	0.636	0.012

The solid lines shown in Fig. 1 are the predicted results by the Langmuir-Freundlich (L-F) equation. As shown in this figure, the proposed model describes the experimental data reasonably well for the whole systems. The obtained heterogeneity parameters from the adsorption of XAD-7 and XAD-1600 are 0.547 and 0.614 for 2-CP and 0.621 and 0.636 for 2,4-DCP, respectively. On the other hand, the values of heterogeneity parameters from the adsorption of activated carbon are 0.452 for 2-CP and 0.535 for 2,4-DCP. It was also found that the extracted adsorption heterogeneity values (m) for two chlorophenols decreased in the order, XAD-1600 > XAD-7 > F-400. It suggests that the polymeric adsorbents are energetically more homogeneous than the activated carbon.

Adsorption Energy Distribution Function

Since the porous materials have different structural, textural, and chemical properties, the behaviors of adsorption onto sorbents are very complex and highly depend on the adsorption systems consisting of the adsorbate and the adsorbent. Adsorption energy distributions have been extensively applied for characterizing the numerous adsorption systems and understanding the surface energy heterogeneities concerned physico-chemical networks.

Experimental adsorption isotherm data including a theoretical local adsorption isotherm equation and an adsorption energy distribution function, are crucial factors for characterizing the surface energy heterogeneity of adsorbent.^{11,12} The overall adsorption isotherm on the heterogeneous solid surface can be written in the form of

$$\theta_T(p) = \int_{\Delta} \theta_L(p, U) \cdot F(U) dU \quad (4)$$

where p is the equilibrium pressure, Δ is the integration region, U is the adsorption energy, $F(U)$ is the wanted energy distribution function, $\theta_L(p, U)$ is a local adsorption isotherm and $\theta_T(p)$ is the experimental adsorption isotherm data. This is the well-known linear Fredholm integral equation of the first kind and the calculation of adsorption energy distribution is a wrong approach of the problem. There are some difficulties in solving the equation since (i) a small variations of the adsorption isotherm data with inevitable experimental errors may lead to the large changes in the energy distribution function, and (ii) a large set of possible solutions to this equation can produce a distorted result. Therefore, several techniques, namely, 1) analytical methods, 2) numerical methods (*i.e.*, iterative, regularization, and integral transformation), and 3) local adsorption isotherm approximation methods, have been widely developed to get a proper and a stable solution of the linear Fredholm integral equation. Among them, the regularization method has been extensively studied for obtaining a reliable and stable adsorption energy distribution. For the current work, we investigated the GENEREG based on smoothness constraint (Tikhonov regularization) and edge preserving regularization methods. Thus, the GENEREG can avoid the difficulties that result from the ill-posed nature of an adsorption integral equation.¹³ The local adsorption isotherms such as Langmuir, Volmer, Fowler-Guggenheim, Hill-de Boer, and BET equations are frequently applied for evaluating the adsorption energy distribution in gas phase.^{11,12} On the other hand, the fundamental adsorption integral equation of the dilute solutions on energetically heterogeneous solid surfaces is given as follows:^{6,14}

$$\theta_T(c) = \int_{E_{12\min}}^{E_{12\max}} \frac{\Phi x \exp(E_{12}/RT)}{1 + \Phi x \exp(E_{12}/RT)} F(E_{12}) dE_{12} \quad (5)$$

where $\theta(p)$ is the total fractional coverage, E_{12} is the energy difference of components, $\Phi = \Phi(c, \theta_T)$ is a model dependent function (*i.e.*, the molecular interactions between bulk and surface phases), $F(E_{12})$ is the energy distribution function, $x = \frac{c}{c_{sol}}$, where c_{sol} is the solubility of adsorbate, R is the gas constant, and T is the absolute temperature. The function (Φ) is closely related with the model of the bulk and surface phases and the surface topography.

To verify the possibility of the GENEREG as a reliable solution technique, the energy distribution was compared for a representative energy distribution having three gaussian peaks. Here, Langmuir local adsorption isotherm and simulated adsorption experimental data were used for this purpose.¹⁵ The postulated distribution function with the three gaussian energy distribution peaks are presented in Fig. 2.

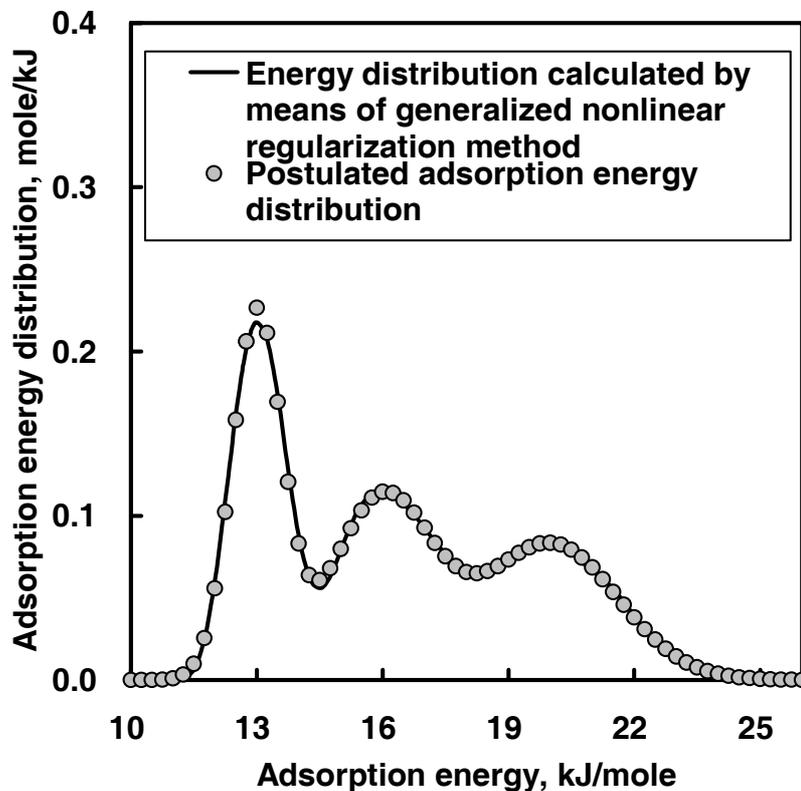


Fig. 2 – Comparison of postulated and calculated energy distributions.

The energy distribution function was calculated with GENEREG using the regularization parameter $\alpha = 1 \times 10^{-3}$. As shown in this figure, the obtained result is reasonably well consistent with the simulated data. This result confirms that GENEREG method is also a very reliable one for treating the adsorption surface heterogeneity such as INTEG and CONTIN.^{16,17} Fig. 3 shows the influence of the heterogeneity parameter on the adsorption energy distribution. The reference adsorption equilibrium isotherm parameters used are $K=11.193$ and $m=0.535$. For smaller value of the heterogeneity parameter (m), the calculated adsorption energy peaks become divided into three main peaks and covered a larger adsorption energy area. As the value of heterogeneity parameter (m) increased (*i.e.*, close to unity), the energy distribution function showed narrower and sharper peak which indicates a decrease of the energetic heterogeneity of adsorbents studied.

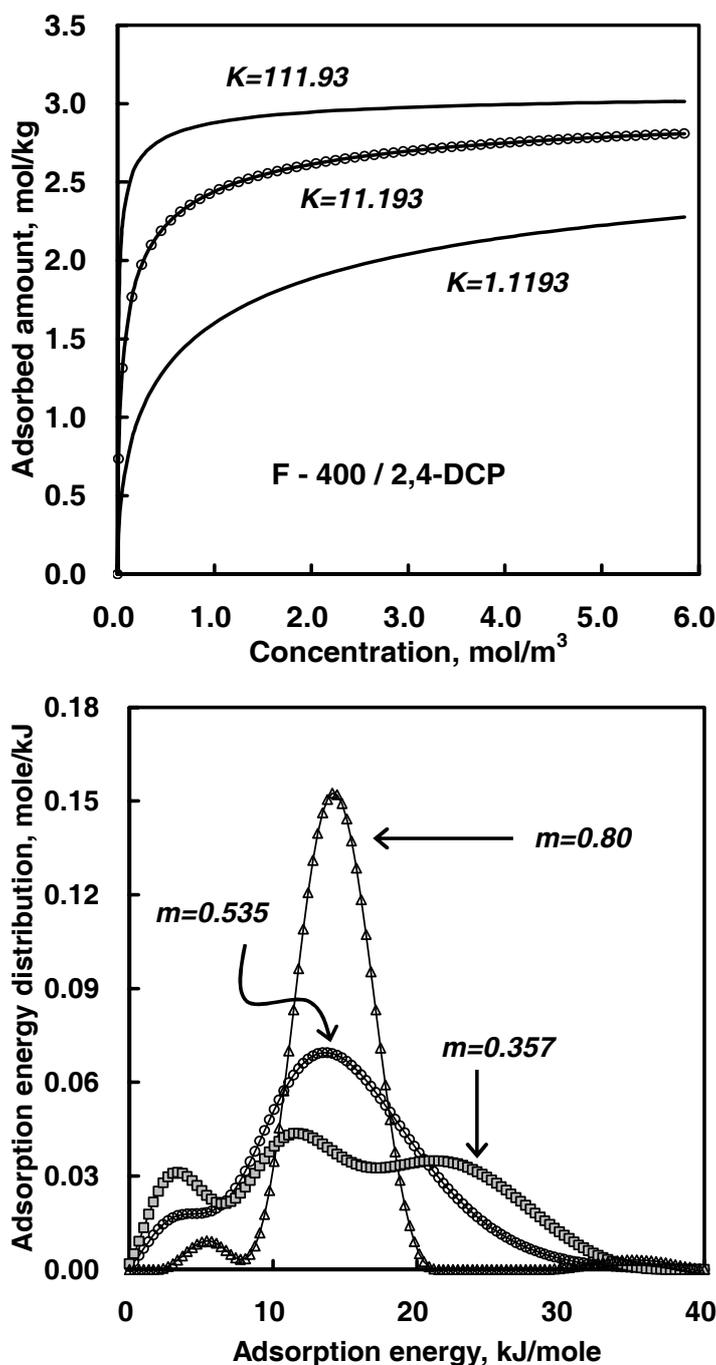


Fig. 3 – Effect of heterogeneity parameters on the adsorption energy distribution of 2,4-DCP on activated carbon (F-400).

The adsorption energy distribution of 2-CP(top) and 2,4-DCP(bottom) on three different adsorbents is presented in Fig. 4. The energy distribution curves are calculated using the generalized regularization method

with the regularization parameter $\alpha = 1 \times 10^{-1}$ and experimental data up to the monolayer adsorption amount. The symbols represent the obtained distribution curves of F-400 (circle), XAD-1600 (triangle), and XAD-7 (rectangle), respectively. The adsorption energy distribution curves of 2-CP for two polymeric adsorbents have the single peak while activated carbon exhibits two peaks. The highest adsorption energy peaks for XAD-1600 and XAD-7 were found to be around 9.08 and 8.07 kJ/mol, respectively. In addition, F-400 has the two main adsorption energy peaks. For example, the calculated high-energy peak is located at 9.08 kJ/mol and the maximum of low energy peak reveals at 29.6 kJ/mol. Also the energy intensity of the second peak is about 1.34 times lower than that of the first. In the case of 2,4-DCP, however, the patterns of energy distribution are reversed. In other words, number of adsorption energy distribution curves of F-400 decreased from two to one and polymeric adsorbents have the two main energy peaks compared to the results of 2-CP. As shown in Fig. 4 (bottom), the adsorption energy peak for F-400 appeared at 14.8 kJ/mol.

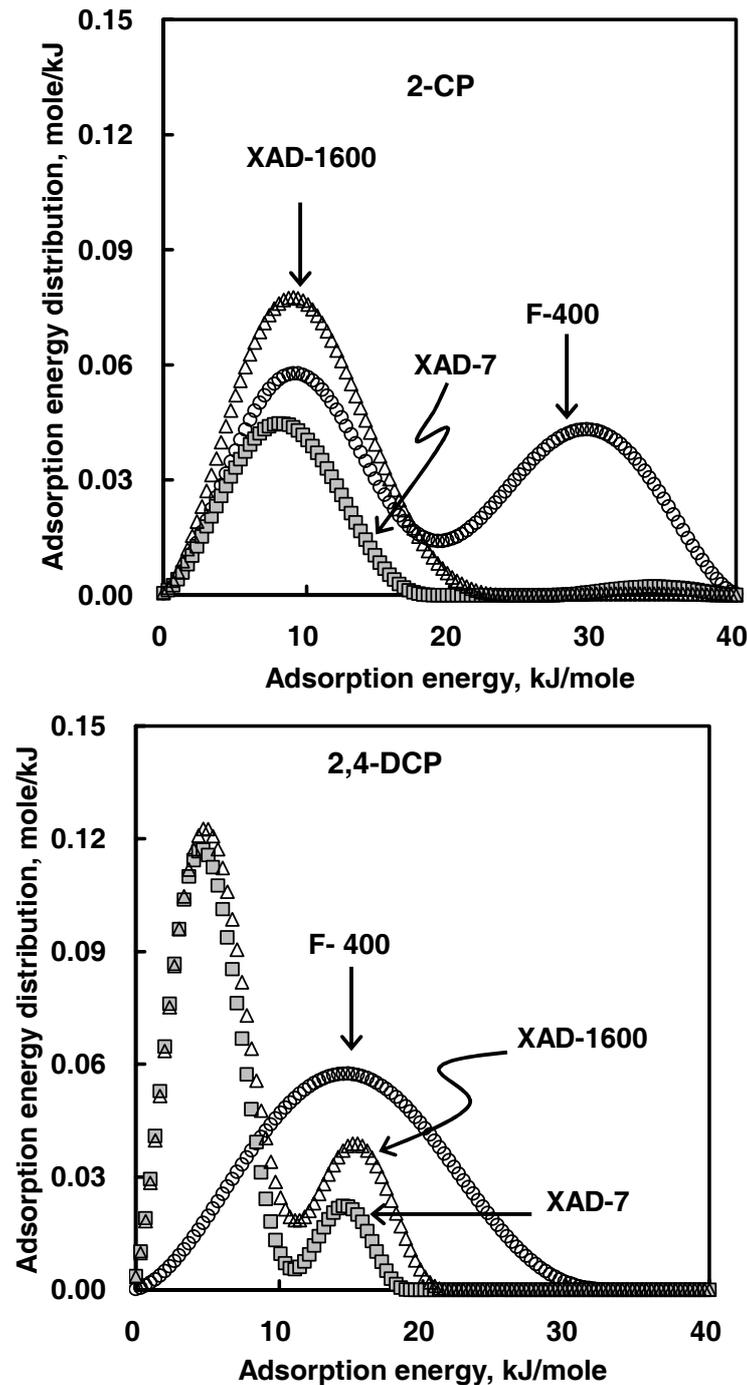


Fig. 4 – Adsorption energy distributions of 2-CP (top) and 2,4-DCP (bottom) on different adsorbents.

In the case of polymeric adsorbents, however, the first pronounced peak evolves at 4.71 kJ/mol and the maximum of low energy peaks are about 15.46 kJ/mol (XAD-1600) and 14.45 kJ/mol (XAD-7), respectively. In addition, heights of the first energy peaks were about 5.25 (XAD-7) and 3.15 (XAD-1600) times larger than the second peaks. On the whole, activated carbon with relative large surface area and small pore size possess a wide range of adsorption energy for whole system. It has been shown that the shape and the intensity of adsorption energy distribution curve are related with the microporosity of adsorbent and the heterogeneity parameter. As the micropore volume of adsorbent increases and the adsorption heterogeneity parameter decreases, the shape and intensity of adsorption energy distribution become broader and lower.⁶ From the above results, the surface energy heterogeneities on porous adsorbents are closely associated with the number of adsorption energy peaks which exhibit the structural differences of adsorbates.

CONCLUSION

Adsorption equilibria of two chlorophenols (2-CP and 2,4-DCP) on different porous adsorbents F-400, XAD-1600, and XAD-7 were investigated for characterizing the surface energy heterogeneity. The obtained adsorption data were correlated with Langmuir-Freundlich isotherm and the adsorption capacity of 2,4-DCP was always greater than that of 2-CP on activated carbon and polymeric sorbents. The adsorption energy distribution functions were calculated successfully by using the generalized nonlinear regularization method (GENEREG) to solve the linear Fredholm integral equation of first kind. It was also found that F-400, with relative large surface area and small pore size, possess a wide range of adsorption energy for all cases. On the basis of the results of current work obtained, it seems that the surface energy heterogeneity highly depends on not only the heterogeneity parameter (m) but also the structural differences of adsorbates on a given adsorbent.

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