

## Research Article

# The Removal of Phenol and Its Derivatives from Aqueous Solutions by Adsorption on Petroleum Asphaltene

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This research describes the adsorption of phenol and *o*-substituted phenols and xylene isomers on petroleum asphaltene from aqueous solution. The results revealed that the adsorption equilibrium data were best fitted with the generalized and Freundlich isotherms. For *o*-substituted phenols, it was found that electron-withdrawing groups increase the adsorption capacity. The uptake of these phenols decreases in the order: *o*-nitrophenol > *o*-chlorophenol > *o*-aminophenol > *o*-cresol > phenol, while the adsorption of xylene isomers decreases in the order: 2,6-xylene > 2,5-xylene > 3,5-xylene > 3,4-xylene. Batch equilibrium results at different temperatures suggest that the adsorption of 2,6-xylene and 3,5-xylene onto asphaltene is an endothermic process,  $\Delta G$  values obtained were positive indicating a nonspontaneous process with increasing randomness at the solid-solution interface. The influence of solution pH on the adsorption of 3,5-xylene on asphaltene was also investigated. The adsorption process was found to be independent on the solution pH. The adsorption capacity of 3,5-xylene was found to increase with the decrease in particle size of the adsorbent.

## 1. Introduction

Phenol and phenolic compounds are organic pollutants found in many industrial effluents. Their presence in wastewater even at low concentrations causes many problems for aquatic environment [1–3]. Because most of phenolic compounds are toxic [4] and carcinogenic [5], their removal or destruction from waste streams has become an environmental concern of significance. Because of their toxicity, phenolic compounds have been included in the US Environmental Protection Agency (EPA) list of priority pollutants [4].

Various water treatment technologies have been proposed for the removal of phenolic wastes. Among these techniques, adsorption is the well-established technique for the removal of low concentrations of organic pollutants from aqueous solutions [1, 6].

In recent years, there has been increasing interest in developing low-cost, naturally occurring adsorbents. Such low-cost adsorbents include palm ash [7], clays [8, 9], chitosan, zeolites, clay, or certain waste products from industrial

operations such as fly ash, red mud, sludges and oxides [10], seaweed, peat moss, modified wool, modified cotton, iron-oxide-coated sand [11], and polymeric adsorbents [1].

Petroleum asphaltene is that portion of a crude oil or bitumen which precipitates on the addition of a low-molecular-weight paraffin hydrocarbon. Asphaltene is brown-to-black amorphous solids containing carbon, hydrogen, nitrogen, oxygen, and sulphur [12].

Asphaltene is composed of condensed aromatic rings, bound by alkyl chains and containing various functional groups such as hydroxyl, carboxyl, ether, ester, aldehyde, ketone, amine, and amides [13]. Owing to these functional groups, asphaltene is able to create a surface charge at the interface. Because of this interfacial activity, asphaltene is of special interest from a colloidal point of view [14, 15].

It was postulated that the mechanism of asphaltene precipitation in organic solvents is the result of two significant observations. The first one is that asphaltene is not a mixture of high-molecular-weight compounds (400–400,000 g/mol) but a mixture of low-molecular-weight

compounds (500–1000 g/mol). The second observation is that the resulting precipitate is not soft and pliable but hard and crystalline in nature [16].

Interaction of phenols with asphaltene was used to characterize the density of basic sites of asphaltenes [17]. This approach was used in this study to investigate the adsorption of different phenols on asphaltenes. To the best of our knowledge, there is no available data in the literature about this topic. In this work, the adsorption capacity of asphaltenes to remove some phenols was studied. The effect of molecular structure of phenols and the effect of several physicochemical parameters such as pH, temperature, and particle size were also discussed.

## 2. Materials and Methods

**2.1. Adsorbent.** Asphaltenes used in this study were isolated from asphalt samples of the heavy crude oil taken from a field in northern Iraq. Isolation of asphaltenes was achieved by a physical method of separation based on solubility. Asphalt was firstly dissolved in toluene and filtered in order to remove minerals and resins. Precipitation of asphaltenes was then achieved by the addition of excess n-hexane (40.0 mL : 1.0 g of asphalt at 25°C). The precipitate was separated by filtration and washed with excess fresh n-hexane. Asphaltenes were further demineralized by dissolution in benzene followed by centrifuging and decanting the solution from the mineral matter. The process was repeated twice and mineral-free asphaltenes were precipitated with excess n-hexane at 25°C. After precipitation, asphaltenes were dried in a vacuum oven at 60°C/40 mmHg for 1 hour and sieved by using available sieves of nominal sizes (59, 90, and 145 μm). Particle sizes of 90 μm were used in all experiments throughout this work; the other sizes were used to study the effect of particle size on adsorption.

Elemental analysis was carried out on demineralized and carefully purified asphaltenes sample. Perkin-Elmer 2400 CHN analyzer was used to determine carbon, hydrogen, and nitrogen in asphaltene. Sulphur content was quantitatively determined by X-ray method using Telsec instrument with Fe<sup>55</sup> source (Oxford, England), whereas oxygen content was determined by difference. Results of C, H, N, S, and O weight percentages (% w/w) and their atomic ratios in asphaltenes are shown in Table 1.

**2.2. Adsorbates.** All chemicals were obtained from Aldrich Chemical Company with declared purity of ≥99%. All chemicals used were of analytical grade, and they were used without further purification. The adsorption isotherms were all determined using distilled water, and all chemicals used were readily soluble in water.

**2.3. Adsorption Experiments.** Stock solutions of the adsorbates were prepared with distilled water in the desired initial concentration, and subsequent concentrations were made by dilution. Batch adsorption experiments were carried out by adding 0.0250 g of asphaltene (Sartorius analytical balance model BL210 S measures to the nearest of 0.0001 g) to 50 mL

of pollutant solution of known concentration in a 100 mL glass-stoppered flasks. The flasks were then placed in a temperature-controlled GFL 1083 (Germany) orbital shaker and agitated at a constant speed of 150 rpm at a constant temperature of 298 K and pH 7.0. At the end of the desired equilibrium period, the contents of the flasks were filtered, centrifuged for 20 min at 5000 rpm using mLw T5 (Germany) centrifuge, and the supernatant was subsequently analyzed for residual concentration of the adsorbate. The concentration of phenols in solutions was typically in the range of 20–200 mg L<sup>-1</sup>. The initial and equilibrium concentrations of phenols were determined using a single beam UV/Visible spectrophotometer (Pye-Unicam-8700, Philips, England) using a (1.0 cm) light-path cell. Each equilibrium concentration value was an average of three measurements. The adsorption capacity or amount of adsorbate adsorbed by asphaltenes ( $q_e$ , mg·g<sup>-1</sup>) was calculated as follows:

$$q_e = \frac{(C_o - C_e) \cdot V}{m}, \quad (1)$$

where  $C_o$  is the initial concentration (mg L<sup>-1</sup>);  $C_e$  is the equilibrium or residual adsorbate concentration (mg L<sup>-1</sup>);  $V$  is the volume of the solution (L); and  $m$  is the mass of adsorbent (g).

The effect of temperature, pH, and particle size on the removal of 3,5-dimethylphenol by asphaltene was studied using the above described procedure at different temperatures, pH values, and different particle sizes.

## 3. Results and Discussion

**3.1. Adsorption Isotherms.** Adsorption isotherms of phenol, o-substituted phenol, and xylenol isomers are illustrated in Figures 1 and 2. The shape of adsorption isotherms indicates S4-behaviour according to Giles et al.'s classification [18]. This type of isotherm implies that adsorption becomes easier as the concentration of the adsorbate in the liquid phase increases. This behavior is observed when the solute molecules have a moderate intermolecular attraction leading to a vertical packing in the adsorbed layer and meets a strong competition from solvent molecules for the adsorption sites. This implies association with the aromatic nuclei face-to-face and perpendicular to the surface [19].

The mechanism of adsorption of phenols by asphaltene presumably involves H-bond formation between the phenolic hydroxyl and H-bonding sites on asphaltene surface. The addition of substituents to phenol can affect H-bonding, and hence adsorption, by their effect on acidity or basicity of the phenolic hydroxyl. The adsorption of ortho substituted phenols decreases in the following order:



It seems that e-withdrawing groups strongly enhance the adsorption capacity on asphaltene surface. Siddiqui [20] has shown that the interaction between asphaltene and phenols is mainly through hydrogen bonding. This is due to the presence of high amounts of heteroatoms that leads

TABLE I: Elemental composition of asphaltene.

Composition (% w/w)					Atomic ratios			
C	H	N	S	O	H/C	N/C	S/C	O/C
80.41	8.16	2.17	1.13	8.12	1.220	0.012	0.038	0.020

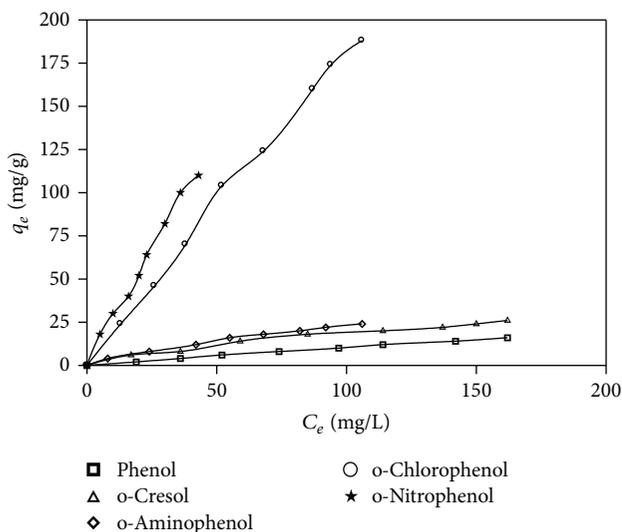


FIGURE 1: The adsorption isotherms of substituted phenols.

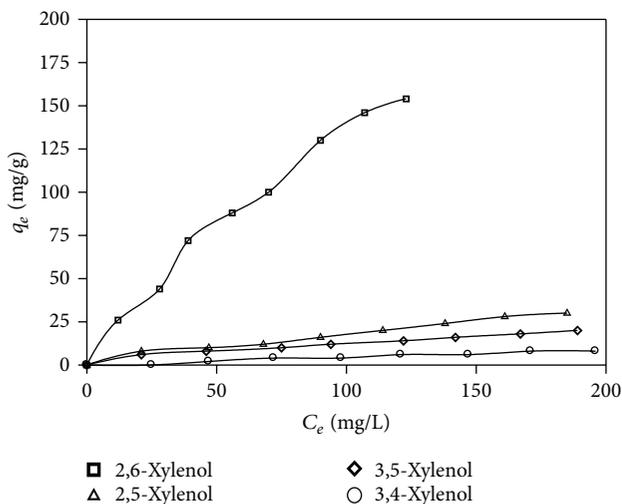


FIGURE 2: The adsorption isotherms of xylenol isomers on asphaltene from aqueous solution at 25 °C.

to the maximum enthalpy of hydrogen bond formation. The relatively high N/C ratio (0.012) of asphaltene used in this study provides comparative information about the basic functional groups present in the asphaltene molecule, which leads to strong hydrogen bonding between phenols and nitrogen atoms of asphaltene.

In the case of xylenols, the high adsorption capacity of 2,6-xylenol may be attributed to the presence of the two

bulky methyl groups near the hydroxyl group that results in decreased solvation and hence increasing the adsorption capacity.

As compared to the literature studies on the same subject, this study indicated high adsorption capacity of asphaltene for different phenolics. Maximum adsorption capacities between 12.16 and 546.28 mg g<sup>-1</sup> were observed which is clearly higher than those reported in the literature.

Several adsorption isotherm models have been published in the literature to describe the experimental data. In this work, four adsorption models were applied to understand the interaction between the adsorbate and adsorbent, Langmuir, Freundlich, Langmuir-Freundlich, and Temkin isotherm models.

**3.1.1. Langmuir Isotherm.** The Langmuir isotherm model [21] has been successfully used to describe the monolayer adsorption. The Langmuir equation assumes that no further adsorption can take place at that site if adsorbate occupies a site. The linear form of this model can be represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e, \quad (2)$$

where  $K_L$  is adsorption equilibrium constant (L mg<sup>-1</sup>) that is related to the apparent energy of adsorption,  $q_m$  is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent (mg g<sup>-1</sup>), and  $q_e$  is the amount adsorbed on unit mass of the adsorbent (mg g<sup>-1</sup>) when the equilibrium concentration is  $C_e$  (mg L<sup>-1</sup>).

The values of  $K_L$  and  $q_m$  can be evaluated from the slope and intercept of the linear plot of  $C_e/q_e$  versus  $C_e$  (Table 2).  $R^2$  values obtained for this isotherm are very small indicating that this isotherm model cannot be used to describe the experimental data for the adsorption of these phenolics on to asphaltene. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equation parameter  $R_L$  that is given by the equation [22]

$$R_L = \frac{1}{1 + K_L C_o}, \quad (3)$$

where  $C_o$  is the highest initial concentration. The value of ( $R_L = 0$ ) indicates that the isotherm is reversible, ( $0 < R_L < 1$ ) favorable, ( $R_L = 1$ ) linear, and ( $R_L > 1$ ) indicates the unfavorable adsorption. As seen from Table 2,  $R_L$  values between 0 and 1 indicate that the adsorption of studied phenolics on asphaltene is favorable.

TABLE 2: Isotherm constants and regression data for Langmuir and Freundlich adsorption isotherms for adsorption of substituted phenols on asphaltene from aqueous solutions.

Adsorbate	Langmuir			Freundlich			
	$q_m$	$K_L$	$R^2$	$R_L$	$K_F$	$n$	$R^2$
Phenol	127.32	0.114	0.604	0.981	0.128	1.047	0.996
o-Cresol	46.23	0.330	0.905	0.945	0.854	1.496	0.979
o-Aminophenol	45.69	0.445	0.911	0.950	0.892	1.414	0.997
o-Chlorophenol	376.89	2.940	0.298	0.630	1.848	1.000	0.997
o-Nitrophenol	548.28	3.152	0.364	0.764	4.088	1.147	0.987
2,6-Xylenol	398.94	2.060	0.832	0.708	3.262	1.231	0.975
2,5-Xylenol	64.23	0.274	0.608	0.948	1.475	1.903	0.908
3,5-Xylenol	30.90	0.241	0.858	0.954	1.350	2.097	0.979
3,4-Xylenol	12.16	0.097	0.854	0.981	0.029	0.901	0.970

3.1.2. *Freundlich Isotherm.* The Freundlich isotherm model [23] is an empirical equation employed for modeling the adsorption on heterogeneous surfaces. Freundlich equation can be written as

$$q_e = K_F C_e^n, \quad (4)$$

where  $K_F$  ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ ) is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and  $n$  is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. The Freundlich coefficients can be determined from the plot of  $\log q_e$  versus  $\log C_e$  based on the linear form of equation as given by

$$\log q_e = \log K_F + n \log C_e. \quad (5)$$

Values of  $n > 1$  represent a favorable adsorption condition [24] and are indicative of cooperative adsorption [25]. It was found that the coefficients of determination obtained from Freundlich isotherm model ( $0.908 < R^2 < 0.997$ ) are higher than those for Langmuir isotherm model as given in Table 2.

Jaynes and Boyd [26] proposed that the adsorption conforms to the Freundlich model when the value of correlation coefficient ( $R^2$ ) is greater than 0.89. The  $R^2$  values shown in Table 2 are greater than 0.89, indicating that the Freundlich isotherm model can be used to describe the adsorption data. The applicability of this isotherm model to all investigated systems implies that heterogeneous surface conditions exist under the experimental conditions studied.

3.1.3. *Langmuir Freundlich Isotherm.* This isotherm fuses both Langmuir and Freundlich isotherms together. It has been used in the following form [27]:

$$\log \left( \frac{q_m}{q_e} - 1 \right) = \log K_G - N_b \log C_e, \quad (6)$$

where  $K_G$  is the saturation constant ( $\text{mg L}^{-1}$ );  $N_b$  is the cooperative binding constant;  $q_m$  is the maximum adsorption

TABLE 3: Isotherm constants and regression data for Langmuir-Freundlich and Temkin isotherms for adsorption of substituted phenols on asphaltene from aqueous solutions.

Adsorbate	Langmuir-Freundlich			Temkin		
	$K_G$	$N_b$	$R^2$	$A_T$	$b_T$	$R^2$
Phenol	1166.16	1.010	0.998	0.056	382	0.944
o-Cresol	121.21	0.970	0.975	0.089	275	0.953
o-Aminophenol	86.00	0.954	0.986	0.154	316	0.929
o-Chlorophenol	7547.45	1.00	0.997	0.079	30	0.937
o-Nitrophenol	154.75	0.96	0.982	0.216	56	0.886
2,6-Xylenol	178.52	0.98	0.987	0.098	43	0.936
2,5-Xylenol	139.82	0.89	0.913	0.067	233	0.854
3,5-Xylenol	82.29	0.90	0.927	0.090	396	0.894
3,4-Xylenol	20.28	0.62	0.320	0.997	0.632	0.958

capacity of the adsorbent ( $\text{mg g}^{-1}$ ) (obtained from the Langmuir isotherm model); and  $q_e$  and  $C_e$  are the same as in Langmuir and Freundlich isotherms. The isotherm constants  $K_G$  and  $N_b$  are obtained from the slope and intercept of the plot of  $\log[(q_m/q_e) - 1]$  versus  $\log C_e$  (Table 3).

This model offers a flexible analytical framework for modeling both Langmuir- and Freundlich-type sorption effects. The coefficients of determination,  $R^2$ , obtained for this isotherm model (Table 3) indicate that the Langmuir-Freundlich isotherm can adequately describe the adsorption data.

3.1.4. *Temkin Isotherm.* The derivation of the Temkin isotherm assumes that the heat of adsorption of all the molecules in the adsorption layer decreases linearly with the coverage of molecules due to the adsorbate-adsorbent repulsions, and the adsorption of adsorbate is uniformly distributed [28, 29]. In addition, it also assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich isotherm. The Temkin isotherm has generally been applied in the following form:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e). \quad (7)$$

This equation can be linearized as given by the following equation:

$$q_e = B_T \ln A_T + B_T \ln C_e, \quad (8)$$

where  $B_T = (RT)/b_T$ ;  $T$  is the absolute temperature in  $K$  and  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The constant  $b_T$  is the Temkin constant related to the heat of adsorption ( $\text{J mol}^{-1}$ ).  $A_T$  is Temkin isotherm constant ( $\text{L}\cdot\text{g}^{-1}$ ) it is known as equilibrium binding constant corresponding to the maximum binding energy [30]. The plot of  $q_e$  versus  $\ln C_e$  should yield a straight line if the Temkin equation is obeyed by the adsorption equilibrium data. The slope and the intercept of this line yield the isotherm constants  $A_T$  and  $b_T$  (Table 3).

**3.2. Effect of Temperature.** The effect of temperature on the adsorption of 2,6-xylenol and 3,5-xylenol on asphaltene was studied at temperatures of 278, 288, 298, and 308 K, with these adsorption isotherms being shown in Figures 3 and 4. The adsorption capacity of both phenolics increased at higher temperature. It was well known that increasing temperature would increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for particular adsorbate [30].

As for asphaltene, it seems that increasing temperature causes the stripping of some of the unit sheets in the molecule. This process allows activated centers to be created and hence increasing adsorption capacity [13].

Thermodynamic parameters such as free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), and entropy change ( $\Delta S$ ) were calculated from the following equations [31]:

$$\begin{aligned} \Delta G &= -RT \ln K_c, \\ \Delta G &= \Delta H - T\Delta S, \end{aligned} \quad (9)$$

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R},$$

where  $K_c$  is the equilibrium constant calculated by [32]

$$K_c = \frac{C_{as}}{C_e}, \quad (10)$$

where  $C_{as}$  and  $C_e$  are equilibrium concentrations ( $\text{mg/L}$ ) of adsorbate on the adsorbent and the solution, respectively.  $\Delta H$  and  $\Delta S$  for adsorption are assumed to be temperature independent. They were calculated from the slope and intercept of the plot of  $\ln K_c$  versus  $1/T$  (Figure 5). Table 4 shows the values of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ . Positive values of  $\Delta H$  indicate the endothermic nature of adsorption process and the magnitude of  $\Delta H$  (13.00–14.00  $\text{kJ/mol}$ ) is due to the physisorption [33].  $\Delta G$  is positive and decreases with increasing temperature, which indicates more driving force and results in more adsorption capacity at higher temperatures. The positive value of  $\Delta G$  indicates the nonspontaneous nature of the adsorption process at the range of temperatures studied [34].

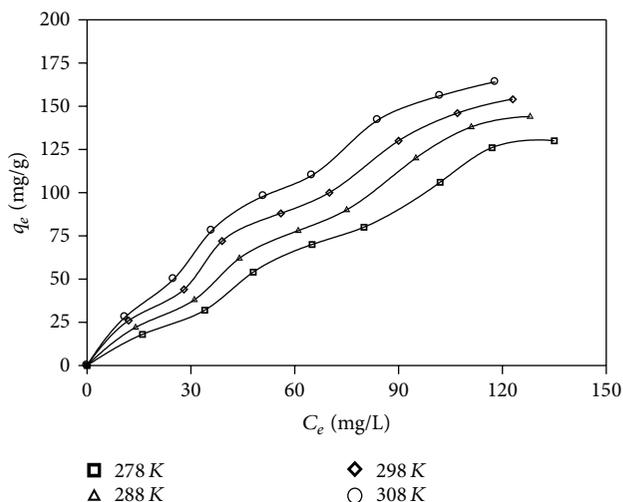


FIGURE 3: Effect of temperature on the adsorption of 2,6-xylenol onto asphaltene.

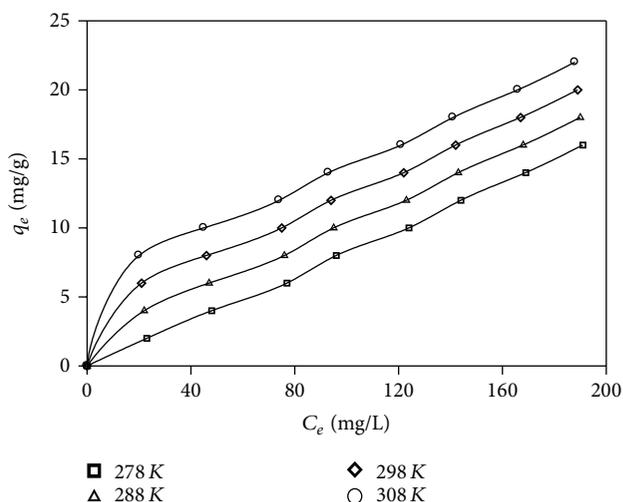


FIGURE 4: Effect of temperature on the adsorption of 3,5-xylenol onto asphaltene.

TABLE 4: Adsorption thermodynamic parameters of xylenols adsorption onto asphaltene.

Adsorbate	$T$ (K)	$\Delta G$ ( $\text{kJ mol}^{-1}$ )	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$\Delta S$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$R^2$
2,6-Xylenol	278	1.514	13.962	44.777	0.997
	288	1.066			
	298	0.618			
	308	0.171			
2,5-Xylenol	278	7.353	14.004	23.924	0.999
	288	7.114			
	298	6.875			
	308	6.635			

The positive values of  $\Delta S$  show the affinity of asphaltene for xylenols and suggest some structural changes during

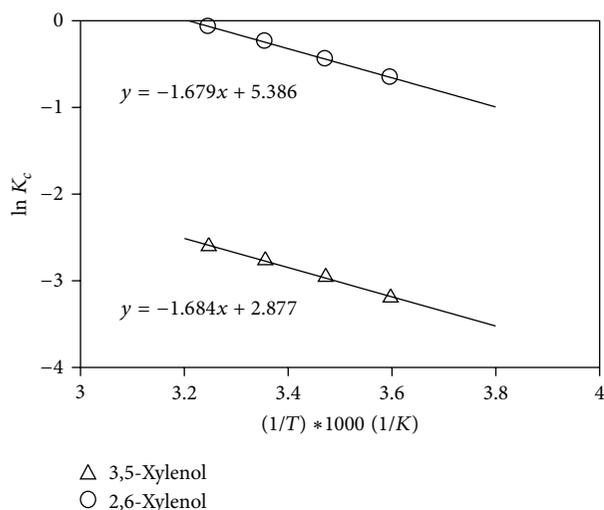


FIGURE 5: Plot of  $\ln K_c$  versus  $1/T$  for estimation of thermodynamic parameters for the adsorption of 3,5-xyleneol and 2,6-xyleneol onto asphaltene.

the sorption process, which leads to an increase in the randomness at the solid-solution interface during adsorption [35, 36]. In the solid-liquid adsorption system, adsorption of solute onto the adsorbent and desorption of solvent from the adsorbent both exist; the former one is accompanied by entropy reduction, and the latter is a contrary process. The entropy change of the adsorption is the sum of the two processes. In this system of the adsorption of xyleneols onto asphaltene, probably, desorbed water molecule is larger than that of the adsorbed xyleneol molecules as these molecules are large compared with water molecules; therefore, several water molecules may be desorbed by adsorption of xyleneol molecule. Therefore, the driving force for adsorption is due to both enthalpy effect and entropy effect [37].

This phenomenon has also been observed in the adsorption of 2,4-dichlorophenol on palm pith carbon [38] and in the adsorption of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon [25].

**3.3. Effect of pH.** To observe the effect of pH on the adsorption of 3,5-xyleneol on asphaltene, adsorption isotherms were studied at different pH values (Figure 6). It appears that there is no change in the adsorbed amount at different pH values. This may be attributed to the amphoteric nature of asphaltenes. At low and high pH, their hydrophilic behavior increases and makes them more surface-active [39].

**3.4. Effect of Particle Size.** The effect of particle size for a constant weight of asphaltene on the adsorption of 3,5-xyleneol is shown in Figure 7. These plots reveal that the adsorption is higher for smaller particle size of the adsorbent. This is because adsorption is a surface phenomenon, so the increase in the uptake by smaller particles was due to the greater accessibility to pores and to the greater surface area for bulk adsorption per unit mass of the adsorbent [40].

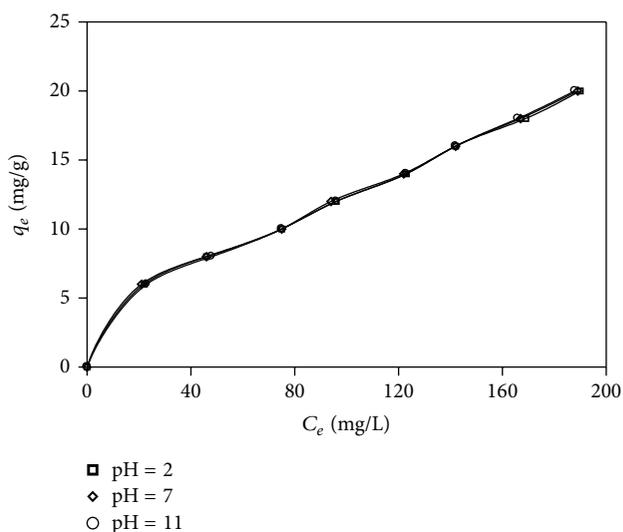


FIGURE 6: Effect of pH on the adsorption of 3,5-xyleneol onto asphaltene.

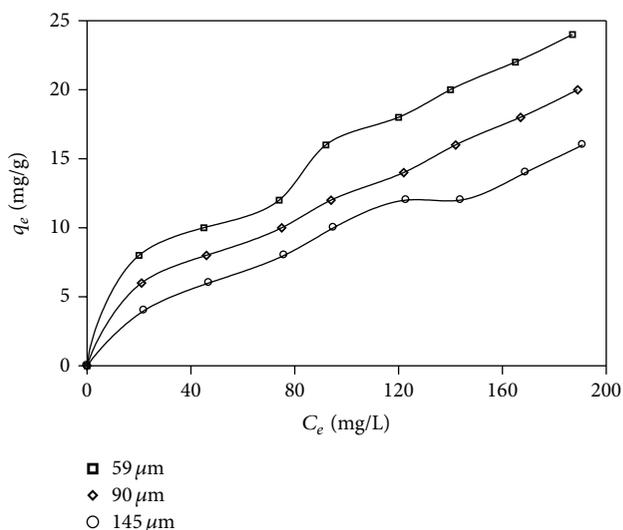


FIGURE 7: Effect of particle size on the adsorption of 3,5-xyleneol onto asphaltene.

## 4. Conclusions

The present work showed that petroleum asphaltene was an effective material for the adsorption of phenol and *o*-substituted phenols and xyleneols from aqueous solution. The adsorption of *ortho* substituted phenols decreases in following the order:

*o*-nitrophenol > *o*-chlorophenol > *o*-aminophenol > *o*-cresol > phenol.

The generalized and Freundlich models were demonstrated to provide the best correlation for the adsorption data of these phenolics onto asphaltene.

The adsorption process of 2,6-xyleneol and 3,5-xyleneol onto asphaltene was found to be endothermic in nature with

a positive value of  $\Delta S$  suggesting the increasing randomness at the solid-solution interface. The positive value of Gibbs free energy ( $\Delta G$ ) indicates that the adsorption is nonspontaneous process.

It can be concluded that the solution pH has no influence on the adsorption isotherms of 3,5-xyleneol and that the adsorption capacity increases with increasing particle size of the adsorbent.

## Conflict of Interests

Regarding this paper, the authors want to say that they do not have any direct financial relation with the trademarks mentioned in the paper. There were no any external funding sources for this study. The authors of the paper had access to all study data and took responsibility for the decision to submit the paper for publication.

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