

Modeling the Adsorption of Phenol and Aniline on Active Carbon

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Introduction

The adsorption of phenol and aniline from aqueous solutions onto activated carbon has been studied. Experimental adsorption data were obtained as a function of pH and temperature. Previous analysis of these data have shown that the often used Ideal Adsorbed Solution (IAS) model [1] does not characterize the data effectively, primarily because there are significant discrepancies between the experimental and predicted values of the free immersion energy. In this paper, the utility of the more general Adsorbed Solution Theory (AST) [2] is examined. In particular, the problems with estimating the pore capacity and the adsorbed layer thickness have been addressed using the genetic algorithm optimization technique. It was shown that AST provides an improved description of the phenol adsorption behavior. However, it does not adequately describe the adsorption of aniline. The poor results with the AST model suggests that the assumption of a homogeneous adsorbed phase might not be suitable.

To include the effects of heterogeneity of the surface, the Dubinin-Polanyi (D-P) potential theory [3] has been examined. It has been demonstrated that this theory provides an adequate description of the adsorption equilibria in terms of both surface excess and surface free energy isotherms.

Experimental

The materials and methods used to obtain the adsorption isotherms have been described in detail elsewhere [1]. Briefly, two types of activated carbon, granular activated carbon Darco G-60 (BET area = 633 m²/g) and Kureha SAC-LP (BET area = 952 m²/g) were used. Adsorption isotherms were obtained by agitating a solution of known volume and composition

with a weighed amount of carbon in 35 ml glass bottles. The bottles were sealed and agitated in a constant temperature water bath at 100 rpm for six days. After equilibration, the adsorbent and the solution were separated by a combination of centrifugation and filtration. The filtered solution was analyzed by UV spectrophotometry, and a mass balance was used to calculate the amount adsorbed.

Results and Discussion

The AST model requires that the pore capacity of each adsorbate be known *a priori*. Since experimental pore capacity data cannot be obtained for liquid adsorption, a modification of the estimation technique developed by Dada and Wenzel [4] was used. In the modified approach, the genetic algorithm was used to minimize the objective function, since this approach is more likely to identify the global minimum. Shown in Table 1 are typical pore capacities (m_i) estimated from the adsorption data. The effective layer thickness (t_i) was estimated from this pore capacity and the monolayer capacity calculated from the McClellan-Harnsberger [5] equations.

Table 1 Phenol (1)/ Water(2) Adsorption on Darco G-60

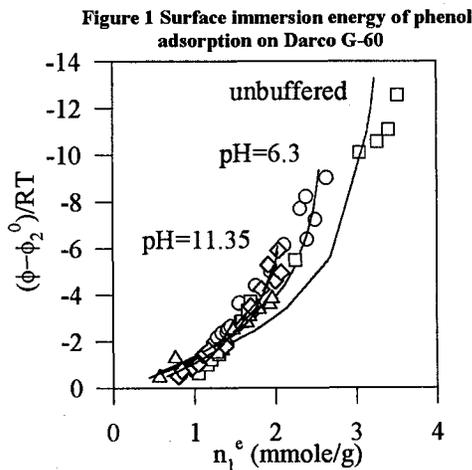
pH	m_1	t_1	m_2	t_2
unbuff	3.32	1.28	7.18	0.50
6.3	2.62	1.01	3.29	0.23
3.07	2.35	0.90	3.10	0.21
11.25	2.17	0.83	4.65	0.52

The effects of pH and temperature on the effective layer thickness are generally consistent with mechanisms that have been proposed for the adsorption of phenolic compounds on activated carbon. For the adsorption of phenol on Darco G-60, multilayer adsorption of phenol

is only observed from unbuffered solution. In other cases, the adsorption of phenol is monolayer or less. This variation can be attributed to a number factors: degree of dissociation of the solute in the liquid phase, the influence of surface oxygen groups, repulsion of charged groups on the surface, and the formation of water clusters. Leng [6] has provided a detailed discussion on how these mechanisms are influenced by solution pH.

The effect of temperature on effective layer thickness for phenol adsorption was also found to be consistent with expectations. As the temperature increases, the effective layer thickness decreases, which corresponds to the decrease in adsorption capacity usually observed for phenol adsorption on carbon.

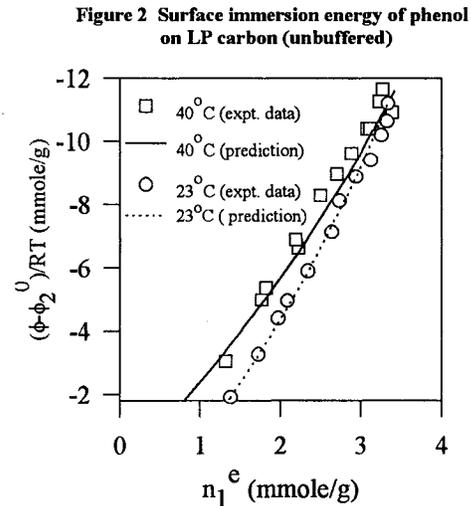
The coefficients of the AST model obtained from the GA optimization for the phenol/water and aniline/water systems generally gave good characterizations of the surface excess isotherms. However, the improvement over the corresponding characterizations of the much simpler IAS model was generally found to be small. Additionally, like the IAS model the AST model did not characterize the surface free immersion energy isotherms effectively. Shown in Figure 1 is a typical case.



As can be seen, while the AST model predicts significantly non-linear behavior, the experimental data were found to vary linearly with surface coverage. This poor characterization could be attributed to the assumption of a homogeneous adsorbed surface.

The D-P potential theory was applied to

check the significance of the homogeneous surface assumption. It was found that this theory is capable of effectively characterizing the adsorption with respect to both the surface excess and the surface free immersion energy isotherms. In particular, this model's predictions of surface immersion energy are far superior to the AST model, especially for phenol adsorption. Shown in Figure 2 is a typical case. As can be seen, the linear behavior is correctly predicted.



This improvement in characterization indicates that surface heterogeneity must be considered in developing an effective model for adsorption of phenol and aniline on carbon.

References

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