Adsorption of Phenolic Compounds on Fly Ash

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Adsorption isotherms for adsorption of phenol, 3-chlorophenol, and 2,4-dichlorophenol from water onto fly ash were determined. These isotherms were modeled by the Freundlich isotherm. The fly ash adsorbed 67, 20, and 22 mg/g for phenol, chlorophenol, and 2,4-dichlorophenol, respectively, for the highest water phase concentrations used. The affinity of phenolic compounds for fly ash is above the expected amount corresponding to a monolayer coverage considering that the surface area of fly ash is only 1.87 m^2/g. The isotherms for contaminants studied were unfavorable, indicating that adsorption becomes progressively easier as more solutes are taken up. Phenol displayed a much higher affinity for fly ash than 3-chlorophenol and 2,4-dichlorophenol.

Introduction

The major solid waste byproducts from coal-fired power plants are ash from the burning of coal and sludge from gas desulfurization. Fly ash is produced as a fine, noncombustible residue carried off in the flue gas with relatively uniform particle size distribution in the 1−10 μm range. Today fly ash is predominantly used in soil stabilization, as a source of metals (i.e., aluminum recovery), and as a pozzolanic cement additive (Usmen, 1988; Berry and Malhotra, 1982; Lane and Best, 1982; Jun-Yuan et al., 1984; Halse and Pratt, 1984). About 70 million tons of fly ash is produced annually in the United States with only about 15% of the ash produced being put to practical use, the rest being landfilled. Environmental and economic concerns have prompted both the government and industry to find effective ways to utilize fly ash and reduce the solid waste volume that is landfilled.

The high percentage of silica and alumina in fly ash makes it a good candidate for utilization as an inexpensive adsorbent for bulk use. One possible such use of fly ash might be as landfill lining material to retard seepage of organics from landfills; a similar use might be for the enhancement of cutoff barrier performance (Mott and Weber, 1992). In order to evaluate such potential uses, it is necessary to determine adsorption isotherms of organics on fly ash from aqueous solutions. This study focuses on adsorption of phenolics, specifically phenol, 3-chlorophenol, and 2,4-dichlorophenol, on fly ash.

Adsorption of organics from aqueous solutions onto solid matrices is characterized in terms of either type I−V Brunauer−Emmett−Teller (BET) isotherms (Brunauer, 1944) or isotherms that are divided into four main classes according to the initial slope of the isotherm curve (Giles et al., 1959). These curves are called the S curve, L curve, H curve, and C curve. Phenol, 3-chlorophenol, and 2,4-dichlorophenol have the strong functional group −OH. Moreover, in the presence of water, these phenolic compounds compete for adsorption sites, since H^+ and OH^- are known to readily adsorb on charged surfaces. Therefore, an S type curve is expected for adsorption of phenolic compounds on polar surfaces such as alumina and silica from polar solvents such as water (Giles et al., 1960). The S curve results from "cooperative" adsorption, indicating that adsorption becomes progressively easier as more solutes are taken up. The increase in adsorption is the direct result of the vertical orientation of the adsorbed molecules at the surface of the adsorbent. In cooperative adsorption, therefore, there is a side-by-side association between adsorbed molecules. This type of adsorption curve is expected when the solute molecule (a) is monofunctional, (b) has moderate intermolecular interaction, and (c) meets competition for adsorption sites from solvent molecules. Because of the shape of the S curve (i.e., absence of a plateau), the adsorption model best suitable for parameter estimation and data fitting is the Freundlich isotherm

$$q_e = KC_e^{1/n} \quad (1)$$

where q_e is the adsorbed phase concentration in equilibrium with the fluid phase concentration C_e, and K and n are empirical constants which determine the curvature and steepness of the isotherm.

Table 1. Chemical Analysis[a] of a TMPA Fly Ash Sample

metal oxide	% present	metal oxide	% present
silica, SiO_2	64.5	potassium, K_2O	0.97
aluminum, Al_2O_3	21.1	manganese, MnO_2	0.12
iron, Fe_2O_3	3.05	sulfur, SO_3	0.13
calcium, CaO	6.87	phosphorous, P_2O_5	0.20
titania, TiO_2	0.71	LOI[b]	0.0
sodium, Na_2O	1.04	total	99.77

[a] Analyses done by Inter-Mountain Laboratories, Inc., College Station, TX. [b] Loss on ignition, indicates the carbon content.

Table 2. Solubilities at 25 °C

compound	solubility in water/(g/L)
phenol	87
3-chlorophenol	27
2,4-dichlorophenol	5

Experimental Section

The fly ash samples used in this study were obtained from the Texas Municipal Power Agency (TMPA). The chemical composition of the fly ash is given in Table 1. The samples had a nitrogen BET surface area of 1.87 m^2/g.

To obtain adsorption isotherms of the phenolics, five solutions of concentrations in the range of 10−90% of the solubility limit of the phenolic compound (phenol, 3-chlorophenol, 2,4-dichlorophenol) in water were prepared prior to data acquisition. The solubilities are given in Table 2. The adsorption isotherms are obtained by using frontal analysis chromatography principles. A schematic repre-

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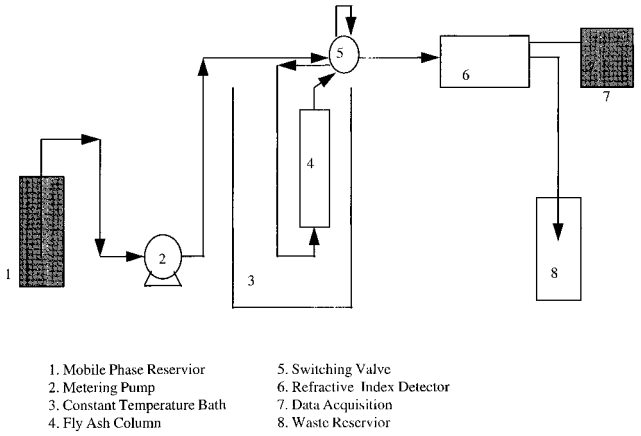

Figure 1. Experimental setup based on frontal analysis chromatography.

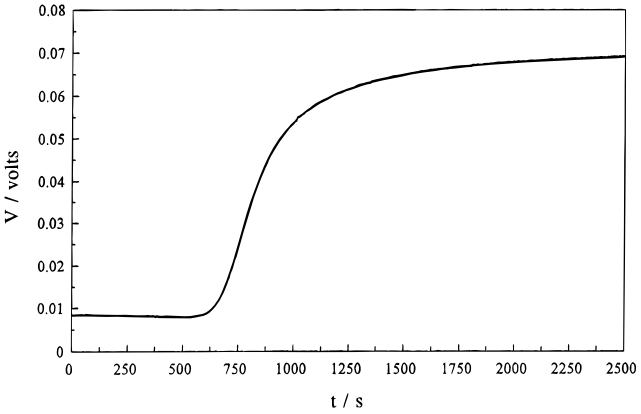

Figure 2. A typical breakthrough curve for adsorption of 3-chlorophenol on fly ash.

sentation of the experimental setup is shown in Figure 1. The system is equipped with a metering pump, a refractive index detector, a switching valve, a voltmeter, and a computer for data acquisition. At the start of each experiment, the fly ash column was bypassed and a steady state voltage output from the refractive index detector for each of the five different organic concentrations was recorded. This enabled us to determine a calibration curve which was later used to convert voltage to concentration prior to data analysis for adsorption isotherms.

After a steady state voltage reading was obtained, the switching valve was switched to the column, the phenol solution was pumped through the column containing an accurately weighed amount of fly ash, and the response of the bed was monitored on-line with the detector. Subsequently, the calibration curve was used to convert the voltage to concentration. The calibration curves were linear with R^2 values of >0.99. Figure 2 shows a typical breakthrough curve for adsorption of phenol on a TMPA fly ash sample. Each adsorption experiment was terminated when the effluent concentration from the column reached a steady state value equal to the inlet concentration. The analysis of the breakthrough curve yields a point on the adsorption isotherm. The mass balance on the fly ash column during the adsorption process is given by

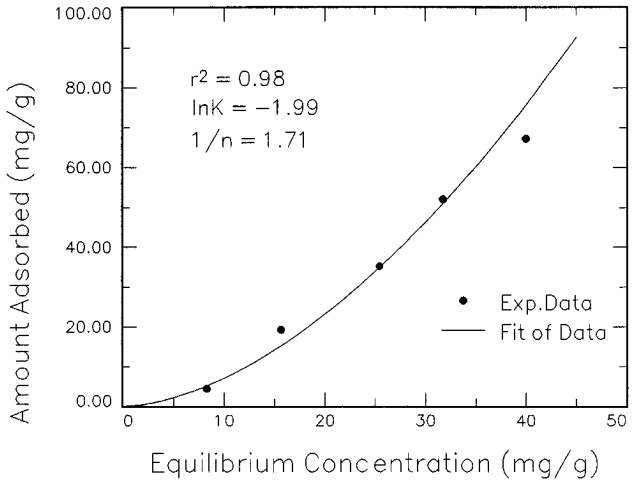

Figure 3. Adsorption isotherm of phenol on fly ash.

$$m_{in} - m_{out} = m_{accumulated} \quad (2)$$

where m_{in} and m_{out} are the mass flow rates in and out of the adsorption column which in turn are given by

$$m_{in} = \int_0^t C_0 v(t)\, dt \quad (3)$$

and

$$m_{out} = \int_0^t C_{eff}(t)\, v(t)\, dt \quad (4)$$

where $v(t)$ is the volumetric flow rate and C_0 and C_{eff} are the concentrations at the inlet and the effluent, respectively. Then the mass accumulated in the column is given by

$$m_{accumulated} = \int_0^t (C_0 - C_{eff}(t)) v(t)\, dt \quad (5)$$

The flow rate, $v(t)$, can be assumed to be constant and equal to the water feed rate to the column, v_0. After accounting for the column void space, the mass adsorbed on the fly ash column is given by

$$m_{adsorbed} = m_{accumulated} - C_0 v_0 \epsilon \quad (6)$$

Results and Discussion

Data on phenol, 3-chlorophenol, and 2,4-dichlorophenol adsorption on TMPA fly ash at 293.15 K are presented in Table 3, and the adsorption isotherms are given in Figures 3−5, respectively. All three isotherms are categorized as

Table 3. Adsorption Isotherm Data

	equilibrium concentration/(mg/g) in the water phase	adsorbed amount/(mg/g)	equilibrium concentration/(mg/g) in the water phase	adsorbed amount/(mg/g)
phenol	8.26	4.4	31.74	52.0
	15.65	19.2	40.00	67.2
	25.43	35.2		
3-chlorophenol	4.51	0.78	16.80	16.40
	9.43	5.94	21.57	20.16
	14.12	11.56		
2,4-dichlorophenol	0.879	0.952	3.333	15.71
	1.724	3.214	4.000	22.17
	2.636	10.86		

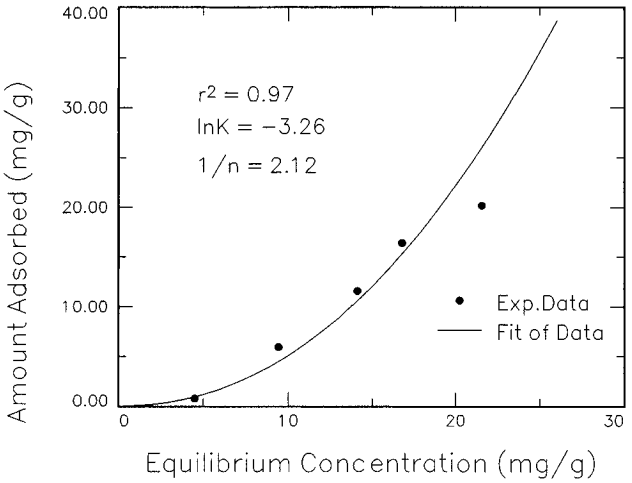

Figure 4. Adsorption isotherm of 3-chlorophenol on fly ash.

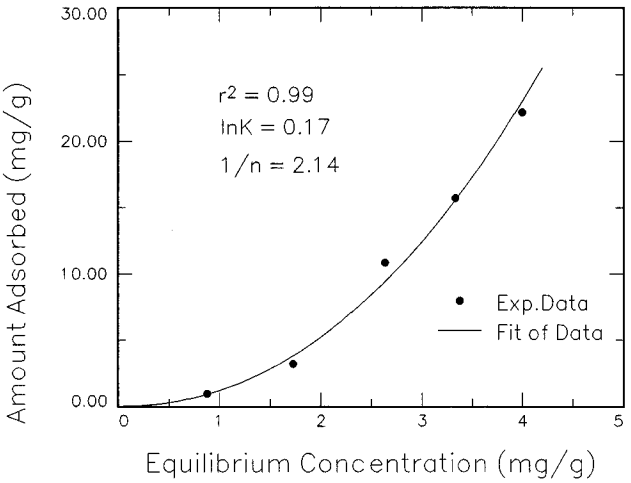

Figure 5. Adsorption iostherm of 2,4-dichlorophenol on fly ash.

unfavorable (BET type III) or cooperative (curve S). The isotherms can be characterized by a convex Freundlich isotherm (i.e., $n < 1$) indicating that no significant adsorption takes place at low concentrations but adsorption becomes significant at higher concentrations (Freundlich isotherm parameters are also given in the figures). Previous research indicates that unfavorable (cooperative) adsorption isotherms are expected for adsorption of phenolic compounds on metal oxides such as silica and alumina (Giles et al., 1960). We attribute the unfavorable (cooperative) nature of the adsorption more to the behavior of the adsorbates. Phenols have a strong hydroxyl functional group which interacts with the adsorbent surfaces, resulting in vertical alignment of the molecule on the surface. Moreover, additional adsorption is motivated and consequently strengthened by the interaction between the adsorbed molecules. This phenomenon is known to contribute significantly to the cooperative nature of adsorption and hence an S type curve (Giles et al., 1960). TMPA fly ash adsorbs 67, 20, and 22 mg/g for phenol, 3-chlorophenol, and 2,4-dichlorophenol, respectively, for the highest concentrations used. The affinity of phenolic compounds for fly ash is much above the expected amount corresponding to a monolayer coverage considering that the surface area of fly ash is only 1.87 m^2/g. It is common practice to calculate

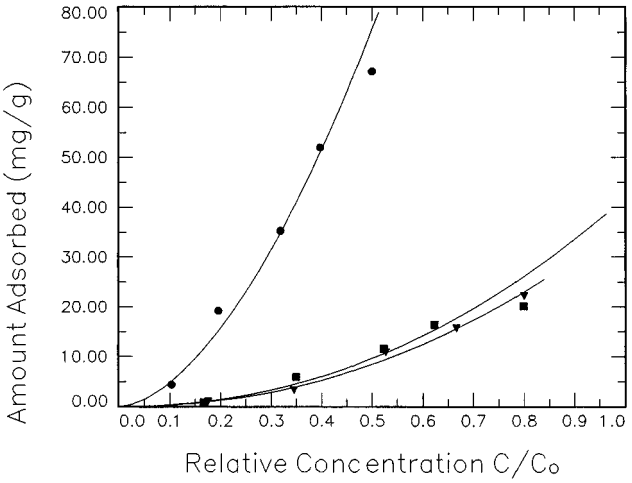

Figure 6. Adsorption comparison using normalized concentrations: ●, phenol (C_0 = 80 mg/g); ■, 3-chlorophenol (C_0 = 27 mg/g); ▼, 2,4-dichlorophenol (C_0 = 5 mg/g).

the amount of adsorbate required for monolayer adsorption in terms of the projected area of a molecule in flat orientation. Considering spherical molecules and hexagonal close packing (Smith, 1970), rough estimates of the amounts required for monolayer coverage of the fly ash surface by phenol, 3-chlorophenol, and 2,4-dichlorophenol are 0.62, 0.71, and 0.75 mg/g, respectively, compared to the adsorption data given in Table 3. However, as discussed previously, molecules with strong functional groups align themselves vertically on the surface; moreover, these adsorbed molecules can interact with other molecules, making the next adsorption layer energetically and statistically more favorable. We believe that the three phenolic compounds, having a very strong functional group as well as strong molecular interaction, display this type of behavior.

Figure 6 is the comparison of adsorption isotherms for the three contaminants in terms of their normalized concentrations in the liquid phase. Although there is not much difference between the isotherms of chlorophenols, clearly phenol has a higher affinity for fly ash.

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