

ADSORPTION OF TOLUENE AND ANILINE BY MODIFIED ACTIVATED CARBON FIBERS

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Introduction

The industrial and technological expansion of our society over the past several decades has resulted in a general deterioration in the quality of our natural water sources. A prime example of immediate concern to the field of water supply is the marked increase in the incidence of water contamination by synthetic organic chemicals (SOCs). The Safe Drinking Water Act Amendments of 1986 were promulgated in response to this growing contamination problem. Given increasingly stringent water quality standards and public concern over environmental issues, environmental engineers must aggressively pursue innovative, selective, and versatile treatment technologies for solving current pollution problems and preventing new ones, therefore minimizing the risk on public health.

Carbon fibers (CFs) are, perhaps, the most innovative and successful carbon material developed within the past forty years. Their applications have been examined in a number of fields to the point where today carbon fibers are used from sporting goods to aircraft structures. However, limited research has been conducted to examine the efficacy of using CFs in environmental engineering applications. The primary goal of this study was to systematically investigate the efficacy of using carbon fibers for the removal of selected SOC from aqueous solutions. Specifically, the roles of fiber porosity and surface chemistry on the removal of toluene and aniline were examined.

Experimental

Adsorbents. Two virgin activated carbon fibers (ACF10 and ACF20H, American Kynol, Inc.) and five surface modified ACF10 carbons are used in this study. These adsorbents are microporous materials with different surface characteristics.

Various surface modified ACF10 fibers are: (1) **ACF10,O**: slightly oxidized under oxygen atmosphere at 180°C for 2hr; (2) **ACF10,He**: heat-treated under helium at 900°C for 2hr; (3) **ACF10,He,16NO**: heat-treated under helium at 900°C for 2hr, then oxidized in boiling concentrated nitric acid for 1hr; (4) **ACF10,He,16NO,4N1H**: heat-treated under helium at 900°C for 2hr, then oxidized in boiling concentrated nitric acid for 1hr followed by ammonia treatment at 400°C for 1hr; and (5) **ACF10,He,16NO,8N1H**: heat-treated under helium at 900°C for 2hr, then oxidized in boiling concentrated nitric acid for 1hr followed by ammonia treatment at 800°C for 1hr.

Adsorption isotherms. Constant-dose aqueous phase isotherm experiments for a wide range of toluene and aniline initial concentrations were performed using both virgin and modified carbon fibers. Preliminary tests showed that toluene adsorption was independent of dissolved oxygen concentration; therefore toluene isotherms were performed under oxic conditions. For aniline isotherms, it was found that uptake could be affected by presence of dissolved oxygen. Therefore stock solutions were vigorously purged with nitrogen to reduce the concentration of dissolved oxygen to less than 0.5 mg/l. Oxygen measurements of anoxic solutions at the end of the experiments showed that oxygen contents were below 1 mg/l. Ten milligrams of carbons were equilibrated with various solute concentrations in 250-ml amber glass bottles (head-space free) for one week on a rotary tumbler at the room temperature of $21 \pm 3^\circ\text{C}$. After the equilibration period, reactors were sampled and analyzed by UV absorbance measurements at 262nm (toluene) and 231nm (aniline). Isotherms were conducted at three pH values of 3, 6, and 11. The stock solution pH was adjusted using HCl or NaOH solutions. The pH's of equilibrated solutions were measured at the end of experiments and remained relatively constant during the isotherms.

Characterization of adsorbents. Various characterization methods have been used to determine physical and chemical characteristics of activated carbons. These methods are: (i) pH_{PZC} and total HCl and NaOH uptake for determination of carbons' surface acidity/basicity; (ii) X-ray Photoelectron Spectroscopy (XPS) for the surface elemental analysis; and (iii) Surface area and pore size distribution using the nitrogen isotherms. Details of these methods were described elsewhere [1].

Results and Discussion

Physicochemical characteristics. Physical and chemical characterization results of virgin and modified activated carbon fibers with different characteristics are tabulated in Table 1. ACF10, and ACF20H are highly microporous fibers with different surface area and pore size distribution but similar surface chemistries (as demonstrated by their pH_{pzc} and surface elemental analysis data). In comparison to virgin ACF10, heat-treated fiber (ACF10,He) has similar characteristics with slightly higher surface basicity and larger surface area and average micropore width.

Mild gas-phase oxidation of ACF10 had no effect on the total surface area, micropore volume, and average micropore width of the modified carbon (ACF10,O). This treatment slightly increased the surface acidity (lower pH_{pzc}) and polarity (higher oxygen content). On the other hand, nitric acid oxidation of heat-treated ACF10 significantly increased its surface polarity (demonstrated by a substantially higher oxygen content) and acidity. This treatment also increased the average micropore width and decreased surface area and micropore volume. Ammonia treatment of oxidized fiber at two temperatures produced fibers with larger average micropore widths (similar to ACF20H), higher surface area and pore volumes, and different levels of surface polarities (from the contribution of N- or O-containing functionalities).

Table 1. Physicochemical characteristics of activated carbons.

Carbon	SA _{BET}	V _{micro, DR}	V _{total}	W ^a ,	Pore volume distribution ^b , %				pH _{PZC}	NaOH uptake	HCl uptake	O	N	C
	m ² /g	cm ³ /g	cm ³ /g	Å	<7Å	7Å-10Å	10Å-20Å	>20Å		meq/g		atom%		
ACF10	963	0.382	0.374	6.8	76.43	14.65	8.92	0.00	8.6	0.156	0.294	4.1	0.8	94.6
ACF20H	1983	0.811	0.860	10.5	27.62	18.83	49.93	3.63	9.6	0.091	0.451	3.3	0.4	96.1
ACF10,He	1057	0.410	0.407	7.4	53.51	17.57	11.35	17.57	10.0	0.086	0.381	3.6	0.4	94.9
ACF10,O	996	0.391	0.382	6.8	54.97	35.03	6.25	3.75	7.4	0.152	0.286	7.0	0.4	91.7
ACF10,He,16NO	768	0.302	0.305	8.1	48.92	22.51	28.57	0.00	1.9	3.046	0.000	13.3	2.5	83.4
ACF10,He,16NO,4N1H	1053	0.420	0.503	9.9	31.39	14.11	38.20	16.30	7.8	0.790	0.348	7.6	4.1	87.1
ACF10,He,16NO,8N1H	1272	0.509	0.606	10.2	32.60	12.60	39.20	15.60	9.7	0.291	0.488	3.8	2.7	91.7

a. Average micropore widths of activated carbons determined from DFT (Density Functional Theory) distribution results in <20Å range.

b. Determined from DFT.

Toluene adsorption isotherms. Adsorption isotherms of toluene by virgin and modified activated carbon fibers, conducted at the pH of 3, are shown in Figure 1. Results obtained (not shown) at other pH values of 6 and 11, as well as those obtained at pH = pHpzc, showed similar uptakes. This indicates that adsorption of non-dissociating and non-polar toluene molecules is independent of pH and surface charge.

Water vapor uptakes at the low relative pressure range (e.g., 0.0 to 0.4) can be related to the extent of water cluster formation or degree of hydrophilicity (or polarity) of carbon surface. Water vapor isotherms of adsorbents that were previously obtained are shown in Figure 2 [2]. Based on this figure, hydrophilicity of treated ACF10 carbons can be classified as: Nitric acid oxidized > ammonia-treated > virgin > heat-treated.

Toluene adsorption isotherms show that from low to intermediate concentrations, surfaces with the most hydrophilic characteristics (i.e., nitric acid-oxidized followed by ammonia-treated) have the lowest uptakes. This is most likely due to the effect of developed water clusters on hydrophilic sites that prevent or hinder access of toluene molecules to the micropore region for utilizing the adsorption sites. On the other hand, at high concentrations, close to or at the saturation level, toluene uptake is predominantly governed by the pore volume.

A comparison of ACF10 and ACF20H fibers with relatively similar hydrophobic surfaces but different pore size distribution can illustrate the effect of porosity on the adsorption of toluene from dilute solutions. ACF10 with a smaller average micropore width, in comparison to ACF20H (Table 1), is showing higher uptakes at lower concentrations. This observation confirms the overlapping potential effect of micropore walls, when the size of adsorbate is close to that of the pore width, on the enhanced toluene uptake.

Adsorption isotherms of aniline. Adsorption isotherms of aniline by virgin and surface-modified ACF10 carbons under anoxic conditions and at the pH of 11 are shown in Figure 3. Preliminary results indicated higher aniline uptakes under oxidic conditions at neutral or slightly acidic pH values. This subject is currently under investigation to further confirm and explain the oxidic/anoxic observations.

Since aniline at the pH of 11 is an uncharged molecule, adsorption isotherms of various modified ACF10 carbons at this condition show a similar trend to those of toluene results (Figures 1 and 3). Similar to the toluene adsorption and due to the negative effect of water clusters (formed on polar sites), the lowest uptake is observed by highly oxidized and polar fiber followed by ammonia-treated and finally other less hydrophilic activated carbon fibers.

Figure 4 shows the effect of pH on aniline adsorption under anoxic conditions. There was no noticeable difference between aniline adsorption isotherms at pH values of 6 and 11, but they were significantly higher than adsorption at the pH of 3. Aniline is protonated at pH values below its pKa (i.e., 4.6). At the same time when the pH of experiment is below the pHpzc of carbon (pHpzc of ACF10 is 8.6, Table 1) the carbon surface is also positively charged. Therefore, at pH =3 repulsion forces between the

same charged aniline ions and the carbon surface result in a reduction in the aniline removal from water. On the other hand at other pH values of 6 and 11, aniline is an uncharged molecule and such repulsion forces do not play a major factor.

Conclusions

Adsorption isotherms of toluene by virgin and modified activated carbon fibers, conducted at different pH values showed that adsorption of non-dissociating and non-polar toluene molecules is independent of pH and surface charge. These isotherms indicated that from low to intermediate concentrations, surfaces with the most hydrophilic characteristics (i.e., nitric acid-oxidized followed by ammonia-treated) had the lowest uptakes. This is most likely due to the effect of developed water clusters on hydrophilic sites that prevent or hinder access of toluene molecules to the micropore region for utilizing the adsorption sites.

Preliminary results of aniline adsorption indicated higher aniline uptakes under oxic conditions at neutral or slightly acidic pH values. Adsorption isotherms of various ACF10 carbons under anoxic conditions and at pH values above aniline's $pK_a = 4.7$ showed a similar trend to those of toluene results. On the other hand at the pH of 3 due to repulsion forces between positively charged aniline and carbon surface, a considerable reduction in the aniline removal from water was observed.

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References

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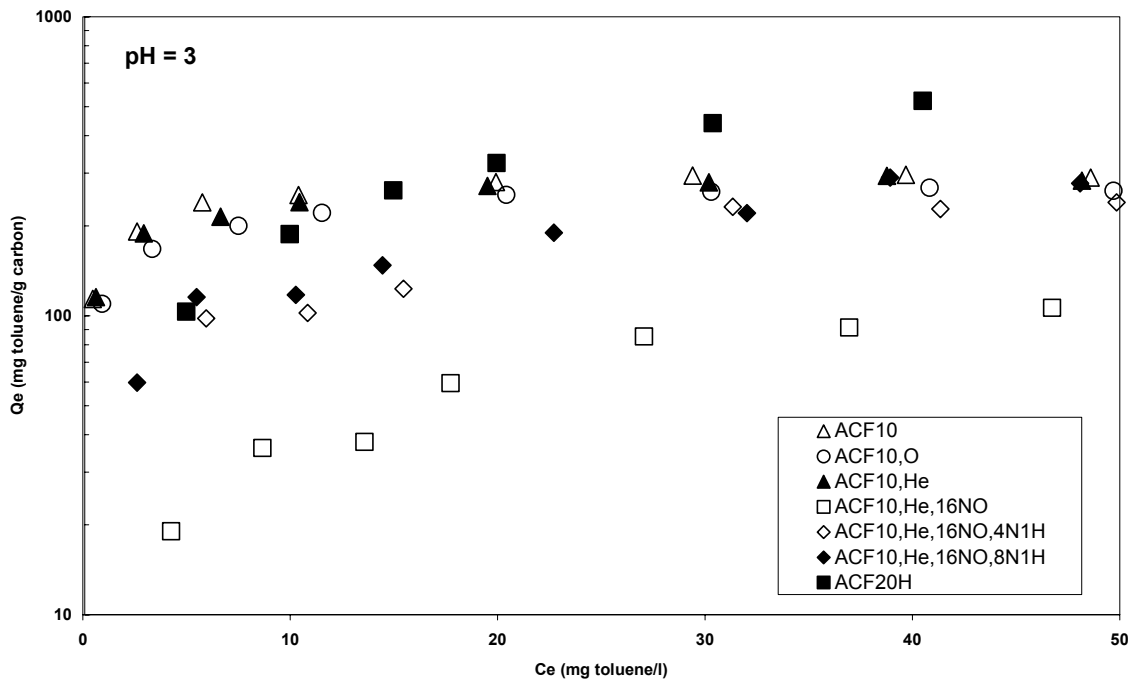


Figure 1. Adsorption isotherms of toluene by virgin and modified activated carbon fibers at pH = 3.

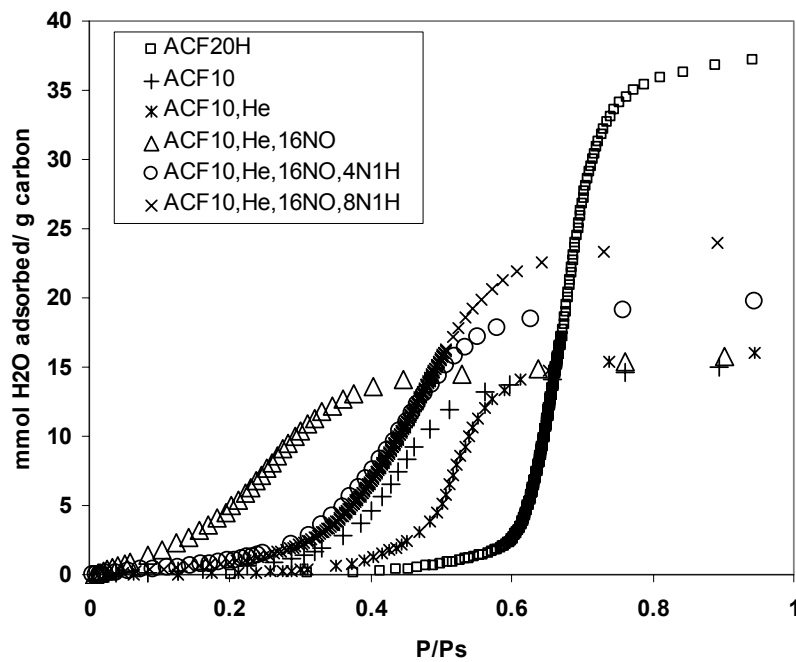


Figure 2. Water vapor isotherms of activated carbon fibers [TCE paper]

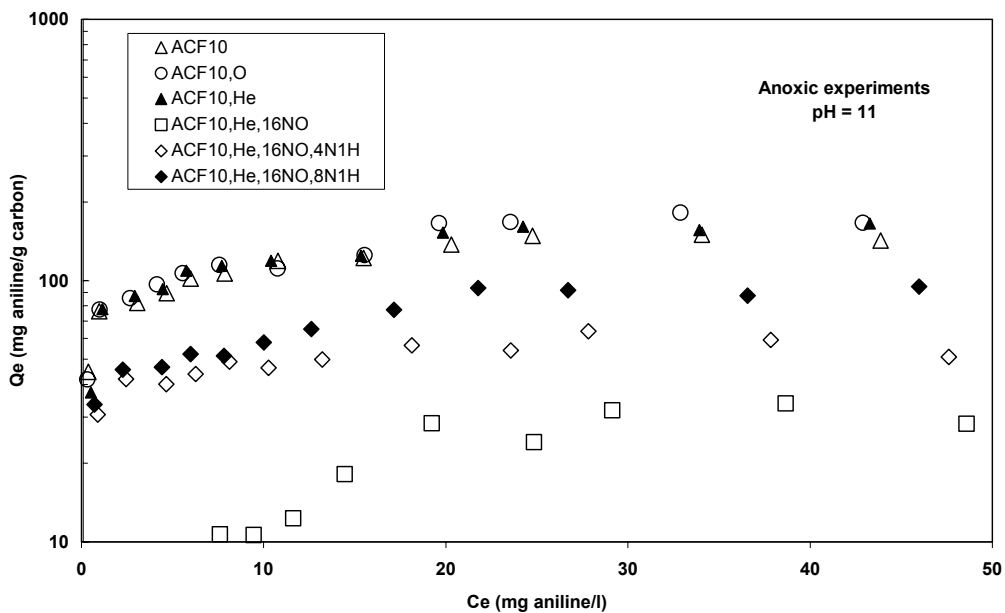


Figure 3. Adsorption isotherms of aniline by virgin and modified activated carbon fibers at pH = 3 and under anoxic conditions.

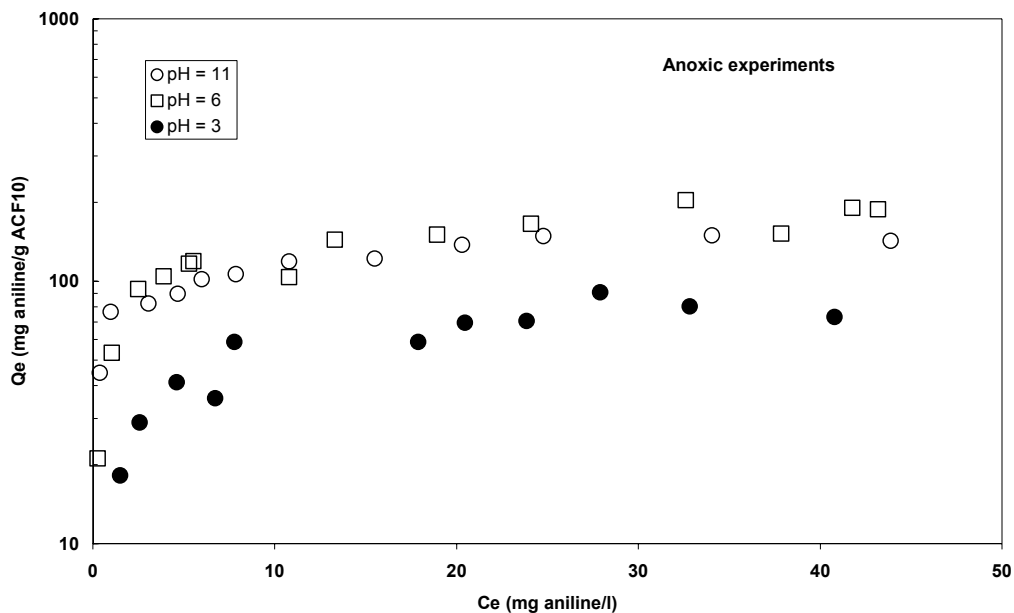


Figure 4. Adsorption isotherms of ACF10 at different pH values and under anoxic conditions.