ADSORPTION OF TRICHLOROETHYLENE BY FIBROUS AND GRANULAR ACTIVATED CARBONS IN THE PRESENCE OF NATURAL ORGANIC MATTER

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Introduction

Adsorption by granular activated carbon (GAC) has been widely employed to remove various synthetic organic contaminants (SOCs) from water supplies [1]. A factor complicating the design and effectiveness of activated carbon for the treatment of potable waters is the presence of naturally occurring dissolved organic matter (NOM) in natural waters. The presence of NOM can significantly reduce the efficiency of activated carbon processes, by competing with targeted SOCs, and thus reducing SOC uptake and rate of adsorption. In fixed-bed reactors, the mass-transfer zone of NOM components can move more rapidly than that of the targeted SOCs. Therefore, at some positions within the bed, the NOM adsorbs ahead of the SOC, and fouls or "*preloads*" the carbon. It has been shown that the preloading phenomenon can significantly reduce the performance of fixed bed adsorbers [2,3]. Ideally, an activated carbon that exhibits maximum SOC removal but minimum NOM uptake is expected to provide a longer service time reducing the overall cost of water treatment process.

In a previous investigation it was demonstrated that ACF10 (an activated carbon fiber with extremely narrow micropores) was resistant to NOM adsorption, mainly due to inaccessibility of its surface area by large NOM species [4]. On the other hand it was also found that ACF10, which had a substantial portion of its surface are located in pores with widths close to the dimensions of SOC molecules (e.g., 5-8Å for Trichloroethylene, TCE), was an excellent adsorbent for SOC removal [5]. Therefore, it was hypothesized that carbon fibers, if designed (or selected) properly, can be promising materials for minimizing the impact of NOM on the removal of SOCs from water.

The main objective of this study was to investigate the effect of NOM preloading on the TCE uptake by granular and fibrous activated carbons. The practical implication of this research is to find the optimized activated carbon characteristics for the selective TCE removal in the presence of NOM.

Experimental

Adsorbents. Two granular (F400 and Macro) and two fibrous (ACF10 and ACF20H) activated carbons were used in this study. F400 (Calgon Corp.) is a microporous, coal-based, and steam-activated, while Macro (Westvaco Inc.) is a mesoporous, wood-

based, and phosphoric acid-activated carbon. Two phenol formaldehyde-based activated carbon fibers (American Kynol, Inc.) are microporous materials with relatively uniform but different pore size distributions. ACF10 and ACF20H were used without any further treatment, while F400 and Macro were heat-treated under helium at 900°C for 2hr (shown by code "He").

Adsorption isotherms. Constant-dose aqueous phase isotherm experiments for a wide range of TCE initial concentrations were performed for both series of single solute and preloading experiments. For single-solute experiments, 10mg of carbons were equilibrated with various TCE concentrations in 250ml amber glass bottles (head-space free) for two weeks on a rotary tumbler. For preloading experiments, 10mg of carbons were initially contacted with 20mg/l (dissolved organic carbon, DOC) of a NOM solution (Charleston SC, USA) in 250ml bottles for two weeks. Then, predetermined amounts (<1cc) of TCE solutions were injected into the isotherm bottles to provide the desired initial TCE concentration. TCE-spiked headspace-free bottles were tumbled for two additional weeks.

After the equilibration period, reactors were sampled and analyzed, after hexane extraction, by gas chromatography using an electron-capture detector. All isotherms were conducted in the presence of a phosphate buffer at the pH of 7 and room temperature (21 ± 3°C). The NOM loading of activated carbons was determined by conducting control experiments (i.e., in the absence of TCE), and measuring NOM concentration in solution before and after adsorption using a dissolved organic carbon (DOC) analyzer.

Characterization of adsorbents. Various characterization methods have been used to determine physical and chemical characteristics of activated carbons. These methods included: (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 nitrogen isotherms. Details of these methods were described elsewhere [4].

Results and Discussion

Physicochemical characteristics. Physical and chemical characterization results of activated carbons are tabulated in Table 1. ACF10 and ACF20H are highly microporous fibers with different surface area and pore size distribution. The total surface area and micropore volume of ACF20H are almost twice those of ACF10. ACF10 has a smaller average micropore width and, unlike ACF20H and granular carbons, majority of its pore volume is located in pores smaller than 7Å. As indicated from pH_{pzc}, HCl and NaOH uptakes, and surface elemental analysis data, these fibers have similar basic and hydrophobic surfaces.

The objective of heat treatment of F400 and more importantly Macro carbons was to reduce their surface polarity and acidity, by removing surface oxygen functionalities, and enhance surface hydrophobicity. **F400,He** and **Macro,He** are microporous and

mesoporous activated carbons, respectively, with relatively similar total surface area but different pore volume distributions. In terms of their surface chemistries, they have different basic or acidic characteristics, but have relatively similar oxygen contents.

Adsorption isotherms. TCE adsorption isotherms of activated carbons, with and without NOM preloading, are shown in Figure 1. The amount of preloaded NOM on each carbon is also shown in the same figure.

NOM preloading. In order to obtain a considerable amount of NOM loading, experiments were conducted at a high NOM concentration (i.e., ~20mg DOC/l). Consistent with our previous results, ACF10 did not show any NOM uptake, while other carbons demonstrated a high amount of NOM loading. This is due to the small average micropore size of ACF10 that provides almost no accessible surface area for the adsorption of large NOM macromolecules. On the other hand the other microporous activated carbon fiber (i.e., ACF20H) that has a considerable pore volume in pores larger than 10Å (i.e., supermicropores) showed a substantial amount of NOM uptake. The highest NOM loading was observed for F400 carbon, due to its favorable surface chemistry (i.e., basic surface) and porosity (i.e., sufficient amount of accessible surface area). Macro that had a less favorable surface chemistry but higher accessible surface area showed also a considerable amount of NOM loading.

Single-solute TCE isotherms. In the absence of NOM, ACF10 had the highest TCE uptake, while other carbons showed similar TCE removal (Figure 1). The superior performance of ACF10, in comparison to other carbons tested in this study, is due to its favorable pore size distribution. When carbon pore dimensions approach to the dimensions of a SOC, a maximum uptake is observed. This is known as microporosity effect. TCE is a planner molecule with 3.6Å*6.2Å*6.6Å dimensions [4]. On the other hand, the average micropore width of ACF10 is 6.8Å and ~75% of its pore volume is found in pores having widths of less than 7Å [Table 1].

TCE isotherms of preloaded carbons. Adsorption isotherms of all preloaded carbons, except ACF10, showed significantly reduced TCE uptakes compared to their single-solute isotherms. This significant reduction is a result of NOM loading, filling or coverage of carbon pores and leading to a considerable reduction in the overall accessible surface area for TCE adsorption. This explanation is currently being investigated by conducting surface area and porosity characterization of preloaded carbons using nitrogen isotherms.

Observed overlapping behavior of ACF10 isotherms (i.e., single-solute and preloaded) is consistent with the resistance of ACF10 to NOM loading (Figure 1). This clearly demonstrates that ACF10 fiber has an excellent selectivity toward small-size SOC molecules (e.g., TCE) and its performance will not be reduced by loading or competition effect of background NOM in practical water treatment conditions.

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	76.4	14.7	8.9	0.0	8.6	0.156	0.294	4.1	0.8	94.6
ACF20H	1983	0.811	0.860	10.5	27.6	18.8	49.9	3.7	9.6	0.091	0.451	3.3	0.4	96.1
F400,He	1058	0.416	0.545	10.2	25.4	22.9	31.5	20.2	9.8	0.098	0.494	4.6	0.4	93.8
Macro,He	1261	0.469	0.992	11.3	12.1	4.1	19.5	64.3	2.8	0.637	0.000	5.8	0.8	92.5

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

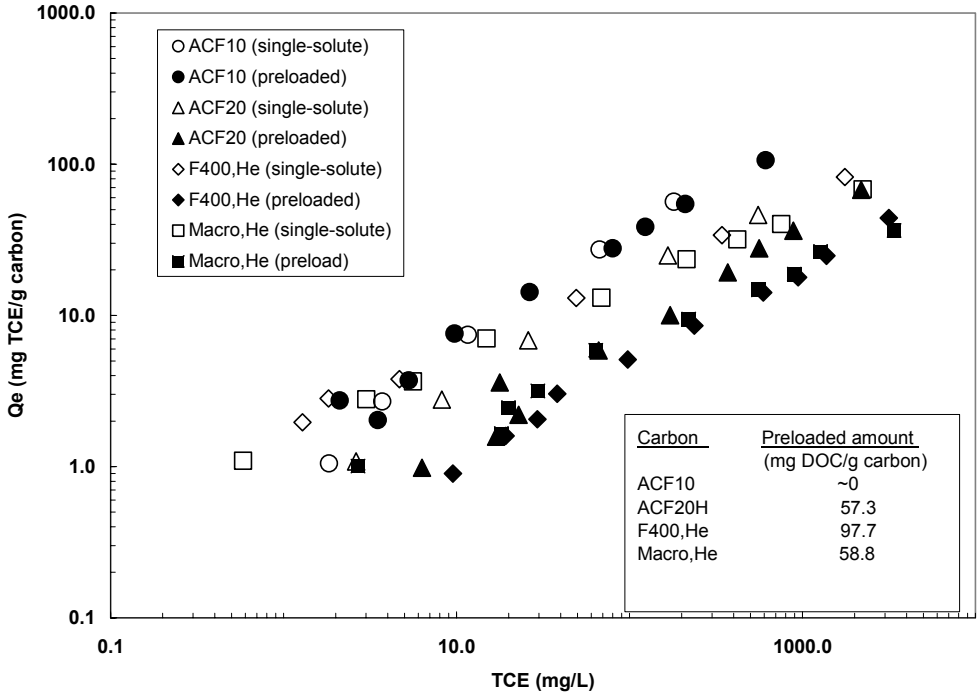

Figure 1. TCE adsorption isotherms of various "fresh" and "preloaded" activated carbons.

Conclusions

A side-by-side study of TCE adsorption by granular and fibrous activated carbons, with or without NOM preloading, was conducted. Results indicated that ACF10, an activated carbon fiber with an average micropore width of 6.8Å, had the highest TCE uptake. The high affinity of ACF10 for TCE adsorption was not reduced by the NOM presence. Consistent with their high NOM loading, other preloaded fibrous or granular carbons showed several times of reductions in TCE removal, in comparison to fresh carbons.

Overall, the findings in this study indicate that activated carbon fibers with narrow pore size distributions that are inaccessible to large NOM macromolecules, but at the same time provide optimized conditions for the adsorption of small SOC molecules can be promising materials for water and wastewater treatment applications.

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