

# THE EFFECT OF ACTIVATED CARBON SURFACE ACIDITY ON COMPETITION BETWEEN NATURAL ORGANIC MATTER AND TRICHLOROETHYLENE

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## Introduction

Activated carbon is widely used in water treatment applications, and granular activated carbon (GAC) adsorption has been identified by the Safe Drinking Water Act Amendments of 1986 as the best available technology for removing synthetic organic contaminants (e.g. trichloroethylene, TCE) from potable water supplies. All natural waters also contain naturally-occurring, dissolved organic matter (DOM) that can compete with TCE and thus significantly reduce the efficiency of activated carbon adsorbers (Kilduff et al. 1998a,b). Because of their prevalence and relative stability, humic substances (humic and fulvic acids) are thought to be the DOM components which most significantly affect TCE adsorption. DOM components generally move through fixed-bed adsorbers more rapidly than TCE, and therefore foul or preload the carbon ahead of the pollutant.

We have investigated various forms of carbon surface modification as a strategy for reducing the effects of DOM competition on TCE uptake. Previous work in our laboratories has shown that by increasing carbon surface acidity and negative surface charge, a significant reduction in the uptake of natural organic foulants can be effected. We have extended that work to examine the uptake of TCE by a series of carbons having different surface acidity that had been preloaded with humic and fulvic acids.

## Experimental

The surfaces of a thermally-activated coal-based carbon (Calgon F400) and an acid-activated wood based carbon (Westvaco WVB) were modified using liquid-phase oxidation ( $\text{HNO}_3$ ) and heat treatment in an inert atmosphere ( $\text{N}_2$ ). The goal was to investigate the role of carbon surface chemistry on adsorption by preparing carbons having different type and surface density of acidic surface functional groups while maintaining the same surface area and pore structure. Ash components and alkaline impurities were removed using 2-N HCl in a Soxhlet extractor for 42 hours. Samples were then heat treated under a nitrogen atmosphere at 1000 °C for 24 hours (designated as H1) to remove oxygen-containing functionality. A portion of the heat treated carbons were

oxidized in aqueous solutions of 70%  $\text{HNO}_3$  at different temperatures (50 to 90 °C) and for different reaction times (2 to 9 hrs) to increase surface acidity (designated as OX followed by the oxidation time in hours and temperature in °C e.g. OX9/70). A portion of oxidized carbons were subsequently heat treated at 650 °C for 24 hours to remove strongly acidic and other  $\text{CO}_2$  evolving groups. Isotherm experiments were conducted using the completely mixed batch reactor (CMBR) bottle-point method. As-received or surface treated carbons were equilibrated with humic substances, TCE or both in 250-ml amber-colored glass bottles which were kept well-mixed. Humic substances were equilibrated for 30 days, while TCE was equilibrated for 21 days, times sufficient to reach an operational equilibrium. Hexane extracts of TCE were analyzed using gas chromatography; humic substances were quantified by total organic carbon. All isotherms were conducted in the presence of a 0.01 M phosphate buffer, at pH 7 and room temperature of  $21 \pm 3$  °C.

The ability to control humic and fulvic acid adsorption through modification of surface chemistry is demonstrated by the data in Figure 1.

## Results and Discussion

The ability to control humic and fulvic acid adsorption through modification of surface chemistry is demonstrated by representative data in Figure 1. The uptake of several model humic substances and natural organic matter isolated from surface waters decreased significantly with increasing surface acidity as measured by NaOH neutralization (Karanfil et al. in press). Because TCE is adsorbed by a hydrophobic adsorption mechanism, and because increasing surface acidity reduces the hydrophobicity of the surface, a similar decrease in TCE uptake was observed as surface acidity increased, as shown in Figure 2 (Karanfil et al. in press). Our objective, then, was to optimize the surface treatment and carbon starting material to minimize the impacts of humic substance preloading while maintaining high TCE uptake. The impact of surface acidity on the effects of preloading are shown in Figure 3. The change in uptake after humic substance preloading as a function of TCE concentration for different surface treated carbons. The points were

generated using best-fit Freundlich isotherm parameters. A constant percent reduction indicates that the slopes of the isotherms were the same before and after preloading. As demonstrated by inspection of Figure 3, surface treated carbons generally showed a resistance to fouling effects - the reduction in uptake resulting from fouling was less for the surface treated carbons. This is consistent with the effects of surface treatment on humic substance uptake (Figure 1). However, even though the effects of preloading were lower, the uptake was also lower in most cases, because surface treatment lowered TCE uptake (Figure 2). One surface treated carbon, WVB heat treated at 1000 C, showed great promise for both minimizing the impacts of preloading and maintaining a high capacity (Figure 4). This carbon exhibited uptake similar to the coal-based F400 carbon in the absence of preloading, and was completely resistant to fouling effects. Uptake by this carbon after preloading is significantly higher than all other carbons tested.

## References

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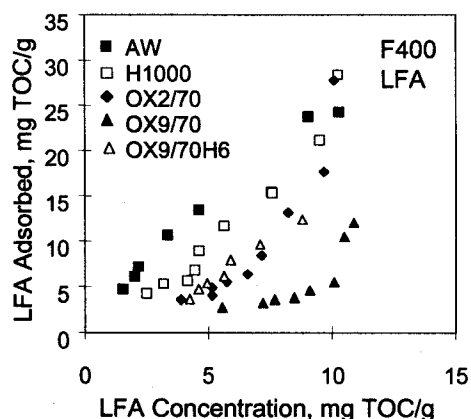


Figure 1. Uptake of Laurentian fulvic acid by surface-treated carbons.

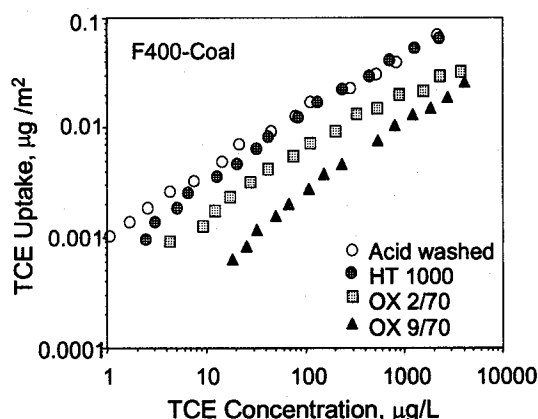


Figure 2. Uptake of TCE by surface treated coal-based carbons.

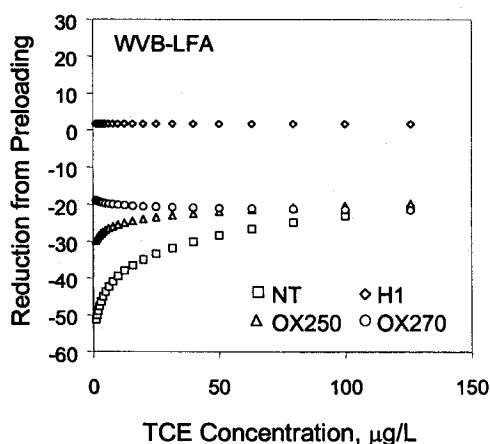


Figure 3. The % reduction in uptake resulting from preloading for different surface treated carbons.

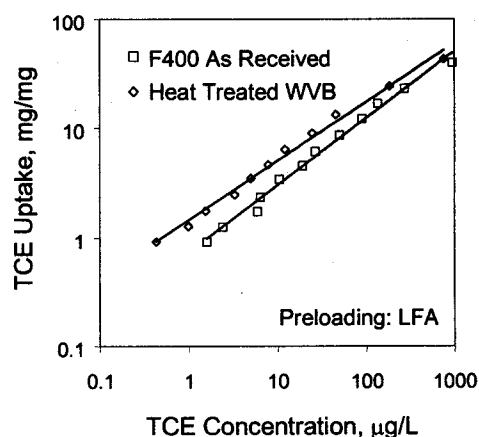


Figure 4. Uptake of TCE by preloaded WVB H1 and as-received F400 carbon.