

THE ROLE OF SURFACE CHARACTERISTICS ON THE UPTAKE OF ORGANIC MACROMOLECULES BY GAC

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Introduction

Natural organic matter (NOM), which is present in nearly all potable water sources, is considered to be the major source of precursors to disinfection by-products (DBPs) formed during water treatment operations [1]. The Environmental Protection Agency (EPA) is planning to impose more stringent standards on DBPs (i.e., the D/DBP rule) because of concern about public health risks, and has designated granular activated carbon (GAC) adsorption as a "best available technology" for removing DBP precursors [2]. Molecular size has been shown to be an important parameter for adsorption of NOMs by GAC [3]. Interactions between these substances and GAC surfaces have also been shown to influence their uptake [4], but little is known specifically about how GAC surface chemistry affects this uptake.

Objectives and Hypothesis

The objectives of this study were to: 1) elucidate how surface characteristics influence uptake of humic compounds by GAC; 2) separate the effects of carbon pore structure and surface chemistry in the adsorption of NOM; 3) determine how molecular properties of NOM influence adsorption on different surfaces; and, 4) provide a rational basis for selecting adsorbents for DBP precursor removal. The hypothesis guiding this study is that sorptive affinity of a GAC for NOM depends, in part, on the properties of the carbon's surfaces.

Experimental Materials and Methods

A thermally-activated coal-based carbon (Calgon, F400) and an acid-activated wood-based carbon (Westvaco WVB) were selected because they exhibit significant differences in pore structure. All carbons used in the research were sonicated and rinsed. Some coal-based carbons were pretreated further to remove ash components and alkaline impurities using 2-N HCl in a soxhlet extractor for 24 hours. Heat treatment of acid-washed carbon samples under nitrogen was employed to remove oxygen-containing functionality selectively. Several carbons heat treated at 1000°C were subsequently oxidized in aqueous solutions of HNO₃ (at different temperature and for

different reaction times) to create new surface carboxyl, lactonic and phenolic groups and thus increase surface acidity.

Humic materials included polymaleic acid (PMA), a fulvic acid surrogate; Laurentian soil fulvic acid (LaFA); Chelsea soil humic acid (CSHA); and Aldrich humic acid (AHA), purified to remove its ash components. Humic substances were equilibrated with activated carbon for one month in well-mixed batch reactors at pH 7 in the presence of excess molecular oxygen. After equilibration, an aliquot of solution was filtered and analyzed for UV absorbance and total organic carbon (TOC).

Results and Discussion

The effects of carbon surface treatment depended on both the humic material and the carbon type; nevertheless, some general trends were observed. As-received F400 carbon exhibited higher uptake than WVB despite having lower surface area, lower pore volume, and smaller average pore size. Its lower surface acidity appeared to be more important than the different pore characteristics.

Effects of Surface Treatment on F400: NOM uptake by treated carbons were generally lower than as-received carbon. The trends of uptake for as-received and heat treated carbons F400 correlated well with size and acidity of NOM; uptake increased with decreasing molecular weight and increasing phenolic acidity (Figure 1). Heat treatment completely removed acidic functional groups but did not change HCl uptake. NOM uptake remained the same or decreased slightly as a result of heat treatment, suggesting that the low degree of surface acidity initially present on F400 carbon (i.e., 0.14 eq/m²) did not interfere significantly with the uptake. Oxidation with HNO₃ increased carbon surface acidity; NaOH uptake increased while HCl uptake decreased with increasing reaction time and temperature. Uptake by oxidized surfaces was lower for all humics, however, greater reductions were observed for polar fulvic acids. Comparison of two fulvic acids (i.e., PMA and LaFA) having similar molecular weights showed that the impact of oxidation was more severe for the one having higher carboxylic acidity (i.e., PMA). At

severe oxidation conditions, the trend between the uptake and the molecular weight and phenolic acidity of NOM disappeared (Figure 2), indicating that size and chemical composition of NOM became less important when the acidic functional group density on the surface increased, as reflected by high NaOH and low HCl uptake values. Subsequent heat treatment after surface oxidation decreased surface acidity (i.e., NaOH uptake) and restored some capacity for NOM. Surface functional group type, in addition to acidity, seems to play a role in NOM uptake.

Effects of Surface Treatment on WVB: In contrast to the F400 carbon, NOM uptakes by the treated WVB carbons were generally higher than values for the corresponding as-received samples. Heat treatment decreased surface acidity by half and increased NOM uptake significantly, particularly for fulvic acids. Uptake increased with decreasing molecular weight and increasing NOM phenolic acidity, a trend also observed for low acidic F400 carbons. Oxidation of the WVB surface increased surface acidity but lowered uptake remarkably. As was observed for the F400 carbon, the trend between uptake and the molecular weight and phenolic acidity of NOM generally disappeared for the WVB carbons after oxidation, although in some cases, higher uptakes were observed despite higher surface acidities. The results suggest that NOM uptake depends on both the *densities* and *types* of surface acidic functional groups.

Conclusions

Carbon surface acidity appeared to be more important than pore characteristics for DBP precursor uptake. Carbons with high surface acidity exhibited generally low uptake. As-received F400 exhibited higher uptake than as-received WVB carbon. Trends in the uptake of different DOMs appear to depend primarily on surface acidity.

References

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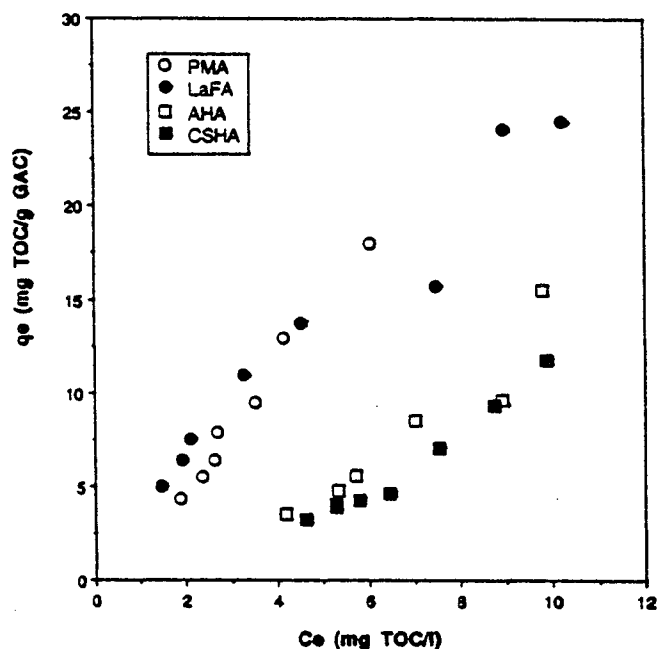


Figure 1. Uptake of NOMs by as-received F400

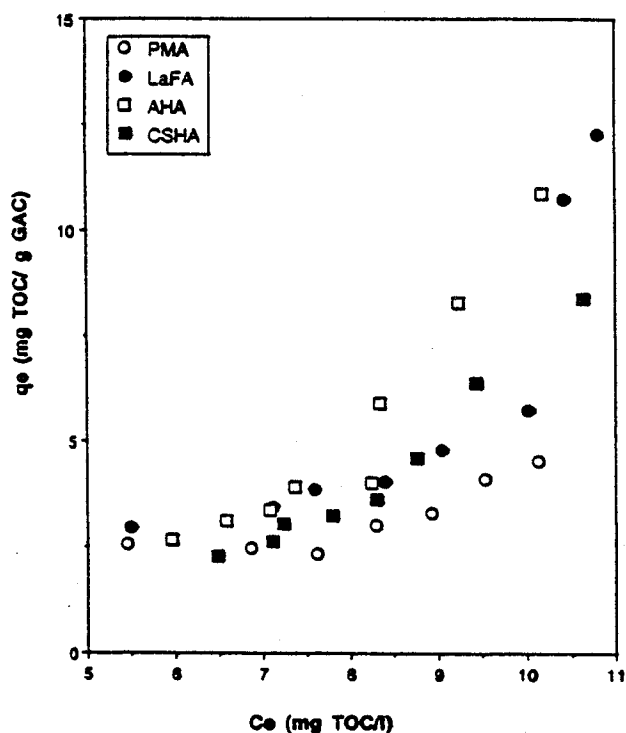


Figure 2: Uptake of NOMs by F400 heat treated at 1000°C and subsequently oxidized with HNO₃ at 70°C for 9 hours