

EXPLORING ADSORPTION OF NATURAL ORGANIC MATTER FROM NATURAL WATERS BY SURFACE-MODIFIED ACTIVATED CARBONS

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Introduction

Naturally-occurring organic material (NOM) in dissolved, colloidal and particulate forms is ubiquitous in surface and ground waters. NOM is a heterogeneous mixture of complex organic materials including humic substances, hydrophilic acids, proteins, lipids, carboxylic acids, polysaccharides, amino acids, and hydrocarbons [1]. The dissolved and colloidal forms (i.e., DOM) are the most problematic and undesirable fractions of NOM with regard to water treatment and supply. A major concern for water utilities is the formation of disinfection by-products (DBPs) resulting from reactions between DOM fractions and chlorine or other disinfectants/oxidants.

Activated carbon adsorption is one of the recommended technologies for removal of DOM from water [2]. However, the exact mechanism of DOM adsorption by activated carbons is not known. This is mainly due to the complexity of both DOM mixtures and activated carbon surfaces.

The main objective of this work is to investigate DOM-carbon surface interactions in order to enhance the removal of DOM by activated carbons. This study is conducted by using: (i) surface-modified activated carbons with different porosities and surface chemistries that previously found to enhance the DOM adsorption; and (ii) different raw and treated natural waters that represent DOM mixtures with different compositions.

Experimental

Adsorbents. Two granular activated carbons, GACs, (i.e., F400; Calgon Corp. and HD3000; Norit Inc.) and two fibrous activated carbons (i.e., ACF10 and ACF20H, American Kynol, Inc.) were used in this study. Both GACs are coal-based and steam-activated carbons. The former is a microporous, whereas the latter is a mesoporous carbon. GACs were modified using: (1) heat treatment under helium at 900°C for 2hr (**He**); (2) heat treatment under helium at 900°C for 2hr followed by oxidation with concentrated nitric acid and finally ammonia treatment at 800°C for 2hr (**He,16NO,8N2H**); and (3) heat treatment under helium at 900°C for 2hr followed by oxidation with concentrated nitric acid then iron impregnation by ion-exchange method and finally ammonia treatment at 800°C for 2hr (**He,16NO,Fe3E,8N2H**). Sequence of various treatment steps following the carbon precursor's name shows the name of each modified carbon. For example "**F400,He,16NO,8N2H**" is the name of F400 carbon that

was heat-treated under helium then oxidized by nitric acid, and finally treated with ammonia at 800°C for 2hr. Details of the modification protocols can be found elsewhere [3]. GACs within the 30/40 mesh size were used for all experiments.

Surface chemistry of activated carbons was characterized by conducting pH_{PZC} and HCl/NaOH uptake experiments. Surface area, pore volumes, and pore size distribution of adsorbents were determined using classical or DFT adsorption models applied to nitrogen isotherms. Details of these methods were described elsewhere [3].

Natural waters. Natural water samples were collected from Charleston (Ch) and Spartanburg (Sp) drinking water treatment plants in South Carolina (USA). The “raw water” (R) samples were collected from the influent to the plants, and the “treated waters” (T) were collected after the coagulation, flocculation and sedimentation process (C/F/S). Both raw and treated waters were concentrated using a reverse osmosis system [4].

SUVA₂₅₄ and size exclusion chromatography (SEC) measurements were used to characterize water samples before and after adsorption experiments. SUVA₂₅₄ is defined as the ratio of ultraviolet (UV) light absorbance at the wavelength of 254nm to the DOC concentration of the water (i.e., $\text{UV (m}^{-1}\text{)}/\text{DOC (mg/L)}$). Thus SUVA₂₅₄ value provides a semi-quantitative measure of the carbon aromaticity. The molecular size distribution of DOM macromolecules in the natural waters, before and after isotherm experiments, was determined from size exclusion chromatography results.

Adsorption isotherms. Constant-dose isotherm experiments with 0.5 g/l carbon dose and a wide range of initial DOM concentrations were performed for all natural water samples at a neutral pH [3]. Water samples, before and after adsorption experiments, were analyzed for UV absorbance, DOM, and molecular weight distribution (using SEC).

Results and Discussion

Characteristics of adsorbents. Physicochemical characteristics of virgin and treated activated carbons are shown in Table 1. A detailed discussion about the effect of each treatment on precursor’s characteristics can be found elsewhere [3]. The objective of heat treatment under helium, “He”, was to decrease the surface acidity (or increase the surface basicity) of activated carbons.

Ammonia treatment of preoxidized GACs at high temperature produced adsorbents with enhanced surface basicities (from decomposition of acidic groups at high temperature and development of basic nitrogen-containing functionalities). Due to the etching effect of ammonia, mesopore volumes of immediate precursors (oxidized carbons, not listed in Table 1) of ammonia-treated GACs were considerably increased.

Iron-impregnated carbons (**He,16NO,Fe3E,8N2H**) contained relatively high iron amounts with basic surfaces, two desired characteristics that expected to have positive

Table 1. Physicochemical characteristics of activated carbons.

Carbon	SA _{BET}	V _{micro}	V _{total}	V _{meso+macro}	DFT surface area distribution, m ² /g				pH _{PZC}	NaOH uptake	HCl uptake
	m ² /g	cm ³ /g	cm ³ /g	cm ³ /g	>0.6nm	>1nm	>2nm	>3nm		meq/g	
F400	1035	0.404	0.553	0.149	637	208	42	14	8.5	0.238	0.411
F400,He	1011	0.394	0.511	0.118	692	199	30	8	9.6	0.082	0.556
F400,He,16NO,8N2H	944	0.356	0.543	0.187	590	271	88	11	9.0	0.192	0.497
F400,He,16NO,Fe3E,8N2H	922	0.348	0.543	0.195	567	272	82	11	9.6	0.221	0.243
HD3000	676	0.265	0.711	0.445	421	174	93	52	6.9	0.565	0.223
HD3000,He	668	0.262	0.659	0.397	420	143	66	36	10.6	0.063	0.515
HD3000,He,16NO,8N2H	928	0.359	0.898	0.539	500	215	79	32	9.7	0.157	0.615
HD3000,He,16NO,Fe3E,8N2H	756	0.296	0.733	0.437	377	134	46	24	8.4	0.218	0.521
ACF10	997	0.366	0.381	~0	191	46	0	0	8.6	0.156	0.294
ACF20H	1983	0.811	0.860	0.051	1023	519	26	1	9.6	0.091	0.451

Table 2. SUVA₂₅₄ and average molecular weights of natural waters tested in this study.

Charleston Raw			Charleston Treated			Spartanburg Raw			Spartanburg Treated		
SUVA	MWw	MWn	SUVA	MWw	MWn	SUVA	MWw	MWn	SUVA	MWw	MWn
4.1	1860	1013	2.0	949	481	2.7	1624	689	1.5	886	591

impacts on DOM adsorption [3]. Surface area and pore size distribution of both ammonia-treated and iron-impregnated F400 carbons were similar. However, for HD3000 carbons surface area and pore volumes of ammonia-treated carbon were considerably higher than those of the iron-impregnated.

ACF10, and ACF20H are highly microporous fibers with different surface area and pore size distribution but similar surface basicity. Almost all of surface area of ACF10 is distributed in pores less than 1nm in width and only a small fraction of its surface area can be found in the 0.6-1nm range. On the other hand the surface area of ACF20H is evenly distributed in <0.6nm, 0.6-1nm, and >1nm ranges.

Characteristics of waters. Both Charleston and Spartanburg raw waters had relatively larger average molecule weights and higher SUVA₂₅₄ values than their treated waters. This indicated that raw waters contained higher fractions of large and hydrophobic DOMs (having more unsaturated bonds and higher degree of aromaticity). Larger DOM components were preferentially removed by coagulants during the coagulation/flocculation process. The results also showed that Charleston raw and treated DOMs had higher SUVA and molecular weight compared to the Spartanburg raw and treated water DOMs.

Adsorption isotherms. Adsorption isotherms of different natural waters showed different degrees of DOM removal by various modified activated carbons. Due to space limitation, isotherms are not shown in this extended abstract. However a classification of the extent of DOM removal by different carbons from different waters is presented in Table 3. Second and third columns of this table show a classification of overall DOM uptake, evaluated based on the adsorption isotherms (on accessible surface area- and mass-basis). The raw water results showed that only pores larger than 1nm in width of ACF10 and ACF20H were accessible to adsorption of DOM molecules. On the other hand ACF10 adsorption isotherms of treated waters (containing smaller fractions of DOM) demonstrated a minor DOM uptake. As a result, adsorption isotherms of raw and treated waters were normalized based on the surface area distributed in pores larger than 1 nm. The fourth and fifth columns in Table 3 show orders of selective DOM removal of large or small fractions, determined from the SEC results.

Previously, it was shown that increasing the surface basicity through heat treatment (under an inert or ammonia atmosphere) could enhance the adsorption of DOM uptake from Myrtle Beach raw water [3]. Furthermore it was demonstrated that iron-impregnated carbons with basic surfaces had increased uptakes.

As summarized in Table 3 (second column) and consistent with the previous observations, results indicated that in case of HD3000 series, iron-impregnated carbon (with basic surfaces) showed the highest uptakes followed by ammonia- and heat-treated carbons. For F400 series, in most cases no considerable improvement in the surface chemistry of modified carbons for DOM uptake can be observed. Enhanced DOM uptakes observed on mass-basis F400 isotherms were primarily due to increases in the accessible surface area. Observed differences between the DOM uptakes by

HD3000 and F400 carbons were attributed to the differences in their porosity. Virgin HD3000 had a mesoporous structure, therefore the effect of various treatments was predominantly reflected on its surface chemistry. On the other hand, it was found that for microporous F400, the benefit obtained in the DOM uptake from the increased mesoporosity (or supermicroporosity) exceeded those obtained from surface chemistry. Characterization results of waters, before and after adsorption, show decreases in SUVA and increases in average molecular weight values, as a result of adsorption by all activated carbons. This indicated a selective removal of hydrophobic and low molecular weight DOM components by activated carbons.

Conclusions

The results obtained in this study showed that the accessibility of DOM macromolecules to carbon pores is a key factor in the DOM adsorption. Therefore, carbon with larger pore volumes in pores > 1nm should be used or produced for DOM removal. Once the DOM molecules access the carbon pores, carbon surface chemistry becomes an important factor. Basic surface characteristics are required for adsorption of DOM. The presence of iron on the carbon surface also enhances the DOM uptake.

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Table 3. Classification of the extent of DOM removal by different carbons.

Water	Overall uptake (surface area basis)	Overall uptake (mass basis)
	F400	
Ch,R	He>N=Fe=V	N=Fe=He=V
Ch,T	He=Fe=N=V	He>N=Fe=V
SP,R	He>N=Fe=V	N>He=Fe>V
Sp,T	N=He=Fe=V	He>V>N>Fe
HD3000		
Ch,R	Fe>He=N>V	N>Fe>He>V
Ch,T	Fe>He=N>V	N=Fe>He>V
SP,R	Fe>He=N>V	Fe=N>He=V

Abbreviation codes:

Carbons: V: virgin, He: He-treated, N: He,16NO,8N2H, and Fe: He,16NO,Fe3E,8N2H.

Waters: Ch: Charleston, SP: Spartanburg, R: raw, T: treated.

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