

Unexpected Role of Activated Carbon in Promoting Transformation of Secondary Amines to *N*-Nitrosamines

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Activated carbon (AC) is the most common solid phase extraction material used for analysis of nitrosamines in water. It is also widely used for the removal of organics in water treatment and as a catalyst or catalyst support in some industrial applications. In this study, it was discovered that AC materials can catalyze transformation of secondary amines to yield trace levels of *N*-nitrosamines under ambient aerobic conditions. All 11 commercial ACs tested in the study formed nitrosamines from secondary amines. Among the different ACs, the *N*-nitrosodimethylamine (NDMA) yield at pH 7.5 ranged from 0.001% to 0.01% of initial amount of aqueous dimethylamine (DMA) concentration, but at 0.05–0.29% of the amount of adsorbed DMA by AC. Nitrosamine yield increased with higher pH and for higher molecular weight secondary amines, probably because of increased adsorption of amines. Presence of oxygen was a critical factor in the transformation of secondary amines, since ACs with adsorbed secondary amines dried under air for longer period of time exhibited significantly higher nitrosamine yields. The AC-catalyzed nitrosamine formation was also observed in surface water and wastewater effluent samples. Properties of AC play an important role in the nitrosamine yields. Preliminary evaluation indicated that nitrosamine formation was higher on reduced than oxidized AC surfaces. Overall, the study results show that selecting ACs and reaction conditions are important to minimize analytical errors and undesirable formation associated with nitrosamines in water samples.

Introduction

N-Nitrosamines are potent rodent carcinogens and probable human carcinogens, with water concentrations as low as 0.2 ng/L associated with an upperbound 10^{-6} lifetime cancer risk (1). Nitrosamines are well-known to form from nitrosation of amines in food products, and, more recently, during water disinfection processes that use chloramines, chlorine, and

ozone, qualifying them as an important class of unregulated disinfection byproducts (DBPs) (2). *N*-Nitrosodimethylamine (NDMA) is the most commonly detected nitrosamine in drinking water with reported concentrations up to 180 ng/L (3). *N*-Nitrosomorpholine (NMOR), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosopiperidine (NPIP), and *N*-nitrosodiphenylamine (NDPhA) have also been detected in drinking water at maximum concentrations about 3, 71, 118, and 2 ng/L, respectively (4, 5). In wastewater effluent, nitrosamines have been detected at concentrations 1 or 2 orders of magnitude higher than their drinking water levels (6–8).

Although there are no federal regulations controlling nitrosamines in drinking water in the United States or in Canada, the U.S. Environmental Protection Agency (EPA) has added NDMA, NPYR, *N*-nitrosodiethylamine (NDEA), *N*-nitroso-*n*-methylethylamine (NMEA), *N*-nitrosodi-*n*-propylamine (NDPA), and *N*-nitrosodi-*n*-butylamine (NDBA) to the Unregulated Contaminant Monitoring Rule 2 (UCMR-2) (9), and NDMA, NDEA, NDPA, NPYR and NDPhA to the third version of the Contaminant Candidate List (CCL3) (10). The Ontario Ministry of the Environment has a maximum allowable concentration (MAC) of 9 ng/L for NDMA (11), whereas the California Department of Public Health has established a notification level of 10 ng/L for NDMA, NDEA, and NDPA, and a public health goal (PHG) of 3 ng/L for NDMA (12).

Considering such low target levels, analysis of nitrosamines in water requires preconcentration steps such as solid-phase extraction (SPE) or liquid–liquid extraction (LLE) followed by high resolution or tandem GC/MS or LC/MS analysis. SPE is more commonly employed than LLE for nitrosamine analysis in recent years because it uses less hazardous solvents (13). Supporting Information, Table S1 summarizes the AC adsorbents that have been commonly used for nitrosamine extraction in the literature. These adsorbents include synthetic as well as coconut shell-based and charcoal-based carbonaceous particles. Taguchi et al. (14) were the first to demonstrate the synthetic Ambersorb 572 (Rohm and Haas, Philadelphia, PA) as an effective SPE adsorbent for nitrosamines. It soon became the preferred choice for extraction of nitrosamines in aqueous media as demonstrated by numerous studies conducted using this adsorbent (Supporting Information, Table S1). EPA's Method 521 (15) for nitrosamine analysis uses coconut shell-based carbonaceous adsorbents for SPE. A number of other carbonaceous adsorbents (Supporting Information, Table S1) have been reported for SPE of nitrosamines in water as well as in foods and beverages with lower extraction efficiencies than Ambersorb 572. However, Rohm and Haas discontinued Ambersorb 572 production in 2007 (16), leading to an increase in the demand for alternate carbonaceous SPE materials including coconut shell-based (17) and charcoal-based (18) carbons.

AC materials are also widely used in drinking water and wastewater treatment, primarily for removal of small molecular weight organic compounds. Liquid-phase applications of AC constitutes 80% of the total AC demand in the U.S. (>500 million pounds), of which the removal of water contaminants represents the major market (55%) (19). Of the total U.S. water treatment market for AC adsorbents, about 50% is in drinking water, 40% is in wastewater, and the rest is in groundwater applications (19). Potable water is the largest end-use market for AC, accounting for more than 100 million pounds. Demand for AC in public service water is expected to grow at approximately 4.5% annually (20).

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AC materials are also frequently used as catalyst supports or in some cases catalysts in various industrial processes including hydrogenation, oxidation, polymerization, and halogenation (21, 22). For example, the production of phosgene (carbonyl chloride) and oxidation of pollutant gases in air pollution control employ AC catalysts. ACs are less used as catalysts for the abatement of organic pollutants in the liquid phase. However, the use of ACs for catalytic wet air oxidation (CWAO) of organic pollutants in waste streams is developing. CWAO of phenolic compounds has been studied in detail (23). Apart from phenols, ACs have been shown as effective catalysts for CWAO of ammonia, aniline, dimethylamine, methylamine, 1,3,6-naphthalene trisulphonic acid, hydrogen peroxide, cyclohexanone, and *N*-phosphonomethyliminodiacetic acid (23, 24).

As to be documented in this paper, while examining various AC materials for SPE of *N*-nitrosamines, it was discovered that many ACs can catalyze transformation of secondary amines to form *N*-nitrosamine under ambient aerobic conditions. Because of the widespread applications of AC materials in water analysis and water treatment, this finding has significant implications in a broad range. This is also a novel discovery since to the best of our knowledge, only one prior work by Dietrich et al. (25) reported that AC particles can catalyze nitrosation of a secondary amine (*N*-methylaniline) with nitrite to form *N*-nitroso-methylaniline. Currently, there is little information in literature regarding the transformation of secondary amines on AC surfaces to form nitrosamines, the potential role of AC in catalyzing nitrosamine formation, the impact of reaction conditions, or the involved reaction mechanisms. Without such knowledge, nitrosamine analysis will continue to be susceptible to this potential error. Furthermore, understanding the roles of AC materials and water treatment conditions on nitrosamine formation will be important to assess the significance of these findings for practical applications.

As an initial effort to address the important information need on this topic, we systematically examined the formation of nitrosamines from amine precursors on various AC surfaces under typical nitrosamine analysis conditions with the objective to identify critical factors influencing this reaction. This study reports the reaction yields in reagent and real water matrices, and the factors including AC properties, amine properties, and environmental conditions that influence the nitrosamine formation.

Materials and Methods

Chemicals. Sources of chemicals and reagents are provided in the Supporting Information, Text S1.

ACs' Modifications and Characterization. Eight types of AC particles (Ambersorb 572, PSC, AqC, OLC, F400, HD4000, GAC, UCT) and three types of AC fibers (ACF10, ACF15, ACF20H) were investigated in this study. Sources and descriptions of these synthetic, coconut shell-based, or coal-based ACs are provided in Supporting Information, Text S2. These AC materials were selected to represent ACs of different origins, uses, and properties. They are also widely used in environmental applications. For example, Ambersorb 572 and UCT represent AC particles used for SPE of nitrosamines, AqC, PSC and GAC represent carbons that are supplied to water and wastewater treatment plants by leading AC suppliers, F400, OLC and HD4000 have been commonly employed in adsorption studies of organic compounds, and carbon fibers possess special properties such as more uniform pore size distribution. Four types of ACs were also pretreated using different approaches (details in Supporting Information, Text S2) to modify their surface characteristics. The PSC particles were pretreated with H₂SO₄, HCl, or ozone, or were baked at 600 °C. For F400, OLC, and HD4000, the particles were pretreated with hydrogen or nitric acid at

elevated temperature. The physicochemical characteristics of both untreated and treated ACs were characterized using established methods as described in Supporting Information, Text S2.

Drinking Water and Wastewater Effluent Samples. Grab samples of surface water (SW) and wastewater effluent (WW) were collected from a municipal drinking water treatment plant (DWTP) and a wastewater treatment plant (WWTP) in the Southeastern U.S. SW sample was collected from the reservoir supplying source water to the DWTP. WW sample was collected after activated sludge secondary treatment and gravity filtration, but prior to chlorine-based disinfection process. Selected properties of the SW and WW samples are provided in Supporting Information, Text S3.

Experimental Setup and Nitrosamine and Amine Analyses. Batch experiments were conducted in either deionized water or natural waters (i.e., SW or WW) using amber borosilicate bottles with Teflon-lined caps. Experiments followed the literature-established protocol (14): AC particles (150–200 mg) were added to 100 mL of DMA or other secondary amine solution (at 1–444 μM) containing 31.25 nM (or 1.25 nM in real water experiments) of NDMA-d₆ or NDPA-d₁₄ surrogate standard and 10 mM phosphate buffer. The isotope-labeled surrogates are used to correct for nitrosamine extraction efficiency and matrix effect in the isotope dilution method (6, 14, 26). The above amine concentrations were selected to obtain substantial differences in nitrosamine formation from different AC particles, as well as to assess factors influencing nitrosamine formation. The amine+AC solution was shaken on a platform shaker at 200–250 rpm for 1.5–2 h at room temperature (22.5 °C) and filtered through a glass-fiber filter (Millipore, Jaffrey, NH). The collected carbon particles were air-dried for 3–6 h typically unless specified otherwise, transferred to a GC vial, and 0.5 mL dichloromethane (DCM) was added to desorb nitrosamines from the particles. Note that because drying the SPE phase is important to facilitate satisfactory elution of nitrosamines (3), reported studies commonly employed air drying of ACs for 3 h or more (27, 28). Then, the DCM layer was analyzed for nitrosamines by GC/MS. For control experiments (samples without AC particles), LLE was used to extract nitrosamines, in which 100 mL (deionized water) or 500 mL (real water) of reaction solution as described above was extracted with 25 or 100 mL DCM, respectively, by vigorous shaking for 2 min. The DCM layer was separated, concentrated down to 0.5 mL by evaporating under vacuum, and analyzed for nitrosamines by GC/MS.

For secondary amines, 2 mL of reaction aliquot were taken before the filtration step and spiked with DMA-d₆ at 1.96 μM from a freshly prepared aqueous stock. The sample aliquot was adjusted to pH 9.0 by 10 mM borate buffer and added with 5 mM 4-methoxybenzenesulfonyl chloride as derivatizing agent. The resulting solution was agitated for 2 h and extracted with 2 mL DCM for 2 min. The extracts were analyzed for derivatized secondary amines by GC/MS. Details of GC/MS conditions for nitrosamines and amines and detection limits are provided in Supporting Information, Text S4.

Results and Discussion

AC-Catalyzed Nitrosamine Formation. Experimental results unambiguously showed that secondary amines can transform to *N*-nitrosamines in the presence of AC particles. This phenomenon was observed, to different extent, on all AC particles and AC fibers tested in this study (Table 1). When 100 mL of DMA-containing (200–222 μM) solutions were subjected to SPE using AC particles at pH 7.5, 0.16 to 2.14 nano moles of NDMA were formed (Table 1), approximately 0.001% to 0.01% of initial amount of DMA in water. In contrast, no nitrosamine formation was detected when the

TABLE 1. NDMA Formation from DMA in the Presence of AC Materials

carbon materials	specific surface area S_{BET} (m^2/g)	pH_{zpc}	test conditions	NDMA (nano moles)	NDMA (ng/L)	NDMA (ng/L) by NDMA- d_6 isotope dilution
Amborsorb 572	1020	7.0	<i>a</i>	0.45 ± 0.33^c	333 ± 244	972 ± 702
AqC	1202	9.6	<i>a</i>	2.14 ± 0.18	1584 ± 133	11337 ± 954
PSC	1114	9.7	<i>a</i>	0.57 ± 0.07	422 ± 52	4971 ± 618
UCT	NA	NA	<i>a</i>	1.68 ± 0.09	1243 ± 67	4463 ± 249
GAC	819	7.4	<i>a</i>	0.28 ± 0.03	207 ± 22	2316 ± 258
F400	1044	9.2	<i>b</i>	0.61 ± 0.08	451 ± 59	3773 ± 509
OLC	983	9.3	<i>b</i>	0.86 ± 0.02	636 ± 15	5794 ± 141
HD4000	706	6.6	<i>b</i>	0.60 ± 0.01	444 ± 7	4459 ± 74
ACF 10	972	7.3	<i>b</i>	0.17 ± 0.01	126 ± 7	1275 ± 73
ACF 15	1520	8.9	<i>b</i>	0.21 ± 0.01	155 ± 7	1558 ± 71
ACF 20H	1740	9.5	<i>b</i>	0.16 ± 0.02	118 ± 15	627 ± 80

^a 222 μM DMA, 200 mg carbon, 2 h suspension shaking time, 3 h carbon drying time. ^b 200 μM DMA, 150 mg carbon, 1.5 h suspension shaking time, 6 h carbon drying time. ^c Experiments were conducted with regenerated Amborsorb 572 particles which were washed with methanol and then dichloromethane, followed by drying in an 100 °C oven. All reaction suspensions were buffered at pH 7.5 by 10 mM phosphate buffer. Instrument detection limit for NDMA = 2 pico moles; Mean \pm standard deviation ($n = 3$); NA = not available; pH_{zpc} : zero point of charge.

amine solution was subjected to LLE without using AC. These results corresponded to 118–1,584 ng/L of NDMA in mass concentrations. Further, if NDMA concentration was quantified by isotope dilution method with NDMA- d_6 which corrected for NDMA extraction efficiency, as is the current practice for SPE protocol, the above NDMA concentrations increased by an order of magnitude to 627–11,337 ng/L (Table 1). Since the carbon-catalyzed NDMA formation from DMA varied significantly among the AC materials (Table 1), the results indicated that AC properties play a role in the NDMA formation. While Amborsorb 572 and AC fibers exhibited the lowest yields, Siemens Aquacarb particles (AqC) showed the highest yield.

These findings were carefully verified with a number of control experiments. Extractions of secondary amine stocks and carbon particles by DCM showed no nitrosamine contamination. Furthermore, similar levels of NDMA formation were observed when the same experiments using AqC and Prominent Systems carbon (PSC) particles were conducted in commercial HPLC-grade water instead of the deionized water available in our lab. Because AC has the potential to catalyze nitrosation of secondary amines with nitrite to yield nitrosamines (25), nitrite was measured using a colorimetric method (29) and found to be below the method detection limit (MDL \sim 70 nM) in the deionized water used in the experiments and in DMA stocks. Spiking various amounts of nitrite in solutions showed that additional NDMA formation compared to no nitrite spiking did not occur until nitrite concentration reached 500 nM (0.023 mg/L) (Supporting Information, Table S2). These results confirmed that nitrite at concentrations below the MDL, if it existed in the deionized water, was not a contributing factor to the observed NDMA formation.

The AC-catalyzed nitrosamine formation could occur (i) while in the suspension state when carbon particles were immersed in solution, and (ii) during drying of carbon particles after filtration. To distinguish the contributions from these two different steps, the amount of nitrosamine formed while in the suspension state was determined by the following procedures: water in the amine+AC aqueous suspension was decanted to collect the carbon particles; DCM was immediately added to the carbon particles in a centrifuge tube followed by centrifugation; afterward, the DCM layer was analyzed for nitrosamines by GC/MS. The amount of nitrosamine formed during carbon drying was then determined by subtracting the amount formed while in the suspension state from the overall nitrosamine formation. It was found that more nitrosamine formed during drying of

AC particles. For example, results with the PSC particles showed that 0.05 ± 0.00 nano moles of NDMA were formed during shaking (1.5 h) of amine+AC suspension, while total NDMA formation for air-dried AC particles, including contribution during shaking (1.5 h shaking and 1.5 h drying), was 0.44 ± 0.03 nano moles. Hence, more than 90% of total NDMA formation occurred during drying of AC particles. It is for this reason that the nitrosamine concentrations to be presented later in all figures were direct measurements, not quantified by the isotope dilution method that corrected for extraction recoveries. In this way, the amount of nitrosamine reported is likely lower than the real amount and thus represents a conservative estimate.

Surface Water and Wastewater Samples. To examine the significance of the above results obtained in deionized water, experiments were also conducted in SW and WW samples. A larger sample volume (500 mL) was subjected to SPE to achieve a lower MDL for NDMA. Samples were extracted by two different carbons (Calgon F400 and Siemens AqC) using procedures described above. AqC and F400 were used in these experiments because they represent ACs with high and low capability to catalyze NDMA formation, respectively, based on our results (Table 1). For comparison, the natural water samples were also fortified with DMA (1 μM [45 $\mu\text{g}/\text{L}$] in SW and 10 μM [450 $\mu\text{g}/\text{L}$] in WW) before SPE. The selected spiking concentrations represent the upper concentration ranges of DMA and other secondary amines found in environmental samples. Previous studies reported DMA concentrations ranging from 1–3 $\mu\text{g}/\text{L}$ (30) in surface waters to up to 235 $\mu\text{g}/\text{L}$ in rivers that receive considerable discharge of wastewater effluents (31). Similarly, diethylamine (DEA) was detected in surface waters at 9–13 $\mu\text{g}/\text{L}$ (31, 32). High incidence of multiple secondary amines in wastewaters has been documented in numerous studies with concentrations of DMA and other amines at 20–1,000 $\mu\text{g}/\text{L}$ (6, 8, 33, 34). Secondary amines have also been employed at varying concentrations as high as 180 mg/L (35, 36) in laboratory studies involving AC particles for extraction of nitrosamines.

A total of five sets (Table 2) were analyzed for each sample with the first set being controls (marked as blank) which employed LLE to quantify residual concentrations of secondary amines and nitrosamines in the SW and WW samples. In the others sets, 200 mg of AC particles were used to extract samples. Both SW and WW had residual NDMA levels below MDL (2–3 ng/L). DMA was not detected (<0.1 $\mu\text{g}/\text{L}$) in SW, while WW had 0.8 $\mu\text{g}/\text{L}$ of DMA. For SW, NDMA did not form above MDL when DMA was not added to the sample, while 0.3 ± 0.0 ng/L (or 8 ± 0 ng/L by NDMA- d_6 isotope dilution)

TABLE 2. NDMA Formation in Surface Water and Wastewater Effluent in the Presence of AC Particles^a

sample	water pH	initial DMA ($\mu\text{g/L}$)	NDMA (nano moles)	NDMA (ng/L)	NDMA (ng/L) by NDMA- d_6 isotope dilution
SW blank	6.3	ND	ND	ND	ND
SW + F400	6.4	ND	ND	ND	ND
SW + AqC	6.9	ND	ND	ND	ND
SW + DMA (1 μM) + F400	6.6	45.8 \pm 0.9	0.002 \pm 0.000	0.3 \pm 0.0	8 \pm 0
SW + DMA (1 μM) + AqC	7.3	46.3 \pm 4.1	0.022 \pm 0.007	3.2 \pm 1.0	59 \pm 15
WW blank	6.9	0.8 \pm 0.0	ND	ND	ND
WW + F400	7.1	0.6 \pm 0.1	0.003 \pm 0.001	0.4 \pm 0.2	10 \pm 0
WW + AqC	7.1	0.6 \pm 0.1	0.006 \pm 0.003	0.9 \pm 0.4	16 \pm 3
WW + DMA (10 μM) + F400	7.3	459.2 \pm 0.8	0.071 \pm 0.002	10.6 \pm 0.2	210 \pm 30
WW + DMA (10 μM) + AqC	7.3	457.1 \pm 4.7	0.340 \pm 0.007	50.3 \pm 1.0	686 \pm 66

^a SW: Surface Water; WW: Wastewater. Experiments used 200 mg carbon (F400 or AqC) and conditions (a) in Table 1 except that the water pH was not adjusted. Instrument detection limit for NDMA = 2 pico moles; ND = non-detectable; Mean \pm standard deviation ($n = 2$).

and 3.2 \pm 1.0 ng/L (or 59 \pm 15 ng/L by NDMA- d_6 isotope dilution) of NDMA formed with F400 and AqC particles, respectively, when 1 μM DMA was added. For WW not fortified with DMA, 0.4 \pm 0.2 (or 10 \pm 0 ng/L by NDMA- d_6 isotope dilution) and 0.9 \pm 0.4 ng/L (or 16 \pm 3 ng/L by NDMA- d_6 isotope dilution) of NDMA formed with F400 and AqC particles, respectively. When WW was fortified with 10 μM DMA, 10.6–50.3 ng/L (or 210–686 ng/L by NDMA- d_6 isotope dilution) of NDMA formed (Table 2). WW samples showed higher NDMA yields than SW samples when normalized by the spiked DMA concentration. This might be partly due to the presence of residual nitrite (0.4 mg/L) in the wastewater samples, and nitrosation was catalyzed by AC. The AqC consistently showed higher NDMA yield than F400, as observed in deionized water matrix. These results further confirm that ACs can catalyze nitrosamine formation from amine precursors in natural water matrixes, and the choice of SPE carbons can significantly impact the analytical results of nitrosamine measurements.

Effect of Reaction Conditions. The AC-catalyzed nitrosamine formation was further evaluated for the impact of reaction conditions including secondary amine concentration and structure, solution pH, and presence of oxygen. PSC particles were used throughout this part of study for consistency. PSC was selected because it formed intermediate levels of NDMA among the ACs (Table 1) and was abundantly available in our lab.

Role of Amine. The effect of amine concentration was evaluated using the same nitrosamine SPE protocol described above by spiking DMA from 1 to 444 μM to solutions buffered

at pH 7.5. Two hundred milligrams of PSC particles were added for extraction of NDMA. As shown in Figure 1A, the amount of NDMA formed was linearly ($R^2 = 0.97$) correlated with DMA concentration in the solution. Control experiment without DMA addition showed non-detectable amount of NDMA formation.

Similar experiments were also conducted on four other secondary amines, MEA, DEA, DPA, and DBA, using 222 μM initial amine concentration and 200 mg PSC particles at pH 7.5. The secondary amines formed corresponding *N*-nitrosamines, that is, MEA to NMEA, DEA to NDEA, DPA to NDPA, and DBA to NDBA (Figure 1B). Each amine formed only its corresponding *N*-nitrosamine and no nitrosamines formed in the absence of AC. A linear relationship between NDBA formation and DBA concentration in the solution was also observed (Supporting Information, Figure S1). In general, the amount of nitrosamine formed was higher for higher molecular weight secondary amines (Figure 1B), possibly because of their increased hydrophobicity and, hence, increased adsorption efficiency on AC particles. Experiments showed that the amount of amine adsorbed to the PSC particles, determined based on the difference between the initial and final (after shaking) amine concentrations, was 1.4%, 2.7%, 3.2%, 6.8%, and 67.6% for DMA, MEA, DEA, DPA, and DBA, respectively. The yield of nitrosamine formation was calculated based on the amount of nitrosamine formed divided by the amount of adsorbed amine (both in nano-moles) on PSC particles. At pH 7.5, the nitrosamine yield was around 0.10% for the above five secondary amines for the PSC particles. Similarly, the nitrosamine formation yield was

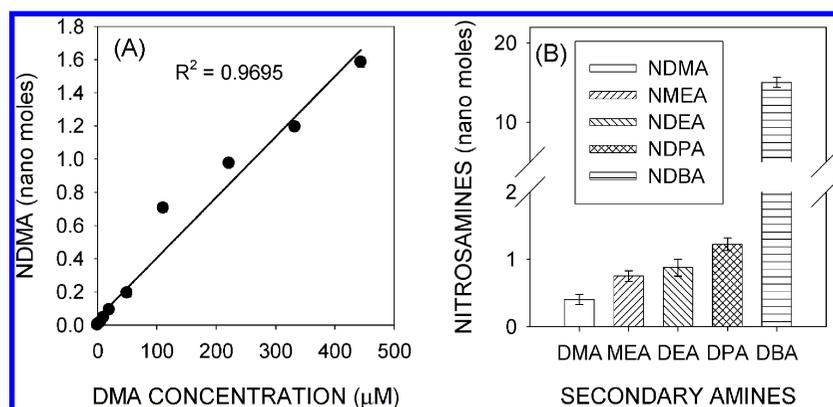


FIGURE 1. Nitrosamine formation from secondary amine in the presence of AC particles: (A) NDMA formation as a function of DMA concentration, (B) Formation of corresponding nitrosamines from five secondary amines. Experiments used 200 mg PSC particles and conditions (a) in Table 1 except that the DMA concentration varied and the carbon drying time was 6 h in (A). (Nitrosamine concentration was not corrected by isotope surrogate recovery; Error bars represent one standard deviation of the means; $n = 3$).

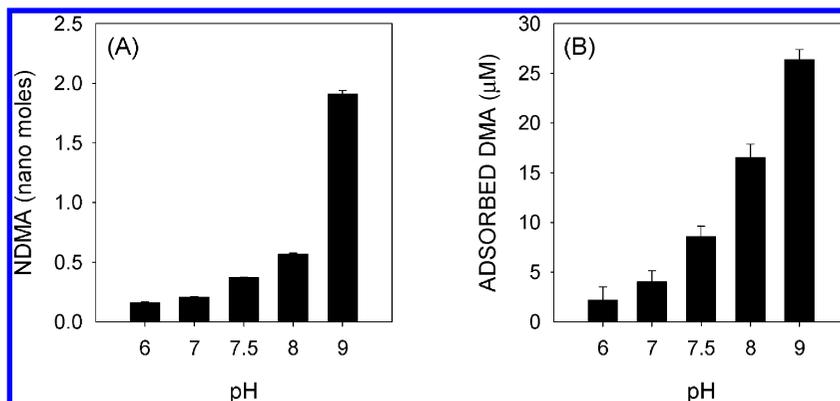


FIGURE 2. Effect of solution pH on (A) NDMA formation from DMA in the presence of AC particles, (B) adsorption of DMA to AC particles. Experiments used 200 mg PSC particles and conditions (a) in Table 1. (NDMA concentration was not corrected by NDMA- d_6 recovery; Error bars represent one standard deviation of the means; $n = 3$).

calculated to be around 0.05%, 0.07%, 0.19%, and 0.29% for F400, HD4000, OLC, and AqC, respectively, based on the amount of NDMA formed divided by the amount of DMA adsorbed at pH 7.5.

These results confirm that secondary amines are precursors of nitrosamines in the AC-catalyzed nitrosamine formation, and the concentration and structure of amine strongly influence the reaction. However, similar patterns of the AC-catalyzed nitrosamine formation from different amines suggest that the involved reaction mechanisms are likely similar.

Effect of pH. The effect of pH was studied at pH 6.0, 7.0, 7.5, 8.0, and 9.0 (buffered by 10 mM phosphate buffer and NaOH) using 222 μM secondary amine and 200 mg of PSC particles. NDMA formation increased non-linearly with increase in pH and was particularly higher at pH 9 (Figure 2A). A similar pH trend was observed for NDBA formation from DBA in the presence of AC (Supporting Information, Figure S2A). The increased nitrosamine formation at higher pH is likely related to greater adsorption of secondary amines to the AC surfaces as at higher pH more of the amines are in the unprotonated forms ($pK_a \sim 10\text{--}11$ for aliphatic secondary amines (37)) and, hence, are more susceptible to adsorption by PSC with zero-point-of-charge (pH_{ZPC}) of 9.7 (Table 3). Indeed, the amount of DMA or DBA adsorbed increased with increase in pH (Figures 2B and S2B). However, amine adsorption alone could not fully explain the amount of nitrosamine formed at different pH as the formation yield (amount of nitrosamine formed/amount of amine adsorbed) was doubled from pH 6.0 (0.1%) to pH 9.0 (0.2%). Other mechanisms also play a role and require further study to fully understand the pH effect. Also, the observed pH trend contradicts with the acidic conditions favored by nitrosation

involving nitrite with or without the presence of AC (25, 38), further supporting that a different mechanism than nitrosation is responsible for the observed catalyzed nitrosamine formation.

Effect of Oxygen. As mentioned earlier, more nitrosamine was formed during the drying step of AC particles than in aqueous suspension. As the drying time increased, nitrosamine formation also increased (Figure 3A); the correlation was linear ($r^2 > 0.99$) until up to 12 h and deviated from linearity at longer drying duration. Further, it was observed that significantly less amount of nitrosamine formed when drying of AC particles was conducted under pure nitrogen gas instead of air (data not shown). Thus, oxygen gas was suspected to play an active role in transformation of secondary amines to nitrosamines. Hence, subsequent experiments were conducted to test the effect of oxygen flow on nitrosamine formation in a controlled environment during drying of AC particles. DMA was spiked at 222 μM in a pH 7.5 buffered solution, and 200 mg PSC particles were added for SPE. After 2 h of shaking, particles were filtered and then transferred to 125 mL glass reactors. Reactors were immediately sealed with rubber stoppers and aluminum crimps upon transferring of the AC particles. An inlet and outlet were supplied in the reactor for oxygen circulation. Pure oxygen was employed for drying of AC particles at three different flow rates of 50, 100, and 200 mL/min for the duration of 3 h after which NDMA formed was quantified. When oxygen velocity was increased, nitrosamine formation was also increased, with a preliminary linear relationship ($R^2 > 0.99$) between oxygen velocity and NDMA formation (Figure 3B). The impact of particle drying time and oxygen gas flow rate on the AC-catalyzed NDBA formation from DBA showed very similar trends as those for NDMA formation (Supporting

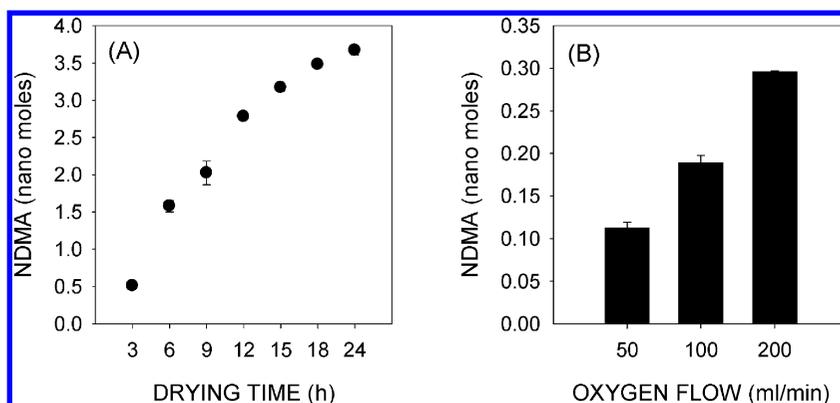


FIGURE 3. Effect of oxygen during drying of AC particles: (A) NDMA formation as a function of drying time, (B) NDMA formation as a function of oxygen flow. Experiments used 200 mg PSC particles and conditions (a) in Table 1. (NDMA concentration was not corrected by NDMA- d_6 recovery; Error bars represent one standard deviation of the means; $n = 3$).

TABLE 3. Effect of Pretreatment of AC Particles on NDMA Formation from DMA in the Presence of AC Particles

carbon particles	specific surface area S_{BET} (m ² /g)	pH _{ZPC}	test conditions	adsorbed DMA (micro- moles)	NDMA (nano moles)	NDMA (ng/L)	NDMA (ng/L) by NDMA-d ₆ isotope dilution
PSC_untreated	1114	9.7	<i>a</i>	0.55 ± 0.02	0.57 ± 0.07	422 ± 52	4971 ± 618
PSC_untreated (w/Na ₂ S ₂ O ₃)	1114	9.7	<i>c</i>	NA	0.86 ± 0.02	636 ± 15	5815 ± 145
PSC_H ₂ SO ₄ treated	1134	2.5	<i>a</i>	0.77 ± 0.01	ND	ND	ND
PSC_HCl treated	NA	NA	<i>a</i>	NA	0.51 ± 0.12	377 ± 89	4450 ± 1051
PSC_O ₃ treated	1088	6.9	<i>a</i>	0.59 ± 0.00	0.26 ± 0.02	192 ± 15	2285 ± 183
PSC_baked at 600 °C	NA	NA	<i>a</i>	0.64 ± 0.05	1.16 ± 0.10	858 ± 74	10109 ± 873
F400_untreated	1044	9.2	<i>b</i>	1.93 ± 0.11	1.01 ± 0.04	747 ± 30	6224 ± 815
F400_H ₂ treated	1075	10.2	<i>b</i>	1.59 ± 0.18	1.30 ± 0.17	962 ± 126	10701 ± 1410
F400_HNO ₃ treated	980	3.7	<i>b</i>	1.69 ± 0.19	0.66 ± 0.02	488 ± 15	5461 ± 179
OLC_untreated	983	9.3	<i>b</i>	0.45 ± 0.03	0.84 ± 0.04	622 ± 30	6011 ± 248
OLC_H ₂ treated	1080	10.2	<i>b</i>	0.69 ± 0.07	1.22 ± 0.11	903 ± 81	9073 ± 822
OLC_HNO ₃ treated	1030	3.5	<i>b</i>	2.79 ± 0.04	0.28 ± 0.01	207 ± 7	2103 ± 81
HD400_untreated	706	6.6	<i>b</i>	0.90 ± 0.06	0.63 ± 0.03	466 ± 22	4783 ± 92
HD4000_H ₂ treated	838	9.9	<i>b</i>	1.10 ± 0.07	1.80 ± 0.19	1332 ± 140	13338 ± 1409
HD4000_HNO ₃ treated	714	3.2	<i>b</i>	2.64 ± 0.03	0.65 ± 0.04	481 ± 30	4823 ± 306

^a 222 μM DMA, 200 mg carbon, 3 h carbon drying time; ^b 222 μM DMA, 200 mg carbon, 12 h carbon drying time; ^c Similar to (a) conditions but also with 222 μM Na₂S₂O₃. Reaction suspensions were buffered at pH 7.5 by 10 mM phosphate and shaken for 2 h prior to filtration. pH_{ZPC}: Zero Point of Charge Instrument detection limit for NDMA = 2 pico moles and for DMA = 0.01 pico moles; ND = nondetectable; NA = not available; Mean ± standard deviation (*n* = 3).

Information, Figure S3). On the basis of these results, oxygen exposure is determined to be a critical factor for the AC-catalyzed nitrosamine formation from secondary amines.

Role of AC Materials. The above results established that AC can induce transformation of secondary amines in the presence of oxygen to generate *N*-nitrosamines, and the reaction occurs on the AC surfaces as adsorption of secondary amines to AC surfaces is a critical factor. Owing to different properties of ACs, nitrosamine formation varied with different AC materials (Table 1). However, no specific correlation was found between nitrosamine formation and the specific surface area of ACs. On the other hand, carbons with lower pH_{ZPC} appeared to be weaker at catalyzing nitrosamine formation than carbons with higher pH_{ZPC}, suggesting the composition of carbon's surface functional groups may be important.

To further evaluate AC's capability to catalyze transformation of secondary amines to form nitrosamine, some of the AC particles were subjected to different pretreatments to modify carbon's surface composition. As shown in Table 3, pretreating PSC particles with H₂SO₄ or ozone significantly lowered AC's capability to catalyze nitrosamine formation, while baking the carbon particles at 600 °C prior to usage resulted in carbons that were stronger at catalyzing nitrosamine formation. Pretreatment of F400, OLC, and HD4000 particles under hydrogen atmosphere at high temperature resulted in greater nitrosamine formation for all three carbons, while pretreatment of carbons with nitric acid lowered nitrosamine formation for F400 and OLC. It was also found that the carbon-catalyzed nitrosamine formation was greater when thiosulfate was present in the sample, a reductant frequently added to drinking water or wastewater samples to quench residual disinfection oxidants.

Treating AC particles with H₂SO₄ or ozone oxidizes surface functional groups resulting in more carboxylic groups, while baking carbon particles at higher temperature liberates oxygen from surface functional groups and makes carbon surface more basic (39). Heat treatment under hydrogen flow removes considerable portion of oxygen surface functionalities, reduces surface functional groups, and decreases the surface acidity of carbons, while treatment with nitric acid oxidizes carbon's surfaces and increase the surface acidity

(40–42). These modifications are evident from the pH_{ZPC} values measured for the modified carbons (Table 3). The finding that the presence of thiosulfate reductant can enhance the AC-catalyzed nitrosamine formation is also consistent with the trend observed with reduced versus oxidized carbons. In contrast, the carbon modifications did not result in significant change in carbon's specific surface area (Table 3). Notably, acid treatment of carbons actually resulted in greater adsorption of DMA to the carbon surfaces, while the carbon-catalyzed nitrosamine formation was significantly lowered for OLC and did not increase for F400 and HD4000. Although not characterized in this study, acid treatment also reduces inorganic impurities on carbon surfaces. Thus, these results suggest that the composition of surface oxygen functional groups and maybe also inorganic impurities on AC surfaces play a role in the carbon-catalyzed nitrosamine formation reactions.

While literature is scarce regarding carbon-catalyzed transformation of amines under ambient aerobic conditions, our experimental results show some similarity with AC-based catalytic wet air oxidation (CWAO) of amines. In the work by Aguilar et al. (43) that utilized ACs as catalysts in the CWAO (at 195 °C and 16 atm) of methylamine and DMA, the authors found that the quinone surface groups (releasing CO by temperature programmed decomposition (TPD)) on ACs were responsible for the catalytic activity, while carboxylic, lactone, and anhydride groups (releasing CO₂ in TPD) were responsible for a catalytic activity inhibition, despite that the latter groups exhibited stronger adsorption of the amines. Methylamine and DMA were oxidized to nitrogen, water, CO₂, and traces of nitrite and nitrate under the employed CWAO conditions. In another study by Gomes et al. (24), AC-based CWAO of aniline generated a range of byproducts including nitrosobenzene and azobenzene. The authors proposed that the oxidizing species are oxygen either in the bulk or adsorbed and hydroxyl radicals readily formed under CWAO's high temperature and pressure conditions, and the catalytic removal of aniline was related to the presence of quinone-type surface functional groups.

Furthermore, it has been well documented in the literature that some AC surfaces can catalyze oxidation of adsorbed phenolic compounds under environmental oxic conditions,

leading to the so-called “irreversible adsorption” of phenols on AC surfaces (44–46). The oxidation of phenols results in dimers and higher polymeric products (47). Dissolved oxygen is involved in the above reaction. It has been proposed that radical species formed from interactions of oxygen with carbon surfaces oxidize the phenols (44, 46). The presence of basic surface functional groups promotes irreversible adsorption of phenols while acidic surface functional groups exhibit the opposite effect (48).

On the basis of our results and comparison to the literature, we speculate that AC surfaces may catalyze oxidation of adsorbed amines in the presence of oxygen to yield nitrosamines. More research is currently underway in our lab to further identify the reaction mechanisms and the role of carbon surface characteristics in the catalyzed nitrosamine formation reactions.

Analytical and Environmental Significance. Overall, the findings in this study are highly relevant for both nitrosamine analysis and water treatment operations. The NDMA yield observed with a variety of ACs at pH 7.5 ranged from 0.001% to 0.01% based on the molar ratio of NDMA concentration to the initial aqueous DMA concentration. Thus, for water that contains 0.1 μ M of DMA (4.5 μ g/L), AC-based SPE may generate about 0.1–0.7 ng/L of NDMA. If the NDMA concentration is corrected by NDMA- d_6 recovery as would normally be conducted in nitrosamine analysis by isotope dilution, up to 3–4 ng/L of NDMA can be reported assuming 20% extraction efficiency. Thus, the AC’s catalytic effect alone could contribute to the trace levels of nitrosamines detected. It is important to note that the above estimation is only an example and will be influenced by the type of AC, the amount of DMA in the water and water matrix. The results show that this analytical artifact is important for natural water samples, particularly in wastewater, where higher amounts of amine precursors, nitrite, and other unknown constituents are present. This analytical error is also greater for higher molecular weight nitrosamines, and can become significant in laboratory studies that often employ elevated amine concentrations. Not evaluated in this study, SPE cartridges with packed AC particles are also currently being used for nitrosamine extraction. In those cases, nitrosamine formation may be lower because of less exposure of carbons to air but will depend on the adopted SPE protocol. Our evaluation on the impact of carbon surface characteristics offers useful information in selecting carbon pretreatment methods to minimize this analytical error.

While relevant, the implications on water treatment operations are probably less than those in analytical methods considering that most surface water contains only low concentrations of amines, the typical contact time during AC processes (in PAC or GAC mode) are rather short, and the formation of nitrosamines was significantly higher during drying phase than in the solution. However, it is possible for amines to accumulate on AC surfaces (used in water treatment processes or in household water filtration device) over time and gradually transform to yield nitrosamines because of the catalytic effect of AC in the presence of oxygen. Furthermore, AC-based processes are commonly coupled with preoxidation by ozone or other oxidants. Such preoxidation processes may generate intermediates such as nitrite that can contribute to nitrosamine formation via catalyzed nitrosation by AC surfaces. More research is needed to further understand the practical implications of findings obtained in this study.

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Supporting Information Available

Additional information in the form of Text S1–S4, Tables S1 and S2, and Figures S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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