Transformation of Amines to Nitrosamines on Activated Carbons [Project #4343]

ORDER NUMBER: 4343

DATE AVAILABLE: November 2013

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OBJECTIVES

The objectives of this project were to (1) minimize potential analytical errors caused by activated carbon (AC)-catalyzed nitrosamine formation reactions and identify the involved reaction mechanisms, and (2) evaluate the potential of AC-catalyzed nitrosamine formation under AC-based water filtration applications. The goal was to develop effective and practical strategies for the water industry to minimize undesirable nitrosamine formation associated with AC adsorbents in nitrosamine analysis and water treatment.

BACKGROUND

Nitrosamines are a group of potent carcinogens that have been shown to form as disinfection by-products (DBPs) from water disinfection processes. AC is the most common solid phase extraction (SPE) material used for analysis of nitrosamines in water. AC is also widely used for the removal of organics in water treatment and as a catalyst or catalyst support in industrial applications. Results reported in recent research indicate that AC materials may catalyze oxidation of amines under ambient aerobic conditions, and catalyze nitrosation of amines with nitrite, to generate nitrosamines. The potential capability of AC materials to promote nitrosamine formation has significant implications for the water industry and beyond. Prior to this project, information regarding the potential role of AC in catalyzing nitrosamine formation and the impact of reaction conditions was severely limited. Without such knowledge, nitrosamine analysis continued to be susceptible to potential analytical errors and public health risk might be generated in practical applications of ACs pertaining to water purification. This project was conducted to address this critical information need. Systematic research was conducted to evaluate potential analytical errors that could be caused by the AC-catalyzed nitrosamine formation reactions under the commonly used nitrosamine analytical protocols, and to assess the potential of AC-catalyzed nitrosamine formation under water filtration applications.
APPROACH

Research for this project was conducted in two parts:

Part I. Evaluating the catalytic effect of AC SPE materials in promoting transformation of amines to yield nitrosamines under nitrosamine analytical procedures, identifying the critical influencing factors, and developing strategies to minimize analytical errors

Part II. Assessing potential catalyzed nitrosamine formation in AC-based water filtration processes, evaluating the impact of pre-oxidation prior to the AC process, and developing strategies to minimize nitrosamine formation

In the Part I research, the AC-based SPE methods for nitrosamine analysis were divided into the “particle method” and the “cartridge method”, in which the AC was applied as loose particles or in pre-packed cartridges, respectively. The particle method was simpler and more convenient than the cartridge method and thus was used for evaluating a wide range of influencing factors systematically. The influencing factors investigated included impact of environmental conditions, SPE procedures, amine properties, and carbon properties. The results from the particle method were extended to, and investigated for, the flow-through cartridge method. The impact of solution pH, ionic strength, temperature, oxygen content, contact time, and real water matrices on the AC-catalyzed nitrosamine formation was investigated. The impact of amine properties was evaluated among various secondary, tertiary, and quaternary amines. The impact of carbon properties was evaluated by investigating a range of commercial AC materials commonly used for nitrosamine analysis or in water treatment under a set of similar experimental conditions. All of the results were combined and examined carefully to identify the most important factors and the involved reaction mechanisms.

Results from Part I showed that, in contrast to the particle method, the cartridge method had low tendency to catalyze nitrosamine formation from amines. Thus, the tendency of AC-catalyzed nitrosamine formation during rapid AC-based water filtration is also likely low. Part II focused on evaluating the adsorption of nitrosamines and secondary amines to AC materials and on the effect of pre-oxidation intermediates/products that may facilitate the AC-catalyzed nitrosamine formation. The latter was on the basis that AC-based water filtration processes are commonly coupled with pre-oxidation by oxidants and such oxidation reactions of real waters can generate intermediates/products that may enhance nitrosamine formation.

RESULTS/CONCLUSIONS

A wide range of commercial AC materials, when applied in the typical particle method for nitrosamine extraction, can catalyze transformation of dimethylamine (DMA) in water to yield trace levels of N-nitrosodimethylamine (NDMA) under ambient aerobic conditions. All of the tested ACs were found to promote nitrosamine formation from secondary amines but the yield varied significantly, likely due to different AC properties. Among the different ACs, the NDMA yield at pH 7.5 ranged from 0.001% to 0.01% of the initial amount of aqueous DMA concentration, but at 0.05–0.29% of the amount of adsorbed DMA by AC. The AC-catalyzed NDMA formation also increased linearly with DMA concentration throughout a wide range (1–444 μM).

The AC-catalyzed nitrosamine formation increased with higher pH and higher ionic strength. The effect of temperature was less pronounced but higher AC-catalyzed NDMA
formation occurred at higher temperature (35°C) than at lower temperatures (5°C and 25°C). The AC-catalyzed nitrosamine formation occurred in clean water matrices, as well as in real water matrices (surface waters [SW] and wastewater [WW] effluents). ACs that have a higher yield of catalyzed nitrosamine formation in deionized (DI) water also promoted a greater amount of nitrosamine formation in the real water matrices than ACs that have a lower yield. The AC-catalyzed nitrosamine formation was greater in the WW matrices than in the SW matrices. The AC-promoted formation of NDMA and N-nitrosomorpholine (NMOR) was quite significant in the real water matrices. Significant concentrations of NDMA were detected in the secondary wastewater effluent samples, whereas NMOR was detected at high concentrations in both surface water and wastewater samples.

ACs can promote transformation of all secondary amines to form their corresponding N-nitrosamines. The nitrosamine yield increased for higher molecular weight secondary amines, likely due to increased adsorption of amines to the AC materials. The AC-catalyzed nitrosamine formation did not occur with the quaternary amine (dimethyl)benzalkonium chloride. Investigations with several tertiary amines that possess the DMA functional groups yielded mixed results due to the presence of the secondary amine DMA impurities in some of the tertiary amine standards. After excluding the impact of DMA impurities, ranitidine was the only tertiary amine among the tested (ranitidine, trimethylamine, dimethylbenzylamine, 5-dimethylaminomethyl furfuryl alcohol, 2,4,6-tris(dimethylaminomethyl)phenol and 2-[(Dimethylamino)methyl]phenol) to be susceptible to the AC-catalyzed NDMA formation. Evidently, it is more difficult for tertiary amines and quaternary amines than secondary amines to yield nitrosamines on the AC surfaces since the transformation will require additional cleavage of C-N bonds.

The cartridge method using the UCT cartridges and the EPA Method 521 was evaluated under a range of conditions. Three different amines (DMA, pyrrolidine [PYR] [and di-n-butylamine (DBA)], a wide pH range (5–9), and several water matrices (DI, SW, and WW) were tested. Despite of significantly greater adsorption of amines to the AC compared to that in the particle method, no catalyzed nitrosamine formation was observed. These results indicate that the tendency of the cartridge method to catalyze nitrosamine formation is quite low.

Experiments with controlled oxygen gas exposure and nitrogen gas exposure showed that exposure of ACs to oxygen and nitrogen was critical for the AC-catalyzed nitrosamine formation. The above results combined with examination using isotope-labeled nitrite and DMA confirmed that molecular oxygen is likely the source of oxidant while molecular nitrogen is the external nitrogen source in addition to amine for nitrosamine formation.

Effect of carbon properties on the AC-catalyzed nitrosamine formation was systematically evaluated among several ACs. AC’s properties play a crucial role as more nitrosamine formation is associated with carbon surfaces with higher surface area, more surface defects, reduced surface properties, higher O2 uptake capacity, and higher carbonyl group content. The study results pointed to a mechanism that the AC’s surface reactive sites react with molecular oxygen to form reactive oxygen species (ROS), which facilitate fixation of molecular nitrogen on the carbon surfaces to generate reactive nitrogen species (RNS) like nitrous oxide and hydroxylamine that can react with adsorbed amines to form nitrosamines. The above nitrosamine formation mechanism involving nitrogen fixation on AC surfaces is among the first to be recognized. Based on the elucidated mechanism, it can be inferred that the low tendency of the cartridge method to catalyze nitrosamine formation is most likely due to the much more
limited exposure of AC to oxygen and nitrogen gases during the cartridge extraction procedures compared to that in the particle method.

Adsorption of DMA and NDMA to ACs was found to be rather weak. The adsorption isotherms can be fitted by the Freundlich equation. Water pH significantly influenced the adsorption of DMA (with greater adsorption at higher pH), but had a small impact on the adsorption of NDMA. The effects of temperature and ionic strength on the adsorption of DMA or NDMA were both modest. Overall, the study results suggest that DMA and NDMA can be easily released from ACs.

Pre-oxidation intermediates/products including nitrite, nitrate, hydroxylamine, and formaldehyde were investigated for their potential to enhance the AC-catalyzed nitrosamine formation. The above compounds were selected because they are common intermediates/products of oxidation of amines by ozone or free chlorine. Among them, nitrite, nitrate, and hydroxylamine were found to enhance the AC-catalyzed nitrosamine formation, while formaldehyde exerted negligible effect. Nitrite and nitrate are nitrosating reagents and their presence likely offered the alternative pathway of nitrosation of DMA to form NDMA, which was catalyzed by the AC surfaces. The presence of hydroxylamine offered an intermediate that could react with DMA via oxidation through catalysis by AC surfaces to form NDMA. Interestingly, the above three compounds (nitrite, nitrate, and hydroxylamine) also promoted transformation of other secondary amines to yield their corresponding N-nitrosamines on AC surfaces. Significantly, nitrite and nitrate were even observed to promote the transformation of some tertiary amines (timethylamine and dimethylbenzylamine) to yield nitrosamines on AC surfaces. The susceptibility of tertiary amines to the AC-catalyzed nitrosation was strongly dependent on the amine structure.

APPLICATIONS/RECOMMENDATIONS

Analytical Implications

Results of this project found that for the two common SPE procedures for nitrosamine extraction and analysis, the “particle method” usually generates some levels of trace nitrosamines while the “cartridge method” does not, if amine precursors are present in the water samples. Using the particle method, the AC’s catalytic effect alone can contribute to the trace levels of nitrosamines detected. The cartridge method, due to less exposure of AC to air, is less susceptible to such analytical artifact. However, the particle method may still be desirable sometimes due to its lower costs, speed, and convenience. In such cases, the mechanistic understanding below is useful to develop strategies to avoid the analytical artifact.

Most secondary amines are susceptible to the AC-catalyzed oxidative transformation to yield levels of corresponding nitrosamines and the effect is greater for higher molecular weight secondary amines. The larger (more hydrophobic) the secondary amine, the greater adsorption to AC and the stronger reaction on AC surfaces. This aspect should particularly be considered when the nitrosamines to be analyzed are significantly larger than NDMA and their amine precursors are commonly found in the environment. NMOR is an example of such a case. In contrast to secondary amines, the AC-catalyzed nitrosamine formation is not productive for most tertiary and quaternary amines, but with exceptions (e.g., ranitidine).

The AC-catalyzed nitrosamine formation also depends strongly on the AC’s properties. Results of this project showed that more nitrosamine formation is associated with carbon
surfaces with higher surface area, more surface defects, reduced surface properties, higher O₂ uptake capacity, and higher carbonyl group content. To minimize the analytical artifact, ACs with fewer of the above attributes should be considered. Pre-treatment of AC particles to generate more oxidized surfaces may also be useful to minimize the AC-catalyzed nitrosamine formation.

The AC-catalyzed nitrosamine formation will be significantly affected by reaction conditions including O₂ exposure, N₂ exposure, water pH, ionic strength, temperature, the presence of other constituents such as nitrite, nitrate and hydroxylamine, and real water matrices. Results of this project demonstrated that the AC-catalyzed nitrosamine formation can take place via two different mechanisms: (i) AC catalyzes reactions of adsorbed amine with O₂ and N₂ to form nitrosamine (i.e., via nitrogen fixation), and (ii) AC catalyzes reactions of amine with nitrite or nitrate that are also present to form nitrosamine (i.e., via nitrosation). When analyzing water samples that are apparently free of any external nitrosating reagents such as nitrite and nitrate, only the pathway (i) may occur. Pathways (i) and (ii) may both occur in analyzing complex water samples such as wastewater. Minimizing exposure of ACs to O₂ and N₂ gases simultaneously (particularly during AC drying) can limit pathway (i). Pathway (ii) will be significant when nitrite or nitrate is present at appreciable concentrations in the water and should be avoided in such cases by choosing the cartridge method.

Implications for AC-Based Water Filtration

Based on the low tendency of the cartridge method to catalyze transformation of amines to yield nitrosamines, the tendency of AC-catalyzed nitrosamine formation during AC-based water filtration is also likely low. This conclusion is on the basis that most surface water contains only low concentrations of amines, the typical contact time during AC processes (in powdered activated carbon [PAC] or granular activated carbon [GAC] mode) are rather short, and the formation of nitrosamines is significantly higher during the drying phase of AC than in the solution (i.e., the tendency for the pathway (i) is low). Results of this project also show that the adsorption of amines and nitrosamines to AC is likely weak during AC-based water filtration. It remains a possibility for amines to accumulate on the surfaces of AC filter media over time and gradually transform to yield nitrosamines due to the catalytic effect of AC in the presence of oxygen and nitrogen. However, such an effect is probably no more important than other potential sources of nitrosamines in the real systems. If the AC-based water filtration is coupled with pre-oxidation by ozone or other oxidants, some of the pre-oxidation intermediates/products such as nitrite and nitrate can facilitate the AC-catalyzed nitrosamine formation by serving as additional nitrosating reagents (i.e., pathway (ii)). More research should be conducted to better understand the significance of pathway (ii) in real water systems and the impact of reaction conditions, amine properties, and AC properties.