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High capacity mercury adsorption on freshly ozone-treated carbon surfaces

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Abstract

A set of carbon materials was treated by a choice of common oxidizers to investigate the mercury capture capacities at varying temperature conditions. It was found that ozone treatment dramatically increases the mercury capture capacity of carbon surfaces by factors up to 134, but the activity is easily destroyed by exposure to the atmosphere, to water vapor, or by mild heating. Freshly ozone-treated carbon surfaces are shown to oxidize iodide to iodine in solution and this ability fades with aging. FTIR analysis shows broad C–O stretch features from 950 to 1300 cm^{−1}, which decay upon atmospheric exposure and are similar to the C–O–C asymmetric stretch features of ethylene secondary ozonide. The combined results suggest that the ultra-high mercury capture efficiency is due to a subset of labile C–O functional groups with residual oxidizing power that are likely epoxides or (epoxide-containing) secondary ozonides. The results open the possibility for in situ ozonolysis to create high-performance carbon-based Hg sorbents.

1. Introduction

Mercury is one of the nation's highest priority pollutants and the target of special emissions regulations such as Clean Air Mercury Rule (CAMR) by the EPA in March 2005 [1]. Methyl mercury has been shown to impair childhood development at extremely low doses [2,3] and represents a significant human health risk through widespread bioaccumulation and fish consumption. Between 1999 and 2002, the Center for Disease Control found that 6% of childbearing age women had a blood methyl mercury level above the recommended reference dose of 5.8 µg/L [4]. Mercury is released to the environment through spills, discharges from industrial or medical facilities such as chlor-alkali plants or dental offices, disposal of Hg-containing consumer products, and incineration or combustion of mercury-containing fuels or wastes. Although mercury is typically oxidized or methylated in the environment prior to reaching a human receptor, it is often in the elemental state at the *point of release*, where Hg concentrations are highest and the conditions for capture most favorable. Elemental mercury can also represent a direct health risk of its own inhalation exposure at 10–30 µg/m³ over long periods of time has been shown to cause neurological impairment [5].

There is great interest in sorbent-based capture of elemental mercury [6–13] with application to spill scenarios, remediation technologies, respirator cartridges, incineration systems, and coal-fired combustion and gasification power plants. Many chemical formulations have been used or evaluated as mercury vapor sorbents, but the most common are based on activated

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carbon materials, which are widely used as sorbents for vapor-phase capture of elemental mercury due to low cost and flexible surface chemistry.

There is great motivation to improve the efficiency of mercury capture by chemical modification of carbon surfaces. Halogenation of activated carbon has been shown to reduce the sorbent mass required to achieve a specific level of mercury removal from combustion flue gases [12]. Hutson et. al. [13] have shown that halogenation likely increases the capacity of activated carbons by providing active sites at which vapor phase elemental mercury is oxidized and then bound [13,14]. Another technique for increasing the mercury capture capacity of activated carbon is treatment with hydrogen sulfide, which was shown to increase the mercury capture capacity of activated carbon fiber by over 30 times even while destroying 95% of the BET surface area [15]. In a study comparing the effect of various sulfur-containing functional groups, Feng et. al. [10] found that one of the most important groups was short chain elemental sulfur (S₂–S₄). Sulfur impregnated carbons have high capacities for elemental mercury, but are too costly and the adsorption kinetics too slow for some important applications.

A common low-cost method for modifying carbon surfaces is oxidation, using reagents that include molecular oxygen, ozone, hydrogen peroxide, nitric acid, and permanganate. Oxidation imparts hydrophilicity to carbon surfaces [16,17], which is desirable for Hg-sorbents used in power station applications, where contamination of fly ash by hydrophobic activated carbon adversely affects the properties of fly ash concrete [16,18]. In previous experiments from our laboratory, ozone treatment did increase the hydrophilicity of activated carbon as desired, but did not enhance the performance of the activated carbon as mercury sorbent, and under some conditions degraded the performance. In contrast, Li et. al. [8,19] report that surface oxygen complexes on carbon are the likely active sites for mercury adsorption in their experiments. It appears that the role of oxide groups on carbon surfaces is complex and requires further systematic study.

Here we present a fundamental study of the role of surface oxygen groups on carbon with special emphasis on ozonolysis. We present the surprising finding that ozone treatment, distinct from air or hydrogen peroxide oxidation, causes dramatic but *transient* increases in the affinity of carbon surfaces for mercury due to the introduction of high-activity oxygen-containing groups that decompose upon modest heating or contact with atmospheric moisture. Spectroscopic and wet chemical assays suggest epoxides or secondary ozonides as the active but labile oxidizing groups.

2. Materials and Methods

Carbon materials used in this study included Darco FGL activated carbon (Norit, 550 m²/g), a granulated activated carbon from Alfa Aesar (900 m²/g), Cabot M-120 carbon black (38 m²/g) and a mesoporous carbon (144 m²/g) with 24 nm average pore diameter fabricated by the glass template method reported by Jian et al. [20]. All surface areas were determined by nitrogen vapor adsorption using the B.E.T. method.

Three different surface treatment methods were used to generate surface oxygen groups on carbon using ozone, air, and hydrogen peroxide. In the first method, 200 mg of carbon was placed in a fritted disk tubular Pyrex reactor and ozone-containing gas mixture passed in with the flow rate of 200±20 cm³/min through the sample bed. The gas mixture was either 0.3–0.35 wt-% ozone in dry air (low concentration condition) or 4.0–4.5 wt-% ozone in oxygen (high concentration condition) generated using a CD10/AD corona discharge system (Clearwater Tech Inc.). The baseline and the ozone concentrations at the exit of the carbon bed were measured by UV absorption using the IN-2000 ozone analyzer manufactured by IN USA, Inc. After treatment the sample bed was flushed with oxygen or dry air for 10 minutes and then

placed under vacuum for 20 minutes to remove free or physically adsorbed ozone. To test for any effect of moisture on the carbon surface, one sample was dried at 130°C for 2 hrs in a nitrogen environment before ozonolysis. The hydrogen peroxide treatment used 500 mg of carbon black in 20 ml of a 30 vol-% aqueous H₂O₂ solution at 50°C for 40 minutes. The solution was transferred to a filter paper and washed twice with de-ionized water. The solid sample was dried by flushing with high purity nitrogen gas at room temperature overnight. Air oxidation experiments on carbon materials were performed in a tube furnace at 400°C in a flow of dry air.

To measure mercury capture capacity, elemental mercury vapor was generated in Argon gas (300 cc/min) at a concentration of $60 \pm 3 \mu\text{g}/\text{m}^3$ using the Hg CAVKIT 10.534 (PS Analytical, Ltd) generator and passed through a fixed bed of sorbent resting on a Pyrex fritted disk inside a tubular Pyrex reactor. The exit Hg concentration was monitored semi-continuously (3.8 min sampling time) by atomic fluorescence using the Sir Galahad II (PS Analytical, Ltd). The mercury capture capacity of the sorbent was calculated by determining the area between the baseline and the breakthrough curve of bed exit concentration data. The system is equipped with a tin chloride reduction unit, but it was bypassed in these particular experiments, where there were no halogens in the system and elemental mercury is the only volatile species at the exit. To confirm that the loss of elemental mercury detected in the gas stream was indeed captured in the bed, selected sorbent samples were analyzed for solid phase elemental and oxidized mercury using a direct mercury analyzer (DMA-80, Milestone Inc.). The capacities obtained by this method were always within 30% of the capacities determined by vapor phase analysis, providing a useful error bound when interpreting the present results.

The oxidizing capability of the ozone-treated carbons was measured using a commercial assay for peroxide. First 400 mg of sample was placed in 12 ml de-ionized water, centrifuged at 4500 rpm and 23°C for 45 minutes, and the supernatant analyzed using a HYP-1 hydrogen peroxide test kit provided by Hach Company. In this test assay, 1 ml of ammonium molybdate solution was added to test cell after which the proprietary starch-iodide reagent was introduced. The presence of peroxides (or equivalent oxidizing species) was observed when the solution turned blue in color. After 5 minutes, the blue-colored solution was titrated with sodium thiosulfate until colorless and the oxidizing capacity accounted as the amount of sodium thiosulfate titrant.

The surfactant adsorption capacity of the treated and untreated carbon black samples was determined by titration procedure referred to as the foam index test [18,21]. Foam index measurements involved placing the test carbon sample [usually about 90 mg] together with 8 grams of Portland cement and 25 ml of de-ionized water into a 70 ml cylindrical jar with a 40 mm I.D., 80 mm length. The jar was then capped and thoroughly shaken for one minute to completely wet the cement and carbon black. In present work, a 5vol-% aqueous solution of Darex II was used as the Air Entraining Admixture (AEA) in the foam index test. The 5vol-% aqueous solution of AEA is added one drop at the time (20 μl per drop) from a pipette gun with a 0.75 ml tube. After each addition the jar is capped and shaken approximately 15 seconds, after which the lid is removed and liquid surface observed. Before the endpoint of the test, the foam on the liquid surface is unstable and breaks in the matter of few seconds. The endpoint is defined when a stable foam is established on the surface for at least 45 seconds. The stable foam endpoint occurs at a relatively constant aqueous concentration of surfactant.

An ATI Mattson Infinity Series FTIR was used to characterize surface functional groups on treated and untreated carbon black samples. Approximately 1wt-% of sample was mixed with FTIR grade KBr powder and pelletized. The FTIR measurements were taken place in laboratory air and in a high purity nitrogen gas environment and the backgrounds of those environments were recorded before each pellet experiment respectively.

3. Results and Discussion

Figure 1 shows the adsorption capacity of the untreated carbon materials for elemental Hg vapor. The capacities decrease with increasing temperature suggestive of an equilibrium adsorption process. Across the suite of test carbon materials, the capacities generally increase with increasing total surface area, but the correlation is crude. The capacities of carbon black and the mesoporous carbon became too low to measure accurately at high temperature and are not reported here. The liquid-crystal-derived mesoporous carbon of Jian et al. [20] was evaluated due to its reported internal surface structure, which consists largely of graphene edge planes, but it has a similar area-specific capacity (9ng/m^2) as carbon black (12ng/m^2), which has a predominately basal surface character. Physical adsorption is a likely contributor to the high capacities at low temperature in this dataset, but is not effective in higher temperature capture processes. For combustion flue-gas capture, a worthy goal is to find surface modification techniques that enhance the chemisorptive component of Hg capture in a way that also imparts hydrophilicity.

To isolate the effect of surface chemistry on chemisorptive Hg capture, a large series of experiments were carried out on carbon black and mesoporous carbon as model systems. These two non-microporous materials are especially suited for study of Hg chemisorption chemistry due to their low physisorption capacity near room temperature and the avoidance of confounding physical effects such as surface area changes due to pore blockage during functional group addition. Figure 2 show results from our early experiments, which indicated no significant enhancement of mercury capture efficiency by ozonolysis, consistent with previous work on activated carbons. One single experiment gave a very different result, however, as seen by the square symbol in Fig. 2 representing about 48 fold capacity increase. This data point arose from a sample treated at high ozone concentration and tested immediately thereafter for Hg adsorption capacity (see Fig. 2).

This experiment on freshly ozone-treated carbon black was repeated and extended to cover different ozone doses and two additional carbon materials. Figure 3 shows these results, which confirm dramatic capacity increases when the adsorption takes place within 30 minutes of ozonolysis. For example, carbon black sample offers as high as 134 fold capacity increase. To ensure that the samples were free of residual ozone, the samples were flushed and placed under vacuum before the adsorption experiment as described in the methods section above. We considered the possibility that the capacity increase was due to adsorbed hydrogen peroxide generated by ozone reaction with surface moisture, but pre-dried carbon black gave similar results.

The capacities presented in Fig. 3 are for carbons treated at the high ozone concentration condition, but similar dose treatments at the lower concentration condition gave capacities well within the 30% experimental error. The dose dependence is slight, and clearly any treatment with ozone above 100 mg/g greatly increases the capacity of the sorbent to capture mercury. The capacity increase for the microporous activated carbon is much less than for the non-microporous carbon black and mesoporous carbon, likely due to micropore blockage by oxygen containing functional groups. Ozonolysis of microporous carbons has been shown to leads to a decrease in surface area because of pore blockage [16,22].

Treatment of carbon black with other oxidizing agents did not lead to a significant capacity increase. Air oxidation at 300°C and 500°C as well as treatment with hydrogen peroxide (see Materials and Methods section) led to carbon blacks with capacities within 30% of the capacity of untreated sample. Both air oxidation and hydrogen peroxide treatment have been shown to generate a variety of different oxygen containing surface functional groups on carbon surfaces [16,23], but these "common" surface oxides are apparently not responsible for the high-activity

Hg capture reported here. The dramatic but unstable surface activation is unique to ozone and worthy of further study.

To better characterize the transient nature of these surface states, a variety of aging studies were carried out on ozone-treated carbon blacks. Figure 4 shows a rapid decrease in capacity when freshly ozone treated carbon black is exposed to room air. Dietz et. al. [22] also report a continuous decomposition of ozone treated charcoals at temperatures greater than 77K. Partial preservation of surface activity by storage of the treated carbon in an inert gas atmosphere suggests some component of air aids in the decomposition of surface functional groups. Introduction of water vapor to the nitrogen flush experiment gives a deactivation similar to that in air, strongly suggesting water involvement in surface functional group decomposition. Annealing in an inert gas atmosphere at 120°C for 4 hours completely destroys the capacity enhancement made by ozone treatment (see Fig. 4).

Chemisorption of mercury on carbon typically involves oxidation and we hypothesize that certain functional groups on freshly ozone-treated carbons possess residual oxidizing ability and can either further oxidize the carbon substrate through decomposition or oxidize "third party" adsorbate species such as Hg. To assess this hypothesis we performed starch-iodine-based peroxide assays on untreated and ozone-treated carbon black samples before and after aging. Table 1 shows that the oxidizing potential of the carbon surface is greatly enhanced by treatment with ozone, and this enhancement decays in air over a period of 24 hours in parallel with the observed behavior toward Hg vapor. Also presented in Table 1 are the foam index values of the untreated, ozonated, and aged ozonated carbon blacks. As can be seen, ozone imparts hydrophilicity (reduces foam index) and the effect does not significantly decay over time. This is consistent with a previous study [16] which suggested that a wide variety of polar oxygen-containing groups contribute to hydrophilicity, and most groups are stable to desorption below about 300°C. In contrast, the sites responsible for Hg capture are likely to be a small subset of these groups that are energetic, oxidizing, and labile. Decomposition or rearrangement of these minority labile oxide groups would not be expected to affect hydrophilicity, which is related to the total fraction of the graphenic carbon surface covered by oxygen groups without a high degree of chemical specificity and thus less sensitive to the nature of those oxygen groups.

There is an extensive literature on carbon surface oxides, but only a few reports of surface groups as active "third party" oxidants [24]. Candidate oxidizing groups include quinones, epoxides, peroxides, and the secondary ozonides (see Fig. 5.I). Figure 5.II shows the classical Criegee mechanism of ozonolysis, involving 1,3 dipolar cycloaddition to carbon carbon double bonds as described by Criegee [25], and later confirmed by ^{17}O NMR spectroscopy [26]. The primary ozonide in Fig. 5.II is a reaction intermediate that decays to a secondary ozonide, which in turn reacts with water to form hydrogen peroxide and ketones [25]. Many secondary ozonides are fleeting intermediates, while others are sufficiently metastable to be isolated and characterized [27–29], including ozonides from polycyclic compounds [28,29], which are relatives of graphenic carbon.

To obtain more information on chemical structure, FTIR spectroscopy was carried out on untreated, ozonated, and aged/ozonated carbon black. In order to focus on the changes during ozonation, the spectrum of untreated carbon black was subtracted from that of the ozonated and aged ozonated spectra and a time series of subtraction spectra shown in Figure 6. As can be seen, ozonolysis introduces a broad feature in the wave number range 1000–1300 cm^{-1} and a smaller peak near 950 cm^{-1} , both of which decay with time. Features near 1100 cm^{-1} are widely associated with C–O stretch and on carbon surfaces have been assigned to various C–O containing functional groups including ethers, esters, ring and ethers [30–33]. In organic compounds epoxide peaks are typically present between 830 and 890 cm^{-1} [34] but have been reported as high as 910 cm^{-1} [35] and 950 cm^{-1} [34]. The peak at 940 cm^{-1} has been cited as

indicative of epoxide groups on carbon [30], but also may arise from O-H deformation in carboxylic acids [34]. Sablinskas et. al. [36] report doublet peaks at 956.1 cm^{-1} and 1082.1 cm^{-1} in a high resolution FTIR study of ethene secondary ozonide, which is similar to both features in the fresh spectrum of Fig. 6. The ethene secondary ozonide features are attributable to asymmetric C-O-C stretch, thus to the epoxide portion of the secondary ozonide structure. The peroxide O-O bond is only weakly active in FTIR and difficult to detect.

Based on the data presented in this study, the most likely candidates for the surface functional groups responsible for high Hg adsorption capacity are epoxides and (epoxide-containing) secondary ozonides. Solution phase treatment of single- and multi-walled nanotubes by Bannerjee et. al. [37,38] have shown that various surface functional groups (lactones, ketones, aldehydes, carboxyls, and others) can be generated by the cleavage of surface primary ozonides with various agents including water. They also found that only in the case of SWNTs with high curvature could the sidewalls of the tubes be functionalized, and in the case of MWNTs only the tube ends and defect sites showed reaction with ozone. Secondary ozonide formation of graphene edge sites is a likely mechanism for carbon black. Mawhinney and Yates [31] do not report ozonides in their FTIR study of ozonolysis of an amorphous carbon, but postulate secondary ozonide decomposition as the source of the observed hydroxyl, carbonyl, and ether moieties. It is possible that the H-content of their amorphous carbon is responsible for the different ozonide stability from the present case. Quinones, though common on carbon surfaces, are unlikely to be the key species, as they do not give characteristic IR features in the C-O single bond region, $950\text{--}1300\text{cm}^{-1}$, range and are not expected to decompose upon mild heating.

Isolated epoxides could also be responsible for the observed capacity increase. Dusenbury and Cannon [39] have explained that the reaction between ozone and granular activated carbon results in the formation of epoxides as well as ozonides. He et. al. [24] suggest that the epoxide groups in graphite oxide give it an oxidizing capability and they have shown that these groups decompose after heating to 100°C in an inert gas atmosphere. These characteristics make the presence of epoxides consistent with the aging and oxidation data presented in this study. In general it is difficult to definitively assign FTIR peaks to specific structures on complex carbon surfaces, so isolated epoxides, (epoxide containing) secondary ozonides, or a combination may be involved here in high activity Hg capture.

4. Summary

Ozone treatment of carbon surfaces leads to large increases in Hg vapor capture capacity (up to 134 fold) by formation of labile C-O containing oxidizing groups, which are likely to be epoxides or secondary ozonides. Conventional studies that do not consider aging, or make special arrangements to test freshly ozone-treated samples, are likely not to see this elevated capacity, but rather see much lower capacities on carbon surfaces containing only the more common global reaction products of Fig. 5.III. The present finding opens the possibility of *in situ* carbon ozonolysis to create fresh, super-active Hg sorbents with the additional benefit of sorbent hydrophilicity useful in certain applications. For applications requiring mercury removal from complex gas streams, much more work is needed to examine multicomponent adsorbate interactions, which can mitigate or otherwise alter the role of the active oxygen groups documented here.

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Figure 1.
Capacity for elemental mercury capture on various as-produced (unmodified) carbon materials. Experiments use fixed sorbent beds exposed to flowing Hg vapor ($60 \mu\text{g}/\text{m}^3$) in Argon gas.

Figure 2.

Effect of ozonolysis degree on total Hg adsorption capacity for mesoporous carbon as a non-microporous model for studying surface chemistry effects. The lower points (circles) show the behavior under "normal" laboratory practice, where ozonolysis were carried out in 0.3 wt-% O₃ in air and the adsorption experiments were carried out 3 days after the ozonolysis (an unintended aging). The upper square is the behavior observed following ozonolysis at 4.5 wt-% O₃ in O₂ when the adsorption experiment was carried out immediately afterward. Inlet Hg vapor is 60 μg/m³.

Figure 3.

Mercury capture capacities on freshly ozone-treated carbons. The inlet Hg vapor is 60 μg/m³ and the ozone "dose" is the total mass of ozone passed through the sample bed over the course of the experiment. Ozonolysis is carried out in 4.5 wt-% O₃ in O₂ followed by nitrogen flushing and vacuum treatment to remove any residual trapped ozone.

Figure 4.

Stability of mercury capture capacities on ozone-treated carbon blacks to various aging conditions. Carbon black is used as a non-microporous model for isolating surface chemistry effects. The inlet Hg vapor is $60 \mu\text{g}/\text{m}^3$ and the ozone "dose" is the total mass of ozone passed through the sample bed over the course of the experiment. Ozonolysis is carried out in 4.5 wt-% O_3 in O_2 followed by nitrogen flushing and vacuum treatment to remove any residual trapped ozone.

Figure 5. Candidate structures and pathways to explain the high transient activity for Hg adsorption. I. Functional groups with known oxidizing ability reported on carbon surfaces; II. Classical Criegee mechanism for the ozonolysis of C=C double bonds; III. Typical global reaction products observed from the reactions in II in the presence of water [25].

Figure 6. FTIR spectra of ozone-treated carbon black samples as a function of atmospheric exposure. Curves shown are subtraction spectra obtained as the difference between the ozone-treated samples and untreated carbon black used as reference. Ozonolysis is carried out in 4.5 wt-% O₃ in O₂ followed by nitrogen flushing and vacuum treatment to remove any residual trapped ozone. Aging gradually destroys the multi peak C-O features from 950–1300 cm⁻¹.

Table 1

Oxidizing capacity, Foam Index and Hg capacity.

Sample	Oxidation Assay (ml/g)*	Foam Index (ml/g)**	Hg Capture Capacity (µg/g)
Untreated CB	0.075	0.122	0.5
Ozonated CB, aged 1hr	0.200	0.022	60.4
Ozonated CB, aged 24 hrs	0.05	0.017	3.0

* vol of sodium thiosulfate per wt of carbon

** vol of 5 vol-% Darex II AEA per wt carbon