

Halides on Carbonaceous Materials for Enhanced Capture of Hg⁰: Mechanistic Study

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Use of amorphous carbon particles impregnated with halides has been demonstrated to be very effective for the capture of elemental mercury (Hg⁰) from power plant flue gases. Despite the fact that the halides employed are not oxidants, the Hg⁰ captured is found to be in an oxidized form. Although this approach has been widely accepted for the control of mercury emissions, the mechanism responsible for enhancing Hg⁰ capture and subsequent oxidation is not well-understood. We investigated the chemistry of halogenated carbonaceous materials and propose a mechanism that appears to be able to explain both the enhancement of Hg⁰ capture and its subsequent oxidation. Interaction of microcrystalline graphitic structures in amorphous carbon with halide ions results in the formation of charge-transfer compounds, with halide ions withdrawing electrons from the graphitic lattice, making the carbon particle a stronger Lewis acid and resulting in the enhancement of its ability to attract electrons from the highly polarizable Hg⁰. Upon contact, the electron transfer produces oxidized mercury, with the graphitic structure as a counterion. This study may have implications in other areas; for example, the combination of sea spray and soot could enhance the oxidation of atmospheric mercury vapor, with potential effects on its residency and bioavailability.

Introduction

Mercury is present in the flue gas of coal-fired power plants in three forms: elemental (Hg⁰), oxidized, and particulate-bound mercury. A large fraction of particulate-bound mercury can be easily removed by electrostatic precipitators (ESPs) or fabric filters. The oxidized mercury tends to stick to particulate matter and is water-soluble; consequently, it can be captured by ESPs, fabric filters, or flue gas desulfurization (FGD). Hg⁰, however, is highly volatile and insoluble in water and is thus not readily removed by existing air pollution control devices (APCDs).^{1–5}

Powdered activated carbon (PAC) impregnated with halogen compounds has been extensively tested for the removal of mercury from the flue gas of coal-fired power plants.^{2,6–8} This approach is highly effective when injection of halogenated PAC takes place downstream of air heaters and especially for power plants burning lignite or sub-bituminous coal, where a substantial fraction of the mercury in flue gas is Hg⁰.

Bituminous coal has a naturally high chlorine content, which is known to be associated with large oxidized mercury fractions, facilitating effective mercury removal by existing APCDs.² Kinetic modeling based on gas-phase Hg⁰ oxidation rate constants indicates that the gas-phase homogeneous reaction pathway alone is insufficient to account for the amount of Hg⁰ oxidation observed in field tests.⁹ It is necessary to take gas–particle heterogeneous interactions into consideration. Extensive field tests and computer modeling

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results have pointed to heterogeneous reactions as the primary pathway responsible for the enhancement of Hg^0 oxidation by HCl.^{9–13} Recent laboratory kinetic experiments indicated that HCl adsorbed on unburned carbon (UBC) in various types of fly ash can substantially enhance Hg^0 removal rates from the gas phase.¹⁴ This enhancement largely diminishes after UBC in fly ash is completely removed [i.e., the loss of ignition (LOI) is 0%] by heat treatment.¹⁴ Apparently, the synergism of UBC and HCl is responsible for the enhancement. After the capture of Hg^0 by halogenated PAC, the mercury has been determined to be in an oxidized form.^{15,16} In addition to HCl, the effect of O_2 , CO, H_2O , SO_2 , and/or NO_x on Hg^0 removal by fly ash and/or PAC was investigated in the laboratory^{12,14,17,18} and with coal-fired flue gas in the field.^{19–23} Laboratory control experiments¹⁴ indicated that O_2 and CO did not exhibit a detectable difference on the Hg^0 removal rate compared to N_2 . H_2O vapor exhibited a promotion effect, but the effect dwindled with increasing temperatures. SO_2 inhibited the Hg^0 removal rate, which was attributed to the competition for the same adsorption sites on carbon. NO promoted the Hg^0 removal rate, which was attributed to an increase of active sites on carbon as a result of the adsorption of molecules with an unpaired electron, such as NO. The NO promotion effect decreased with increasing temperatures as the NO adsorption capacity dwindled. However, HCl enhanced Hg^0 removal the most among flue gas components.

Numerous results, as mentioned above, have noted that halogen compound impregnated carbon particles, whether PAC or UBC in fly ash, somehow speed up the oxidation of Hg^0 , despite the fact that some of the halogen compounds were not oxidants.

Previous studies have contributed to the understanding of the chemical process of Hg^0 capture by halogenated carbon particles.^{24–26} Halogen compounds were said to be chemisorbed on PAC, and Hg^0 capture was described as the adsorption on active sites.²⁷ Still, the nature of the active sites is not clear.

It is known that the oxidation of Hg^0 by halogen molecules is catalyzed by surfaces and even by its own reaction products.²⁸ However, not all surfaces are alike; when a silica surface is coated with a layer of halocarbon wax (HW), the catalytic effect is largely absent¹⁴ and activated carbons impregnated with halogen are far more effective than the same without halogen.¹⁴

Amorphous carbon particles, such as PAC, UBC, or soot, possess microcrystalline graphite.²⁹ The microcrystals can be as small as only a few unit cells of the graphite structure. The graphitic structure of the carbon particles is highly imperfect, which results in many possibilities for reactions of the edge carbons, formed as a result of the so-called broken bonds, with their surroundings. The physicochemical aspects of carbon particles have been studied extensively.²⁹ Physical configuration (surface area, pore-size distribution, and defective graphite microcrystallite structure) and chemical composition (surface functional groups and impurity) of carbon particles can affect their adsorption, catalytic, and reactivity properties. The purpose of this study is to improve the understanding of the chemistry of Hg^0 capture by halogenated PAC. Because the microcrystalline graphite-like lattice is a component of PAC, this paper investigates its role in the capture of Hg^0 , especially when interacting with halides. This paper also compares the effectiveness of other components of PAC, produced by the activation of powdered graphite (PG), in Hg capture.

Experimental Section

There is a large variation in the properties of commercial PAC because of different raw materials and manufacturing processes.^{29–31} In view of the irregular and amorphous nature of PAC, PG was chosen as a starting material. The PG was activated using various methods to produce carbon particles possessing specific properties of PAC. The activated PG was then studied for Hg^0 capture kinetics. The comparison of various carbon particles: PG, PAC (Darco-Hg and Darco-Hg-LH), and UBC in fly ash (bituminous) in their Hg^0 capture kinetics was made when appropriate.

The kinetics of Hg^0 capture by carbon particles were investigated using an experimental setup described in detail in our previous papers devoted to the rate constant determination of homogeneous reactions of Hg^0 with Br_2 , $\text{SCl}_2/\text{S}_2\text{Cl}_2$, and Cl_2 and their heterogeneous reactions involving PAC and fly ash (with and without UBC). The reaction took place in a Pyrex flask¹⁴ with a volume of 380 mL and an optical path of 14.5 cm. Because

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Hg^0 is readily adsorbed on solid surfaces, the inner wall of the reactor was coated with a halocarbon wax (HW) to minimize the surface effect. The reactor wall effect was studied and reported.^{14,32,33} It was found that, after coated with HW, the adsorption of Hg^0 on the wall was substantially reduced on the basis of mercury cold vapor atomic absorption spectroscopy. After coating, 0.100 g of PG, PAC, or fly ash was adhered to the surface of the HW. The wax was removed after each individual experiment, and fresh wax was recoated on the inner wall of the reactor before each experiment. Prior to each run, the reactor was evacuated and a volume of nitrogen or air saturated with Hg^0 vapor at 298 K was injected with a syringe (B-D Yale, 100 mL) to a 380 mL spherical Pyrex reactor, which was thermostatic at various temperatures, primarily at 393 K. The concentration of Hg^0 can be calculated from the absorption cross-section and the optical length and/or the vapor pressure at a given temperature and the volume of the reactor. The temperature inside the reactor reached 393 K almost instantaneously. The rapid temperature equilibrium had been established with a thermocouple, although the thermocouple was not used during the experiment to avoid interference with Hg^0 sorption. Subsequently, the pressure was quickly brought to 760 Torr with air or N_2 . For experiments involving HCl, a volume of air or N_2 with a known concentration of HCl was injected into the reactor prior to the introduction of Hg^0 . The vapor pressure of HCl above an aqueous hydrochloric acid solution can be obtained from the literature. A known volume of HCl vapor was injected into the reactor, and the concentration of HCl was calculated. The HCl concentration obtained in this way can be verified with an IR cell at an absorption band at 2886 cm^{-1} . The procedure to reduce the influence of mass transfer on Hg^0 reaction kinetics was discussed extensively in our previous papers and will not be repeated here.^{14,32} Because the kinetics were performed using a large excess of sorbent over Hg^0 , the half-life of Hg^0 , i.e., the time required for the concentration of Hg^0 to fall to one-half of its initial value, can be expressed as $t_{1/2} = \ln 2/k[\text{sorbent}]$.³⁴ Therefore, the half-life is independent of the initial Hg^0 concentration employed. The Hg^0 removal efficiencies were used to compare the relative effectiveness of different carbon treatments.

The Hg^0 concentration in the gas phase was monitored *in situ* by a mercury cold vapor atomic absorption spectrometer (CV-AAS) during the course of reactions.^{14,32} The initial Hg^0 concentration employed for each experiment was 0.2 ± 0.02 ppm.

Several types of treatment were made on PG: (1) heating to about 673 K and then exposure to moist air to generate acidic oxygen functional groups,^{29,30} (2) heating to above 1023 K and then cooling under vacuum to room temperature before exposure to moist air to generate basic oxygen functional groups,^{29,30} (3) impregnating with various inorganic bromides (KBr, NaBr, and NH_4Br) to study the effect of cations, (4) impregnating with various inorganic halides (KI, KBr, and KCl) to study the effect of halide ions, (5) impregnating/mixing with various acids (HCl, H_2SO_4 , and HNO_3) to study the effect of acidity (H^+), (6) impregnating with NaCl and then absorbing a sufficient amount of Hg^0 to compare with the PG, which was impregnated with HgCl_2 , and (7) mixing with aromatic and aliphatic halides (1-bromopyrene, 2,7-dibromofluorene, chloroform, and 1,10-dibromodecane). The impregnation/mixing procedure employed was a weighed amount of an inorganic halogen compound

containing 0.40 g of halogen ion dissolved in 25 mL of deionized water in a 250 mL beaker. Subsequently, 10 g of PG was added into the solution, and the mixture was stirred for 30 min before placing the beaker in an oven at 393 K. The beaker was taken out of the oven, and the mixture was stirred for about 2 min every hour for a total of 12 h to ensure well impregnation and dryness. The procedure was employed for impregnating all of the inorganic compounds studied, including KBr, NaBr, NH_4Br , KI, KCl, NaCl, and HgCl_2 . The weight percent of halogen (in halides) to PG was 4% in all cases. The concentration of acids impregnated into or mixed with carbon particles was also chosen to be 4% by weight and was prepared the same as the salts. A similar procedure was employed for the preparation of the mixture of PG with organics (aromatic and aliphatic halides), except that chloroform was used as a solvent and that the mixture was left in a fume hood at 293 K for 12 h to dryness.

Scanning electron microscopy (SEM) was used to determine the morphology and elemental composition of carbon particles. SEM shows the highly porous structure of PAC, which is largely responsible for their remarkable adsorption properties. The pores observed are about 0.1–0.5 μm in diameter. The major elemental composition of Darco-Hg is Ca, Si, Al, Fe, and S in addition to C. X-ray photoelectron spectroscopy (XPS) was used to determine the change of oxidation states of halogen and mercury on carbon particles. The samples for XPS runs were prepared by placing 0.01 g of Hg^0 and 1 g of KBr-impregnated PG in a 50 mL glass sample bottle. The bottle was then placed in an oven at 393 K for 12 h, with the bottle shaken for 5 min every hour during the heating process. XPS experiments were carried out on a RBD upgraded PHI-5000C electron spectroscopy for chemical analysis (ESCA) system (Perkin-Elmer) with Mg K α radiation ($h\nu = 1253.6\text{ eV}$) or Al K α radiation ($h\nu = 1486.6\text{ eV}$).³⁵ The X-ray anode was run at 250 W, and the high voltage was kept at 14.0 kV, with a detection angle at 54° . The base pressure of the analyzer chamber was about 5×10^{-8} Pa. The sample was directly pressed onto a self-supported disk ($10 \times 10\text{ mm}$) and mounted on a sample holder. Binding energies were calibrated using the containment carbon (C 1s = 284.6 eV).

The chemicals employed were mercury (99.99%), synthetic PG (99.2%; particle size, $\sim 20\text{ }\mu\text{m}$; surface area, $6.5\text{--}10.5\text{ m}^2/\text{g}$), potassium iodide (99%), potassium bromide (99%), potassium chloride (99%), ammonium bromide (99%), sodium bromide (99%), 1-bromopyrene (96%), 2,7-dibromofluorene (99%), chloroform (99.8%), 1,10-dibromodecane (95%), HCl (37%), H_2SO_4 (98%), and HNO_3 (69%) from Sigma-Aldrich Co., HW (Series-1500) from Halocarbon Product Co., and Darco-Hg-LH ($\sim 45\text{ }\mu\text{m}$, $550\text{ m}^2/\text{g}$) and Darco-Hg ($\sim 45\text{ }\mu\text{m}$, $600\text{ m}^2/\text{g}$) PACs from Norit American. HCl standard gas (99%) was from Matheson Co. Fly ash ($< 150\text{ }\mu\text{m}$) from bituminous coal combustion was provided by MobotecUSA. The LOI and Brunauer–Emmett–Teller (BET) surface areas for fly ash were measured to be 12.4% (wt) and $11.35\text{ m}^2/\text{g}$, respectively. The BET surface area of UBC in fly ash was calculated to be $81\text{ m}^2/\text{g}$.

The uncertainty of Hg^0 measured by CVAAS was ± 0.005 ppm. The accuracy of the data reported here was estimated to be within 20%.

Results and Discussion

Several sets of experiments were performed to study various mechanisms reported in the literature for the halogen-enhanced Hg^0 removal rate by carbon particles.^{18,24–26}

Field and laboratory tests have indicated that HCl plays an important role in the oxidation of Hg^0 . Of several potential pathways, we believe that it is unlikely to proceed via the route of gas-phase reactions: $\text{Hg}^0 + \text{HCl} \leftrightarrow \text{HgCl} + \text{H}$, because this reaction is hindered by a high activation energy,³⁶ or $\text{Hg}^0 + 2\text{HCl} \leftrightarrow \text{HgCl}_2 + \text{H}_2$, which should also be very slow because of

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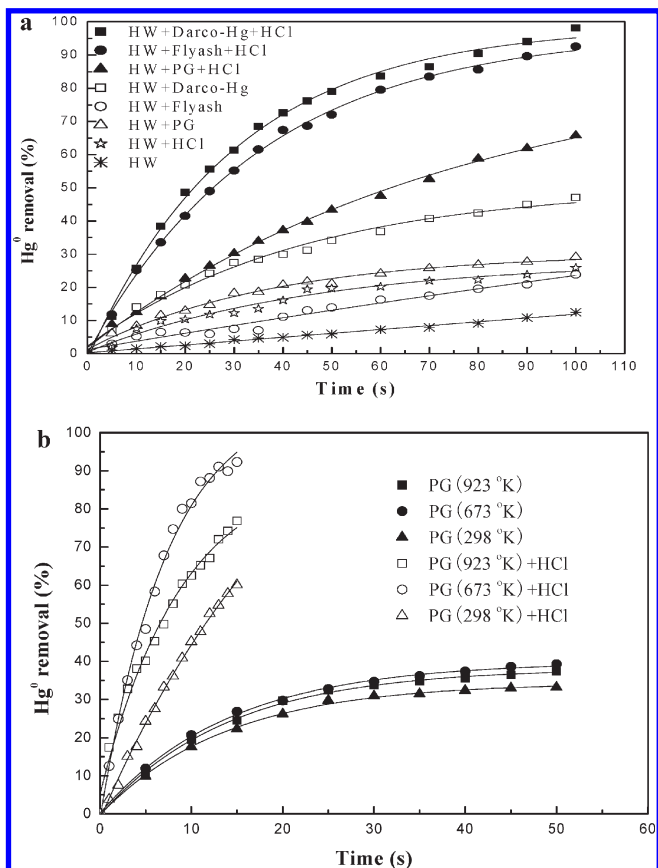


Figure 1. (a) Effect of HCl on Hg⁰ removal efficiency by carbon particles at 373 K. (b) Effect of surface oxygen functional groups on PG on Hg⁰ removal efficiency at 298 K.

the fact that it is a termolecular collision (the chance of three species coming together is small) and the small concentrations of Hg⁰ and HCl typically found in flue gas.

The extent of Hg⁰ oxidation by atomic Cl in the boiler under high-temperature conditions was studied. Although the reaction rate constant of Hg⁰ with atomic Cl was determined to be very large,²⁸ the temperature downstream from the air pre-heater where activated carbon is typically injected is not high enough to decompose HCl to produce atomic Cl, a short-lived species.

The Deacon process, which involves the catalytic conversion of HCl to Cl₂, has been suggested as a possible mechanism for the oxidation of Hg⁰ leading to its capture because Cl₂ is an oxidant. To investigate this hypothesis, Hg⁰ removal was performed under anaerobic conditions and at low temperatures, whereas the Deacon process requires high temperature (> 673 K) in air.³⁷ Because Hg⁰ is still captured at much lower temperatures, we can rule out the Deacon process as the mechanism.

Figure 1a shows that the gas-phase reaction rate of Hg⁰ with HCl appears to be as slow as that of Hg⁰ with other sorbents in the absence of HCl. However, the removal rate increases significantly in all cases after the addition of 35 ppm HCl. It must be noted that PG has a surface area of only 6–10 m²/g, but after exposure to HCl, it became more effective than Darco-Hg (surface area of 600 m²/g), a PAC widely used for comparison in tests for Hg⁰ removal from power plants.

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Because the gas-phase reaction rate of Hg⁰ with HCl is slow, the graphitic lattice in carbon particles apparently plays an important role in promoting Hg⁰ capture following the adsorption of HCl. Fly ash after exposure to HCl exhibited a significant enhancement in Hg⁰ capture, which can be attributed to the interaction of UBC in fly ash with HCl.

Acidity has been suspected of influencing Hg⁰ removal rates by carbon particles.²⁴ To investigate the effect of acidity, PG was treated with HCl, H₂SO₄, and HNO₃ and Hg⁰ removal rates were measured. It was found that PG treated with sulfuric and nitric acids did not exhibit appreciable improvement in Hg⁰ removal rates compared to untreated PG. This implies that the promotion effect was due to chloride ions rather than the increase of the acidity. The results obtained here are consistent with those reported by Olson et al.,²⁴ in that PG impregnated with HCl is far better than that with H₂SO₄ or HNO₃ in the enhancement of Hg sorption. Olson et al.²⁴ found that acid promotion exhibits a specific acid catalysis and not a general acid catalysis, with acids having polarizable halide anions showing a stronger effect than the oxyacids. A mechanism involving the conversion of carbene to carbenium ion oxidant for Hg⁰ oxidation was proposed.²⁴ Theoretical calculations recently performed by Olson et al.³⁸ ruled out a direct covalent bond formation between Hg⁰ and the carbenium ion but suggested the formation of a mercury charge-transfer complex on the cationic center formed by HCl addition. The sorption of HgCl₂ on lignite-activated carbon was attributed to the basic sites on the carbon.³⁹

The role of surface oxygen functional groups in the enhancement of Hg⁰ removal was investigated. Acidic groups include carboxylic and hydroxyl, and basic groups include carbonyl and chromene,^{29–31} although the inherent polynuclear aromatic structure of carbon particles was proposed as providing basic sites for the adsorption of acids in the diffuse double-layer theory.^{29,40,41} Figure 1b shows that both acidic (673 K) and basic (923 K) groups did not exhibit appreciable improvement in Hg⁰ removal rates, in agreement with previous work.^{42,43} Li et al.⁴³ found that oxygen surface functional groups produced by air oxidation are characterized by high phenol and low carbonyl or lactone groups, which contribute to very low Hg⁰ adsorption capacities, but the effect of surface groups on Hg⁰ adsorption kinetics was not investigated. However, after exposure to 35 ppm HCl, the Hg⁰ half-life decreased considerably, reaching 11, 5.5, and 4.5 s for PG without heat treatment, with basic groups, and with acidic groups, respectively. The results indicate that PG, whether without heat treatment or treated to produce acidic or basic functional groups, in all cases is significantly more effective at the removal of Hg⁰ after treatment with HCl.

Halogens (Cl₂, Br₂, and I₂) are oxidants, but halides (KCl, KBr, and KI) are not. The effect of different halide ions impregnated into the PG was studied. Figure 2a shows that Hg⁰ removal efficiency increased with increasing size of halide ions: Cl⁻ < Br⁻ < I⁻. The Hg⁰ capture rate by PG with 4%

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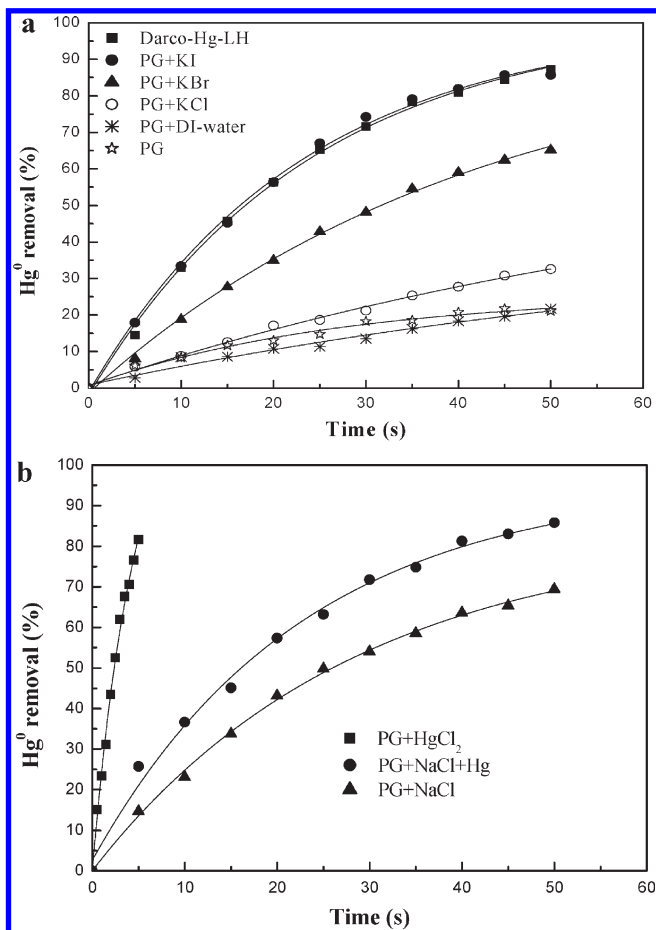


Figure 2. (a) Effect of different halides on Hg⁰ removal efficiency at 373 K. (b) Comparison of Hg⁰ removal efficiencies, at 298 K, by PG impregnated with 1.4% NaCl, 2.4% NaCl with subsequent absorption of 4% Hg⁰, and 3.4% HgCl₂ prior to the kinetic runs.

KI was the largest, followed by 4% KBr and then 4% KCl. Polarizability seems to be more important than electronegativity in influencing the enhancement. For comparison, the Hg⁰ removal rate by Darco-Hg-LH (surface area of 550 m²/g), a brominated PAC, which has been demonstrated to be very effective for mercury control in the utility industry, is shown. The surface area of Darco-Hg-LH was more than 50 times larger than that of PG (6–10 m²/g); however, the Hg⁰ removal rate by Darco-Hg-LH was only twice as fast as that by PG impregnated with KBr.

Experiments that could shed some light on the counterions of the oxidized mercury after the capture of Hg⁰ on carbon particles were conducted. Hg⁰ removal efficiency was determined for PG impregnated with one of three chlorides: 4% NaCl, 4% NaCl with subsequent addition of 4% Hg⁰, and 4% HgCl₂. Hg⁰ half-life was 25 s with only NaCl and decreased to 15 s with NaCl and then Hg⁰. However, Hg⁰ half-life was only 2.5 s with HgCl₂. These results (Figure 2b) indicate that sequential impregnation of NaCl and Hg⁰ into carbon particles did not yield the same effect as the impregnation of HgCl₂, implying that Hg⁰ was probably not associated with Cl⁻ after the adsorption of Hg⁰ on carbon particles. The high Hg⁰ removal efficiency by PG impregnated with HgCl₂ can be attributed to the redox reaction of Hg⁰ with HgCl₂ to form Hg₂Cl₂.

The effect of organic halides was investigated. Neither aliphatic (chloroform and 1,10-dibromodecane) nor aromatic

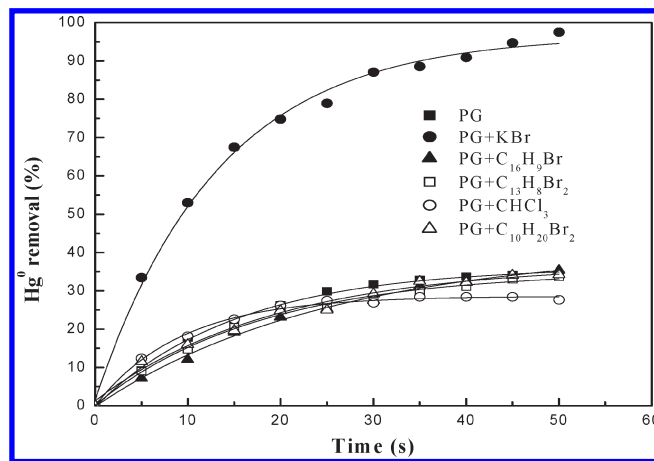


Figure 3. Effect of various organic halides with PG on the Hg⁰ removal efficiency at 298 K. Also shown for comparison is the Hg⁰ removal efficiency by KBr-impregnated PG.

halides (1-bromopyrene and 2,7-dibromofluorene) adsorbed on PG exhibited any enhancement of Hg⁰ capture (Figure 3). The fact that the covalent bonded halides have no effect suggests that the insertion of Hg⁰ into bonding between C and Br or Cl, to form a C–Hg–Br or C–Hg–Cl structure, did not occur.

XPS was used to investigate the charge-transfer mechanism. The shift of core electron binding energy, as measured by XPS, is related to the oxidation state of the element in a molecule. The core electron binding energy increases if elements lose valence electrons, becoming more cationic, whereas the binding energy decreases if the element gains electrons, becoming more anionic. The binding energy of Br 3d_{5/2} electrons is 69.3 eV in KBr, corresponding to a –1 oxidation state.¹⁵ When PG was impregnated with KBr, the binding energy of Br 3d_{5/2} electrons decreased to 68.4 eV (Figure 4a), indicative of Br drawing electrons closer to its nucleus, rendering the PG positively charged. As an electrical conductor, the PG delocalizes the positive charge over the graphitic domain, which would be more likely to attract Hg⁰, a polarizable atom with 80 electrons surrounding its nucleus. Upon contact, charge transfer from Hg⁰ to PG takes place, resulting in the formation of oxidized mercury (cation), with the PG lattice as the counteranion.

PG was also impregnated with Br₂, which produced a Br 3d_{5/2} binding energy of 68.4 eV, identical to PG impregnated with KBr (Figure 4b). After capture and oxidation of Hg⁰, the binding energy of Br 3d_{5/2} in the KBr-impregnated PG returned to 69.3 eV. The binding energy of Hg⁰ 4f_{7/2} is 99.9 eV,¹⁵ which shifts to 101.0 eV, from our results, after capture, evidence for electron transfer forming oxidized mercury. For comparison, the Hg 4f_{7/2} binding energy was 100.5 eV for HgBr₂ and 100.0 eV for Hg₂Br₂, indicative that the oxidized mercury is likely in the mercuric (Hg²⁺) state. The binding energy of C 1s electrons did not exhibit detectable change after impregnation with bromide. We attribute this to the fact that only 4 wt % bromide was impregnated in PG (the atomic ratio of KBr to C is only 0.006 or 1 mol of KBr for every 167 mol of carbon) and the delocalization of the π electrons among carbon atoms in the graphitic lattice.

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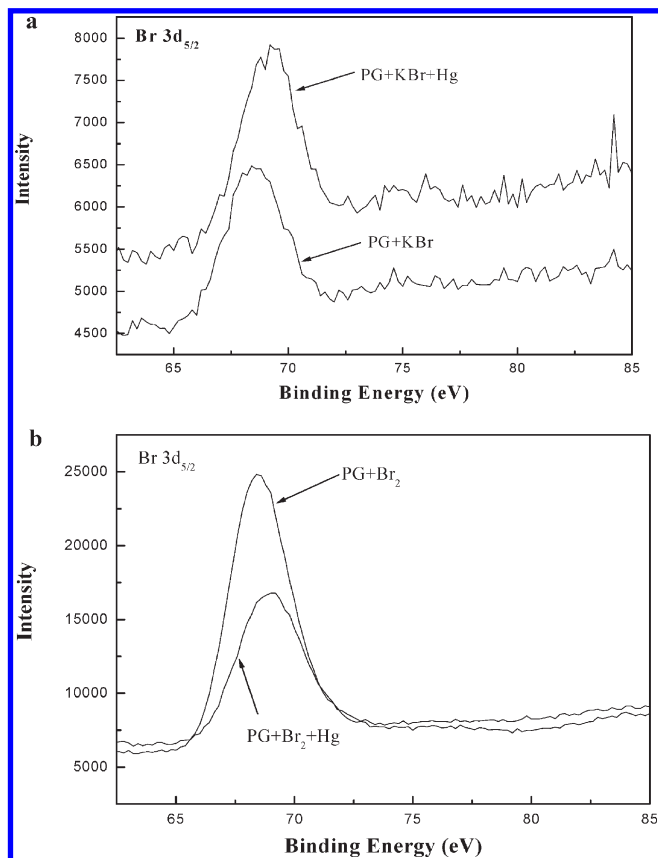


Figure 4. (a) XPS spectra showing the binding energies of Br 3d core electrons in (a) KBr and (b) Br₂ impregnated into PG before and after the capture of Hg⁰.

Papirer et al.^{44–46} studied the bromination of carbon black by XPS and found that different bromine bonding energies are detected depending upon the bromination method and subsequent heat treatment. The Br 3d_{5/2} peak at 68.5 eV was suggested to be the physisorbed HBr because it falls in the range of bromide (Br⁻), which varies between 67.8 ± 0.2 and 69.2 ± 0.2 eV, and the fact that most of the peak disappears after vacuum outgassing at 100 °C for 4 days. However, extensive studies indicate that, if graphite is exposed to Br₂ vapor, bromine intercalation compounds are formed^{47–50} and

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that the absorption is reversible.⁴⁹ Intercalate desorption was found to be thermally activated. The mechanism of desorption depends upon the intercalate concentration. On the basis of the studies mentioned above, the Br 3d_{5/2} peak at 68.4 eV obtained from the interaction of PG with Br₂ is likely a graphite–bromine intercalation compound. Hutson et al.¹⁵ also studied the brominated activated carbon by XPS and questioned the existence of physisorbed HBr because of the high vacuum pretreatment before taking an XPS spectrum. However, the important finding in our study is that PG impregnated with KBr exhibits a binding energy for Br 3d_{5/2} of 68.4 eV, the same as that of graphite–bromine intercalation compounds. Although XRD, which characterizes the crystallographic structure of the bulk sample, did not reveal the existence of intercalation, charge transfer between KBr and the surface layer of PG is apparent from the XPS results. XPS is a technique for the analysis of the surface layer, 2–5 nm depending upon the X-ray energy and inelastic mean free path of emitted electrons. Therefore, it appears that the impregnation method employed did not facilitate the penetration of bromides into the bulk of PG based on XRD; nevertheless, XPS binding energy supports the formation of intercalation of bromides within the surface layer of the graphite lattice.

The graphite intercalation compounds have been studied in the past.^{47–52} The formation of intercalation compounds depends upon the electron transfer between the graphite and the reactant. If the electrons are transferred to the graphite, donor or N-type compounds are formed. If electrons are removed from the graphite, acceptor or P-type compounds, such as graphite bromide, are formed.

Our XPS results appear to support the charge-transfer mechanism, similar to the formation of P-type graphite compounds, for the enhancement of Hg⁰ capture by halogenated carbon particles. This mechanism can also explain the formation of the oxidized Hg²⁺ with graphite lattice as counterions, resulting in N-type compounds. Because Hg⁰ is a large atom with many electrons, it is highly polarizable and the London dispersion forces should play an important role in its interaction with surrounding atoms and molecules. This could explain the enhanced Hg⁰ oxidation when the solid surface is involved,^{10–14,28,34} especially when the solid surface is a strong electron acceptor, such as brominated PAC.

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