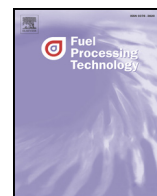




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Experimental and kinetic studies of gas-phase mercury adsorption by raw and bromine modified activated carbon

Qiang Zhou, Yu-Feng Duan*, Ya-Guang Hong, Chun Zhu, Min She, Jun Zhang, Hong-Qi Wei

Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, PR China

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ABSTRACT

Gas-phase mercury capture performance of raw activated carbon (R-AC) and bromine modified activated carbon (AC-Br) was evaluated in a fixed-bed reactor. Effect of flue gas temperature on mercury adsorption efficiency was explored. Sorbent characterization was conducted to feature their morphologies correlated to mercury adsorption efficiency. Adsorption kinetic and thermodynamic analysis of fixed-bed experimental results was also carried out to explore the different mercury adsorption mechanisms of R-AC and AC-Br. The results show that vapor mercury adsorption capacity of AC-Br increases with temperature, but R-AC demonstrates opposite results. The bromine ion (Br^-) remains in the mesopore and the surface of R-AC in the form of amorphous during modification process, leading to the reduction of mesopore volume and the increase of micropore volume. The increase of active site (Br^-) on activated carbon improves chemisorption of vapor mercury on AC-Br at 150 °C and 200 °C. The kinetic analysis shows that mercury adsorption on active sites is the adsorption rate controlling step, in which it can be divided into two steps: surface adsorption and intraparticle diffusion adsorption. Vapor mercury adsorption on AC-Br needs more activated energy due to the enhancement of chemisorption. The initial mercury adsorption rate of AC-Br increases with temperature, which is different from that of R-AC. The thermodynamic analysis shows that the adsorption of gas-phase mercury on both R-AC and AC-Br is spontaneous, endothermic and mainly physical in nature enhanced by chemisorption. The bromine modification enhances chemisorption of vapor mercury on AC-Br leading to the increase of complexity degree of mercury adsorption process.

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1. Introduction

Mercury has been a concerned pollutant due to its toxicity, volatility, persistence, and bioaccumulation in the environment, which is extremely dangerous for ecosystem and human health [1–3]. In 2005, the U.S. EPA issued the Clean Air Mercury Rule (CAMR) proposing that coal fired power plant was the most difficult mercury emission source facing control [4,5]. This is because compared to municipal and medical waste incinerators, which emit high concentration of almost exclusively oxidized mercury (Hg^{2+}), coal-fired power plants emit much lower concentration (ppb) of both elemental mercury (Hg^0) and oxidized mercury (Hg^{2+}) [4]. In general, oxidized mercury (Hg^{2+}) can be easily removed by Wet Flue Gas Desulfurization (WFGD) facilities, because oxidized mercury is highly water-soluble [6,7]. However, elemental mercury (Hg^0) cannot be removed through WFGD and particle control devices (PCDs) because it is insoluble in water and high volatile [8–10]. In addition, due to large quantity and scale of boilers, coal combustion has been the largest anthropogenic source of mercury emission [11–13].

Sorbent injection upstream of PCDs such as Fabric Filters (FFs) and Electrostatic Precipitators (ESPs) is the most promising control technology for removing mercury from coal combustion flue gas [14,15]. The brominated activated carbon (AC-Br), which has been widely tested for mercury capture in coal-fired power plants, is confirmed to be an effective sorbent for removing both Hg^0 and Hg^{2+} [16,17]. However, the limited understanding of the mechanism associated with mercury adsorption on AC-Br has been a major problem on mercury capture. A considerable amount of researches exploring the mechanism of mercury adsorption on AC-Br have been performed [18–21]. Sasmaz et al. [18] investigated the possible binding mechanism of Hg^0 onto brominated fiber and powder activated carbon sorbents by X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) spectroscopy. He found that Hg^0 was oxidized at the brominated carbon surface at both 30 °C and 140 °C, coordinated to two Br atoms with no detectable bonding between Hg and O. Rupp and Wilcox [19] studied the interaction of Hg^0 and flue gas components (SO_2 and NO_x) on brominated AC fibers, and found that NO and NO_2 promoted Hg^0 oxidation on brominated AC fiber, but SO_2 prevented Hg^0 adsorption and oxidation on brominated AC fiber. The interaction of SO_2 and NO_x with Br led to sorbent deactivation. Liu et al. [20] conducted theoretical studies of mercury–bromine species adsorption mechanism on

* Corresponding author. Tel./Fax: +86 25 83795652
E-mail address: yfduan@seu.edu.cn (Y.-F. Duan).

carbonaceous surface by the mean of first principles of quantum mechanical methods based on density functional theory. The results showed that bromine had a positive effect on Hg^0 adsorption on carbonaceous surface due to the transfer of charge. Compared to HgBr_2 adsorption, which was not very stable on the surface, the adsorption of Hg-Br on carbonaceous surface was highly thermally favorable and belonged to chemisorption. Sun et al. [21] studied the Hg^0 adsorption capacity and the dynamics of brominated activated carbon, and found that bromine modification caused enhanced and faster Hg^0 adsorption. The Hg^0 adsorption capacity of activated carbon increased 80 times reaching 0.2 mg/g when the bromine amount was 0.33%. Although the researches of gas-phase mercury adsorption on brominated activated carbon have been widely conducted, the highly complex mercury adsorption procedure results in the limited understanding of mercury adsorption mechanism. Therefore, further studies of mercury adsorption on AC-Br are still needed.

Adsorption kinetic study has been an important way to obtain kinetic parameters, predict adsorption rate controlling step and explore adsorption mechanism. Three widely used kinetic models are pseudo-first order kinetic model, pseudo-second order kinetic model and Weber and Morris intraparticle diffusion model [22–25]. They have been widely applied in the researches of heavy metal adsorption from liquid phase [26]. Sulaymon et al. [23] investigated the kinetic of heavy metal (Pb(II), Cu(II), Cr(III) and Co(II)) adsorption onto activated carbon using pseudo-first order and pseudo-second order equation. He found that the adsorption followed pseudo-second order equation. Somayajula et al. [25] researched the kinetic of Hg^{2+} adsorption from aqueous solution using intraparticle diffusion models, pseudo-first and second order models. He found that the adsorption followed pseudo-second order model and was dominantly divided into a two-step intraparticle diffusion process. Mohan et al. [27] studied the kinetic of mercury adsorption from wastewater using fertilizer waste activated carbon and found that the adsorption followed film diffusion mechanism at low concentrations, and followed particle diffusion mechanism at high concentrations. In addition, the kinetic analysis method has also been applied in the studies of dye, organic vapors, water molecules, carbon dioxide and oxygen gas adsorption on activated carbon [26]. By kinetic studies, different adsorption mechanisms have been obtained, but the number of literatures relating to the kinetic of gas phase adsorption on activated carbon is limited [26]. Vidic et al. [28] studied the kinetic of gas-phase mercury adsorption by virgin and sulfur-impregnated activated carbons, and found that the formation rate of HgS was the rate-limiting step. However, he did not use kinetic models and give specific kinetic parameters, including activation energy, free energy, enthalpy and entropy. G. Skodras et al. [26] researched the kinetic of vapor elemental mercury adsorption on commercial activated carbon using four kinetic models, including Fick's intraparticle diffusion equation, pseudo-first and second order models and Elovich kinetic equation. He found that mass transfer limitation affected mercury adsorption procedure and chemical adsorption rate was the controlling step, but he did not investigate the difference between mercury adsorption on raw and modified activated carbon from the kinetic of view. Although the kinetic studies of gas-phase mercury adsorption on activated carbon have been started, the comprehensive kinetic adsorption mechanism is still not very clear. Therefore, it is necessary to conduct further research on the kinetic and thermodynamic properties of gas phase mercury adsorption on R-AC and AC-Br.

This current work evaluated a brominated activated carbon (AC-Br) in a fixed-bed adsorption reactor, and raw activated carbon (R-AC) was also tested for comparison. Both of R-AC and AC-Br were characterized to feature their morphologies correlated to mercury adsorption efficiency. Adsorption kinetic and thermodynamic analysis of fixed-bed experimental results was also carried out to explore the different mercury adsorption mechanisms of R-AC and AC-Br. Therefore, this work has

been performed in an attempt to elucidate mercury adsorption mechanism of AC-Br and to provide a foundation for understanding more complex systems.

2. Experimental

2.1. Sorbent preparation

The R-AC tested in this work was prepared from a commercial activated carbon by crushing and sieving, with a geometric mean particle diameter of 75 μm . The R-AC purity is 93.94%. The AC-Br was prepared by adding 10 g R-AC sample into 200 ml 1% (mass ratio) NH_4Br solution and stirring for 12 h, then filtering out the particles, drying them in an oven at 45 $^\circ\text{C}$ and cooling them in a desiccator.

2.2. Sorbent characterization

The prepared R-AC and AC-Br samples were characterized by N_2 adsorption, scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX) and X-ray diffraction (XRD) to feature their morphologies correlated to mercury adsorption efficiency. Specific surface area and porous structure parameters of the sorbents were obtained by adsorbing and desorbing N_2 at 77 K using an automatic volumetric multipoint apparatus (ASAP 2020, Micromeritics). As shown in Fig. 1, steep increase of adsorbed volume at low relative pressure illustrates the existence of large numbers of micropores (<1 nm), and increase of adsorbed volume at high relative pressure verifies the presence of mesopores (2 nm–50 nm) and macropores (>50 nm) in sorbents [29]. Fig. 1 indicates that the R-AC and AC-Br have similarly a well-developed micropore structure. The modification on the R-AC does not change its micropore structure, but reduce the volume of mesopores and macropores. As Fig. 2 shows, the pore diameter between 3 nm and 30 nm of AC-Br is visibly less than that of R-AC, which demonstrates that part of the modifier remains in mesopores after modification. Generally, micropores provide activated sites for mercury adsorption, mesopores serve as transportation channels and macropores function as entry portals to carbon particle [30]. As shown in Table 1, the R-AC and AC-Br have similar specific surface area, which is obtained by the Brunauer–Emmett–Teller (BET) equation. The AC-Br has larger micropore volume proportion and smaller mean pore diameter due to the decrease of mesopore volume. The EDX analysis shows that approximate 1.47% bromine remains on the surface of R-AC after modification.

Fig. 3 shows that the R-AC and AC-Br have similar spectrum with no significant peak related to inorganic and organic crystalline compounds except silicon dioxide (SiO_2) detected at 20.88 $^\circ$ and 26 $^\circ$. It confirms that

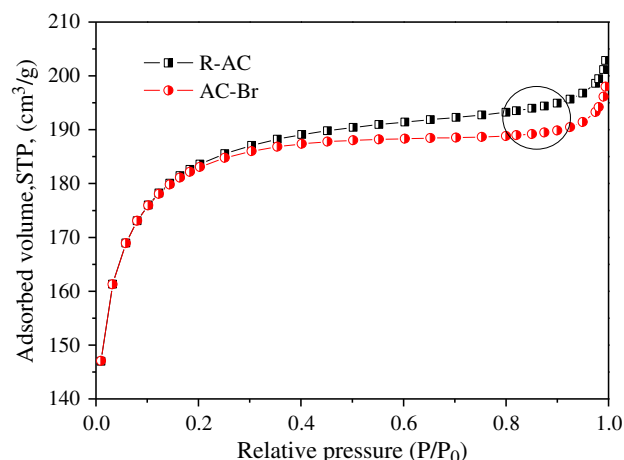


Fig. 1. N_2 adsorption isotherms of R-AC and AC-Br.

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