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Influence of Main Components in Exhaust Gas on Mercury Adsorption Capacity of Brominated Activated Carbon

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Abstract

Brominated activated carbon (AC-Br), which was produced from coconut shell activated carbon (AC) and brominated by wet way with elemental bromine, was determined as a material with super high adsorption capacity of mercury vapor. But in real exhaust gases, there are many components such as SO_2, NO_x, CO, CO_2, HCl, H_2O can influence on adsorption ability of the AC-Br. In this paper, these influences were studied and compared them between initial AC and AC-Br. Each component has different effect on AC and AC-Br and followed by its particular mechanism.

Keywords: brominated activated carbon; mercury vapor adsorption; exhaust gas influences

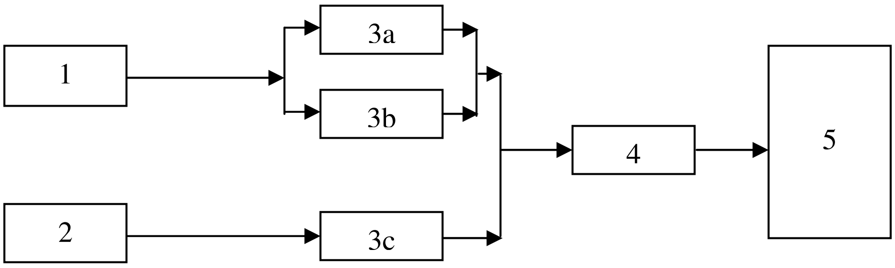
1. Introduction

Mercury emissions are the source of serious health concerns. Worldwide mercury emissions from human activities are estimated to be 1000 - 6000 tones per year, which accounts for 30-55% of global atmospheric mercury emissions (Lee *et al*., 2006). Anthropogenic sources of mercury are numerous. Mercury is produced by the mining and smelting of cinnabar ore, it is used in chloralkali plants, in paints, in electrical switching equipment and batteries, in thermometers and medical equipment, in mercury vacuum apparatus, as a catalyst in chemical processes, in mercury quartz and luminescent lamps, in the production and use of high explosives using mercury fulminate, in copper and silver amalgams in tooth-filling materials, and as fungicides in agriculture (WHO, 2000). Mercury entering the atmosphere is mainly from combustion sources, including medical waste incinerators, municipal solid waste incinerators and coal-fired utilities. The largest source is believed from coal-fired power plants. U.S. coal-fired power plants emitted 44.2 tones of mercury into the air in 2004, which accounts for 40% of the total U.S. anthropogenic emissions. Canadian power plants emitted 1.96 tones of mercury in 2004, which accounts for 25% of total Canadian anthropogenic emissions (IJC, 2006).

Currently, two methods exist to reduce mercury emissions from combustion sources: reduce the mercury content in the combusted materials or use advanced flue gas treatment technologies to capture the mercury (Yang *et al*., 2007). Numerous mercury adsorbents such as coal chars (Wu *et al*., 2000), calcium sorbents (Ghorishi and Sedman, 1998), petroleum coke (Lee *et al*., 2006), zeolites (Morency, 2002), fly ash (Senior *et al*., 2004), activated carbon and chemical treated activated carbon (Yang *et al*., 2007) have been studied. Among them, activated carbon impregnated halogens or sulfur have shown the more extensively for capturing mercury vaporthan others. At this time, brominated activated carbon appears to be the best performing mercury adsorbent. The bromination causes enhanced and faster mercury adsorption. The adsorption capacity increases 80 times to 0.2 mg/g when bromination is 0.33% (Sun *et al*., 2006). Liu *et al*. (2007) used bromine vapor injected to exhaust gas from coal electric power plant to help enhancing efficiency of mercury vapor removal to more than 90%.

The mercury adsorption depends on several factors (Yang *et al*., 2007). The surface functional groups, such as bromine, chlorine and sulfur species, can strongly affect mercury adsorption through the chemical adsorption mechanism. Sorbent properties, such as size, shape, surface area, micropore volume and pore size distribution may affect sorbent adsorption performance also. Besides, flue gas chemical composition is the important factor that significantly affects mercury adsorption.

In this paper, theinfluences of the main components in exhaust gas, including SO_2, NO_x, CO, CO_2, HCl, H_2Oon mercury vapor adsorption of brominated activated carbon are studied.



Note: 1, Spiking gas; 2, Clean air; 3a, 3b and 3c Gas flow adjusters; 4, Gas mixer and 5, Equipment for mercury vapor adsorption study

Figure 1. Gas spiking system

2. Materials and Methods

2.1. Brominated AC and spiking gases

Brominated AC was prepared from coconut shell AC soaking in lightly acidic solution of elemental bromine for 3 hours at temperature around 45°C and normal pressure. The ratio of bromine per AC was 3%. After bromination, the material was washedby deionized water and dried at 105°C for 4 hours.

Spiking gases were commercial standard gases and spiked to mercury vapor current by a standard equipment as described in Fig. 1.

2.2. Experimental methods

The AC or brominated AC (0.5-1.0 mm of size) was mixed with quartz sand with the same size under the weight ratio of 1:10 and filled into adsorption columns which were used for determination of dynamic adsorption capacity (Tran Hong Con *et al.*, 2015). Experiments'conditions of inlet mercury vapor concentration was 32.267 mg/m^3, adsorption temperature was 50°C, adsorbent quantity was 0.2 g, gas flow rate was 0.5 L/min. Outlet mercury vapor (after adsorption) in each fraction was fixed in oxidative solution of $KMnO_4$ dissolved in nitric acid and determined by AAS connected with cool vapor generator (APHA, 1995).

The influencing gas was supplied through gas spike gate and then mixed with clean air to meet designed concentration, then mixed with mercury vapor current before contact with adsorption column. The apparatus for this investigation was described in Fig. 2.

The dynamic equilibrium adsorption capacity was determined in the conditions mentioned above. At each concentration level of spiked gases, adsorption process was carried out continuously and after every 60 min adsorption (equal 30 L gas passed the adsorption column) the fractions were taken. The examination was continued until the mercury concentration in the effluent almost equal the inlet concentration. Average mercury concentration in the fractions was determined. The dynamic equilibrium adsorption capacity (q_e) was calculated by following formula:

$$q_e = \frac{C_o \,.\, t_T . w^n - \sum_i C_i \,.\, t_i . w \;\; (mg/g)}{m} \qquad (1)$$

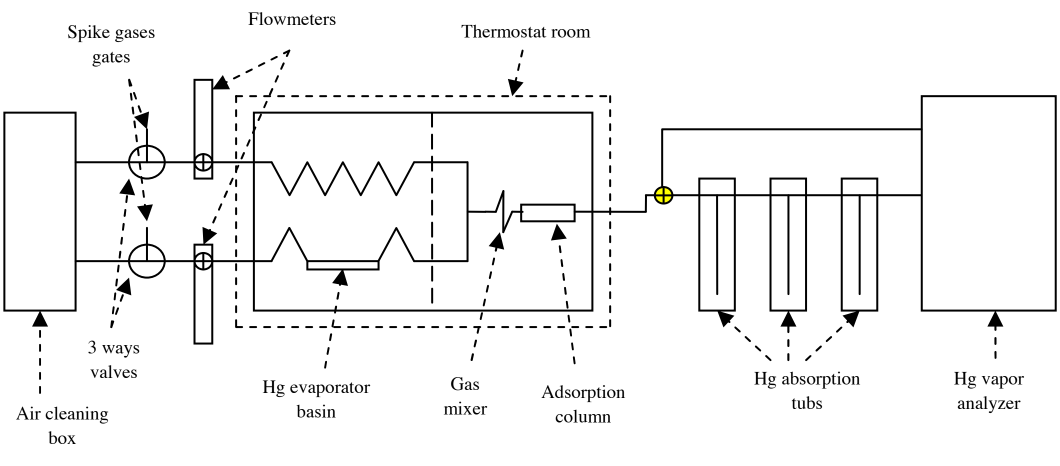


Figure 2. The apparatus for the Hg vapor adsorption study

Where C_o is inlet mercury concentration (mg/m^3), C_i is outlet mercury concentration in fraction i (mg/m^3), t_T is total adsorption time (min), t_i is the time of each fraction (min), w is flow rate (L/min) and m is adsorption material quantity (g).

3. Results and Discussion

3.1. Influence of SO_2 concentration on dynamic equilibriumadsorption of mercury vapor on AC and AC-Br

The dynamic equilibrium adsorption of original AC and AC-Br was carried out according to the experimental procedure presented in the section 2.2 with spiked SO_2 concentration increased from zero to 1000 ppm and calculated following the formula (1). Investigation results are reported at Figs. 3 and 4.

According to the results showed in Figs. 3 and 4, the influence of SO_2 concentration on adsorption capacity of mercury vapor on AC was different. For original AC, the adsorption capacityof mercury vapor was increased significantly when spiked SO_2 concentration increased from zero to 100 ppm; then decreased when SO_2 concentration increased until to 1000 ppm. The reason of this phenomenon assumed that, at the concentration lower than 100 ppm, when SO_2 contacted with AC surface, the reductive functional groups in AC possibly reduced SO_2 to form elemental sulfur. Elemental sulfur itself was strong adsorption center of mercury vapor. But at the higher concentration, SO_2 can react with elemental sulfur to form deferent disulfur compounds which have lower affinity with mercury vapor. So the adsorption capacity of the material (AC) was then decreased.

In the case of AC-Br, the increase of SO_2 concentration decreased mercury vapor adsorption capacity of the material. Until now, the reason of this phenomenon was not clear yet. It seemed reasonable to assume that (1) after bromination, strongest reductive groups in the AC surface were oxidized, so they could not reduce SO_2 to elemental sulfur and (2) in the space of high concentration of SO_2 and partly brominated AC, neutral SO_2 molecules could massively adsorbed on the AC surface; those obstruct adsorption of mercury vapor.

3.2 Influence of NO_2 concentration on dynamic equilibrium adsorption of mercury vapor on AC and AC-Br

Investigation of NO_2 gas influence was carried out as the same procedure as for investigation of SO_2 above. But concentration of NO_2 gas was changed in the range from zero to 100 ppm. The dynamic equilibrium adsorption capacity of the materials AC and AC-Brafter spiking NO_2 gas was measured and calculated flows those presented in section 2.2. The result is showed in Fig. 5.

The results in Fig. 5 showed that NO_2 presented in mercury vapor current had positive effect on adsorption of mercury vapor on both AC and AC-Br. In the previous studies (Olson *et al*., 2009),authors showed out that, mercury vapor adsorbed onto AC almost was in the oxidized forms, Hg(I) or/and Hg(II). Therefore, before or during adsorption, mercury vapor was oxidized by any oxidation process. In this study, NO_2 was an oxidant, so NO_2 could directly oxidize Hg element or support a certain oxidation reaction with elemental Hg. Those resulted in forming of activated Hg or/and Hg(I), Hg(II)species. These species more easy adsorbed

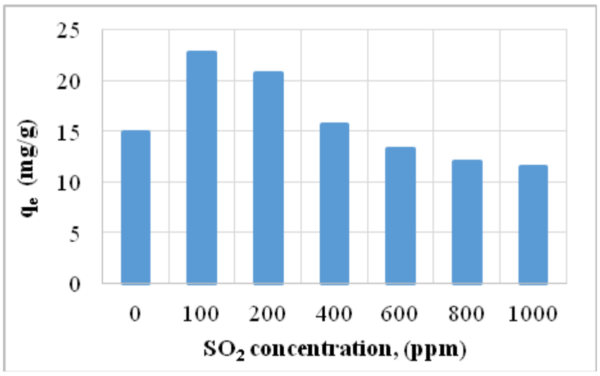


Figure 3. Influence of SO_2 on adsorption capacity of AC

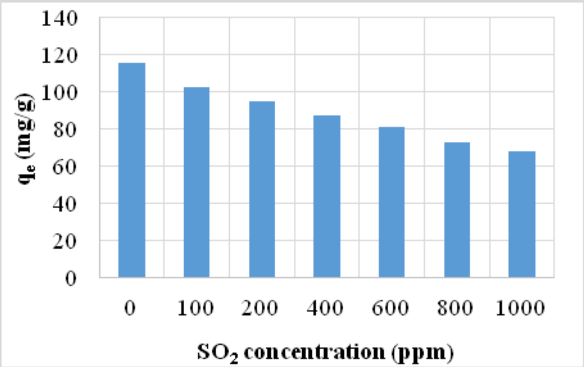


Figure 4. Influence of SO_2 on adsorption capacity of AC-Br

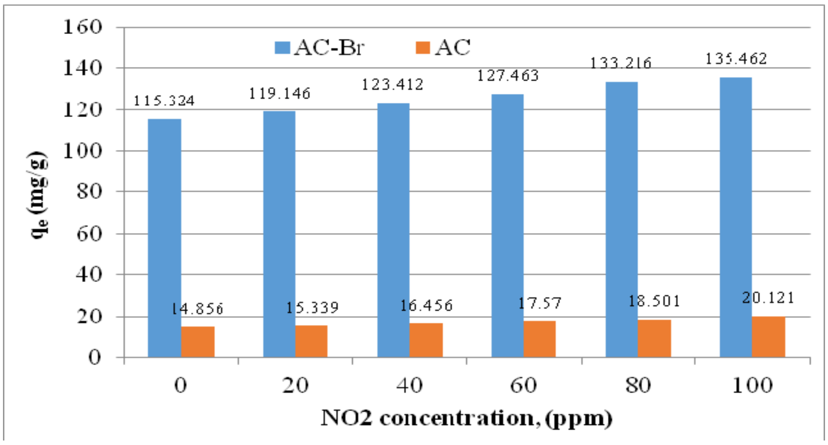


Figure 5. Influence of NO_2 concentration on adsorption of AC and AC-Br

on non-brominated AC surface in the form of Hg oxides or on brominated AC centers through -Br-Hg or -Br-Hg-O- or other complex bonds (Granite and Presto, 2008). The explanation above for increasing of NO_2 concentration intensified adsorption capacity of mercury vapor on AC and AC-Br is needed somewhere more indentified, but it is mostly acceptable.

3.3 Influence of CO_2 concentration on dynamic equilibrium adsorption of mercury vapor on AC and AC-Br

Investigation of CO_2 influence on adsorption capacity of mercury vapor onto AC and AC-Br materials was carried out under the same experimental conditions as those for NO_2 or SO_2 and concentration of CO_2 increased from zero to 15% (maximum CO_2 concentration in exhaust gases). The result is present in Fig. 6.

According to the data presentedin Fig. 6, in the case of original AC, when CO_2 concentration increased from zero to 3%, the adsorption capacity slightly increased and then decreased while CO_2 concentration increased continuously to 15%. For explanation of this phenomenon, there is a hypothesis that, in adsorption space, where CO_2 concentration was still small enough, CO_2 molecules possibly bound with carbon atoms on AC surface, especially carbons in the edge of broken carbon net or carbenes, and formed stronger oxidative centers. These centers enhanced Hg adsorption potential. However, in the higher concentration, the dense adsorption layer of CO_2 on AC surface obstructed adsorption of mercury vapor on AC. In the case of AC-Br, CO_2 had negative influence on adsorption capacity in any concentration level. But the decrease was not significant; in maximum CO_2 concentration (15%), the adsorption capacity decreased only about 14%. The reason could be the obstruction of the dense adsorbed CO_2 molecules on the surface of the materials.

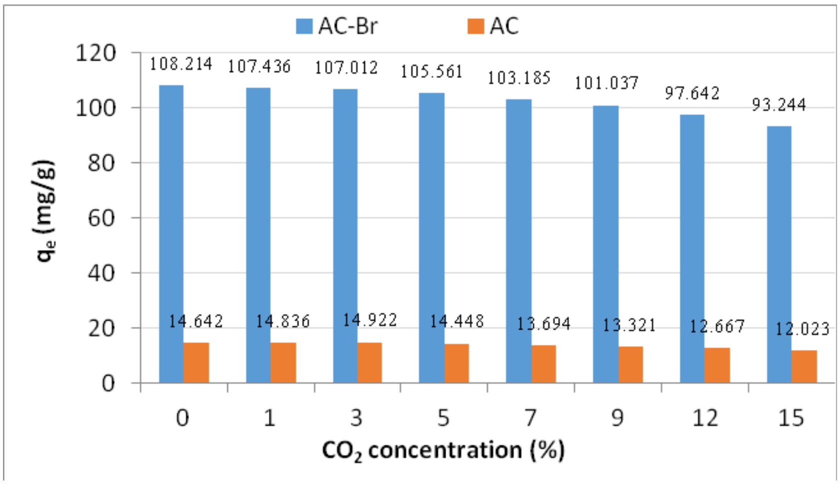


Figure 6. Influence of CO_2 concentration on adsorption capacity of AC and AC-Br

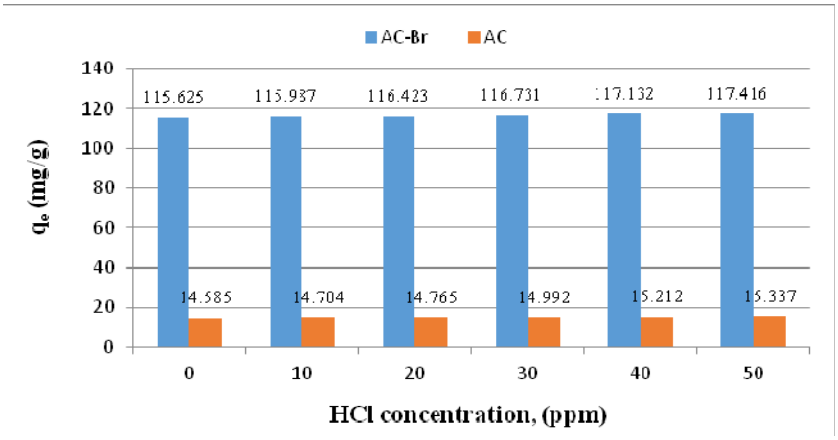


Figure 7. Influence of HCl vapor concentration on adsorption capacity of AC and AC-Br

3.4 Influence of HCl vapor concentration on dynamic equilibrium adsorption of mercury vapor on AC and AC-Br

In this investigation, the HCl vapor concentration was in the range of zero to 50 ppm and experimental conditions were the same as those for other gases above. Result of the investigation is present in Fig. 7.

Investigation result showed that, when HCl vapor increased from zero to 50 ppm, adsorption capacity of original AC continuously increased, but almost negligible, total increase was about 5% in comparison with adsorption process without HCl vapor. The reason and mechanism of this phenomenon is not clear yet. But there is a hypothesis that, presence of HCl vapor, HCl molecules possibly adsorbed onto AC surface and create active adsorption center for mercury vapor. Hg could link with carbon on AC surface though Cl atom, likely Hg adsorbed on chlorinated AC. In the case of AC-Br, HCl was almost unaffected. In the maximum concentration of HCl (50 ppm), the adsorption capacity increased only 1.5%.

3.5 Influence of water vapor concentration on dynamic equilibrium adsorption of mercury vapor on AC and AC-Br

This investigation was carried out at 80°C to avoid water vapor condensation. The water vapor concentration spiked to the gas current were zero, equal to saturated in 40°C, 60°C and 80°C. The other experimental conditions were kept the same as used for investigation of spiked gases above. The influence of water vapor on adsorption capacity is showed in Table 1.

According to data in Table 1, there is different effect of water vapor on adsorption of mercury vapor on AC and on AC-Br. Increase of water vapor in gas current decreased adsorption capacity of AC significantly, but that for AC-Br was slightly increased. Water is easy to adsorb onto AC surface and obstructed Hg species contact with adsorption centers on AC surface. But in the case of AC-Br, it is possibly that water adsorbed onto the centers containing bromine atoms create favorable conditions for Hg react with bromine, therefore adsorption capacity of AC-Br increased.

Table 1. Influence of H_2O vapor on adsorption of Hg vapor on AC and AC-Br

Exp. No	H_2O vapor concentration	(g/m^3)	q_{cb} (mg/g)	
			AC	AC-Br
1	Dried air at 80°C	0.0	8.823	103.792
2	Saturated in 40°C	59.1	8.202	108.425
3	Saturated in 60°C	130.5	7.711	112.356
4	Saturated in 80°C	293.8	7.234	117.482

Table 2. Composition of gases in gas mixture

Experiment No	NO_2 (ppm)	SO_2 (ppm)	HCl (ppm)	CO_2 (%)
1	0	0	0	0.32
2	100	100	5	3.5
3	200	200	20	8.5
4	300	300	40	12.0
5	500	1,000	50	15.0

3.6 Influence of mix gases on dynamic equilibrium adsorption of mercury vapor on AC and AC-Br

Mixture of gases used for study experiments in this investigation was present in Table 2. Other experimental conditions were kept the same as for investigation of single gas present in section 2.2.

The result present in Fig. 8 showed that increase of spiked gases concentration from matrix 1 to matrix 5 decreased adsorption capacity of AC up to 74% but that of AC-Br only near 30%. The investigation also showed that total effect of gases was not equal simple algebraic sum of gases effects. This is more complicated due to interactions between gases, mercury vapor and functional groups on AC and AC-Br surface. These interactions are almost not clear yet and they need to be further investigated.

4. Conclusions

Both AC and AC-Br have possibility to adsorb mercury vapor in exhaust gases; therefore the dynamic equilibrium adsorption capacity of AC-Br is almost ten times higher than that of AC. The influence of main components in stack gas (SO_2, NO_2, CO_2, HCl, H_2O) and mixture of the gases on the adsorption capacity of AC and AC-Br was different. Beside different mechanism of adsorption of mercury vapor onto AC and AC-Br (adsorption onto AC is predominantly physical and that on AC-Br is mainly chemical),there are complex interaction processes. A part of these interactions and processes were explained in this study. The influence of gas mixture on adsorption capacity of AC was significant (up to 74% decreased) but on AC-Br only about 30% in challenging condition. So AC-Br was appreciated as an excellent material for stack mercury vapor treatment.

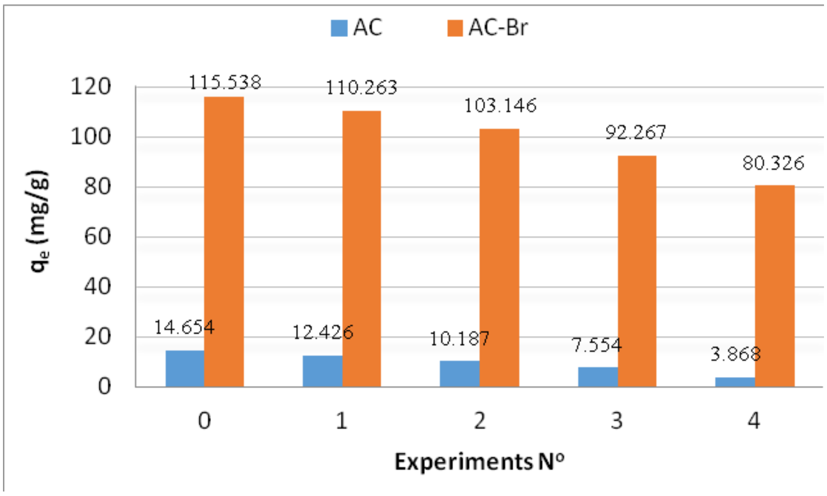


Figure 8. Influence of gas mixture on adsorption capacity of AC and AC-Br

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