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Preparation of gold- and chlorine-impregnated bead-type activated carbon for a mercury sorbent trap

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HIGHLIGHTS

- Hg sorbent trap is prepared using impregnated bead-type activated carbon (BAC).
- BAC is impregnated with chlorine and/or gold (BAC^C, BAC^{Au}, and BAC^{Cl-Au}).
- Hg spiking efficiency of BAC^{Cl-Au} is 23% higher than that of virgin BAC.
- Hg adsorption efficiency higher than 95% is obtained by BAC^{Cl-Au}.

ARTICLE INFO

ABSTRACT

This study aimed to develop a mercury (Hg) adsorption trap, which can be used to measure the concentration of elemental Hg in emissions from a Hg discharge facility, and evaluate its adsorption efficiency. The Hg spiking efficiency was compared by impregnating metallic and halogen materials that have high affinity for Hg into activated carbon (AC) to determine an accurate spiking method for Hg on AC. The Hg spiking efficiency was compared according to the type and content of the impregnated substances. AC impregnated with Cl and Au had a 15–20% higher Hg spiking efficiency compared to virgin AC. For Au impregnation at weight ratios of 0–20 wt% of adsorbent, spiking efficiencies of over 97% were observed under certain conditions. The Hg adsorption properties of the above adsorbent were determined experimentally, and the results were used to test the adsorption performance of Hg adsorption traps.

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1. Introduction

Stringent regulations and continuous and accurate monitoring of atmospheric Hg emissions are now mandated as a result of the Minamata Convention on Mercury (Hg) (UNEP, 2013).

Despite the complexity of sample collection and pretreatment prior to measurement, wet processes for the examination of Hg emissions in air such as the Ontario Hydro Method (ASTM D6784, 2008) have been used for some time. A wet process involves the constant inhalation of gas in the stack by sampling equipment, followed by trapping in an absorption solution. The strong acids used as the absorption solution, such as $KMnO_4-H_2SO_4$, should be contained in an impinger. However, wet processes could lead to

large errors in the measured value because of the complex sample collection and pretreatment processes.

Dry processes have been developed to overcome the shortcomings of wet processes. The most widely used dry process is US EPA Method 30 B (US EPA, 2007). Technical difficulties in obtaining both homogeneity and stability of the Hg-spiked reference section of the sorbent trap have prevented this method from being commercialized until recently (Zhang et al., 2016).

Continuous emission monitoring (CEM) equipment was recently introduced and is advantageous in that it can determine the concentration of Hg discharged in real time. However, CEM is disadvantageous in terms of its high initial cost. US EPA Method 30 B uses an adsorption trap, which is easy to install and sample as well as inexpensive. However, because the adsorption trap cannot measure particulate Hg, it can be only used under low particulate concentrations. Nevertheless, the sorbent trap can be used by itself or to verify CEM readings and is comparatively easier than a typical wet

process.

To properly analyze the concentration of Hg in emitted gas, the amount of Hg spiked in the adsorbent (activated charcoal) should be accurate when producing the adsorption trap. Although existing adsorption traps have an efficiency of over 90% for highly concentrated spiked Hg, these traps lead to high error rates at low spiking concentrations. In this study, a halogen and transition metal (Kobiela et al., 2003), which have high binding affinity for Hg, were impregnated to compensate for the abovementioned disadvantage (Chingombe et al., 2005). Impregnating chlorine (Cl) as the deactivated catalyst (Zhang et al., 2016) activates the activated carbon (AC). Furthermore, the halogen, i.e., Cl, has strong binding affinity. Because gold (Au) is the most stable transition metal and has strong binding affinity for Hg, its binding with Hg is not broken at high temperatures (700 °C) (Kobiela et al., 2003).

2. Experimental

2.1. Materials

A sorbent trap involves an absorbent that is situated in a narrow pipe. To maintain the uniformity of the shape and size of the trap, bead-type activated carbon (BAC) was selected instead of powdered AC, which often causes a pressure drop.

Aqua regia was used for Cl impregnation. Halogens restore disabled AC because they bond strongly to Hg. The reagents used in the experiment are detailed below (Granite et al., 1998).

The fact that bonds between Hg and Au, as well as impregnated Au, are not broken at temperatures below 700 °C indicates high bond strength (Portzer et al., 2004). A Au standard solution was prepared to impregnate Au. Overly impregnating Au can disrupt Hg absorption. A 1 ppm Au standard solution was prepared by diluting a Au stock solution (Kanto Chemical Co. Inc., Tokyo, Japan).

2.2. AC impregnation

To increase the efficiency of Hg adsorption to BAC (Kanto Chemical Co. Inc., Tokyo, Japan), BAC was impregnated with 5% aqua regia and a 5 wt% Au standard solution; 5% aqua regia consisted of an HCl solution mixed with a solution of HNO_3 at a ratio of 3 to 1, which was subsequently diluted. After soaking the BAC in 5% aqua regia, the sample was heated at 90 °C for 30 min using a heating block (SCP Science, Quebec, Canada). After heating, the sample was baked at 90 °C in an oven for 48 h. After adding 40 mL of deionized (DI) water to the sample after the baking was completed, a 5 wt% Au standard solution of BAC was bound to the sample. After stirring for 2 h using a stirrer at 350 rpm, the solution was filtered using a 0.45-μm membrane filter. Afterward, the sample was stored in a glass bottle after drying for 48 h at 110 °C.

BAC was impregnated using 1) 5% aqua regia, 2) a Au solution, and 3) both 5% aqua regia and a Au solution and named BAC^{Cl}, BAC^{Au}, and BAC^{Cl-Au}, respectively.

2.3. Hg spiking

The Hg concentration in the spiked section of the sorbent trap that the experimenter was aware of must have been absorbed (US EPA, 2007). Therefore, the Hg vapor adsorption experiment is essential to ensure the accuracy of the data. Hg-spiked BAC^{Au} was produced as follows. After the insertion of BAC^{Au} was complete, the impregnation of Cl and Au in the Hg standard solution was conducted for 4 h using a stirrer at 350 rpm. After stirring, the samples were baked for 48 h at 90 °C.

The spiked concentration of Hg varied depending on the concentration and flow rate of Hg gas. The Hg concentration to be spiked can be calculated using Eq. (1):

$$C_c = \frac{C_{sol} \times V_{sol}}{W_c} \tag{1}$$

where C_c is the Hg concentration (ng g^{-1}) in the Hg-spiked BAC^{Au}, C_{sol} is the Hg concentration (μg L^{-1}) in the Hg standard solution, V_{sol} is the volume of the Hg standard solution, and W_c is the weight (g) of BAC^{Au}.

2.4. Hg adsorption

Each experiment was conducted to analyze the adsorption properties of the different impregnated materials. The adsorption rate and adsorbed amount were confirmed according to the variations in the contact time and initial concentration. The adsorbed concentration and removal concentration were identified using experiments that were dependent on the contact time. The initial Hg concentration was 1000 ng mL^{-1}.

The maximum adsorption capacity was confirmed based on the variation of the initial concentration of Au. The Au contents were 0, 5, 10, and 20 wt%; the Hg concentrations were 50, 100, 200, 300, 400, 500, 600, and 700 mg L^{-1}. Each sample was analyzed after a 12 h reaction.

2.5. Performance evaluation of the sorbent trap

Hg adsorption in the gas phase was conducted to estimate the capacity of the sorbent trap. The Hg concentration was set using the standards for thermoelectric power plants and the cement industry (Granite et al., 2000). The inhalation flow rate and adsorption time were set as 0.4–1 lpm and 60 min, respectively (Gómez-Giménez et al., 2015). A Hg^0 calibration unit (Model 3310, Tekran Instruments Corp., Toronto, Canada) was used to generate a flue gas with a highly precise Hg^0 concentration. After passing through the reactor, the adsorption efficiency was analyzed using a continuous, real-time, on-line, gas-phase Hg^0 analyzer (VM-3000, Mercury Instruments, Karlsfeld, Germany). A cold vapor atomic absorption spectrometry (CVAAS) Hg analyzer (RA-915$^+$/RP-91, Lumex Ltd., St. Petersburg, Russia) was used to measure the Hg concentration on the AC in the sorbent trap. Fig. 1 shows the adsorption efficiency estimation and mimetic diagram.

3. Results and discussion

3.1. Characterization of the impregnated ACs

The prepared BAC samples were analyzed using Fourier transform-infrared spectroscopy (FT-IR; PerkinElmer Spectrum 100 Series) to ensure impregnation. Virgin BAC, BAC^{Cl}, and BAC^{Au} were analyzed. Under the same conditions, the peak changes were measured as a function of the Au content, for which the impregnated Au content varied from 5 to 10 wt%. The Au NPS peaks were observed at 1048-1203 cm^{-1} and 2910-3100 cm^{-1}.

No peak was observed for both virgin BAC and BAC^{Cl} in the relevant ranges, whereas BAC^{Au} produced peaks near 1100 and 2900 cm^{-1} (Fig. 2). There was no significant difference between the peaks as a function of the Au content.

X-ray diffraction (XRD; MiniFlex, Rigaku Co., Tokyo, Japan) analysis was used to determine the impregnation status of BAC impregnated with Cl and Au. Virgin BAC was used as a reference. In the case of Cl, unique peaks were observed at 23, 28, and 80 (2θ). In the case of Au, unique peaks were observed at 37, 44, and 69 (2θ). These results were because of a quality decision. Fig. 3 shows the results of the XRD measurements. Cl produced peaks at 23, 28 and