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Full Length Article

Kinetic studies of mercury adsorption in activated carbon modified by iodine steam vapor deposition method

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HIGHLIGHTS

- The iodine vapor deposition method was put forward to modify the raw activated carbon.
- AC modified by the iodine steam vapor deposition method has good mercury adsorption capacity.
- The pseudo-second model was the best fit to the actual mercury adsorption behavior onto AC-I_2 sorbent.
- A general dynamic equation was determined to predict mercury adsorption by AC-I_2 sorbent.

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ABSTRACT

The objective of this study was to develop a high efficiency activated carbon (AC) sorbent for mercury removal. The vapor deposition method was used to modify the raw AC. This method is relatively easy to carry out and uniformly modifies the AC. The results of this study indicate that AC modified by iodine steam vapor deposition has much better Hg capturing capacity than AC modified by bromide deposition under the same experimental conditions. London dispersion forces and exposure of the sorbent surfaces play important roles in elemental mercury (Hg^0) adsorption. Adsorption kinetic behavior was also studied under different experiment conditions. Results indicated that the pseudo-second model was the best fit to the actual mercury adsorption behavior onto AC-I_2 sorbent. The effect of adsorbent mass and gas flow rate on adsorption behavior were examined. Results indicated that increasing the sorbent mass led to an increase in Hg adsorption capacity, while increasing the gas flow rate resulted in a significant decrease in Hg adsorption capacity. Decreases in Hg adsorption capacity were likely due to a shorter contact time and lower partial pressure reducing the number of contact opportunities between the Hg atoms and the sorbent surface. Finally, a general dynamic equation was determined that can be used to help predict Hg adsorption curve of AC-I_2 sorbent without completing a real fixed-bed Hg adsorption experiment.

1. Introduction

Mercury is harmful to human health and the environment due to its toxicity and bioaccumulation in the food chain [1]. Coal-fired utility boilers consume large quantities of coal and are the largest anthropogenic source of atmospheric Hg, accounting for 30% of total anthropogenic Hg emissions [2]. The latest emission standard of air pollutants for thermal power plants was promulgated by the Chinese Ministry of Environmental Protection in 2011 (GB13223—2011); Hg emissions for coal-fired boilers should be less than $0.03\ mg\ m^{-3}$ in 2015, presenting new challenges for the coal-fired power plants to control Hg pollution. There are three main forms of Hg present in the flue gas: particulate-bound (Hg^p), oxidized (Hg^{2+}), and elemental mercury (Hg^0). Hg^p refers to the Hg adsorbed onto residential particulate (e.g. fly ash), it canbe captured by current air pollution control devices such as electrostatic precipitator (ESP) and fabric filter (FF). Hg^{2+} can be removed efficiently by wet desulfurization device since it is water-soluble [3,4]. Conversely, Hg^0 is most difficult to remove because of its high vapor pressure and low water solubility. Many researchers have determined that Hg^0 can be partly converted to Hg^{2+} by oxidizing species in the flue gas, mainly chlorine and oxygen [5,6]. If the chlorine content of the feed coal is high, the HCl concentration in the flue gas is also higher, increasing the extent of elemental mercury oxidization [7,8]. The feed coals in China, however, have a

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lower chlorine content (63–318 mg kg^{-1}) than the average value of US coals (628mg kg^{-1}) [9]. Therefore, using chlorine to convert Hg^0 to Hg^{2+} as a means of Hg capture and control is a less viable option for China.

Because Hg^0 is not soluble in water and lower chlorine content, many power plants in china will need separate Hg removal systems to meet the necessary emission limits. For such power plants, activated carbon injection is a reliable option. When activated carbon is injected into the flue gas upstream of the particle control equipment, the gas-phase Hg contacts the sorbent and attaches to its surface. Existing particle control equipment, either an electrostatic precipitator (ESP) or a fabric filter, collects the fly ash and sorbent with the Hg attached [10,11]. Raw, untreated activated carbon (RAC) has a very limited Hg adsorption capacity and therefore needs chemical modification. Impregnation of activated carbons using halides greatly increases Hg removal capacity. Eswaran and Stenger studied the effects of halogen acids such as HCl, HBr and HI on Hg^0 conversion in flue gas and determined that HBr and HI oxidized Hg^0 very effectively, while HCl was less effective [12,13]. In a similar study, De et al. reported that mercury removal efficiency increases in the following order: AC < Cl-impregnated AC < Br-impregnated AC < I-impregnated AC [14]. Sun et al. observed that brominated activated carbon was effective in removing Hg, with the adsorption capacity increasing 80-fold at a bromination loading of 0.33 wt.% [15]. Currently, the commercial activated carbon used in power plants is mostly modified by bromide. Although the cost of bromide modification activated carbon is much more cheaper, iodine modification is more effective, and the iodine vapor deposition method is more convenient for application in power plant.

Adsorption kinetic studies are useful for investigating adsorption mechanisms. Four widely used kinetic models are Pseudo-first-order model, Pseudo-second-order model, Intra-particle diffusion model and Elovich model. They have been widely applied in studies of heavy metal adsorptionfrom a liquid phase. Mohan et al. studied the kinetics of Hg adsorption from waste water using fertilizer waste activated carbon and found that the adsorption followed the film diffusion mechanism at low concentrations, and followed the particle diffusion mechanism at high concentrations [16]. 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, although literature related to the kinetics of gas phase adsorption on activated carbon is limited. Skodras et al. researched the adsorption kinetics of Hg^0 vapor on commercial activated carbon using the four kinetic models mentioned previously. He found that mass transfer limitation affected the mercury adsorption process and chemical adsorption rate was the controlling step [17].

The adsorption of Hg^0 on Br modified AC has been widely studied, but research into the process and mechanism of mercury adsorption on iodine modified AC are limited. Especially, the research related to the activated carbon modified in iodine steam vapor deposition method is less. There are significant differences between bromine and iodine in atom size and chemical properties and the theories applied to the bromide modified AC may not completely apply to the iodine modified AC. Therefore, further studies of Hg adsorption on iodine modified AC (AC-I_2) are still needed.

2. Experimental

2.1. Sorbent preparation

The RAC tested in this work was obtained from a commercial activated carbon by crushing and sieving, with a particle size range from 180 μm to 250 μm. The AC-$I_2$was prepared by adding 50 mg solid iodine in a stainless steel reaction kettle, then heated to 150 °C for 1 h to ensure all solid iodine sublimation, adding 10 g RAC sample to the reaction kettle, shaking in the oscillator and cooling at room temperature. In the process of cooling, activated carbon has a good contact with iodine vapor and adsorbs on the pore structure of RAC. Alternatively, as the temperature inside of the reaction kettle gradually decreases, the iodine vapor condenses on the RAC surface or on its pore structures.

2.2. Characterization

The structural properties of the AC samples were determined by nitrogen adsorption at −196 °C using a Quanta chrome autosorb iQ instrument. The density functional theory (DFT) model was used to explore the pore size distribution of the AC samples prepared at different conditions. The thermal stability of samples was measured by TA Instrument TG Q500. A sample size of 10 mg was used in these experiments. All samples were heated in N_2 for pyrolysis. The flow rate was 60 ml min^{-1} and the heating range was from 30 to 800 °C at 10 °C min^{-1}. For accuracy, samples were taken randomly and each experimental condition was carried out in triplicate. Calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) was used to verify the performance of the TG system. To determine the loading of halogen on samples, the EPA method 1311, Toxicity Characteristic Leaching Procedure (TCLP) was utilized. ADionex ICS-1100 Ion Chromatography (IC) instrument was used to quantify the halogen content in the solutions.

2.3. Kinetic sorption experiment

The Hg kinetic sorption experiment was carried out in a fixed-bed system. As shown in Fig. 1, the apparatus consists mainly of a fixed-bed adsorption reactor, elemental mercury (Hg^0) permeation source- PSA Cavkit, and a PSA Hg analyzer (Sir Galahad), which can measure the concentration of Hg^0 every 5 min. Teflon was used for all gas lines, joints, and valves to prevent Hg^0 adsorption by the system.

The Hg^0 permeation source is designed to generate and release a constant concentration of Hg^0 vapor at a selected temperature of 40 °C. Compressed air with a pressure of at least 40 psi was supplied as a carrier gas to transport Hg^0 vapor out of the permeation source. Two mass flow controllers were used in the system, one to regulate the air into the Hg permeation source (flow rates on the order of milliliter per minute) and a second to regulate a dilution gas (flow rates on the order of liters per minute). The total gas flow rate of the system is the sum of the inlet air for the permeation source and the dilution gas. In this work, the concentration of Hg was set and remained at 50 μg m^{-3} and three different gas flow rates including 6 L min^{-1}, 7 L min^{-1} and 8 L min^{-1} were selected to estimate the effect on Hg kinetic sorption parameters.

A fixed-bed sorption reactor was placed inside an oven, which can be accurately controlled within ±1 °C. The inside diameter of the reactor is 10 mm. Each experiment involved placing approximately 0.06, 0.08, 0.1 g of AC sample in the bottom of the fixed-bed reactor as the sorbent. Subsequently, silica cotton, known to be inert to Hg during the adsorption process, was added to keep the AC stationary during the experiment. The fixed-bed reactor temperature was initially set at 50 °C. The Hg^0 gas vapor was controlled by the PSA Cavkit and flowed into the fixed-bed reactor. The outlet flow of the reactor with variable Hg concentration was continuously monitored by the PSA system. Finally, the Hg removal efficiency (η) was calculated using the following equation.