



# Preparation and characterization of benzoic acid-modified activated carbon for removal of gaseous mercury chloride



Jinjing Luo<sup>\*</sup>, Jingjing Lu, Qiang Niu, Xiaobao Chen, Zhongye Wang, Jieru Zhang

College of the Environment & Ecology, Xiamen University, Xiamen, Fujian, PR China

## HIGHLIGHTS

- Activated carbon was modified with pre-heating treatment and benzoic acid impregnation.
- Gaseous HgCl<sub>2</sub> adsorption experiments on activated carbon were conducted.
- Experiments showed that carboxylic and carbonyl groups promoted HgCl<sub>2</sub> adsorption process.
- Carboxylic groups are believed to contribute the most to HgCl<sub>2</sub> capture.

## ARTICLE INFO

### Article history:

Received 28 April 2015

Received in revised form 20 July 2015

Accepted 3 August 2015

Available online 8 August 2015

### Keywords:

Activated carbon

Benzoic acid

Surface oxygen-containing functional groups

Mercury chloride adsorption

## ABSTRACT

This article investigates the properties of surface oxygen-containing functional groups (SOFG) on activated carbons, and their effects on removal of gaseous mercury chloride (HgCl<sub>2</sub>). For this purpose, the surface of a coal-based commercial activated carbon BPL was modified by heating in an inert atmosphere and then impregnated with benzoic acid solution. Afterwards, all carbonaceous samples were tested for their HgCl<sub>2</sub> adsorption capacities. Nitrogen (N<sub>2</sub>) adsorption, Fourier Transform Infrared Spectroscopy (FT-IR) and Boehm titration were applied to study the surface characteristics of carbon samples. It was found that after benzoic acid impregnation, the amounts of SOFG improved with the increasing of benzoic acid concentration, especially carboxylic and carbonyl groups. Adsorption experiments showed that higher HgCl<sub>2</sub> adsorption capacities were obtained with more carboxyl and carbonyl groups. And the largest capacity obtained in this study was 484.7 μg/g of carbon with carboxyl and carbonyl concentrations of 0.570 mmol/g and 0.706 mmol/g, respectively. This suggests that carboxylic and carbonyl groups play predominant roles in HgCl<sub>2</sub> removal. And carboxylic groups are believed to contribute more than that of carbonyl groups in HgCl<sub>2</sub> capture process.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Activated carbon is widely used for removal of pollutants from the environment due to its special porous structure and surface chemical properties [1,2]. It has been shown that the surface oxygen-containing functional groups (SOFG) on activated carbons are important factors influencing its adsorption performance [3], since the qualities and quantities of SOFG can affect the adsorption sites, hydrophilicity or hydrophobicity and the surface charge distribution on carbon surface [4–6], which can directly impact on the adsorption performance of target pollutant by activated carbon.

Waste incineration is one of the most important sources for global anthropogenic mercury emissions [7]. Due to the high concentration of hydrogen chloride (HCl) in waste incineration flue gas,

most of the mercury exists in the form of HgCl<sub>2</sub>, which corresponds to 70–80% of total mercury [8]. Activated carbon has gained global attention as one of the most promising adsorbents for mercury removal [9–11]. It is well known that mercury capture performance was greatly influenced by the chemical composition on the carbon surface, Saha et al. [12] studied the mercury capture efficiency by Brominated and Sulfur-treated activated carbon sorbents, and Rupp and Wilcox [13] investigated the complicated interaction between the Brominated activated carbons sorbents, Hg and combustion flue gas. It is also believed that SOFG play major roles in mercury capture by providing active sites for mercury bonding [14]. Recently, strong oxidants are generally chosen to introduce additional SOFG onto carbon surface to improve mercury capture efficiency. Li et al. [15] used HNO<sub>3</sub>-treated carbon sample to remove elemental mercury (Hg<sup>0</sup>), and Wu et al. [16] applied liquid-phase ozone (O<sub>3</sub>) oxidation to obtain SOFG on carbon surface. Other oxidants like sulfuric acid (H<sub>2</sub>SO<sub>4</sub>),

<sup>\*</sup> Corresponding author. Tel.: +86 0592 2188119; fax: +86 0592 2180655.

E-mail address: [luojj27@xmu.edu.cn](mailto:luojj27@xmu.edu.cn) (J. Luo).

hypochlorous acid (HClO) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and so on were also tested [2,17]. Although these modified activated carbons perform well in mercury removal, it is not clear which particular SOFG is participating in mercury adsorption process due to the multiple functional groups with high concentrations generated on those strong oxidants-treated carbon surfaces [15].

In recent year, extensive research efforts have been conducted to evaluate the impacts of carbon–oxygen surface complexes on  $\text{Hg}^0$  adsorption [18]. However, only a few studies have been done to understand the bonding mechanism between carbon surface and gaseous  $\text{HgCl}_2$  [19,20]. Therefore, this paper aims at identifying the functional groups responsible for  $\text{HgCl}_2$  removal on carbon surface. In this study, benzoic acid was chosen as modification agent, hoping that the weak oxidant could cause limited but noticeable changes in SOFG on the carbon surface, especially for carboxylic groups, thus it will be more convenient to study the effects of SOFG on  $\text{HgCl}_2$  adsorption. Nitrogen adsorption was conducted to characterize the pore structure of the samples, and the chemical characteristics of the carbon samples were determined by Fourier Transform-Infrared Spectroscopy (FT-IR) and Boehm titration methods [21].  $\text{HgCl}_2$  adsorption experiments were tested to assess the feasibility of the adsorbents. Adsorption mechanisms of  $\text{HgCl}_2$  removal by the adsorbent was also elaborated in this study.

## 2. Experimental

### 2.1. Sample preparation

Commercial coal-based granular activated carbon (BPL, Calgon Carbon Corporation, Tianjin, P.R. China) was used as as-received material in this study. The samples were thoroughly washed with deionized water to remove impurities and then dried at  $105^\circ\text{C}$  until reaching a constant weight. The dried samples were grinded into powder with the size of 100–200 mesh, heated in a quartz boat reactor under a  $\text{N}_2$  flow of 0.5 L/min and a heating rate of  $10^\circ\text{C}/\text{min}$ , to remove most SOFG and other surface functional groups present originally on the carbon surfaces. After cooling to ambient temperature, the obtained samples (designated as BPL-1000) were immersed into 200 mL benzoic acid solution, with concentration of 0.08, 0.16, 0.24 and 0.32 g/L. The mixtures were stirred continuously at  $25^\circ\text{C}$  for 24 h, and then separated through vacuum filtration. The filtered carbon was washed with deionized water until the pH of the filtrate was stable. The treated samples were marked as BPL-CX1-4 and stored in a drying chamber for future use.

### 2.2. Sample characterization

The surface area and pore parameter of activated carbon samples were analyzed by nitrogen adsorption at 77 K using surface area and porosimetry analyzer (ASAP2020, Micrometrics, USA) [22–24]. The results were obtained through adsorption isotherms of samples. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation, and the pore volume was measured by applying t-plot models.

FT-IR experiments on the carbon samples were carried out by a FTIR spectrometer (NEXUS 470, Thermo Nicolet, USA). About 1.5 mg of dry sample was mixed with 200.0 mg of KBr (Spectrography Purity), and the mixture was pressed into a pellet and then placed in the sample room for scanning. The spectra were obtained in wavenumber range of  $4000\text{--}400\text{ cm}^{-1}$  at a resolution of  $4\text{ cm}^{-1}$ .

Base-acid titration of the carbons was performed to measure the SOFG of carbon samples based on Boehm titration theory [21]. Based on this theory, about 1.0000 g of carbon sample was placed in a

conical flask containing a 60 mL solution (0.05 N) of: sodium bicarbonate ( $\text{NaHCO}_3$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium hydroxide ( $\text{NaOH}$ ), and sodium ethoxide ( $\text{NaOC}_2\text{H}_5$ ). The flask was sealed and stirred constantly at  $25^\circ\text{C}$  for 24 h, and then filtered. A total of 20 mL of each base filtrate was pipetted and titrated with HCl to neutralize the excessive base. The specific SOFG were measured from the base titration experiment based on the following theory:  $\text{NaHCO}_3$  neutralizes only carboxylic groups, while  $\text{Na}_2\text{CO}_3$  titrates both carboxylic and lactone groups,  $\text{NaOH}$  reacts with carboxylic, lactone and phenol groups, and  $\text{NaOC}_2\text{H}_5$  neutralizes carboxylic, lactone, phenol and carbonyl groups.

### 2.3. Mercury adsorption

Fig. 1 showed the experimental setup for  $\text{HgCl}_2$  adsorption system, which consists of a gas feeding system, a gaseous  $\text{HgCl}_2$  generating device, a fixed bed reactor and a gas purification device. An  $\text{HgCl}_2$  permeation tube (VICI Metronics, USA) was used as gaseous  $\text{HgCl}_2$  source. It was placed in a sealed U-shape quartz tube immersed in a temperature-controlled water bath, providing a constant supplier of  $\text{HgCl}_2$  in the system by adjusting the temperature of the water bath and the flowrate of the carrier gas. Nitrogen gas with a flow rate of 200 mL/min was used as a carrier gas. Total gas flow rate was controlled at 1.0 L/min through mass flow controllers (MFC). The concentration of  $\text{HgCl}_2$  was measured by Ontario Hydro Method (OHM) [25]. Initial  $\text{HgCl}_2$  concentration was  $425\text{ }\mu\text{g}/\text{m}^3$ . A mixture of 0.0030 g of carbon sample and 5.0000 g of quartz sand was packed into a fixed adsorption bed, which was placed in a temperature-controlled oven, and the adsorption temperature was maintained at  $140^\circ\text{C}$ . Mercury measurement instrument (MA-3000, Nippo Instrument Corporation, Japan) was applied to analyze mercury adsorption capacities.

## 3. Results and discussion

### 3.1. Sample characterizations

Table 1 showed the BET surface and pore parameters of samples with and without treatment. The test results illustrated that the

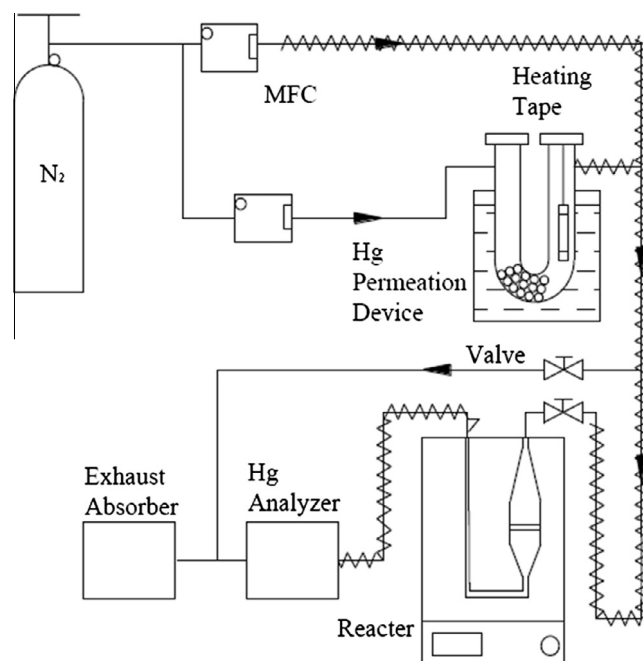


Fig. 1. Experimental setup for  $\text{HgCl}_2$  adsorption.

Download English Version:

<https://daneshyari.com/en/article/205566>

Download Persian Version:

<https://daneshyari.com/article/205566>

[Daneshyari.com](https://daneshyari.com)