Fuel 229 (2018) 60–67

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

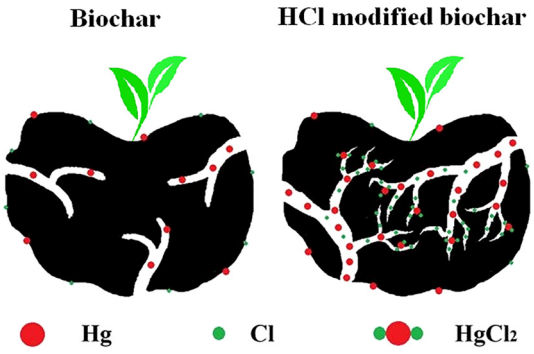
Full Length Article

Increasing the chlorine active sites in the micropores of biochar for improved mercury adsorption

Tao Wang[a], Jiawen Wu[a], Yongsheng Zhang[a,*], Jun Liu[a], Zifeng Sui[a], Huicong Zhang[a], Wei-Yin Chen[b], Pauline Norris[c], Wei-Ping Pan[a,c]

[a] Key Laboratory of Condition Monitoring and Control for Power Plant Equipment, Ministry of Education, North China Electric Power University, Beijing 102206, China
[b] Department of Chemical Engineering, University of Mississippi, 134 Anderson Hall, University, MS 38677, USA
[c] Institute for Combustion Science and Environmental Technology, Western Kentucky University, Bowling Green, KY 42101, USA

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Chlorine modification
Biochar
Mechanism
Elemental mercury
Flue gas

ABSTRACT

A series of biochars were prepared from rice(RI), tobacco(TO), corn(CO), wheat(WH), millet(MI), and black bean straw(BB). These biochars were used to study the mechanism of elemental mercury(Hg^0) adsorption by hydrochloric acid modified biochars. The biochars were modified by 1 M hydrochloric acid (HCl) and then used in a fixed-bed Hg^0 adsorption experiment. As would be expected, the results indicated that HCl modification increased the Hg^0 adsorption performance of the six biochars. After modification, the Hg^0 adsorption efficiency of tobacco biochar increased from 8.2% to 100.0%, and the average Hg^0 adsorption capacity of the biochars increased by 61 times. The acid modification dissolved the metal compounds in the biochar, reducing the metal content and increasing the average surface area of the biochar. The average surface area of the raw biochars increased from 29.9 to 110.1 m^2/g after HCl modification. The extra surface area was mostly created in the micropores, leading to a significant increase in the amount of micropores. These micropores effectively adsorbed the Cl atoms, which acted as active sites for Hg^0. In the adsorption process, Hg^0 diffused into the interior of modified biochars via mesopores, and finally the adsorbed Cl in the micropores reacted with Hg^0 to form $HgCl_2$.

1. Introduction

Mercury has received growing worldwide concern due to its toxicity. Mercury emission from coal combustion is one of the largest sources of mercury pollution. Coal consumption in China accounted for 50.6% of global mercury coal consumption in 2016. It is estimated that

* Corresponding author.
E-mail address: yszhang@ncepu.edu.cn (Y. Zhang).

https://doi.org/10.1016/j.fuel.2018.05.028
Received 6 March 2018; Received in revised form 4 May 2018; Accepted 6 May 2018
Available online 09 May 2018

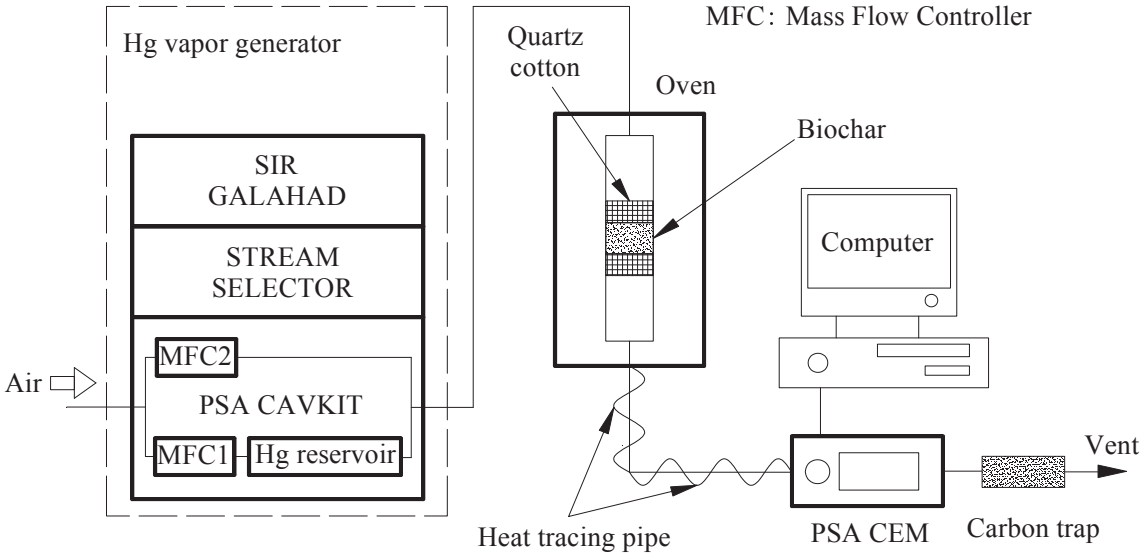


Fig. 1. Schematic diagram of Hg^0 adsorption.

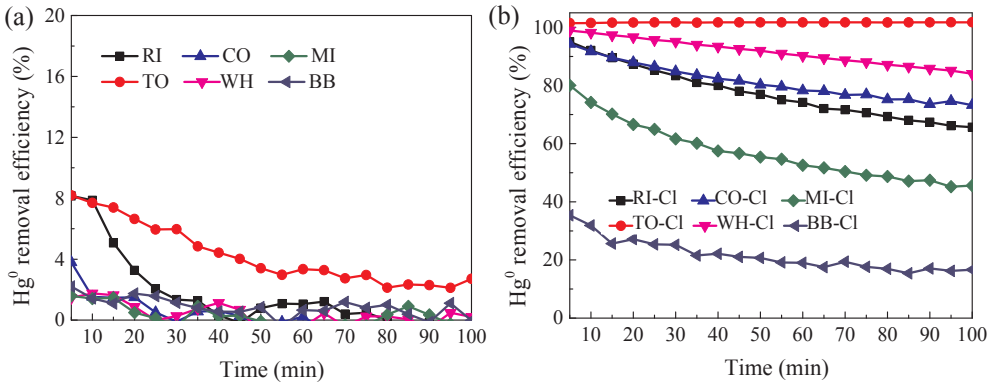


Fig. 2. Hg^0 removal efficiency of raw and modified biochars.

70% of the mercury pollution in China comes from coal combustion, which accounts for 25%–40% of global mercury emissions [1–4]. Hg^0 is more difficult to remove than oxidized or particle-bound mercury due to its low reactivity, low water solubility and high volatility. Activated carbon injection methods have been reported as the most promising technology for Hg^0 removal [5–7]. Activated carbon, injected into the flue gas before the particulate control devices, adsorbs the Hg^0 from the flue gas and is then captured by the particulate control devices. However, the high operational cost of activated carbon injection limits large-scale applications. Discussions regarding the development of low-cost adsorbents have dominated research in recent years.

Biochar pyrolyzed from agricultural biomass would be attractive as a low cost and abundant sorbent. Unfortunately, the Hg^0 adsorption capacity of unactivated biochars is at least 2–3 orders of magnitude lower than activated carbon [8]. Therefore, many physical and chemical activation techniques have been used to promote biochar adsorption capacity. Li et al. reported that the adsorption capacity of chemically modified biochar was 2–3 greater than biochar modified by physical techniques [9]. Chemical techniques mainly add active functional groups on the biochar by acid [10–13], alkali [14,15], metal [16–18], sulfur [19–23] and halogen [24–29] modification, which promotes the removal of elementary mercury. Hg^0 can react with Fe^{3+} to form oxidized mercury, resulting in an increase in Hg^0 removal efficiency from 40.0% to 99.9% after $FeCl_3$ modification [30]. Hg^0 removal efficiency increased by 32.1% after KOH modification [14] and Hg^0 adsorption capacity of NaOH modified coconut husk biochar increased by 31.0% [31]. In a study by Klasson et al., HCl modified biochar adsorbed over 95% of the Hg^0 from the flue gas [32]. In another study by Johari et al., the Hg^0 adsorption capacity of HCl modified biochar reached 6067 μg/g and the Hg^0 removal efficiency of HCl-impregnated biochar was 34 times greater than that of raw biochar [11]. Though previous studies have shown that HCl modification leads to an obvious increase in the Hg^0 adsorption capacity, mechanisms of Hg^0 adsorption on HCl modified biochar are not clear. Johari [11] reported that HCl modification enlarged the surface area, improving the physical adsorption of Hg^0. Klasson's work showed no direct correlation between Hg^0 adsorption capacity and surface area after HCl modification and indicated that Hg^0 was adsorbed via chemisorption [32]. While Shen indicated that HCl modification added the C—Cl group on the surface of biochar, which reacted with Hg^0 to form $HgCl_2$ [33].Clearly, more research is needed to determine the mechanism of Hg^0 adsorption on HCl modified biochar.

In this paper, rice, tobacco, corn, wheat, millet, and black bean straw were prepared in high purity nitrogen at 600 °C to produce biochars, which were then impregnated by 1 M HCl. The effect of HCl modification on Hg^0 adsorption by six biochars was studied. Biochar composition, Brunauer–Emmett–Teller (BET), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), inductively coupled plasma optical emission spectrometry (ICP-OES), temperature programmed desorption (TPD), and Ion chromatography were used to discuss the possible mechanisms of Hg^0 adsorption on HCl modified biochar.