



The mechanism of sulfur component in pyrolyzed char from waste tire on the elemental mercury removal



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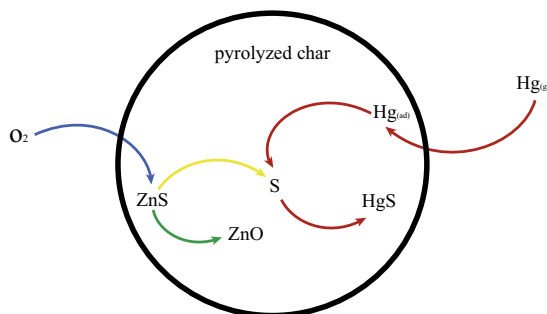
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HIGHLIGHTS

- The waste tire char pyrolyzed at 600 °C was demonstrated to be an innovative Hg⁰ adsorbent.
- Sulfide on the surface of the pyrolyzed tire chars was considered as a key factor in Hg⁰ removal.
- The Hg⁰ removal mechanism of pyrolyzed char was developed by XPS analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

A kind of cost-saving pyrolyzed char from waste tire was investigated in the capture of gas phase elemental mercury in presence of O₂. Various pyrolysis/testing temperatures and acid treatment methods were introduced to evaluate their effects on Hg⁰ removal by the char. Textural characteristics, elemental contents and surface functional groups analysis were also measured using nitrogen adsorption, scanning electron microscope (SEM), elemental analysis, Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and X-ray photoelectron spectroscopy (XPS), respectively. The waste tire char pyrolyzed at 600 °C was demonstrated to be a promising gas phase mercury adsorbent when compared with commercial activated carbon. Acid treatment decreased the Hg⁰ removal efficiency of the char because of the loss of sulfide from the surface. It indicated that the mechanism of Hg⁰ removal by the char was mainly chemisorption and the sulfide groups on the surface served as active sites for Hg⁰ removal. The main reaction route for the Hg⁰ removal was assumed that ZnS on the surface of the char reacted with O₂ to form S first, and then Hg⁰ reacted with S to form HgS.

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1. Introduction

More than 330 million waste tires are disposed each year in the world [1]. There are several ways to dispose this residue such as tire retreading, mechanical grinding, rubber reclaim, landfill,

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incineration and pyrolysis etc. Some of them were piled up illegally, and sometimes open burning is even directly applied to extract steel from tires, resulting in a serious problem of environmental. In contrast, tyre pyrolysis is carried out at medium temperature (350–600 °C) in an inert ambient, and the volatile (over 60%) from the pyrolysis is condensed to form oil while the un-condensation gas is always combusted directly to provide energy [2]. Pyrolysis of the waste tire may be optimized to produce some high value products, such as oil, char, gas and residual steel products.

Most of the sulfur in tyre remained in pyrolysis char, so the air pollution is lower for pyrolysis than the directly incineration [3–5]. Landfill is not a good method to treat waste tyre because the degradation of waste tyre is difficult. Pyrolysis can be considered as a more attractive method compared with landfill and incineration treatments because of a minor environmental impact. Although the pyrolyzed char may be further activated and used as activated carbon or carbon black, their qualities are limited because of their complicated compositions [6–8].

The emission of gas phase elemental mercury (Hg^0) from combusted flue gas has received attention in recent years, because Hg^0 is easy to pass through the post-combustion control units and cause a series of environmental pollution. Injecting activated carbon (AC) upstream into the dust-control unit is considered as one of effective technologies for mercury removal and is used in industry. Activated carbon modified with sulfur and halogens performs well in the adsorption of Hg^0 in flue gas [9–13]. However, the high price of activated carbon makes this technology economically unfavorable for the removal of Hg^0 from coal combustion system. In order to look for AC alternatives, various inexpensive carbonaceous absorbent materials were extensively studied, such as the carbonaceous absorbent materials from waste tires [14], mulberry twig [15], bamboo [16], and coconut shells [17]. Compared with other alternatives, pyrolyzed char derived from waste tiers had a relative poor pore properties yet had high content sulfur.

As a type of inexpensive carbon material, the pyrolyzed char from waste tire used instead of activated carbon to capture Hg^0 had been studied in some previous papers [14,18,19]. These studies focused either on the impregnation of sulfur or halogen, or on the pore property enhancement with the CO_2 or steam [9,10]. The waste tire usually contains high sulfur compound since sulfuration technology is widely applied to performance improvement in productive process. However, very little attention was drawn to the effect of intrinsic sulfur content of waste tire and its char on the mercury removal, although the impregnated sulfur had been proved to effectively increase the Hg^0 removal [9,12]. In addition, different sulfur forms in the char may affect the Hg^0 capture greatly, however there are very limited papers concerning this topic and the Hg^0 adsorption mechanism for the pyrolyzed char needs to develop further.

The aim of this study is to investigate a new and cost-saving pyrolyzed char from waste tire for the Hg^0 removal in combusted flue gas and the Hg^0 adsorption mechanism is also discussed at the end.

2. Materials and methods

2.1. Sample preparation

The bias tire is chosen in this study because bias tire is more possible to treat by pyrolysis due to its large amount, whereas the radial tire is recycling directly often. The proximate and ultimate analysis of bias tire was listed in Table S1. According to Table S1, the bias tire includes high volatile (62.2 wt.%) and fixed carbon (29.4 wt.%) and low ash (7.1 wt.%). The C and H are the main element component, and the N, S, O and Zn elements are relative low.

The waste tire was shredded and crushed to a size of 0.8–1.0 cm. 16.0 g of the tire was pyrolysed in a fixed bed quartz reactor (3.0 cm in diameter \times 16 cm in height). The reactor was under oxygen-free ambience with pure N_2 flow of 200 ml/min. The reactor was heated to a final pyrolysis temperature (500, 600 and 700 °C) at 20 °C/min and remained 60 min. The reactor was then cooled to room temperature. The derived chars (30–35 wt.% of

the waste tire) pyrolysed at 500, 600 and 700 °C were denoted as T5, T6 and T7, respectively.

The T6 char was mixed with H_2SO_4 (2.0 mol/L) and HNO_3 (4.0 mol/L) at the ratio of solution/solid at 10 ml/g. The mixtures were stirred for 24 h, then filtered and adequately washed with deionized water. After that, the chars were dried in an oven at 105 °C for 12 h. The chars treated by H_2SO_4 and HNO_3 solutions were denoted with T6S and T6N, respectively.

All the pyrolyzed chars were sieved to 40–60 mesh before the mercury adsorption.

2.2. Characterization techniques

The proximate analysis of the char was carried out according to Chinese National Standards (GB/T 212-2008). Specific surface area (S_{BET}), micropore (<2 nm) specific surface area ($S_{\text{BET}(\text{micro})}$), pore volume (V_{total}), micropore pore volume (V_{micro}) and average pore diameter (D_{avg}), were determined by N_2 adsorption at -196 °C on a ASAP 2020 automated gas adsorption system (Micromeritics, USA). The N_2 isotherms were employed to calculate the S_{BET} according to the Brunauer–Emmett–Teller (BET) model at a relative pressure ranging from 0.05 to 0.35, and the V_{total} at a relative pressure of 0.98. The $S_{\text{BET}(\text{micro})}$ and V_{micro} were estimated on the basis of t -plot method [20]. The D_{avg} was based on the differential pore volumes of Barrett–Joyner–Halenda (BJH) desorption branch. Scanning electron microscope SSX-550 (SHIMADZU CO. Ltd, Japan) was used to analyze the surface morphology of chars. Elementar EA3000 (LEEMAN, China) and Inductively Coupled Plasma-Optical Emission Spectrometer IRIS Advantage (Thermo, USA) were used to analyze the element content of the chars. The element valence state on the surface of the chars was measured by X-ray photoelectron spectroscopy (XPS) using Axis Ultra DLD (Kratos Analytical Ltd, Britain) with Mg X-ray source. The binding energies were calibrated by the C1s peak at 284.6 eV.

2.3. Experimental setup and method

The experimental setup used to evaluate the performance of Hg^0 adsorption by the chars was shown in Fig. S1 (in supporting information). In order to lessen the influence of acid gas, the simulation flue gas only contained N_2 and O_2 (6 vol.%). The simulated flue gas went through the mixer maintained at 120 °C. A N_2 flow (200 mL/min), serving as carrier gas, passed through an Hg^0 permeation tube placed in a U-type glass tube. The U-type glass tube was placed in a temperature-controlled thermostat water bath to maintain the Hg^0 concentration at 29.0 ± 1 $\mu\text{g}/\text{m}^3$, which was designed to simulate the typical concentration in the flue gas. The quartz fixed reactor, 10 mm inner diameter and 400 mm length, was put in a temperature-controlled electric furnace kept at reaction temperature. 0.1 g chars were placed in the reaction zone of the reactor and kept for over 4 h at the reaction temperature before the entrance of simulation flues. The Gas Hourly Space Velocities (GHSVs) is 25000 h^{-1} . The inlet and outlet gas line were all kept warm at 120 °C to avoid Hg^0 condensation. The total gas flow passing through the reactor was kept at 850 mL/min. Before conducting the adsorption testing, it was necessary to take enough time (over 4 h) to maintain a constant HgCl_2 concentration. Mercury concentration at the inlet and outlet of the reactor was measured continuously by using the H11-QM201H online cold vapor atomic mercury analyzer (Jiangsu Qinan instrument Co. China). The mercury concentration at inlet of the reactor was the initial concentration (C_{in}) and the mercury concentration at outlet of the reactor was outlet concentration (C_{out}). The mercury concentration was measured every 10 min by the mercury analyzer.

The adsorption activity of the sorbent was determined by the Hg^0 removal efficiency ($\eta\%$) according to Eq. (1).

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