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Elemental mercury removal by the modified bio-char from medicinal residues

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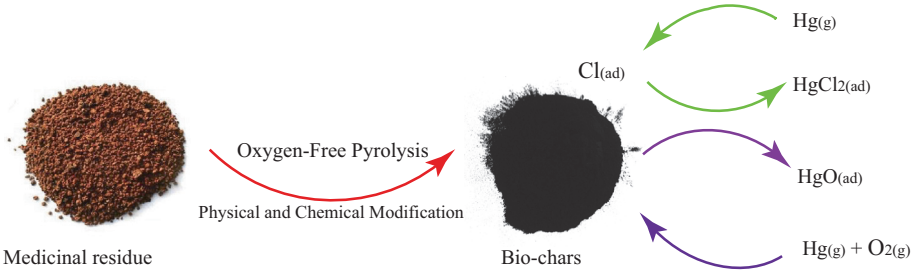
HIGHLIGHTS

- The bio-char from medicinal residue was used in Hg^0 removal from flue gas.
- Physical activation and chemical impregnation were used to modify the bio-chars.
- Hg^0 capture mechanism was investigated by the experimental and kinetic methods.
- The modified bio-chars are cheap and efficient in comparison with CACs based sorbents.

GRAPHICAL ABSTRACT



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ABSTRACT

The purpose of this paper is to investigate the bio-char from medicinal residue in gas phase elemental mercury removal. The bio-char was derived from pyrolysis char modified by both physical and chemical modification. Physical activation (microwave and steam) improves pore structure and introduces oxygenic functional groups. Chemical activation (chloride-impregnated) significantly promotes elemental mercury capture capacity. Mercury adsorption by NH_4Cl-impregnated bio-char was much better than those by $ZnCl_2$-impregnated and HCl-impregnated bio-chars. A combination kinetic model presents a strong correlation with the adsorption data for the chloride-impregnated bio-chars. The model results reveal the importance of mass transfer during the initial stages of element mercury adsorption for these materials. Furthermore the overall element mercury adsorption process is strongly governed by chemisorption for the chloride-impregnated bio-chars. The studies showed that the modified bio-chars derived from medicinal residue might be cost effective sorbents with high activity, which can be used as an alternate to commercial activated carbons (CACs) or modified CACs in the removal of element mercury.

1. Introduction

Medicinal residue is an industrial waste of the Chinese pharmaceutical process in the production of herb medicines. It is reported that the output of Chinese traditional medicine reached approximately 3.1 million tons in China in 2013. Medicinal residue accounted for about 70% of the raw feedstock, therefore medicinal residue yield was over 7.0 million tons from Chinese traditional medicine manufacture in 2013. Conventional treatment methods for these industrial wastes mainly included landfill or incineration [1,2]. However, these methods brought about new environmental problems, such as landfill leachate and polycyclic aromatic hydrocarbons (PAHs) emissions. The pyrolysis of the medicinal residue offered a new manner for waste treatment, which effectively

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reduced the emission of pollutants [3]. Bio-gas and bio-oil from waste pyrolysis could be combusted as a fuel whereas how effectively use bio-char needed to be considered, because the amount of bio-char always possessed 1/3 of pyrolysis products.

Coal combustion is considered as a dominating stationary source for atmospheric mercury emissions via human activities [4]. The elemental mercury (Hg^0) is receiving much attention due to its volatility, high toxicity, ability to bio-accumulate within the environment [5]. Injecting activated carbon (AC) has been commercially used to abate Hg^0 emissions from coal combustion system. However, the high cost for AC injection is beyond the economic tolerance of combustion system. Consequently, various inexpensive carbonaceous absorbent materials were extensively studied, such as the carbonaceous absorbent materials from mulberry twig [6], bamboo [4], coconut shells [7] and coke [8]. Some kinds of inexpensive inorganic materials were also considered as promising absorbents, for example bentonite [9], natural mineral sorbents [10] and fly ash [11]. The use of bio-char derived from medicinal residue as a sorbent for mercury removal will be very valuable. But until now, there has few papers reported about this topic. It is interesting to investigate the characteristics and feasibility of using the modified bio-chars from medicinal residue to remove gas elemental mercury.

The resource of Chinese traditional medicine contains three kinds: herbs, animals and minerals. The herbs make up the largest medicine proportion, accounting for over 50 percent. In this paper, the medicinal residue came from a pharmaceutical factory, which adopts the herbs as raw materials. Activation by steam or CO_2 at high temperatures (>800 °C) is a common method for AC preparation. In this study, activation will be performed by use of microwave as auxiliary heater in order to save energy. The halogens (Cl, Br and I) are regarded as effective reagents for Hg^0 adsorption by the modified AC or bio-char [12]. In the process of halogens impregnation, the halogens could react with the carbon and form many active groups. These groups can offer more adsorption site for the Hg^0 and produce oxidized mercury, like Hg_2X_2 and HgX_2 (X represents halogens). The modification by Br/I has been demonstrated to be a marked improvement in Hg^0 removal in comparison to that by Cl [13]. However, chlorine is more cost effective and chemically stable, which makes it an ideal reagent for industrial applications [14].

A number of kinetics models are available for the investigation of adsorption. Some of them focus on the process of mass transport, such as pseudo-first order and intraparticle diffusion models. Others concentrate on the reaction on the surface of sorbent and consider the chemisorption as the controlling step at adsorption process, such as pseudo-second order and Elovich models [15,16]. It is interesting to investigate the characteristics of mercury adsorption on the surfaces of biochar from medicinal residue. However, there are few available literatures focusing on the adsorption kinetics of gas phase Hg^0 on the biochar from medicinal residue.

In this study, a series of chloride based agents (HCl, $ZnCl_2$ and NH_4Cl) are adopted to chemically modify the bio-chars derived from medicinal residue. The main purpose of this study is to investigate the potential feasibility of bio-char from medicinal residues by the combination of physical and chemical activation as an alternate to AC or modified AC in the removal of Hg^0 from flue gas.

2. Materials and methods

2.1. Characteristics of medicinal residues

The elemental analysis of the raw medicinal residues was measured by Elementar Vario EL CUBE (German). The proximate analysis of the raw medicinal residues was determined according to Chinese National Standards (GB/T 212-2008). The ash analysis (from raw medicinal residues) was measured by an energy dispersive X-ray spectrometer (EDX, Bruker AXS Microanalysis GmbH Berlin, German). The measuring accuracy of X-ray spectrometer is 0.1%.

2.2. Sample preparation

2.2.1. Biomass char

Raw medicinal residues were from a Chinese herb pharmaceutical factory (Tianjin Pharmaceutical Factory of Traditional Chinese Medicine, China). The main ingredients in raw medicinal residues contained *Folium eriobotryae*, liquorice, *Platycodon grandiflorum*, *Rhizoma typhonii flagelliformis*, menthol, fluorite fluoritum, furnace soil, etc. The raw medicinal residues were ground into the size of 5–18 mesh. The raw residues were pyrolysed in a fixed bed reactor (160 mm in length and 30 mm in inner diameter), under a N_2 atmosphere (30 mL/min). The reactor was heated at 20 °C/min to a final temperature of 600 °C and kept for a residence time of 60 min. The final temperature was selected because 600 °C was the optimal temperature among 500, 600 and 700 °C when the mercury removal capacity was considered (in Fig. S.1 in supplementary data). The reactor was then cooled to room temperature under a N_2 atmosphere. The derived bio-char by pyrolysis process is denoted as S6.

2.2.2. Physical activation

2.0 g of the sample (S6) was placed in a quartz tube reactor (5 × 10 cm) under a N_2 atmosphere (100 ml/min) and the reactor was placed in a microwave heated oven (950 W and 2.45 GHz frequency). Deionized water (2.0 mL/h) was injected into the reactor by a peristaltic pump to form steam. The activation time for the sample was 4 h. The temperature in the quartz tube reactor might be 400–700 °C. The product from the physical activation (with microwave and steam) is denoted as S6 W.

2.2.3. Chemical activation

The pyrolysed (S6) and physically activated (S6W) bio-chars were impregnated with various solution volumes of HCl, $ZnCl_2$ and NH_4Cl at a concentration (1 mol/L for Cl^-) in proportion to a 5 wt% loading of HCl, $ZnCl_2$ and NH_4Cl (based on S6 or S6W). These mixtures were stirred for 12 h, and dried using a water bath for 4 h at 80 °C. The samples were dried for a further 12 h at 90 °C at the end. The samples were then sieved to a particle size range of 60–80 mesh prior to the Hg^0 adsorption experiments. The final products prepared from the pyrolyzed bio-chars (S6) were denoted as S6H5, S6Z5 and S6N5, respectively. The final products prepared from the chemically activated bio-chars (S6W) were denoted as S6WH5, S6WZ5 and S6WN5, respectively.

2.3. Sample characterization methods

The specific surface area, pore volume and pore size distribution of the samples were determined by N_2 adsorption at −196 °C on a NOVA 2000 automated gas adsorption system (Quantachrome Instruments, USA). The total surface area and pore volume were evaluated by the Brunauer–Emmett–Teller (BET) method. The pore size distribution was calculated by the Barrett–Joiner–Halenda (BJH) method using the adsorption isotherm data. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet Magna-560 infrared spectrometer (U.S. Bio-rad co.) over a range of 4000–400 cm^{-1}. The mercury element on the surface of adsorbents was analyzed by photoelectron spectroscopy (XPS) using X-ray photoelectron spectrometer of Axis Ultra DLD (Kratos