



Adsorption of vapor-phase elemental mercury (Hg^0) and mercury chloride (HgCl_2) with innovative composite activated carbons impregnated with Na_2S and S^0 in different sequences

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HIGHLIGHTS

- We successfully develop an innovative composite $\text{Na}_2\text{S} + \text{S}^0$ PACs.
- The adsorptive capacity of Hg^0 and HgCl_2 was much higher than previous studies.
- The removal of Hg^0 was higher than HgCl_2 .

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ABSTRACT

As powdered activated carbon (PAC) is being widely used for mercury adsorption, its efficiency can be enhanced by sulfur impregnation. In this study, innovative composite PACs impregnated with two sulfur species, vapor-phase elemental sulfur (S^0) and aqueous-phase sodium sulfide (Na_2S), in different sequences were developed for investigating the removal of gaseous elemental mercury (Hg^0) or mercury chloride (HgCl_2) with respect to the adsorptive capacities and adsorption rates at different influent Hg^0 or HgCl_2 concentrations and different adsorption temperatures. The effects of sulfur impregnation on the physicochemical characteristics of the PACs, including specific surface area, volumes of various pore sizes, and sulfur content, were also examined. In the results, the PACs impregnated with aqueous Na_2S , followed by the subsequent gaseous Hg^0 impregnation exhibited higher adsorptive capacities of both mercury species. At elevated adsorption temperatures (200 and 300 °C), the adsorption of Hg^0 is more effective onto the surface of the composite sulfur-impregnated PACs, whereas the composite PACs provided elevated capacities for HgCl_2 at a lower adsorption temperature (150 °C), suggesting possible variation of mercury control strategies under different circumstances. These findings provide insight into the application of this innovative composite PACs for the removal of gaseous Hg^0 or HgCl_2 . Higher adsorptive capacities of Hg^0 or HgCl_2 compared to those of previous studies were achieved by using the innovative composite sulfur-impregnated activated carbons.

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1. Introduction

The impacts to the environment and public health resulted by the occurrence of various anthropogenic contaminants, notably those containing mercury, have been the issues of high importance to ensure the environmental sustainability. Given the lowest boiling point among metallic elements, Hg is a volatile metal and commonly exists in the gas phase such as flue gases from combustion sources, producing threats to the receiving environment and public health by potentially less restricted gas-phase transport

and transfer. Therefore, mercury-containing compounds in the atmosphere are recognized as hazardous air pollutants (HAPs) that present high risks to the environment and human health, and are currently regulated by the Environmental Protection Agency (USEPA) and the United Nations Environment Programme (UNEP) [1]. Mercury is typically present in the environment in three forms including elemental mercury (Hg^0), mercury ion (Hg^{2+}), and gaseous mercury. Amongst these, Hg^0 and its derivatives have raised additional international concerns given their characteristics of strong toxicity, long-range transport potential due to their persistence, and bioaccumulation in various biotas.

The elemental Hg and the oxidized Hg approximately account for 50% of total Hg in the flue gas emitted from coal-fired power

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plants respectively (5:5), whereas the molar ratio of the oxidized Hg to the elemental Hg ($\text{HgCl}_2/\text{Hg}^0$) in the flue gas emitted from the MSWIs is about 6:4. In comparison to other heavy metals, mercury has unique physicochemical characteristics with low melting point of -39°C , low boiling point of 356°C , high vapor pressure of 0.246 Pa at 25°C , and low water solubility of $6.0 \times 10^{-5}\text{ g/L H}_2\text{O}$ at 20°C [1,2].

Combustion is one of the major sources emitting mercury into the environment [3]. Mercury is emitted mainly in the form of Hg^0 during the combustion processes at high temperatures (up to 1427°C), followed by a homogeneous oxidation forming HgCl_2 during post combustion ranging from 477°C to 627°C . As the temperature of stack gas drops to $125\text{--}325^\circ\text{C}$, the oxidized Hg species (e.g. HgCl_2 , HgO , and HgSO_4) are formed by heterogenous catalytic oxidation. Therefore, Hg mostly reacts with Cl_2 , HCl , and O_2 in the stack gas, and less reacts with other species (e.g. NH_3 , N_2O and H_2S) [4–6]. It is worth noting that HgO can react with H_2SO_4 and SO_2 to form HgSO_4 and Hg^0 at high and low flue gas temperatures (e.g. 300°C and 40°C), respectively, interfering the removal of Hg^0 by many mercury treatment technologies [7].

Activated carbon (AC) is one of the commonly available control technologies for mercury removal [7]. Given the economic concern due to the price and potentially large usage needed for mercury treatment, the production of activated carbons from the pyrolysis of waste tires has been considered a feasible technology [8–12], as the process generating approximately 32–42% of carbon blacks associated with 35–45% of pyrolyzed oil and 5–10% of combustible gasses [13,14]. The thermogravimetric analysis (TGA) has been widely used in the early studies to investigate the characteristics of this production process with respect to the weight variations of PACs at different temperatures, the pyrolysis rate of waste tires, and the adsorption rates of VOCs onto the surfaces of the PACs [15]. One another advantage of using the TGA is its capability to measure the weights of the PACs and temperature variations of the differential thermal gravimetry (DTG) in the meantime as the PACs are produced at varying heating rates. In this study, the PACs used were developed from the pyrolysis of waste tires, as the TGA being employed as the major technique for analysis.

Volatile organic compounds (VOCs) are a group of chemicals commonly treated through physical adsorption onto the surfaces of activated carbons [16]. However, for the mercury-containing compounds in the atmosphere such as HgCl_2 , the activated carbons can be impregnated with sulfur to enhance the mercury removal by chemisorption at adsorption temperatures higher than 150°C [17]. The increasing adsorptive capacity of the sulfurized PACs to adsorb HgCl_2 at temperatures higher than 150°C possibly resulted by a shift of the adsorption mechanism from physical adsorption to chemisorptions [18]. Graydon et al. found that the impregnation of PACs with gas-phase SO_2 enhanced the removal efficiency of Hg^0 at high temperatures [19]. With additional sulfur additives (e.g. elemental sulfur and sodium sulfide) being impregnated to PACs, the adsorptive capacities of the sulfurized PACs for Hg^0 were further enhanced [20,21], attributed to more sulfur-bonding activated sites with strong mercury bonding potential being formed in the inner pores of the PACs [17]. As demonstrated previously, the adsorptive capacity of the impregnated PACs for the mercury-containing compounds such as HgCl_2 was increased with the sulfur content and specific surface area of the PACs, the influent mercury concentration, and the adsorption temperature [22]. The effect of multiple impregnation on the adsorption of mercury-containing compounds onto the impregnated PACs has also been investigated. An adsorptive capacity up to $5,236\text{ }\mu\text{g-HgCl}_2/\text{g-C}$, which is approximately 2–3 times higher than the adsorptive capacities of those impregnated with single Na_2S or S^0 , respectively, is observed on the composite PACs impregnated with aqueous Na_2S solution followed by vapor-phase S^0 gas [22].

According to previous studies, the adsorptive capacity of activated carbons for mercury pollutants (i.e. Hg^0 and HgCl_2) decreases as the temperature increases, the adsorptive characteristics of activated carbon surface can be changed by mixing the activated carbon adsorbent with other chemical substances, and thus its adsorptive capacities for specific pollutants can be further enhanced. Previous studies reported that the Na_2S impregnated activated carbons can be used to remove Hg^0 and HgCl_2 vapors emitted from the coal-fired power plants and MSWIs [20,21,23].

As suggested in the previous studies, the adsorptive capacity of the PACs was significantly enhanced by sulfur impregnation [20,21,23]. However, the detailed information regarding the influences of different forms of sulfur and different impregnation sequences on the adsorption of mercury-containing compounds onto the impregnated PACs is rather limited. The objective of this study is therefore to investigate the adsorptive capacities of the PACs impregnated with S^0 and Na_2S in different sequences. Two forms of mercury pollutants, Hg^0 and HgCl_2 , commonly observed in the flue gases were the pollutants of primary interest in this study. In addition to the adsorptive capacities, the adsorption rates and possible mechanisms that determine the adsorption of Hg^0 and/or HgCl_2 onto the sulfur-impregnated PACs were discussed by using a TGA with respect to the effects of adsorption temperature and influent mercury concentration. The effect of sulfur impregnation on the physicochemical characteristics of the PACs including their specific surface area, volumes of various pore sizes, and sulfur content were also examined.

2. Materials and methods

2.1. Preparation of various composite sulfur-impregnated PACs

In this study, the PACs used for sulfur impregnation to improve the associated mercury adsorptive capacity were produced from the pyrolysis and activation of waste tires. The waste tires were initially shredded into $\sim 1\text{ cm}$ scraps and then rinsed with water before undergoing pyrolysis and activation processes. The scrapped tires of 20 g were pyrolyzed and activated to produce activated carbons in a ceramic crucible placed at the center of a tubular oven in the absence of O_2 . Pyrolysis and activation of waste tires were performed at 500°C and 900°C , respectively, by using a water feed rate of $1.0\text{ mg H}_2\text{O}/\text{g-c-s}$ [12].

The effects of sulfur impregnation on mercury adsorption onto the sulfurized PACs were studied given different operating parameters, including the forms of mercury to be treated (e.g., Hg^0 or HgCl_2), the forms of sulfur used for impregnation (e.g. S^0 or Na_2S), and the co-impregnation with both S^0 and Na_2S), the sequences of sulfur impregnation (e.g., gaseous S^0 impregnation followed by aqueous Na_2S impregnation, or aqueous Na_2S impregnation followed by gaseous S^0 impregnation, denoted as $\text{S}^0 + \text{Na}_2\text{S-PACs}$ and $\text{Na}_2\text{S} + \text{S}^0\text{-PACs}$, respectively), and the adsorption temperature. The specific surface areas (SSAs) and pore size distributions of the PACs as well as their sulfur contents before and after impregnation were also analyzed to understand the influences of different sulfur impregnation approaches on the physicochemical characteristics of the PACs.

To impregnate Na_2S on the PACs, Na_2S in solid state (SHIMAKYU'S PURE CHEMICALS, sodium sulfide with purity of 60%) was dissolved in deionized (D.I.) water to prepare 3% w/w aqueous Na_2S solution. Approximately 1.0 g of the raw PACs were rinsed and impregnated with 100 mL of the prepared Na_2S solution, and were oven-dried at 105°C for 24 h [17]. For S^0 impregnation, a mixture of 0.5 g raw PACs with 1.5 g S^0 in solid state (SHIMAKYU'S PURE CHEMICALS, elemental sulfur with purity of 99%) was heated at 400°C for 3 h to impregnate the PACs with the vaporized S^0 in

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