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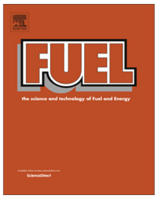

Mercury removal and synergistic capture of SO_2/NO by ammonium halides modified rice husk char

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HIGHLIGHTS

- Renewable biomass waste was recycled to prepare a low-cost and efficient sorbent.
- Hg^0 removal efficiency increased as pH of the halide solutions decreased.
- SO_2 and NO could be synergistically removed by this Hg^0 removal enhanced sorbent.
- This biomass sorbent had comparable performance to commercial activated carbon.

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ABSTRACT

Rice husk, a common agricultural waste and renewable biomass, was pyrolyzed and then impregnated with NH_4Cl and NH_4Br to develop an efficient sorbent for gaseous mercury removal from flue gas. The sorbents' performance was first investigated in a fixed-bed system with N_2 atmosphere at 150 °C and then in an entrained-flow system with real coal-fired flue gas at 150 °C. For comparison, a commercial coal-based activated carbon (CAC) treated with the same impregnation method was also studied. In the N_2 atmosphere, the mercury removal performance of rice husk char (RHC) was significantly enhanced after modification with ammonium halides, which are neither strong oxidants nor strong catalysts. The comparison of the RHC modified with HBr, NH_4Br, $CaBr_2$, $(NH_4)_2SO_4$ and NH_4OH with the same amount of bromine or ammonia confirmed the pivotal role of halogen in mercury removal. Although ammonia was proven to have no beneficial impact, the mercury removal capacity varied as the cation changed and increased as the pH of the halide impregnation solutions decreased. When tested in real coal-fired flue gas with a high concentration of SO_2 (1177 ppmv) and NO (254 ppmv), the ammonium bromide impregnated RHC sorbent which had an excellent mercury removal performance in the fixed-bed still reached about 80% efficiency for gaseous mercury removal. Furthermore, a synergistic effect on SO_2/NO removal was observed for both ammonium halides modified RHC and CAC sorbents injected into the real coal-fired flue gas; the synergistic effect might be due to the oxidation effect of O_2 and H_2O in the flue gas and the catalytic effect of the carbonaceous sorbent. Most micropore structure of the RHC was maintained after ammonium halides impregnation; however, the physisorption energy decreased in various degrees. Overall, in spite that the BET surface area and micropore volume of the RHC sorbent were smaller than the CAC, the RHC sorbent still reached a comparable level of multipollutants capture.

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1. Introduction

Mercury has been brought into global focus due to its continuing and serious damages to both the environment and human health [1]. The risk of exposure to this toxin has significantly increased by industrial activities in the past few decades, and coal burning remains one of the major anthropogenic sources of mercury emissions to the atmosphere [2]. In 2011, the U.S. EPA issued Mercury and Air Toxics Standards (MATS) to reduce mercury pollution from electric utilities [3]. The mercury emission limit of power plants in China was also set at 0.03 mg/N m^3 in 2011 [4], and a more stringent limit of 0.003 mg/N m^3 is expected by 2020 [5].

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Although existing air pollution control devices (APCDs) have good performance on total mercury removal and mercury concentration in flue gas is low with the most common APCDs combination (SCR + ESP + WFGD) [6–8], a significant fraction of mercury is transferred to the fly ash, effluent and gypsum, inevitably causing difficulty in centralized recycle and processing. Activated carbon injection (ACI) has drawn most attention due to its capability in removing mercury effectively and has been tested in various pilot-scale and full-scale facilities [9–12]. ACI's success has led to many efforts into exploring alternative materials with a lower cost and more efficient modification methods for its further industrial application.

As a renewable resource, biomass has advantages of being abundant, sustainable and economic. After pyrolysis under appropriate conditions, with devolatilization and reconstruction of carbohydrate polymers, the produced solid biomass char has a loosely developed physical structure and highly active functional groups on the surface [13,14]. Hence, biomass char has a capacity for physisorption and chemisorption, making it a potential candidate to replace activated carbon. Various biomass wastes, like bamboo and almond shells, have been converted to biomass char, and their capacity for mercury removal has been investigated in bench-scale fixed-bed facilities [15–17]. However, there have been no studies regarding mercury removal by biomass char injected into actual coal fired flue gas. Activation is a common method to further develop biomass char's porous structure and surface reactivity [18–20], yet the additional energy consumption reduces biomass char's economic advantage as compared with commercial activated carbon. Meanwhile, most biomass chars or biomass derived activated carbon without chemical modification have shown limited elemental mercury (Hg^0) removal capacity [21,22]. Hence, whether activation treatment of biomass char for mercury removal is necessary is unclear.

Halogen has been widely recognized to play a beneficial role in oxidizing and adsorbing Hg^0 [23,24]. Liu et al. [25] found that gaseous Br_2 was able to oxidize Hg^0 due to their large diffuse electron clouds and high polarity, and the unburned carbon components in fly ash further promoted the oxidizing ability [26]. Bisson et al. [27] deduced that $CaBr_2$ with excellent thermal stability might be generated during the activated carbon/biomass ash bromination procedure with liquid bromine, resulting in the extension of optimal adsorption temperature (from room temperature to 390 °C). Impregnation with metal halides, such as $CuCl_2$ and $ZnCl_2$, has an excellent effect on promoting Hg^0 removal by activated carbon as well [28,29]. Lee et al. [30] pointed out that $CuCl_2$ impregnated activated carbon not only adsorbed but also oxidized Hg^0 with a higher oxidation potential than commercial brominated activated carbon. The adsorption and oxidation active sites were different on sorbent surface. Li et al. [31] further reported that Hg^0 was oxidized by consuming Cl from $CuCl_2$ doped on α-Al_2O_3 in the absence of HCl and O_2. Some other metal halides, like $CoCl_2$ and $MnCl_2$, generate active halogen elements and transition metal oxides with high catalytic activity during pyrogenation, which may also accelerate Hg^0 oxidation and halogenation [32]. Different from the above mentioned materials, ammonium halides are neither strong oxidants nor strong catalysts. Yet, decomposition of ammonium halides in flue may also produce halogens that can oxidize mercury, although studies about sorbents modified by ammonium halides are essentially non-existing.

Besides mercury, flue gas from coal-fired power plants also contains SO_2 and NO_x. There is a tendency to develop an integrated technology for multi-pollutants control with high efficiency [33]. In the applications to remove SO_2 and NO_x from flue gas, activated carbon shows not only good adsorption performance but also a high catalytic activity for oxidation of SO_2 and reduction of NO_x [34]. It was reported that the SO_2 removal ability of activated carbon could be significantly improved after thermal treatment with ammonia [35–37], due to the introduction of nitrogen atoms and then the increase of surface basicity [34]. On the part of NO_x, Tsuji and Shiraishi [38] reported that the denitration reaction could occur with the catalysis of carbon on its own at temperatures below 473 K, but adsorption rather than catalytic reaction might be the main mechanism at lower temperatures from 373 K to 423 K [34].

In view of the above, treating biomass with ammonium halides may provide a potential solution conductive to both mercury capture as well as the synergistic removal of SO_2/NO. In this study, a biomass char sorbent for efficient and low-cost mercury capture was developed. Its performance in mercury uptake, as well as the co-benefits of SO_2 and NO removal, were investigated in both an inert atmosphere (fixed-bed system) and a coal-fired flue gas atmosphere (entrained-flow system). Its porous structure and surface chemical properties were characterized. For comparison, a commercial coal-based activated carbon (CAC) using the same impregnation method was also studied.

2. Material and methods

2.1. Sorbents preparation

Rice husk (RH) collected from the northern district of Jiangsu province, China, was dried, milled and sieved to retain the particles within 0.15–0.20 mm in diameter. These raw RH particles were pyrolyzed at 600 °C for 10 min in nitrogen. The produced rice husk char (RHC) was treated with 1% (w/v), 2% (w/v) NH_4Cl or NH_4Br solutions for 12 h with a RHC impregnation solution loading of 0.05 g/mL. After impregnation, the materials were filtered and dried at 45 °C in an oven overnight and cooled down to room temperature in a desiccator. These modified sorbents were labeled as RCl1, RCl2, RBr1 and RBr2, where the number represented the concentration of modifying solutions. For comparison, the indigenous commercial CAC (75–80 μm) was impregnated following the same procedure. Additionally, to identify the effect of sorbent impregnation on mercury uptake enhancement, modification with a series of bromides and ammoniums solutions, i.e. HBr, $CaBr_2$, NH_4Br, $(NH_4)_2SO_4$, NH_4OH at the same molarity of bromine or ammonium ($Br/NH_3 \sim 0.204$ mol/L, to be equivalent to 2% w/v) was conducted. Finer sorbent particles were needed during the mercury removal tests in the entrained-flow reactor. Hence, both RHC and CAC were milled and sieved into a size range of 13–25 μm before 1% (w/v) NH_4Br solution impregnation.

2.2. Sorbents characterization

The porous structure properties of the sorbent samples were characterized by N_2 adsorption/desorption at 77 K using an automatic specific surface area and pore size distribution instrument (BELSORP-mini II, BEL Japan Inc., Japan). Samples were pretreated at 200 °C for 12 h before adsorption measurement. The specific surface area and pore volume were determined based on Bru nauer–Emmett–Teller (BET) isotherm equation [39]. The mircopore surface area and volume were calculated using the *t* method [40]. The surface morphology and elemental information of the samples were analyzed by field emission scanning electron microscopy equipped with energy dispersive X-ray spectrometer (SEM–EDX, Sirion 200/Gensis 60S, FEI, Netherlands).

2.3. Fixed-bed system

Fig. 1 illustrates the fixed-bed reactor system designed and constructed to investigate the mercury and SO_2/NO removal performance. The system was composed of a simulated Hg^0 vapor

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