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Full Length Article

# Effect of characteristics of KI-impregnated activated carbon and flue gas components on $Hg^0$ removal

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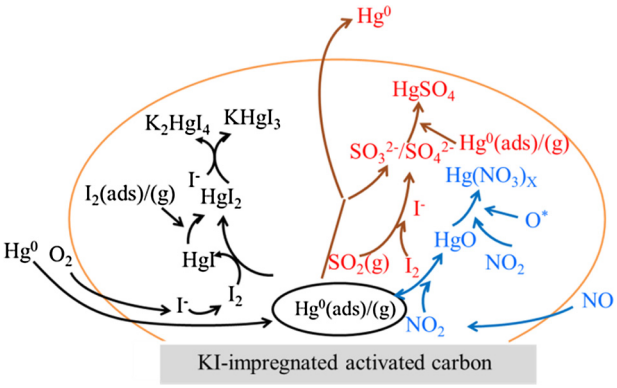
## HIGHLIGHTS

- The relationship between the KI-AC characteristics and $Hg^0$ removal was established.
- The mechanism of $Hg^0$ adsorption under various flue gas components was discussed.
- The binding abilities of mercury and different groups generated over the KI-AC were compared.

## GRAPHICAL ABSTRACT

Proposed adsorption mechanism for $Hg^0$ under the simulated flue gas over the 1% KI-AC.

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## ABSTRACT

The KI-impregnated activated carbon (KI-AC) was synthesized to investigate its capacity for elemental mercury ($Hg^0$) removal under the simulated flue gas. The $Hg^0$ removal performance is significantly promoted by KI loading. The effect of reaction temperature and activated carbon porosity on $Hg^0$ removal, and calculation on desorption activation energy of adsorbed mercury species were employed to identify the relationships between the physicochemical characteristics of the KI-AC and $Hg^0$ removal capacity. Raising the reaction temperature weakens the function of physisorption in the process of $Hg^0$ removal. The Brunauer-Emmett-Teller (BET) surface area and desorption activation energy of the adsorbed mercury species analyses indicate that the $Hg^0$ removal occurs through a combination of physisorption and chemisorption, and the chemisorption dominates the reaction. In addition, the influences of flue gas components on $Hg^0$ removal over KI-AC were evaluated, and the adsorption mechanisms were proposed. Oxidation of $I^-$ ion by the presence of $O_2$ is the substantial reason that facilitates the $Hg^0$ removal. The $Hg^0$ removal performance is promoted by the generation of $SO_3^{2-}/SO_4^{2-}$ and slightly frustrated by the competitive adsorption as well as consumption of $I_2$ molecules. Higher concentration of NO inhibits the generation of HgO products. However, the KI-AC sample remains highly active toward $Hg^0$ removal in the presence of NO because of the reaction with active N-containing groups. Additionally, the affinity capacities between $Hg^0$ and the various groups generated on the KI-AC follow the sequence: N → S-containing groups.



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## 1. Introduction

Over the decades, the great deal of the coal demand in China has caused a variety of environmentally adverse effects [1,2]. Control of mercury emissions is extremely pressing with increasingly stringent standard of power plants. Therefore, as the largest consumer of coal, China has an obligation to cut down the mercury emissions originated from coal combustion of power plants.

The mercury removal capacity substantially lies on its existing forms in the flue gas. Typically, the mercury derived from coal-fired flue gas occurs cardinally as gaseous oxidized mercury ($Hg^{2+}$), particulate-bound mercury ($Hg^{P}$) and elemental mercury ($Hg^{0}$) [3,4]. Among these mercury speciations, most $Hg^{2+}$ and $Hg^{p}$ could be readily separated from the flue gas by current pollution control utilities [5,6]. By contrast, $Hg^{0}$ is difficult to remove due to its lower water solubility and higher vapour pressure [7]. Hence, it is of great importance to develop effective $Hg^{0}$ removal technologies.

Adsorption and oxidation methods have been extensively investigated and reported to facilitate the control of $Hg^{0}$. The catalysts employed in the selective catalytic reduction (SCR) reaction have been proved helpful for the catalytic oxidation of $Hg^{0}$ to $Hg^{2+}$ [8–11], but the oxidation efficiency is strongly restricted by the presence of HCl concentration in the flue gas [12]. Among the various adsorbents, activated carbon (AC) injection upstream of the dedust facilities, where the flue gas temperature is usually below 160 °C, have commercially applied in the industry of the United States of America, and exhibits the highest performance for mercury adsorption [13,14]. Nevertheless, the short contact time between the injected AC and the flue gas requires a high carbon to mercury (C/Hg) ratio and thus results in a large operating expense [15]. Since the high cost limits the development of AC injection techniques, the modified activated carbon has been most widely studied in the area of mercury adsorption [16–18]. Previous studies have investigated numerous modified activated carbons for $Hg^{0}$ removal performances, and found that the I-impregnated ACs possessed the highest mercury adsorption capacity [19,20]. Therefore, in this study, KI-AC acts as the adsorption material to evaluate its removal performance for $Hg^{0}$ at low temperature.

Many researchers have approved that the $Hg^{0}$ removal performance is closely associated with the physicochemical characteristics of the activated carbon [21–25]. It is reported that the AC with larger BET surface area tended to have bigger surface energy, further to generate larger adsorptive driving force between the adsorbate and adsorbent, which was proven to enhance the $Hg^{0}$ physisorption capacity. In addition, the surface oxygen complexes, possibly carbonyl and lactone groups, are the active sites for chemisorption of $Hg^{0}$, while the phenol groups might inhibit $Hg^{0}$ adsorption. However, the effect of physicochemical characteristics on the $Hg^{0}$ removal performance greatly varies in material.

The flue gas components depend strongly on the properties of the coals burned, and the $Hg^{0}$ removal performance is largely affected by the flue gas compositions, including $O_2$, $SO_2$ and NO atmosphere. Laboratory experiments indicated that $O_2$ exhibited a notable promotion in the $Hg^{0}$ capture capacity over the surface of carbonaceous materials by the formation of carbonyls groups [26]. The effect of $SO_2$ on $Hg^{0}$ removal over the AC hasn't reached an agreement. It was reported that $Hg^{0}$ removal capacity over the AC was irrelevant of the concentration of $SO_2$ [27]. Others also found that $SO_2$ alone had a little promotional impact on $Hg^{0}$ adsorption [28]. In addition, the impact of NO on $Hg^{0}$ adsorption varies from ACs. Miller et al. found that 300 ppm NO led to observably positive effect on $Hg^{0}$ capture [28]. Liu et al. indicated that 500 ppm NO had no detectable effect on $Hg^{0}$ capture [29]. In addition, previous literatures predominately concentrated on the impacts of flue gases on $Hg^{0}$ capture, and little attention had been paid to the affinity capacities between $Hg^{0}$ and various groups that formed due to the presence of flue gas components.

On the basis of the above analysis, this study focused on identifying the relationships between the physicochemical characteristics of the KI-AC and $Hg^{0}$ removal performance, and evaluated the impact of the co-existence gaseous components on $Hg^{0}$ removal. Furthermore, the probable reaction pathways were proposed according to the experimental data. The affinity capacities between $Hg^{0}$ and the various groups over the KI-AC sample were also contrasted. The improved understanding of the research will help to provide insight into the potential industrial applications of KI-AC adsorbents in chlorine-free flue gas systems.

## 2. Materials and methods

### 2.1. Sample preparation

The activated carbon support is purchased from the Chengde Jibei Yanshan Activated Carbon Plant of Hebei Province. Prior to use, virgin AC were grinded and sieved to 20–60 Chinese mesh. Subsequently, it was washed and agitated with distilled water for several times and soon dried approximately for 12 h at 120 °C. The KI-impregnated activated carbon were prepared from a KI solution and AC support using an impregnation method. The KI solution was prepared by adding the required amount of KI solid to approximately 150 mL distilled water. Then, the activated carbon was dispersed to the KI solution. After stirred for 3 h, the KI-impregnated activated carbon was dried in an electricity heat drum wind drying oven at 120 °C for 14 h. The adsorbents are denoted as X% KI-AC, where X stood for the weight percentage of KI solid to activated carbon used in the sample preparation progress.

### 2.2. Sample characterization

The activated carbon porosity characteristics were recorded over the whole range of relative pressures at −196 °C, using a $N_2$ adsorption apparatus (ASAP 2020, Micromeritics Instrument Corp). The specific surface areas of the samples were measured using the $N_2$ adsorption isotherms with the Brunauer–Emmett–Teller (BET) method. The micropore volume was determined by the Horvath–Kawazoe (HK) method. The total pore volume was accessed from the amount of the adsorbed $N_2$ at $p/p_0 = 0.99$ from the adsorption data of the isotherm.

### 2.3. Experimental apparatus and removal performance measurement

The adsorption experiments were conducted in a down-flow fixed-bed quartz reactor (6 mm o.d.) as shown in Fig. 1. About 25 mg of the sample, which was laid inside a tubular furnace to regulate the reaction temperature, was used in each experiment. The feed gases consisted of $O_2$, $SO_2$ and NO (when used) balanced in $N_2$, which were accurately adjusted using mass flow controllers (MFC) with the total flow rate of 600 mL/min. An $Hg^{0}$ permeation device (Mercury S56-HE-SR, VICI Metronics), which was sealed in a Teflon tank maintained at 53.7 °C, was used to provide a constant feed of $Hg^{0}$ concentration. The relatively high initial $Hg^{0}$ concentration of 145 ± 1 μg/m$^3$ was adopted to shorten the adsorption time during the experiments. The $Hg^{0}$ concentrations were continuously measured using an online $Hg^{0}$ analyzer (RA-915M+, Lumex). To prevent $Hg^{0}$ deposition further to cause experimental errors, the pipeline system that the $Hg^{0}$ vapour passed through was heated to approximately 60 °C. The $Hg^{0}$ adsorbed on the pipelines were found to be less than 0.4 μg/m$^3$. Before each test, all the activated carbon samples were purged by $N_2$ for 20 min to ensure equal