Hollow microbeads modified with MoS$_2$ for enhanced removal of mercury from coal-fired flue gas

Qian Cai, Ping He*, Naichao Chen, Jiang Wu, Haodong Jia, Rui Shen, Tianyang Hu and Kangsai He

Shanghai University of Electric Power, College of Energy and Mechanical Engineering, Shanghai 200090, China

Abstract. Hollow microbeads, derived from fly ash emitted by power plants, are hollow microbeads composed of various compounds including SiO$_2$ and Al$_2$O$_3$. These microspheres exhibit a high specific surface area and stable chemical properties. In this work, HM-MoS$_2$ was synthesized through a two-step hydrothermal method to address the issues of low adsorption efficiency and high operational costs associated with the utilization of hollow microbeads in actual power plant applications. The experiments demonstrated that under simulated power plant flue gas conditions, the adsorption efficiency of HM-15 for elemental mercury (Hg$^0$) exceeded 96%. Additionally, HM-15 displayed resistance to SO$_2$ and NO gases, indicating its potential as a mercury adsorbent material with promising industrial applications.

1. Introduction

Over the past few decades, as industrialization has accelerated, atmospheric mercury pollution has become a global environmental problem[1,2]. Mercury is a hazardous heavy metal whose volatility and bioconcentration result in long-range environmental transport and accumulation in organisms, posing a serious threat to human health and ecosystems[3,4]. Consequently, the development of efficient and reliable mercury adsorbents has become a crucial research direction in the field of environmental protection.

Mercury emissions from coal-fired power plants primarily exist in three forms: elemental mercury (Hg$^0$), oxidized mercury (Hg$^{2+}$), and particulate-bound mercury (Hg$^0$) [5]. Hg$^{2+}$ can be removed by wet flue gas desulphurization (FGD), while Hg$^0$ is generally removed by electrostatic precipitators (ESP) or activated carbon injection (ACI). However, Hg$^0$ is the most difficult to remove from the tail gas of coal-fired power plants due to its high volatility and chemical stability[6]. Adsorption has received a lot of attention as a simple and relatively low-cost removal technique for elemental mercury[7]. Coal-fired power plant fly ash, as one of the by-products of coal-fired power plants, has unique physical and chemical properties, high specific surface area and adjustable chemical properties. Hollow microbeads, on the other hand, are hollow spherical shaped beads containing various compounds such as SiO$_2$, Al$_2$O$_3$, etc., which are separated from the fly ash of power plants and may be a potential mercury adsorbent[8]. In recent years, research on further improving the adsorption efficiency of mercury by surface modification of adsorbents has increased, and it has become a consensus that utilizing the high affinity between elemental sulfur and mercury can significantly enhance the adsorption effect of adsorbents[9]. In this work, we prepared molybdenum disulfide modified hollow microbeads (HM-MoS$_2$) by two-step hydrothermal method, and systematically tested the mercury removal performance of HM-MoS$_2$ at different temperatures and in various types of flue gas components (N$_2$+O$_2$, SO$_2$, and NO). The physical and chemical properties of the adsorbent were analyzed by BET and XPS, and the adsorption mechanism of HM-MoS$_2$ on mercury was discussed. The mercury compounds contained in the adsorbent were characterized by the programmed warming desorption method (Hg-TPD), and the mercury accumulation pattern in the spent adsorbent was comprehensively investigated.

2. Experimental section

2.1 Synthesis of MoS$_2$

Sodium molybdate dihydrate (Na$_2$MoO$_4$·2H$_2$O) and L-cysteine (C$_3$H$_7$NO$_2$S) were both acquired from Shanghai Titan Technology Co., Ltd. A total of 0.84g of Na$_2$MoO$_4$·2H$_2$O and 2.11g of C$_3$H$_7$NO$_2$S were dissolved in 40 ml of deionized water, and the solution was stirred using a magnetic stirrer for 45 minutes to ensure complete dissolution. The resulting mixture was then transferred to a 100ml autoclave and subjected to hydrothermal reaction at 200°C for 24 hours. After completion, the product was washed three times with deionized water and anhydrous ethanol respectively. Subsequently, the obtained sample was transferred to a drying oven, where it was dried at 60°C for 12 hours and ground to yield a black MoS$_2$ powder.
2.2 Synthesis of HM-MoS$_2$

Hollow microbeads (HM) were sourced from a power plant in Shanghai. Following a similar hydrothermal method, 1g of hollow microbeads and a pre-weighed amount of MoS$_2$ powder were added to 40ml of deionized water. The mixture was stirred magnetically for 45 minutes and then subjected to hydrothermal treatment at 160°C for 24 hours. The product was washed three times with deionized water and anhydrous ethanol, followed by overnight drying in a vacuum oven at 60°C to obtain HM-MoS$_2$ powder. Samples with mass ratios of 5%, 10%, 15%, and 20% were designated as Hm-5, Hm-10, Hm-15, and Hm-20, respectively.

2.3 Hg$^0$ adsorption experiments

Fig. 1 illustrates the experimental setup. Nitrogen gas is employed as the carrier gas to drive Hg$^0$ through a mercury generator (PSA10.536 SIR GALAHAD II, U.K.) at a flow rate of 1 L/min through the main pathway. The adsorbents tested are positioned within a glass tube, secured in place by cotton and quartz wool, and subjected to heating via a fixed heating bed to simulate flue gas temperatures. Subsequently, the mercury vapors are mixed with N$_2$ gas and directed into a mercury analyzer for monitoring. Upon completion of the monitoring, the exhaust gases are expelled through a tail gas treatment unit[10].

The experimental calculation equation (1) is shown below:

\[
\eta_{Hg} = \frac{1}{H_{g_{in}}} \times (H_{g_{in}} - H_{g_{out}}) \times 100\% \quad (1)
\]

In the equation (1), $\eta_{Hg}$ is the Hg$^0$ adsorption efficiency (%), and $H_{g_{in}}$ is the initial inlet Hg$^0$ concentration(μg/m³), $H_{g_{out}}$ is the export mercury concentration(μg/m³).

![Fig. 1. Hg$^0$ adsorption experiment flow chart](image)

As shown in Fig. 2(a)(b), the original hollow microbeads exhibit a largely intact spherical structure. Fig. 2(c)(d) and Table. 1 illustrate that following surface modification, the spherical structure is disrupted into an irregular, fragmented morphology with particle formation on the surface. Contrary to expectations, the specific surface area of the fragmented hollow microbeads did not decrease, suggesting successful attachment of MoS$_2$ to the surfaces of the disrupted microbeads.

![Fig. 2. SEM diagram: (a)(b):HM, (c)(d):HM-15](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HM</td>
<td>17.27</td>
<td>4.26×10$^{-2}$</td>
<td>4.76</td>
</tr>
<tr>
<td>Hm-5</td>
<td>11.04</td>
<td>8.12×10$^{-2}$</td>
<td>11.82</td>
</tr>
<tr>
<td>Hm-10</td>
<td>15.01</td>
<td>1.52×10$^{-1}$</td>
<td>18.62</td>
</tr>
<tr>
<td>Hm-15</td>
<td>18.18</td>
<td>1.48×10$^{-1}$</td>
<td>13.40</td>
</tr>
<tr>
<td>Hm-20</td>
<td>13.42</td>
<td>1.19×10$^{-1}$</td>
<td>13.94</td>
</tr>
</tbody>
</table>

As shown in the Fig. 3, the diffraction peaks of the adsorbent material for the undoped samples are identified at scattering angles $\theta = 22.549^\circ$, $26.033^\circ$, and $51.502^\circ$. 

corresponding to the (4 2 2), (4 4 0), and (1 0 4 2) lattice planes, respectively (PDF#42-0720). Additionally, several indistinct peaks are observed between 20° and 30°, attributable to SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, and other oxygen-containing compounds, confirming the composition of the hollow microbeads[11]. The (1 0 0) and (1 0 7) facets corresponding to MoS$_2$ are noted at 2θ = 32.677° and 62.814°, respectively (PDF#47-0720) [12]. With increasing MoS$_2$ content, the characteristic peaks of SiO$_2$ exhibit a slight leftward shift, and a gradual reduction in peak intensity, indicating a decrease in the SiO$_2$ content on the surface of HM-15 and its partial replacement by MoS$_2$.

![Fig. 3. XRD graph](image)

2.4 Hg$^0$ adsorption experiment

Take 30mg of sample, place it on a fixed bed test bench, and conduct Hg$^0$ removal performance experiments under high-purity nitrogen gas. The experimental results are shown in Fig. 4. At 120 °C, the average mercury adsorption efficiencies for HM, HM-5, HM-10, HM-15, and HM-20 are 50.7%, 87.9%, 96.5%, and 88.7%, respectively. HM-15 exhibits the highest Hg$^0$ adsorption efficiency. Analysis of the mercury adsorption efficiency curves from HM to HM-20 suggests that MoS$_2$ enhances the thermal stability of the adsorbent in simulated flue gas environments. However, excessive MoS$_2$ reduces mercury adsorption efficiency. BET characterization results indicate that this decrease for HM-20 is due to excessive particle aggregation on the surface, reducing the availability of oxygen and sulfur active sites.

![Fig. 4. 2h mercury removal efficiency graph](image)

Considering the feasibility of adsorbents in practical applications and the continuous, long-term adsorption of Hg$^0$, we tested the long-term adsorption performance, cyclic adsorption performance, and adsorption performance of different flue gas components of the HM-15 adsorbent. As shown in Fig. 5, to assess the stability of the sample, HM-15 was operated in an N$_2$ environment for 10 hours.

![Fig. 5. 10h Hg$^0$ removal efficiency graph](image)

It maintained an average mercury adsorption efficiency of over 92%, and the efficiency curve was stable. Furthermore, we evaluated the cyclic performance of HM-15 through cyclic experiments. We prepared a 0.1mol/L dilute sulfuric acid solution to wash mercury and its compounds. The adsorbed sample was placed in 30ml of leachate and magnetically stirred for 30 minutes to precipitate a large amount of mercury and its compounds. Then, it was washed three times with deionized water and ethanol to remove some impurity ions. Finally, it was dried and ground for use in the next cycle. As shown in Fig. 6, after five cycles, the average adsorption efficiency of the adsorbent still maintained above 90%.

![Fig. 6. 5 cycles of Hg$^0$ removal efficiency graph](image)

The Hg$^0$ removal performance of the sample was tested under different flue gas components (N$_2$+O$_2$, SO$_2$, and NO). The experimental results are shown in Fig. 7. Compared to the N$_2$ environment, the atmosphere of N$_2$+5% O$_2$ has a promoting effect on the adsorption of Hg$^0$. This is due to O$_2$ promoting the loss of electrons from Hg0 during the adsorption process, resulting in its
oxidation to Hg⁰. In most common adsorbents, the addition of SO₂ will have a negative effect on adsorption. For metal oxides, such as iron oxide and copper oxide, used as mercury adsorbents in an SO₂ atmosphere, a competitive adsorption reaction occurs with the active oxygen sites on their surfaces to form sulfates. This reaction reduces the effective active adsorption sites[13]. Due to the doping of MoS₂, HM-15 exhibits certain sulfur resistance in a medium to low concentration SO₂ atmosphere. As shown in the following equation(2). In an NO atmosphere, NO can destroy the active sites of the adsorbent, and the adsorbed product HgS may be reduced to Hg⁰ by NO, which is not conducive to the adsorbent's capture of Hg⁰[14].

\[ \text{HgS}(s) + 2\text{NO}(g) \rightarrow \text{Hg}^0(g) + \text{SO}_2(g) + \text{N}_2(g) \] (2)

![Fig. 7. Hg⁰ removal efficiency in Different atmospheres](image)

The problem of poor thermal stability has always interfered with the ability of MoS₂ to adsorb mercury in different environments, and pure MoS₂ is difficult to maintain stable adsorption of mercury in high temperature ranges above 160 °C[15]. The work shows that the modified HM-15 solves the problem of insufficient thermal stability of MoS₂ under high temperature conditions. As shown in the Fig. 8, with the increase of temperature, the adsorption efficiency of HM-15 did not decrease. This is speculated to be due to the decomposition of oxygen-containing free radicals on the surface of the broken hollow microbeads at high temperatures, which supplemented the O defect vacancies.

![Fig. 8. Hg⁰ removal efficiency in Different temperatures](image)

As shown in Fig. 9, after separation from the power plant fly ash, the hollow microbeads exhibit an adsorption efficiency of 50.7%, significantly surpassing the 18% of the fly ash. The adsorption efficiency of HM-15 is notably enhanced after modification with MoS₂, which is higher than that of modified SiO₂[13], and not much lower than that of MoS₂ alone. From an economic usage perspective, only 15% of the MoS₂ amount is required to nearly reach the adsorption efficiency of MoS₂, better balancing cost durability and adsorption performance in practical applications.

![Fig. 9. Hg⁰ removal efficiency by different adsorbents](image)

3. Results and discussion

As shown in the Fig. 10, through the Hg programmed temperature desorption experiment, it was found that there is a clear peak at 108.6 °C, indicating the presence of unreacted Hg⁰ in the low temperature stage. After reaching 200 °C, there are two peaks, 217.9 °C and 379.3°C, representing HgS and HgO products, respectively.

![Fig. 10. Hg-TPD (HM-15)graph](image)

As shown in the Fig. 11 through thermogravimetric (TGA) testing, it was found that HM-15 hardly decomposes at high temperatures. The slight decrease in quality between 160°C and 400°C may be due to the pyrolysis of a small amount of organic matter on the surface of hollow microbeads.
The elemental valence composition of the HM-15 surface was investigated by XPS, in Fig. 12(a), two characteristic peaks were found at 232.62 and 229.38 eV, representing Molybdenum Oxide of Mo 3d\(^{3/2}\) and MoS\(_2\) of Mo 3d\(^{5/2}\), respectively, in addition to a weaker characteristic peak at 226.34 eV, corresponding to Mo\(^{6+}\), which may be due to the sample preparation process with O\(_2\) reaction that occurs with partial oxidation\([16]\). In Fig. 11(b), two peaks were found at 163.47 and 162.18 eV, corresponding to S 2p\(^{3/2}\) and S 2p\(^{1/2}\), respectively, which proves that elemental S is present in HM-15 in the form of S\(_2^-\)\([9]\). In Fig. 12(c), O 1s corresponds to hydroxide (-OH) and lattice oxygen (O\(_L\)) at 531.91 and 530.46 eV, respectively, and the electronic interactions are strengthened in comparison with the standard peak position of MoS\(_2\), which makes the characteristic peaks of HM-15 move towards higher binding energy\([17]\). In Fig. 12(d), it can be observed that Hg is observed at 101.44 eV in the form of Hg\(^{2+}\) valence in HM-15 before adsorption, which may be due to HgS or Hg-containing organic compounds carried by hollow microbeads separated from fly ash.

Fig. 13(a) shows the XPS elemental valence analysis of HM-15 after the adsorption experiment, and the characteristic peaks corresponding to S\(^{2-}\) and S\(^{2-}\) were found at 163.29 eV versus 162.01. Compared with the pre-adsorption period, the peak intensity decreased and the area of the S\(^{2-}\) peak became smaller, which proved that part of the S\(^{2-}\) and Hg\(^{2+}\) finally generated HgS after the adsorption of HM-15. Characteristic peaks corresponding to HgO and HgS appeared at 104.15 and 99.78 eV, respectively, in Fig. 13(b)\([18]\). Observing the area change of the peaks in the figure, it can be found that HM-15 mainly relies on the physical adsorption of hollow microbeads to immobilize Hg\(^2+\), and the lattice oxygen vacancies and defective sulfur sites are involved in the catalytic oxidation, which synergistically promotes the adsorption of mercury.

$$\text{Hg}^0(g) \rightarrow \text{Hg}^0(\text{ad})\ (3)$$
$$\text{Mo}^{6+} + \text{Hg}^0(\text{ad}) \rightarrow \text{Hg} - \text{Mo}\ (4)$$
$$\text{Fe}^{2+}(\text{Fe}_2\text{O}_3) \rightarrow \text{O}_L + \text{Fe}^{3+}\ (5)$$
$$\text{Hg} - \text{Mo} + \text{S}^{2-} \rightarrow \text{HgS} + \text{Mo}^{4+}\ (6)$$
$$\text{O}^L + \text{Hg}^0(\text{ad}) \rightarrow \text{HgO} (\text{ad})\ (7)$$
$$\text{HgO} + \text{S}^{2-} \rightarrow \text{HgS}\ (8)$$

4. Conclusion

This work synthesized four ratios of HM-MoS\(_2\) via a secondary hydrothermal method, enabling successful modification of hollow microbeads with MoS\(_2\). In the
mercury removal experiments using simulated flue gas, HM-15 achieved a mercury adsorption efficiency of 96.5% at 120°C. The adsorption efficiency remained above 90% in both long-term and cyclic tests, demonstrating excellent mercury adsorption performance. The incorporation of MoS$_2$ enhanced the mercury adsorption capacity of hollow microbeads in the presence of SO$_2$. Therefore, HM-15 can be considered an effective mercury adsorbent with potential industrial applications.

Acknowledgments

This work was partially sponsored by “National Key R&D Program of China”(2021YFE0109800).

References

4. V. Kumar, S. A. Younis, J. E. Szulejko, K.-H. Kim, RSER 185, 113659 (2023)
5. Y. Zheng, G. Li, Y. Xing, W. Xu, T. Yue, J ENVIRON SCI 148, 420-436 (2025)
7. X. Yang, C. Gong, Y. Guan, J. Li, F. Li, C. Peng, J. Wu, T. Cui, S. Xiang, Y. Gao, FUEL 344, 128081 (2023)
11. R. Xiao, Y. Zhang, S. Wei, X. Chuai, X. Cui, Z. Xiong, J. Zhang, Y. Zhao, CHEM ENG J 453, 139946 (2023)
15. D. Liu, L. Yang, J. Wu, B. Li, Sci Total Environ 824, 153934 (2022)