

Modeling mercury adsorption on carbon particles in simulated flue gas

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Abstract: A model was developed to describe the adsorption characteristic of mercury in flue gas based on one residual carbon sample and one activated carbon sample. The differential equations were established with mass balance of mercury in the gas phase and in the solid phase. Then the model was solved using a Matlab program with a Runge-Kutta process. The mercury adsorption isotherms of these two adsorbents were obtained by breakthrough column experiments. The results show that at low gas phase mercury concentrations ($< 0.3 \text{ mg/m}^3$), the adsorption equilibrium of residual carbon is in accord with the case of a type II isotherm of the Freundlich theory. Whereas the data of activated carbon falls into the Langmuir relationship, it is the case of a type III isotherm. The experimental data were fitted to the Freundlich model by Matlab software. The variances of mercury concentration are smaller than 0.81 which implies the agreement between measurements and simulation is quite agreeable considering the wide scatter of the measurements. This model is useful for forecasting mercury removal efficiency and is helpful to the mechanism analysis of mercury adsorption on carbon-based adsorbent.

Key words: mercury; adsorption; residual carbon; fly ash; activated carbon

The impact of mercury on the environment and the physiological health of humans are well documented^[1-3]. Presently, the most effective and widely used technology for direct control of vapor-phase elemental mercury is injection of powdered activated carbon into the gas stream^[4-5]. Because the expenses associated with this process could be quite high, ranging from \$ 14 400 to \$ 38 200 per pound of mercury removed^[6], various other sorbents were examined with respect to their ability to adsorb vapor-phase mercury and their applicability in industry^[7-8]. Due to the relatively low production costs, residual carbons would likely be considerably more cost-effective for the removal of mercury from combustion flue gases than other technology. Up to now, the modeling study of mercury adsorption on residual carbon has not been researched so much. In this study a model was developed to describe the adsorption characteristics of mercury in the flue gas based on one residual carbon sample and one activated carbon sample in comparison.

1 Materials and Methods

1.1 Residual carbon

One residual carbon (FS) sample and one activated carbon (HXT) sample are investigated in this study (see Tab. 1). A fly ash sample (FS ash) was selected from a power plant in Fujian province in China. FS carbon is the residual carbon separated from FS by froth flotation (double currents flotation column). For comparison, one commercial activated carbon sample, HXT, which was purchased merchandise (for gas adsorption) was also tested.

Tab. 1 Properties of carbons used in adsorption experiments

Carbon	Average size/ μm	Density/ $(\text{g} \cdot \text{cm}^{-3})$	BET surface area/ $(\text{m}^2 \cdot \text{g}^{-1})$	LOI/%
FS	63	2.01	10.747	73.4
HXT	40		739.445	

1.2 Mercury adsorption equipment

The adsorption experimental apparatus is shown in Fig. 1. The material bed is a U-shaped tube with a diameter of 4 mm. The carbon bed is placed in the second thermal bath to ensure a constant temperature. The feed gas line and the carbon bed are connected by a three-way valve, which allows the measurement of the mercury concentration of the feed gas entering the carbon bed. The exhausted gas exits from the other end of

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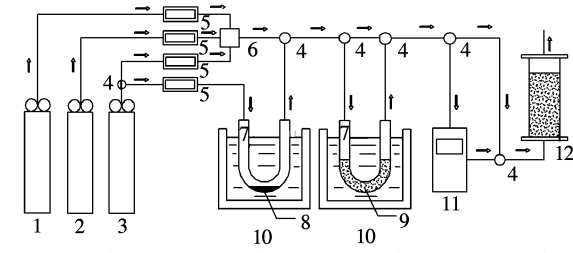


Fig. 1 Schematic diagram of mercury vapor generation and adsorption experiment apparatus

the carbon bed. When measurement of mercury concentration is needed, the gas (either feed gas or exhausted gas) is first collected in a one-liter Tedlar bag and the mercury in the bag is analyzed using the mercury vapor analyzer. The structural and operational parameters for column texts are summarized in Tab. 2.

Tab. 2 Structural and operational parameters for column texts

Carbon loading/g	Bath temperature/°C		Nitrogen flow rate/(mL·min ⁻¹)	Nitrogen pressure/kPa
	Carbon bed	Hg holder tube		
About 0.3	20 to 120	-5 to 80	100 to 200	125

The equilibrium of the absorbed mass of mercury q is calculated as

$$q = \int_0^Q (C_0 - C) dQ \quad (1)$$

where C_0 and C are the influent and effluent concentrations of mercury, and Q is the total gas volume flowing into the column.

2 Model Establishing

The mass balance of mercury in the gas phase and in the solid phase can be derived from the assumption that the velocity of adsorption of the adsorbent particles is roughly equal to that of the flue gas. Another assumption is that the whole system is in a stationary state. A volume element A_d of the flue gas duct is shown in Fig. 2. The mass balance of mercury in the flue gas can be described as

$$\frac{dM_{\text{Hg, gas}}}{dt} = \hat{M}_{\text{Hg, gas, in}} - \hat{M}_{\text{Hg, gas, out}} - D \quad (2)$$

where D is the mass removed in per unit time from the gas phase by adsorption on the adsorbent surface, M is the substance mass, and \hat{M} is the substance mass rate of time.

The mass flow of mercury in the flue gas which enters the volume element is

$$\hat{M}_{\text{Hg, gas, in}} = \hat{M}_{\text{gas}} C_{\text{Hg, gas}} = \rho_{\text{gas}} w A_d C_{\text{Hg, gas}} \quad (3)$$

where $C_{\text{Hg, gas}}$ is the mercury concentration in the gas

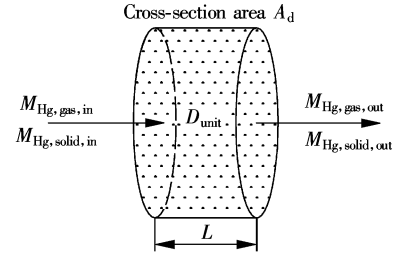


Fig. 2 Schematic diagram of a volume-element of the flue gas duct upstream the particle control device

phase, w is the superficial gas velocity, A_d is the cross-sectional area of duct, and ρ is the mass density.

Then the output mass flow of mercury is

$$\hat{M}_{\text{Hg, gas, out}} = \hat{M}_{\text{gas}} C_{\text{Hg, gas}} + \hat{M}_{\text{gas}} \frac{\partial C_{\text{Hg, gas}}}{\partial L} dL \quad (4)$$

For this stationary case system, it follows that

$$\rho_{\text{gas}} w \frac{dC_{\text{Hg, gas}}}{dL} = -D_{\text{unit}} \quad (5)$$

where D_{unit} represents the mercury adsorption rate in the unit volume of the duct, namely,

$$D_{\text{unit}} = \frac{D}{V} \quad (6)$$

The mercury concentration in the flue gas $C_{\text{Hg, gas}}$ is given as

$$C_{\text{Hg, gas}} = \frac{M_{\text{Hg}}}{M_{\text{gas}}} \quad (7)$$

The mercury adsorbed on the adsorbent surface can be developed based on the equations above. The mercury mass change rate of time is described as

$$\frac{dM_{\text{Hg, solid}}}{dt} = \hat{M}_{\text{Hg, in}} - \hat{M}_{\text{Hg, out}} + D \quad (8)$$

There is a relationship for the stationary case system,

$$\lambda \rho_{\text{gas}} w \frac{dC_{\text{Hg, solid}}}{dL} = D_{\text{unit}} \quad (9)$$

where λ is the solids loading in the flue gas, $C_{\text{Hg, solid}}$ is the mercury concentration in the solid phase, and L is the length of flue gas path.

Then the mercury concentration absorbed on the adsorbent is

$$C_{\text{Hg, solid}} = \frac{M_{\text{Hg}}}{M_{\text{solid}}} = \frac{1}{\lambda} \frac{M_{\text{Hg}}}{M_{\text{gas}}} \rho_{\text{gas}} \quad (10)$$

With the assumption mentioned above, the balance equations can be solved at the base of the following initial conditions: ① The mercury concentration on the solid is zero at $L = 0$ (e. g. at the point of injection); ② The mercury concentration of the flue gas at $L = 0$ is equal to the mercury concentration at the inlet of the bed. The differential equations were solved using a Matlab program with a Runge-Kutta process.

3 Results and Discussion

3.1 Calculation of the adsorption parameters

Through the calculations of experimental data, the equilibrium data of activated carbon were best fitted with the Langmuir relationship, which is the case of the type III isotherm; whereas the data of residual carbon are better fitted by the Freundlich theory, which is the case of the type II isotherm.

On the basis of assuming that the adsorption process is not limited by mass transfer, the kinetic parameters of the adsorption process were calculated from the experimentally determined breakthrough curves. The following modified adsorption kinetics are used for the correlation,

$$D_{unit} = n_{ads} C_{Hg, gas} \lambda A_s (C_{Hg, solid, eq} - C_{Hg, solid}) \quad (11)$$
 where n_{ads} is the adsorption constant, and $C_{Hg, solid, eq}$ is the equilibrium concentration.

For the determination of the kinetic parameter n_{ads} , the breakthrough curves were fitted basically with the model described above. The model was used to calculate the concentration downstream the fixed bed. Tab. 3 shows the values of n_{ads} for the investigated adsorbents.

Tab. 3 Kinetic parameters for FS carbon and activated carbon

Adsorbent	$n_{ads}/(kg \cdot (m^2 \cdot s)^{-1})$	Temperature/°C
FS carbon	0.65	20
HXT carbon	0.007 5	40

3.2 Modeling the mercury captured by fix-carbon-bed adsorption

The series of breakthrough curves were obtained by the column tests and the results are presented in Fig. 3. It can be seen that the distributions of all curves are logarithm shaped and the adsorption capacity at 40 °C is lower than that at 20 °C. This phenomenon, which is in accord with the common rules of physical adsorption, indicates that the mercury adsorption on residual carbon is mainly present in physical adsorption. The higher mercury concentration at entrance, the less time spent for the carbon bed to reach saturation adsorption. Experimental data were fitted to Freundlich model by Matlab software. Tab. 4 summarizes the model parameters for FS and HXT carbon. The comparison of the predicted results and experimental data is presented in Fig. 3. It can be seen that the agreement between measurements and simulation is quite acceptable.

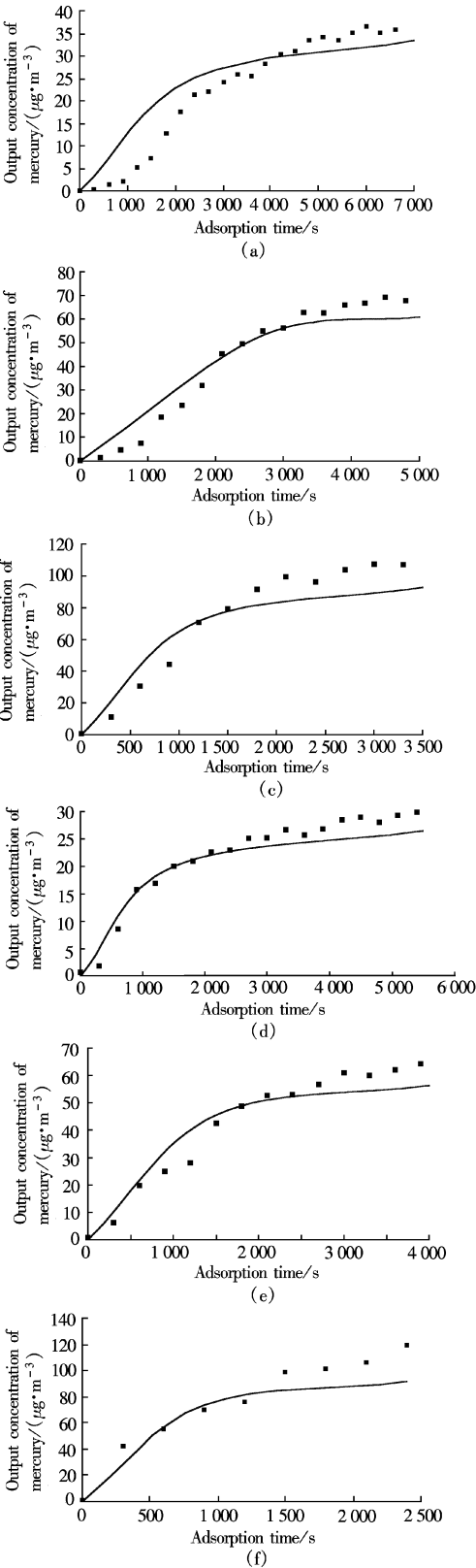


Fig. 3 Comparison of breakthrough profile measured in column test and predicted by models in different situations (FS carbon). (a) At 20 °C, $C_0 = 36 \mu g/m^3$; (b) At 20 °C, $C_0 = 68 \mu g/m^3$; (c) At 20 °C, $C_0 = 107 \mu g/m^3$; (d) At 40 °C, $C_0 = 29 \mu g/m^3$; (e) At 40 °C, $C_0 = 63 \mu g/m^3$; (f) At 40 °C, $C_0 = 102 \mu g/m^3$

Tab. 4 Model parameters for FS and HXT carbons at 20 °C

Para- meters	Langmuir		Para- meters	Freundlich	
	HXT carbon	FS carbon		HXT carbon	FS carbon
N	3.17×10^6	9.91×10^6	n	6.13×10^7	2.15×10^7
$C_{\text{Hg, solid, max}} /$ ($\text{kg} \cdot \text{kg}^{-1}$)	1.65×10^{-3}	4.36×10^{-4}	r	1.469	1.627
S^2	0.81	0.87	S^2	0.83	0.91

4 Conclusion

In this study a model was developed to describe the adsorption characteristics of mercury in flue gas. The mercury adsorption characteristics of two kinds of adsorbents—activated carbon and residual carbon were conducted by the breakthrough experiments. The isotherm of FS carbon is in accord with type II isotherm according to the classification of Brunauer^[9] at low gas phase mercury concentrations ($<0.3 \text{ mg/m}^3$). Whereas the isotherm of activated carbon is similar to that of type III. The necessary adsorption parameters were determined by measuring breakthrough curves in a bench-scale fixed bed. The adsorption equilibrium of activated carbon was best fitted with the Langmuir relationship as in the case of the type III isotherm, whereas the data of residual carbon are better fitted by the Freundlich theory as in the case of the type II isotherm. The fitting quality of the model compared well with the data measured from the breakthrough experiments. The model has potential worthiness for the mechanism analysis of mercury adsorption on carbon-base adsorbent and is useful in the development of mercury removing technology.

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模拟烟气中炭质颗粒的汞吸附模型

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摘要:根据残炭和活性炭的穿透吸附试验数据,提出了残炭吸附等温线的数学模型.通过所取微元内气相汞和固相汞的总量平衡关系建立相关微分方程组,并运用 Matlab 软件结合 Runge-Kutta 过程推导出适用模型.穿透试验结果表明:在与电厂烟气汞浓度相近的低汞浓度条件下 ($<0.3 \text{ mg/m}^3$),残炭的吸附等温线符合 Freundlich 理论的 II 型等温线,而活性炭的数据则明显具有 Langmuir 关系,即属于 III 型等温线.运用 Matlab 软件将实验数据对修正模型进行拟合计算,经过统计分析,出口汞浓度数据方差不超过 0.81,表明在允许的误差范围内,测试数据和模拟结果令人满意.该模型对汞吸附脱除效率预测和炭质吸附剂的汞吸附富集机理研究有重要意义.

关键词:汞;吸附;残炭;飞灰;活性炭

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