Supporting Information

Impact of Nonoxidized Sulfur Species on Elemental Mercury Removal by SO_2 Activated Petroleum Cokes

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1. Adsorption activation energy

The adsorption activation energy E_a represents the minimum energy required to convert normal adsorbate molecules into the activated state before adsorbed. The type of mercury adsorption process on the sorbent can be determined by the activation energy value. In general, the value of E_a in the range of 5~40 kJ/mol represents physisorption, and the value in the range of 40~800 kJ/mol indicates chemisorption.[1] The adsorption activation energy of mercury removal on the sorbent can be figured out by the Arrhenius equation. The linear expression of the Arrhenius equation is listed as follows[1-3]:

$$\ln k_2 = -\frac{Ea}{RT} + \ln k_0 \qquad S(1)$$

where k_2 ($g \cdot \mu g^{-1} \cdot min^{-1}$) is the pseudo-second-order adsorption rate constant obtained from the pseudo-second-order kinetic model; E_a (kJ/mol) is the adsorption activation energy; R is the gas constant, 8.314 J/(mol·K); T (K) is adsorption temperature; k_0 is the temperature influence factor. The pseudo-second-order kinetic equation in the nonlinear form used in this study to obtain k_2 is described as follows[4]:

$$q_t = \frac{q_e^2 \cdot k_2 \cdot t}{1 + q_e \cdot k_2 \cdot t} \qquad S(2)$$

where q_t ($\mu g \cdot g^{-1}$) and q_e ($\mu g \cdot g^{-1}$) are mercury uptake at time t and at equilibrium, respectively; t (min) is reaction time.

As shown in Fig. S3, the pseudo-second-order kinetic model can fit the experimental data very well. The fitting parameters of mercury adsorption on PC-S, PC-NS and PC-SC are listed in Table S1. The obtained correlation coefficient R^2 for the pseudo-second-order kinetic model is close or greater than 0.99 for all conditions,

demonstrating that mercury adsorption on SO_2 activated cokes strongly follows the pseudo-second-order kinetic model.

According to the Arrhenius equation, a straight line can be obtained by plotting $\ln k_2$ against 1/T, and the activation energy can be calculated from the slope of the straight line, which equals to $-E_a/R$. The fitting curves of the Arrhenius equation are shown in Fig. S4, and the obtained values of adsorption activation energy E_a for PC-S, PC-NS and PC-SC are listed in Table S2. As detailed in Table S2, the correlation coefficient R^2 values are close or greater than 0.95, verifying that the E_a values obtained by the Arrhenius equation were tenable within 80~200 ℃. The activation energy of Hg^0 adsorption over PC-S, PC-NS and PC-SC was 68.61 kJ/mol, 54.18 kJ/mol and 96.49 kJ/mol respectively. It illustrates that the mercury adsorption on SO_2 activated cokes PC-S, PC-NS and PC-SC are governed by chemisorption process.[5]

References:

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4. El-Khaiary, M. I.; Malash, G. F., Common data analysis errors in batch adsorption studies. *Hydrometallurgy*. **2011,** 105, (3-4), 314-320.

5. Liu, D. J.; Zhou, W. G.; Wu, J., Texture and structure variation of perovskite $LaFeO_3$/ZSM-5 during high-temperature desulfurization. *Surface Review and Letters*. **2020,** 27, (5) , 1950151.

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Table S1. Kinetic parameters of the pseudo-second-order kinetic model for mercury adsorption onto SO_2 activated cokes at 80~200 ℃.

	Temperature (℃)	q_e (μg/g)	k_2 (g·μg^{-1}·min^{-1})	R^2
PC-S	80	339.15	8.79×10^{-6}	0.989
	120	123.28	7.06×10^{-5}	0.992
	160	67.10	2.26×10^{-4}	0.997
	200	13.62	4.74×10^{-3}	0.999
PC-NS	80	464.02	4.46×10^{-6}	0.990
	120	144.61	5.19×10^{-5}	0.991
	160	71.06	1.65×10^{-4}	0.998
	200	30.81	5.20×10^{-4}	0.989
PC-SC	80	1370.48	4.70×10^{-7}	0.992
	120	204.33	2.26×10^{-5}	0.993
	160	36.85	8.06×10^{-4}	0.992
	200	22.32	1.27×10^{-3}	0.993

Table S2. Fitting Results of the Arrhenius Equation.

Sorbents	Slope	Intercept	R^2	E_a (kJ/mol)
PC-S	-8252.65	11.48	0.946	68.61
PC-NS	-6516.94	6.35	0.984	54.18
PC-SC	-11605.31	18.66	0.955	96.49

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Fig. S1. XPS spectra of S_{2p} for raw high-sulfur petroleum coke.

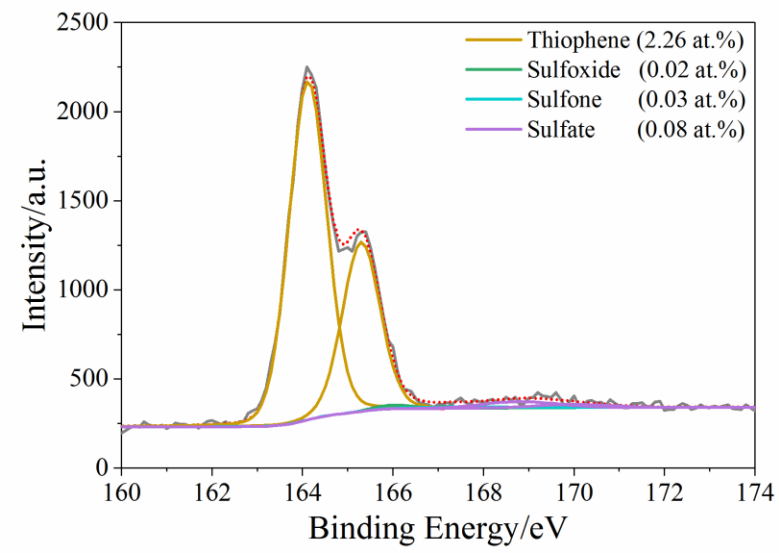

Fig. S2. Hg^0 adsorption performance of raw PC at 35 μg/m^3 and 160℃.

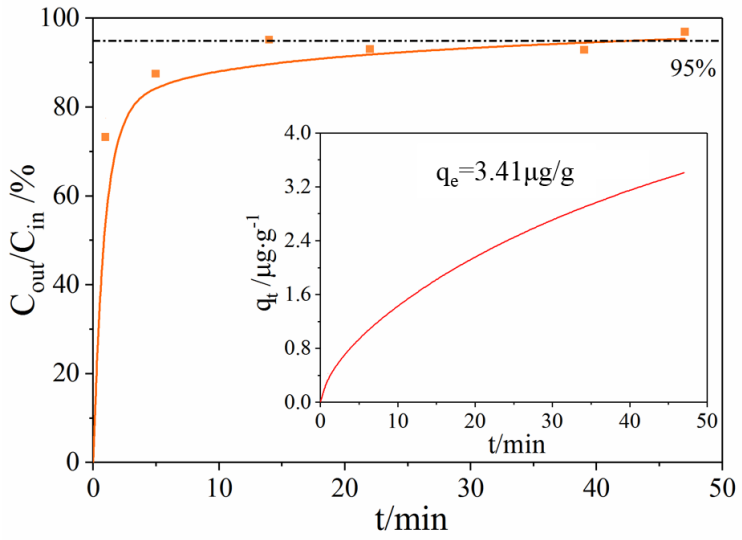

Fig. S3. Fitting curves of the pseudo-second-order kinetic model.

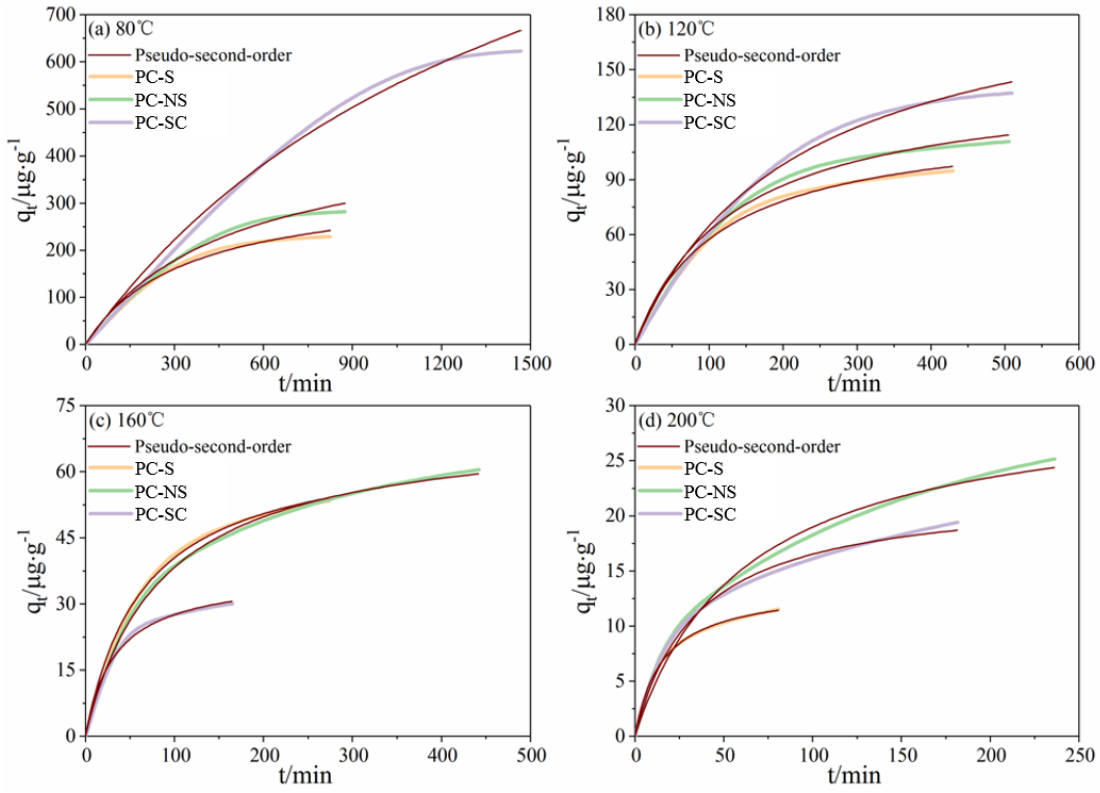

Fig. S4. Fitting curves of the Arrhenius equation.