Adsorption kinetics of SO₂ on powder activated carbon

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Abstract. The flue gas SO_2 adsorption removal by powder activated carbon is investigated based on a fixed bed reactor. The effect of SO_2 inlet concentration on SO_2 adsorption is investigated and the adsorption kinetics is analyzed. The results indicated that the initial SO_2 adsorption rate and the amount of SO_2 adsorbed have increased with increased in SO_2 inlet concentration. Gas diffusion, surface adsorption and catalytic oxidation reaction are involved in SO_2 adsorption on powder activated carbon, which play a different role in different stage. The Bangham kinetics model can be used to predict the kinetics of SO_2 adsorption on powder activated carbon.

1. Introduction

SO_2 adsorption by activated carbon (coke) is a kind of dry flue gas desulfurization technology, which can reduce SO_2 emission, recovery sulphur, and reduce the other pollutants in flue gas (SO_3, NOx, dioxin, mercury, etc.). Activated carbon desulfurization has a broad application prospects[1-4].

Cylindrical coal activated carbons of diameter of 5~9 mm are employed in the industrial applications of activated carbon desulfurization, which has the drawbacks of high inner diffusion resistance and low inner surface utilization ratio but the powder activated carbons present better SO_2 adsorption performance[5]. Ma[5] proposed a technology that SO_2 is removed by powder activated carbon (PAC) in the circulating fluidized bed and performed some researches.

SO_2 adsorption on activated carbon involves gas film diffusion, pore diffusion and surface adsorption and the adsorption occurs when the adsorbate molecules from the gas phase diffuse to the activated carbon's micropore surface. The adsorption rate is controlled by one of the slowest step. Adsorption kinetics is the basis of adsorption rate and adsorption process design, including intrinsic kinetics and apparent kinetics. The intrinsic kinetics is established based on the mechanism model, and the apparent adsorption kinetics is determined by classic and empirical formula. Apparent adsorption dynamics model can reflect a certain adsorption reaction mechanism and also present the change of the dynamic adsorption process using a dynamic model of unified description, which is widely used in describing the adsorption process. The commonly used models include pseudo first-order kinetics model, pseudo second-dynamics model, intraparticle diffusion model, Elovich kinetics model and Bangham adsorption dynamics model[5-9].

In this paper, the flue gas SO_2 adsorption by powder activated carbon is investigated based on a fixed bed reactor. The effect of SO_2 inlet concentration on SO_2 adsorption is investigated and the adsorption kinetics is analyzed.
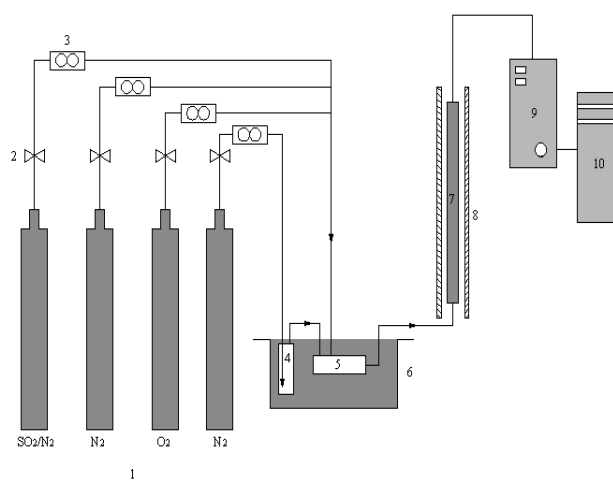
2. Experiments

2.1. Activated carbon

A commercial granular activated carbon was grinded and screened, and a PAC of 0.075 mm in size was selected. The PAC was washed with distilled water and then dried for 24 h at 105 °C in an oven. The pore texture of the activated carbon was characterized by N_2 adsorption isotherms at 77 K using a Micromeritics ASAP2020 instrument. The specific surface area (A_{BET}) was calculated from N_2 adsorption data using the BET equation. The total pore volume (V) was determined by the N_2 adsorption capacity at $P/P_0 = 0.98$. The micropore specific surface area (A_{mic}) and volume (V_{mic}) were calculated using the t-plot method. The average pore size (L) was calculated with $4V/A_{BET}$.

2.2. SO_2 adsorption

The schematic diagram of the experimental apparatus is shown in figure 1[5]. It consists of a unit for preparation of the model flue gas, a glass fixed bed reactor and a gas analysis system. The reactor has a length of 500 mm with a porous glass plate placed at 250 mm from the bottom of the reactor and has an inner diameter of 15 mm. The model flue gas is composed by high purity nitrogen, high purity oxygen, 5% (V/V) SO_2 and H_2O in N_2. Each gas is first individually introduced through a mass flow controller (Sevenstar CS200) and then mixed in the mixing chamber.

All experiments were conducted with a gas flow of 400 ml/min (at 1 bar, 298 K). SO_2 adsorption was performed at 338 K, and the concentration of SO_2 was in the range 0.02~0.3%, oxygen 6%, H_2O 8% and the balance was N_2. A sample of activated carbon of 0.5 g was placed on the porous plate and N_2 of 400 ml/min was kept for 30 min before experiment started to outgas the air. The N_2 was then changed into the model flue gas and the adsorption of SO_2 began. The concentration of SO_2 at the outlet of the reactor was monitored continuously using a Fourier-transform IR flue gas analyser (GASMET, DX-4000).The amount of SO_2 adsorption on powder activated carbon was calculated by SO_2 breakthrough curve.

1-Gas cylinder, 2-Valve, 3-Mass flow controller, 4-Water, 5-Gas mixer, 6-Water bath, 7-Reactor, 8-Electric heating device, 9-FT-IR gas analyzer, 10-Data collection system

Figure 1. Schematic diagram of the experimental system.

3. Results and discussion

3.1. Characterization of powder activated carbon pore texture

Figure 2 shows that the N_2 isotherm of powder activated carbon is of TypeI [10], which shows that it is essentially a microporous solid according to the IUPAC classification. A desorption hysteresis in the region of high relative pressure shows that the powder activated carbon has some mesopores.

Pore structural properties of powder activated carbon are shown in table 1. The powder activated carbon has a large specific surface area and a developed micropore structure. The total pore volume is mainly composed of micropore and a small amount of mesopore. The average pore width is larger than SO_2 diameter, O_2 diameter, and H_2O diameter, which can allow the molecules to diffuse into the pores.
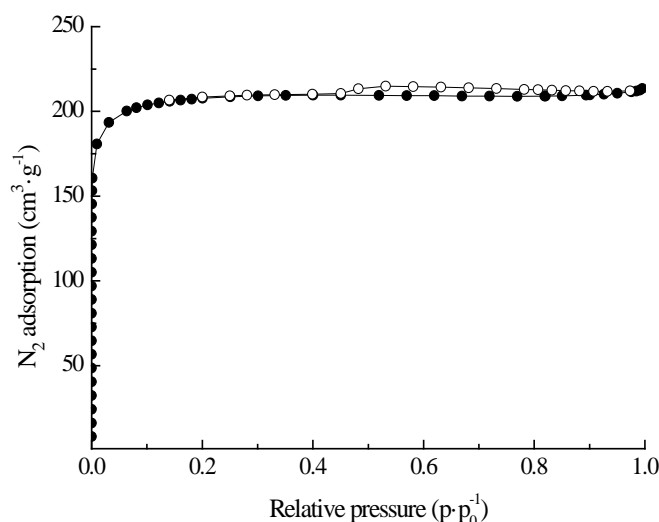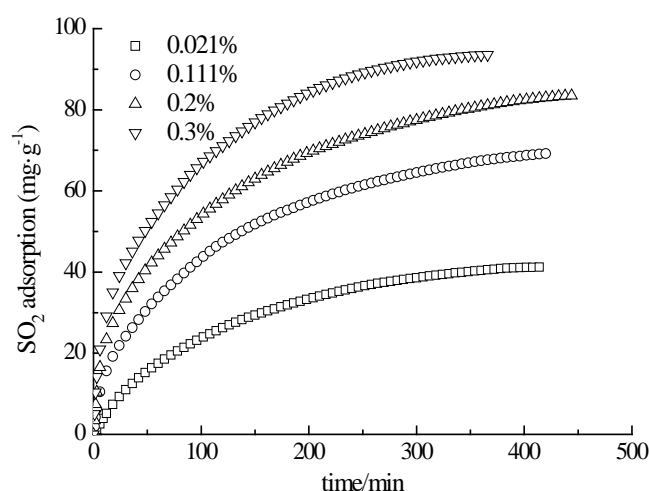
Figure 2. Nitrogen adsorption isotherm (77k) for powder activated carbon.

Table 1. Pore structural characteristics of activated carbon.

Sample	$A_{BET}(m^2 \cdot g^{-1})$	$A_{mic}(m^2 \cdot g^{-1})$	$V_{mic}(cm^3 \cdot g^{-1})$	$V(cm^3 \cdot g^{-1})$	$L(nm)$
PAC	624.3	541.1	0.285	0.328	2.101

3.2. The effect of SO_2 concentration on SO_2 adsorption

Figure 3. The effect of SO_2 inlet concentration on SO_2 adsorption.

The effect of SO_2 inlet concentration on SO_2 adsorption is as shown in figure 3. SO_2 adsorption increases gradually with increased SO_2 inlet concentration. When SO_2 concentration increases from 0.021% to 0.3%, SO_2 saturated adsorption capacity increases from 41.2 mg·g^{-1} to 93.6 mg·g^{-1}. The initial SO_2 adsorption rate increases dramatically and the subsequent adsorption rate tend to be more

consistent with increased SO_2 concentration. The SO_2 concentration difference between the gas and activated carbon surface increases with increased SO_2 inlet concentration, which leading the driving force to overcome the mass transfer resistance between the gas and the activated carbon surface increasing, and then the initial SO_2 adsorption rate and saturated adsorption capacity increase.
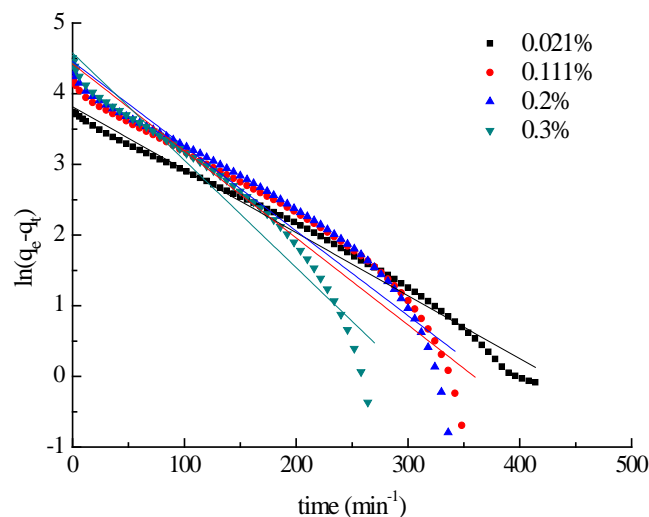
3.3. The adsorption kinetics of SO_2 onto powder activated carbon

3.3.1. Pseudo first-order kinetics model The pseudo first-order kinetics model has the form:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

(1)

Where k_1 is the rate constant of the pseudo first-order adsorption (min^{-1}), and q_e and q_t are the amount of SO_2 adsorbed per unit mass of powder activated carbon (mg·g^{-1}) at time t and equilibrium. After definite integration by applying the initial conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, equation (1) becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

(2)

Figure 4. The pseudo first-order kinetics model for SO_2 adsorption.

The plot $ln(q_e-q_t)$ versus t gives no straight lines as shown in figure 4. The pseudo first-order kinetics describes the surface adsorption is a first order of nature, which is the rate-controlling step. Results in figure 4 show that pseudo first-order kinetics cannot fit well the kinetic results for the entire range of adsorption time, which suggest that SO_2 adsorption onto powder activated carbon is not a first-order process.

3.3.2. Pseudo second-order kinetics model The pseudo second-order kinetics model has the form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

(3)

Where k_2 is the rate constant of the pseudo second-order adsorption (g·(mg·min)$^{-1}$). After definite integration by applying the initial conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, equation (3) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

(4)

Figure 5 shows the plot between t/q_t versus time t. The pseudo second-order kinetics assumes that chemisorption is the rate-controlling step in adsorption process. The pseudo second-order kinetics cannot fit well the kinetic results in the initial stage for SO_2 adsorption onto the powder activated

carbon, which confirm that the adsorption process does not follow a pseudo second-order mechanism and suggest that surface adsorption and reaction is not rate-controlling step in SO_2 adsorption process.
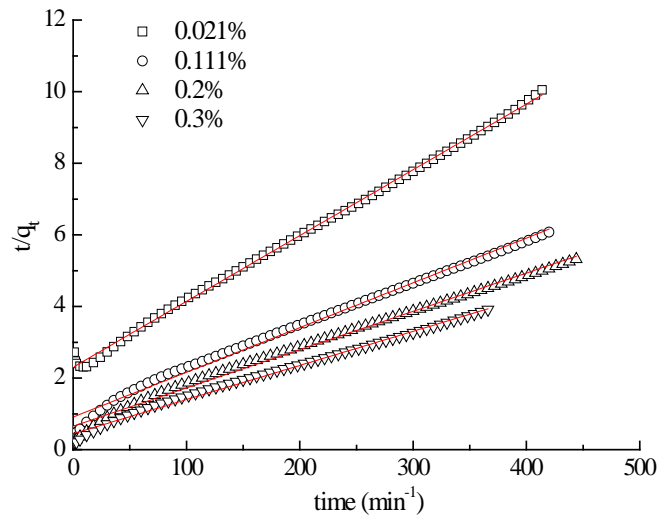
Figure 5. The pseudo second-order kinetics model for SO_2 adsorption.

3.3.3. Intraparticle diffusion model
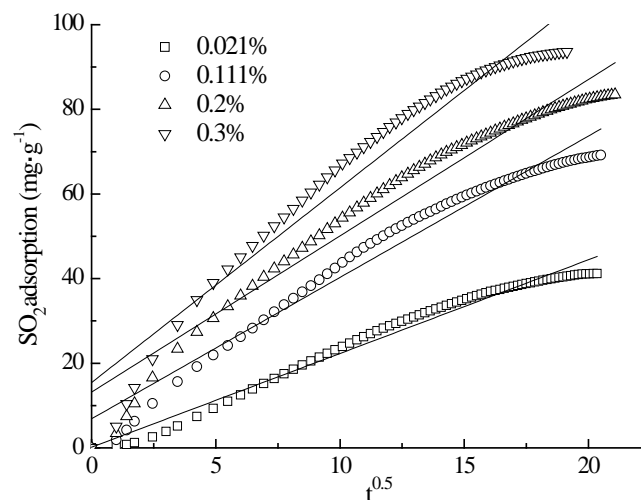
Figure 6. The intraparticle diffusion model for SO_2 adsorption.

The intraparticle diffusion model has the form:

$$q_t = k_{id}t^{0.5} + C \tag{5}$$

Where k_{id} is the rate constant of the intraparticle diffusion model (g·mg^{-1}·min$^{-0.5}$)), and C is a constant (mg·g^{-1}). If the plot of q_t versus $t^{0.5}$ gives straight lines, intraparticle diffusion is the rate-controlling step in adsorption process.

Figure 6 shows the plot of q_t versus $t^{0.5}$. According to equation (5), a plot of q_t versus $t^{0.5}$ should be a straight line when adsorption mechanism follows the intraparticle diffusion process. As shown in figure 6, there is not a straight line between q_t and t in the adsorption process, but the plot of q_t versus $t^{0.5}$ give straight lines in different stage, which suggest that different reactions in different stages are controlling the adsorption process.

3.3.4. Elovich kinetics model A widely used equation to describe the kinetics of chemisorptions of gas on an energetically heterogeneous solid is proposed by Elovich. The Elovich kinetics model has the form:

$$\frac{dq_t}{dt} = a\exp(-bq_t)$$

(6)

Where a (mg·(g·min)$^{-1}$)and b (mg·g^{-1}) are constants. After definite integration by applying the initial conditions q_t=0 at t=0, equation (6) becomes:

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t)$$

(7)

Figure 7 shows the plot of q_t versus $\ln(t)$. According to equation (7), a plot of q_t versus $\ln(t)$ should be a straight line when adsorption mechanism follows the Elovich equation. As shown in figure 7, Elovich model does not fit the data for the adsorption of SO_2 very well. The theoretical curves at high SO_2 concentration are highly deviate from the experimental data.
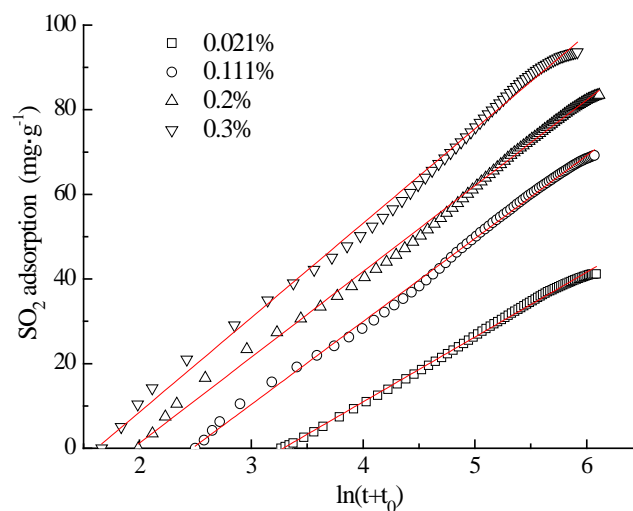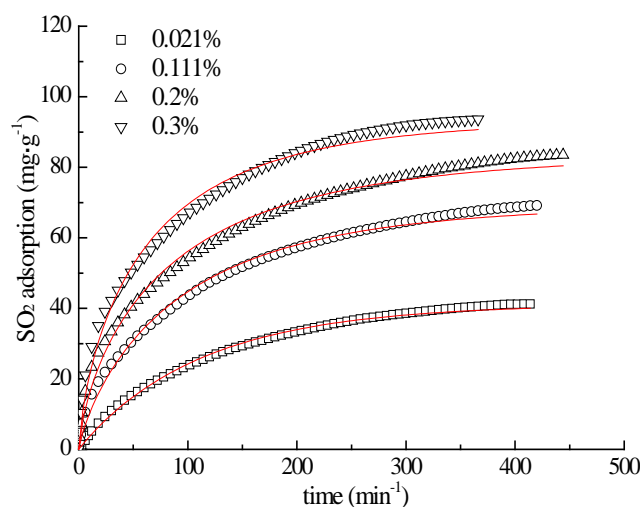

Figure 7. The Elovich kinetics model for SO_2 adsorption.

3.3.5. Bangham kinetics model The Bangham kinetics model has the form:

$$q_t = q_e(1 - e^{-kt^n})$$

(8)

Where k and n are constants.

Figure 8 shows the plot of q_t versus t. The parameters of Bangham model fitting are shown in table 2. As shown in figure 8 and table 2, Bangham model can fit the data for the adsorption of SO_2 very well. Bangham adsorption dynamics model can better describes the adsorption of SO_2 onto powder activated carbon. Gas diffusion, surface adsorption and catalytic oxidation reaction are involved in SO_2 adsorption on powder activated carbon, which play a different role in different stage [5-6].

Figure 8. The Bangham kinetics model for SO_2 adsorption.

Table 2. Parameters of Bangham model fitting.

Sample	SO_2 concentration (%)	q_e(mg·g^{-1})	k (min^{-n})	n	R^2
	0.021	41.2	0.0099	0.975	0.9965
PAC	0.111	69.3	0.0250	0.809	0.9936
	0.2	83.6	0.0404	0.720	0.9902
	0.3	93.6	0.0483	0.724	0.9886

4. Conclusions

The initial SO_2 adsorption rate and the saturated amount of SO_2 adsorbed onto powder activated carbon increase with SO_2 increased inlet concentration. Gas diffusion, surface adsorption and catalytic oxidation reaction are involved in SO_2 adsorption on powder activated carbon, which play a different role in different stage. The Bangham kinetic model can be used to predict the kinetics of SO_2 adsorption on powder activated carbon.

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