Adsorption kinetics of SO2 on powder activated carbon

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Abstract. The flue gas SO2 adsorption removal by powder activated carbon is investigated based on a fixed bed reactor. The effect of SO2 inlet concentration on SO2 adsorption is investigated and the adsorption kinetics is analyzed. The results indicated that the initial SO2 adsorption rate and the amount of SO2 adsorbed have increased with increased in SO2 inlet concentration. Gas diffusion, surface adsorption and catalytic oxidation reaction are involved in SO2 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 SO2 adsorption on powder activated carbon.

1. Introduction

SO2 adsorption by activated carbon (coke) is a kind of dry flue gas desulfurization technology, which can reduce SO2 emission, recovery sulphur, and reduce the other pollutants in flue gas (SO3, 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 SO2 adsorption performance[5]. Ma[5] proposed a technology that SO2 is removed by powder activated carbon (PAC) in the circulating fluidized bed and performed some researches.

SO2 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 SO2 adsorption by powder activated carbon is investigated based on a fixed bed reactor. The effect of SO2 inlet concentration on SO2 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 N₂ adsorption isotherms at 77 K using a Micromeritics ASAP2020 instrument. The specific surface area ($A_{BET}$) was calculated from N₂ adsorption data using the BET equation. The total pore volume ($V$) was determined by the N₂ 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. SO₂ 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) SO₂ and H₂O in N₂. 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). SO₂ adsorption was performed at 338 K, and the concentration of SO₂ was in the range 0.02~0.3%, oxygen 6%, H₂O 8% and the balance was N₂. A sample of activated carbon of 0.5 g was placed on the porous plate and N₂ of 400 ml/min was kept for 30 min before experiment started to outgas the air. The N₂ was then changed into the model flue gas and the adsorption of SO₂ began. The concentration of SO₂ at the outlet of the reactor was monitored continuously using a Fourier-transform IR flue gas analyser (GASMET, DX-4000). The amount of SO₂ adsorption on powder activated carbon was calculated by SO₂ breakthrough curve.

3. Results and discussion

3.1. Characterization of powder activated carbon pore texture
Figure 2 shows that the N₂ isotherm of powder activated carbon is of Type I [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 SO2 diameter, O2 diameter, and H2O diameter, which can allow the molecules to diffuse into the pores.

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

3.2. The effect of SO2 concentration on SO2 adsorption

The effect of SO2 concentration on SO2 adsorption is as shown in Figure 3. SO2 adsorption increases gradually with increased SO2 inlet concentration. When SO2 concentration increases from 0.021% to 0.3%, SO2 saturated adsorption capacity increases from 41.2 mg·g\(^{-1}\) to 93.6 mg·g\(^{-1}\). The initial SO2 adsorption rate increases dramatically and the subsequent adsorption rate tend to be more
consistent with increased SO2 concentration. The SO2 concentration difference between the gas and activated carbon surface increases with increased SO2 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 SO2 adsorption rate and saturated adsorption capacity increase.

3.3. The adsorption kinetics of SO2 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 SO2 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 \( q_t = q_e \) at \( t = t \), equation (1) becomes:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  

(2)

Figure 4 shows the plot \( \ln(q_e - q_t) \) versus time \( t \). The pseudo first-order kinetics assumes that chemisorption is the rate-controlling step in adsorption process. The pseudo first-order kinetics cannot fit well the kinetic results in the initial stage for SO2 adsorption onto the powder activated carbon.

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 \( q_t = q_e \) at \( t = t \), equation (3) becomes:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]  

(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 SO2 adsorption onto the powder activated carbon.
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 SO2 adsorption process.

![Graph](image)

**Figure 5.** The pseudo second-order kinetics model for SO2 adsorption.

### 3.3.3. Intraparticle diffusion model

The intraparticle diffusion model has the form:

\[ q_t = k_{id} t^{0.5} + C \]  

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.

![Graph](image)

**Figure 6.** The intraparticle diffusion model for SO2 adsorption.

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.](image)

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

\[
q_t = q_e (1 - e^{-kt})
\]

(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$^{-1}$) | n | R$^2$ |
|--------|--------------------------|-------------------|--------------|---|-------|
| PAC    | 0.021                    | 41.2              | 0.0099       | 0.975 | 0.9965 |
|        | 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.

References
[1] Jastrzab K 2012 Fuel Process. Technol. 101 16
[2] Izquierdo M T, Rubio B and Mayoral C 2003 Fuel 82 147
[3] Kisiela A M, Czajka K M and Moroń W 2016 Energy 116 1454
[4] Rosas J M, Ruiz-Rosas R and Cordero T 2017 Chem. Eng. J. 307 707
[5] Li B 2012 Experimental study on adsorption removal of SO$_2$ from flue gas by powder activated carbon in circulating fluidized bed (Jinan: Shandong University)
[6] Li B, Jiang H T and Zhang L Q 2012 J. Chin. Coal. Soc. 37 1737
[7] Kennedy L J, Vijaya J J and Sekaran G 2007 J. Hazard. Mater. 149 134
[8] Yin Y S, Zhang J and Sheng C D 2010 Proceedings of the CSEE 30 49
[9] Gao J X 2010 Studies of flue gas purification and sulfur recovery process by carbon moving bed temperature swing adsorption method (Beijing: Tsinghua University)
[10] Zhang Y H 1989 Adsorption (Shanghai: Shanghai Science and Technology Literature Press)