Research Article

Shaopeng Zhang, Zhuang Li*, Yanchun Yang, Weiwei Jian, Danzhu Ma*, and Fengrui Jia*

Kinetics and thermodynamics of SO₂ adsorption on metal-loaded multiwalled carbon nanotubes

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Abstract: To investigate the adsorption kinetics and thermodynamic adsorption mechanism and laws of dry flue gas desulfurization, we prepared a new adsorbent by loading Cr, Cu, and Zn on TiO₂-loaded multiwalled carbon nanotubes. Desulfurization experiments were also carried out. In this study, three kinds of samples were used for simulation and diffusion processes in the dynamic adsorption of different SO₂ volume fractions in flue gas and thermodynamic model analysis of different temperatures in flue gas. Results show that the diffusion coefficient of SO₂ in three kinds of samples ranges from 10⁻¹⁶ to 10⁻¹⁴ m² s⁻¹, and the diffusion may be dominated by configuration diffusion. The intraparticle diffusion model predicts that the performance improves with an increase in the SO₂ volume fraction and a shift of adsorption time. This finding indicates that an increase in SO₂ volume fraction and a change in adsorption time increase the Kundsén diffusion specific gravity and decrease the configuration diffusion specific gravity, thereby increasing the SO₂ diffusion resistance, which becomes faster than the activation energy barrier resistance in the catalytic oxidation reaction. Thus, the diffusion resistance specific gravity increases in the total resistance of the diffusion reaction. One possible mechanism of the adsorption process is the transition to surface reaction control at the early stage of adsorption to joint control of

late diffusion and surface reactions. Adsorption thermodynamics studies show that SO₂ adsorption by three adsorbents is a spontaneous, exothermic, and entropic reduction process, and the increase in temperature is inconducive for SO₂ adsorption in three samples.

Keywords: SO₂, adsorption, kinetics, thermodynamics

1 Introduction

SO₂ produced by coal combustion causes considerable harm to the environment, such as acid rain formation in water ecosystem, terrestrial ecosystem, and buildings in cities [1–4], and results in direct or indirect damage on materials and human health. Thus, flue gas desulfurization is important. Dry flue gas desulfurization is the most effective way to control SO₂ pollution [5,6]. Carbon nanotubes (CNTs) have attracted considerable attention from scholars locally and internationally due to their unique pore structure and excellent adsorption characteristics [7–9].

CNTs can be used as adsorbents to adsorb various industrial waste gases [9–12]. The adsorption capacity of CNTs for organic compounds is generally higher than that of activated carbon and other C-based adsorbents. The doping of metals, such as Fe, Cu, Mn, Ni, and Ti, is an effective method to significantly increase the oxidizing power of carbonaceous catalysts [13–17].

Comparing the prediction results calculated by the adsorption model with the adsorption behavior of different adsorbents under varied experimental conditions is crucial for accurately describing the adsorption process [18]. In all models, adsorption thermodynamics can predict the final state of a system from an initial nonequilibrium mode, and adsorption kinetic can determine the rate of adsorption and the time of the entire adsorption process. Therefore, in the analysis of the adsorption process, it is necessary to use both adsorption thermodynamics and adsorption kinetic to determine the model adsorption parameters. The determination of the model's adsorption parameters permits to optimize the adsorption

* **Corresponding author: Zhuang Li**, Liaoning Shihua University, College of Petroleum Engineering, Fushun, 113006, China, e-mail: lizhuang@lnpu.edu.cn

* **Corresponding author: Danzhu Ma**, Liaoning Shihua University, College of Petroleum Engineering, Fushun, 113006, China, e-mail: madanzhu@lnpu.edu.cn

* **Corresponding author: Fengrui Jia**, Liaoning Shihua University, College of Petroleum Engineering, Fushun, 113006, China, e-mail: frjia@lnpu.edu.cn

Shaopeng Zhang, Weiwei Jian: Liaoning Shihua University, College of Petroleum Engineering, Fushun, 113006, China

Yanchun Yang: Beijing University of Technology, College of Environmental and Energy Engineering, Beijing, 100000, China

mechanism pathways, to express the dependence of the surface properties of the adsorbent on the sorption results, and to determine the adsorbent capacities and design effectively the adsorption systems [19]. Elashgh *et al.* [20] studied the adsorption equilibrium and adsorption kinetics of the basic red 46 on multiwalled CNT (MWCNT). Banerjee *et al.* [21] examined the adsorption effects of CNTs on rhodamine B and methyl orange and performed adsorption equilibrium and adsorption kinetics fitting. Under suitable conditions, when SO₂ in the flue gas adsorbs the catalyst bed through the C-based catalyst, chemical adsorption accompanying the catalytic oxidation reaction occurs, and H₂SO₄ is formed and adheres to the pores of the C-based adsorption catalyst to realize SO₂ removal and recover S resources during adsorbent regeneration [22–24]. During the chemisorption process, two physical and chemical processes, including surface reaction and diffusion, which play different roles in influencing the SO₂ adsorption rate and dynamic adsorption process [25–27], respectively, are involved. The dynamic adsorption and diffusion behavior of SO₂ on C-based adsorbents have rarely been reported by theory or model. In-depth study on the role of diffusion and surface reaction in C flue gas desulfurization and analysis of the role, laws, and mechanisms of diffusion in dynamic adsorption to provide deep insight into the physical and chemical mechanisms of adsorption is important in guiding the process of development.

In this study, three types of adsorbents, namely, MWCNT/TiO₂ + Cr, MWCNT/TiO₂ + Cu, and MWCNT/TiO₂ + Zn, were synthesized by sol–gel method and used for SO₂ adsorption. According to the fixed bed reaction system, the dynamic adsorption of samples in flue gas was studied, and the adsorption kinetics and thermodynamic analysis of these samples were systematically performed.

2 Adsorbent and experiment

The raw MWCNTs (purity: >95%, diameter: 10–15 nm, length: 10–30 mm) were provided by the Chinese Academy of Sciences Chengdu Organic Chemistry Co., Ltd. The new adsorbents, namely, MWCNT/TiO₂ + Cr, MWCNT/TiO₂ + Cu, and MWCNT/TiO₂ + Zn, were prepared by sol–gel method by using tetrabutyl titanate and MWCNTs for SO₂ adsorption experiments. The experimental device is shown in Figure 1. In this experiment, N₂, 9% O₂, 5% H₂O, and SO₂ were used to simulate the flue gas. The flow rates of N₂, O₂, and SO₂/N₂ were precisely controlled by the mass flowmeter. H₂O was carried by a N₂ shock constant

Figure 1: Experimental system. 1 – Gas cylinders (SO₂, O₂, N₂); 2 – reducing valve; 3 – mass flowmeter; 4 – blending gas bottle; 5 – water bubbler; 6 – portable flue gas analyzer; 7 – wet flowmeter; 8 – thermometer; 9 – tube heating furnace; 10 – fix-bed reactor; 11 – flue gas analyzer; 12 – tail gas treatment bottle.

temperature water bath. After the gas was uniformly mixed, it entered the reactor and insulated from the mixer to the reactor inlet line to ensure that H₂O exists in the gas form. The experimental simulated flue gas was accurately measured via flue gas analysis (Gasboard-300) by using flue gas analyzer Testo-365 (Testo Instrument International Trading Co., Ltd., Germany). The preparation, characterization, and performance of MWCNT/TiO₂ + Cr, MWCNT/TiO₂ + Cu, and MWCNT/TiO₂ + Zn adsorbents have been published in an earlier study detailed in *ref.* [28].

The adsorption capacity of conversion of prepared adsorbents was calculated using the following formula:

$$q_t = \frac{(C_0 - C) \cdot M \cdot L}{m} \quad (1)$$

$$q_e = \int_0^t \frac{(C_0 - C) \cdot M \cdot L}{m} dt \quad (2)$$

where C_0 and C are the volume fractions (mg/m³) of SO₂ in inlet and outlet flue gas, respectively, M is the molar mass (g/mol) of SO₂, L is the flow (L/min) of gas, m is the mass (g) of adsorbent, and t is the adsorption time (min) to reach SO₂ adsorption equilibrium.

3 Adsorption kinetic models

The adsorption process usually consists of three steps. First, the adsorbate is transferred from the outside to the outer surface of the adsorbent. Then the adsorbate diffuses to the adsorption site in the adsorbent and finally

the adsorption itself. Adsorption and diffusion are considered the main steps to limit the rate of adsorption. So the fitting to the models permits elucidation of the adsorption mechanism adsorbate.

3.1 Diffusion-type apparent adsorption kinetic model

In adsorption kinetics, the diffusion models assume that the diffusion is the rate-limiting step. And the diffusion models usually obtained a straight line passing through the origin. They are divided in two parts, the external mass transfer model and the internal diffusion models. According to the difference in the details of the particle, Ho divided into particle diffusion and pore diffusion models and discussed it [29]. For intraparticle diffusion, Boyd derived the Boyd intraparticle diffusion model, and Weber and Morris model was used to deduce a pore diffusion model [30].

The intraparticle diffusion model can be solved by diffusion partial differential equations and hypothesized according to different situations [31,32]. In these situations, by solving the partial differential equation describing the microspore diffusion of spherical particles [31,32], equation (3) can be obtained. At the initial stage of adsorption, equation (4) was obtained, where *ierfc* is expressed as the inverse function of the residual error function [33].

$$\frac{\bar{q} - q_0^*}{q - q_0^*} = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_e t}{R^2}\right) \quad (3)$$

$$\frac{q_t}{q_e} = 6 \left(\frac{D_e t}{R^2}\right)^{\frac{1}{2}} \left[\frac{1}{\sqrt{\pi}} + 2 \sum_{n=1}^{\infty} \text{ierfc}\left(\frac{nR}{\sqrt{D_e t}}\right) \right] - 3 \frac{D_e t}{R^2} \quad (4)$$

where $F = q_t/q_e$, $B = \pi D_e/R^2$; and for any shape of the particle, $3V/A$ can be used instead of R of the spherical particle.

When $q_t/q_e < 0.3$ [32], the Boyd–Crank–Ruthven, Weber and Morris I, and Weber and Morris II intraparticle diffusion models were applicable. Boyd et al. [30] also derived the Boyd model that describes the effects of extraparticle fluid films. For intraparticle diffusion effects, the Dumwald–Wagner intraparticle diffusion model can be used to describe the overall intraparticle diffusion effect. According to Ruthven, at the late stage of adsorption, when $q_t/q_e > 0.7$, equation (1) only retains the first term of the series expansion to meet the prediction requirements. Combined with the studies of Boyd and Ho, the Boyd–Ruthven–Ho model can be obtained [30].

Acharya et al. [32] used the Boyd–Ruthven–Ho model to investigate the internal diffusion effect of the flow–solid system over the entire adsorption range.

3.2 Theoretical expression of models

3.2.1 Boyd–Crank–Ruthven model

The Boyd–Crank–Ruthven model assumes that the adsorbent diffuses uniformly in the spherical model and that the surface diffusion rate D_e at all points in the particle is constant.

$$\frac{q_t}{q_e} \approx \frac{6}{\sqrt{\pi}} \left(\frac{D_e t}{R^2}\right)^{\frac{1}{2}} = k_{i, \text{BCK}} t^{\frac{1}{2}} \quad (5)$$

With the spheres initially free of solutes and the solute concentration on the surface kept constant, the Boyd–Crank–Ruthven model provides an accurate solution to this equation at any given time to resolve the average concentration in solids.

3.2.2 Weber and Morris model

Weber and Morris model has shown that the plot of q_t/q_e versus $t^{1/2}$ could be decomposed in two linear plots, the first one corresponding to equation (6):

$$q_t \approx \frac{6}{\sqrt{\pi}} \left(\frac{D_e t}{R^2}\right)^{\frac{1}{2}} q_e = k_{i, \text{WMI}} t^{\frac{1}{2}} \quad (6)$$

and the second one to equation (7):

$$q_t = k_{i, \text{WMI}} t^{\frac{1}{2}} \quad (7)$$

3.2.3 Dumwald–Wagner model

Dumwald–Wagner model should be linear and the rate constant $k_{i, \text{DW}}$ can be obtained from the slope. Dumwald–Wagner model proved to be reasonable to model different kinds of adsorption systems.

3.2.4 Boyd pseudo first model

The Boyd pseudo first-order model is described by the nonreversible equation:

$$\log(1 - F) = -\frac{k_{i,B}}{2.303}t \quad (8)$$

Boyd pseudo first model assumes that adsorption occurs only locally and the interactions between the adsorbed ions are ignored. In addition, the model also considers the energy of adsorption is not dependent on surface coverage. And maximum adsorption corresponds to a saturated monolayer of adsorbates on the adsorbent surface [30].

3.2.5 Boyd–Ruthven–Ho model

$$B_t = -0.4977 - \ln(1 - F) \quad (9)$$

The assumptions are almost the same as for the Boyd pseudo first model.

4 Results and discussion

4.1 Adsorption kinetic simulation results and analyses

The SO₂ equilibrium adsorption amount corresponding to different SO₂ volume fractions of three different samples in the flue gas was obtained by nonlinear fitting of dq_t/dt when $dq_t = 0$. The corresponding q_t is the experimental approximate estimated value and q_e is the SO₂ equilibrium adsorption amount, as shown in Table 1.

The adsorption behavior of different SO₂ volume fractions in flue gas was simulated by diffusion-controlled apparent adsorption kinetic model. The results are shown in Figures 2–5 and Tables 2–4. Among these SO₂ volume fractions, Figure 2 lists the simulation and experimental results of the Dumwald–Wagner and the Weber and Morris I models. Figure 3 lists the simulation results of the Weber and Morris II model. Figure 4 lists the simulation results of the Boyd–Crank–Ruthven intraparticle diffusion model. Figure 5 shows the simulation and experimental results of the Boyd quasi-first-order and Boyd–Ruthven–Ho intraparticle diffusion models. Among them the working condition of SO₂ volume fraction of $2,000 \times 10^{-6}$ in Figure 3 was the baseline, and the results simulated by the Weber and Morris II model were cited. At the same time, due to MWCNT/TiO₂ + Cr, MWCNT/TiO₂ + Cu, and MWCNT/TiO₂ + Zn, the microspores with a pore size of 0.8 nm were mainly used in these samples. Thus, the diffusion resistance in the particles is mainly concentrated in the microspores. The configuration had a

diffusion resistance, whereas the Kundsens diffusion or molecular diffusion resistance of the mesopores and microspores was small. The changes in SO₂ volume fraction and adsorption time resulted in changes in the overall chemisorption behavior by affecting the diffusion and surface reactions.

Figure 2 shows that the Dumwald–Wagner model had low prediction accuracy for MWCNT/TiO₂ + Cr and MWCNT/TiO₂ + Cu, but the prediction accuracy for MWCNT/TiO₂ + Zn was high, and the initial simulation value of SO₂ adsorption deviation of the experimental value was large. The deviation became small at the late stage of adsorption. As the SO₂ volume fraction in the flue gas increased, and the SO₂ volume fraction increased to $2,000 \times 10^{-6}$, the prediction accuracy of the model showed an increment, and deviation decreased.

Figure 3 shows that the three simulated straight lines of the Weber and Morris II model with boundary layer effect parameters did not pass through the origin, thereby indicating that intragranular pore diffusion was not the only rapid control step for SO₂ chemisorption on these samples. Among three simulated straight lines, within 60 min of the pre-adsorption period, the specific gravity (q_t/q_e) of the SO₂ adsorption amount to the SO₂ equilibrium adsorption amount was within 0.3, and the straight line generated by the simulated value of the model was still not the coordinate origin. When the q_t/q_e value was between 0.5 and 0.6, the simulation was predicted within the wide range of adsorption and adsorption time, the deviation between the simulated value and the experimental value was large, and the straight line obtained by the analog value was not the coordinate origin. As the adsorption time progressed, the prediction accuracy of intragranular pored diffusion II increased. This phenomenon indicated that the boundary layer effect was considerably affected at the initial stage of adsorption, and the boundary layer effects decreased with time.

Figure 4 and Tables 2–4 show that the simulated value of the Boyd–Crank–Ruthven intraparticle diffusion model evicted significantly from the experimental value, and the deviation became small with time. As the SO₂ volume fraction increased, the correlation coefficient became large, and the fitting effect improved. This finding indicated that intraparticle diffusion (microporous diffusion) was not a quick-control step of SO₂ adsorption on these samples.

Figure 5 shows that the simulated values of the Boyd first-order model agreed well with the experimental values when the SO₂ volume fraction was low but not with the SO₂ volume fraction. This condition indicated that the extragranular gas film diffusion was not the control step of adsorption. The Boyd–Ruthven–Ho model

Figure 2: Modeling results of diffusion-controlled apparent adsorption kinetics with Dumwald–Wagner model and Weber and Morris I model under different inlet SO_2 volume fractions of flue gas. (a) MWCNTs/TiO₂ + Cr, (b) MWCNTs/TiO₂ + Cu, (c) MWCNTs/TiO₂ + Zn.

Figure 3: Modeling results of diffusion-controlled apparent adsorption kinetics with Weber and Morris II model under different inlet SO_2 volume fractions of flue gas. (a) MWCNTs/TiO₂ + Cr, (b) MWCNTs/TiO₂ + Cu, (c) MWCNTs/TiO₂ + Zn.

Figure 4: Modeling results of diffusion-controlled apparent adsorption kinetics with Boyd–Crank–Ruthven model under different inlet SO₂ volume fractions of flue gas. (a) MWCNTs/TiO₂ + Cr, (b) MWCNTs/TiO₂ + Cu, (c) MWCNTs/TiO₂ + Zn.

Figure 5: Modeling results of diffusion-controlled apparent adsorption kinetics with Boyd pseudo first model and Boyd–Ruthven–Ho model under different inlet SO₂ volume fractions of flue gas. (a) MWCNTs/TiO₂ + Cr, (b) MWCNTs/TiO₂ + Cu, (c) MWCNTs/TiO₂ + Zn.

Table 1: Equilibrium SO₂ adsorption capacity under different inlet SO₂ volume fractions of flue gas

Φ_{SO_2}		500×10^{-6}	$1,000 \times 10^{-6}$	$2,000 \times 10^{-6}$
$q_{\text{e,exp}}/\text{mg g}^{-1}$	MWCNT/TiO ₂ + Cr	25.764	38.751	54.585
	MWCNT/TiO ₂ + Cu	19.793	24.467	37.486
	MWCNT/TiO ₂ + Zn	13.783	17.893	20.653

Table 2: Modeling results of diffusion-controlled apparent adsorption kinetics under different inlet SO₂ volume fraction of flue gas for MWCNT/TiO₂ + Cr

Kinetic models		Model parameters corresponding to inlet SO ₂ volume fraction		
		500×10^{-6}	$1,000 \times 10^{-6}$	$2,000 \times 10^{-6}$
Weber and Morris I intraparticle diffusion model (60 min)	$k_{i,\text{WMI}}/\text{mg g}^{-1} \text{min}^{-0.5}$	0.822	0.992	1.462
	R^2	0.9228	0.9394	0.9457
Weber and Morris I intraparticle diffusion model	$k_{i,\text{WMI}}/\text{mg g}^{-1} \text{min}^{-0.5}$	2.399	1.577	1.848
	R^2	0.9634	0.9682	0.9813
Weber and Morris II intraparticle diffusion model (60 min)	$k_{i,\text{WMI}}/\text{mg g}^{-1} \text{min}^{-0.5}$	1.032	1.223	1.811
	$c/\text{mg g}^{-1}$	1.943	2.061	3.092
	R^2	0.9774	0.9787	0.9786
Weber and Morris II intraparticle diffusion model	$k_{i,\text{WMI}}/\text{mg g}^{-1} \text{min}^{-0.5}$	1.655	1.953	2.525
	$c/\text{mg g}^{-1}$	-5.123	-5.718	-6.423
	R^2	0.9812	0.9834	0.9936
Dumwald–Wagner intraparticle diffusion model	$k_{i,\text{DW}}/\text{mg g}^{-1} \text{min}^{-0.5}$	-0.002	-8.952	-7.566
	R^2	0.923	0.948	0.976
Boyd–Crank–Ruthven intraparticle diffusion model	$k_{i,\text{BCR}}/\text{mg g}^{-1} \text{min}^{-0.5}$	1.557	1.848	2.399
	R^2	0.6624	0.9673	0.9811
Boyd pseudo first model	$k_{i,\text{B}}/\text{mg g}^{-1} \text{min}^{-0.5}$	0.0029	0.0019	0.0017
	R^2	0.9886	0.9982	0.9979

Table 3: Modeling results of diffusion-controlled apparent adsorption kinetics under different inlet SO₂ volume fraction of flue gas for MWCNT/TiO₂ + Cu

Kinetic models		Model parameters corresponding to inlet SO ₂ volume fraction		
		500×10^{-6}	$1,000 \times 10^{-6}$	$2,000 \times 10^{-6}$
Weber and Morris I intraparticle diffusion model (60 min)	$k_{i,\text{WMI}}/\text{mg g}^{-1} \text{min}^{-0.5}$	0.442	0.721	1.032
	R^2	0.8764	0.9155	0.9353
Weber and Morris I intraparticle diffusion model	$k_{i,\text{WMI}}/\text{mg g}^{-1} \text{min}^{-0.5}$	1.115	0.908	1.503
	R^2	0.9421	0.9862	0.9762
Weber and Morris II intraparticle diffusion model (60 min)	$k_{i,\text{WMI}}/\text{mg g}^{-1} \text{min}^{-0.5}$	0.580	0.924	1.285
	$c/\text{mg g}^{-1}$	1.231	1.808	2.248
	R^2	0.9498	0.9826	0.9866
Weber and Morris II intraparticle diffusion model	$k_{i,\text{WMI}}/\text{mg g}^{-1} \text{min}^{-0.5}$	1.001	1.209	1.614
	$c/\text{mg g}^{-1}$	-3.089	-3.089	-3.673
	R^2	0.9732	0.9904	0.9932
Dumwald–Wagner intraparticle diffusion model	$k_{i,\text{DW}}/\text{mg g}^{-1} \text{min}^{-0.5}$	-4.108	-2.880	-2.719
	R^2	0.949	0.969	0.981
Boyd–Crank–Ruthven intraparticle diffusion model	$k_{i,\text{BCR}}/\text{mg g}^{-1} \text{min}^{-0.5}$	0.909	1.115	1.503
	R^2	0.9400	0.9672	0.9753
Boyd pseudo first model	$k_{i,\text{B}}/\text{mg g}^{-1} \text{min}^{-0.5}$	0.0015	0.0012	0.0011
	R^2	0.9971	0.9962	0.9914

linearization curve was a straight line and passes through the origin, thereby indicating that the inner (hole) diffusion was a quick-control step, but the experimental point represented by the Boyd–Ruthven–Ho model in Figure 5 was estimated to a straight line but not the origin. This result indicated that internal diffusion was not a quick-control step for SO₂ adsorption by the sample.

The phenomena and trends represented in Figures 2–5 revealed a certain degree of adsorption mechanism. As the volume fraction of SO₂ in the flue gas increased, the diffusion resistance of SO₂ in the particles and the energy barrier resistance against the activation energy in the catalytic oxidation reaction at the active site decreased, and the resistance against the energy barrier decreased rapidly. The proportion of diffusion resistance in the total resistance of chemisorption increased, and the proportion of the latter decreased. This result showed that the high SO₂ volume fraction corresponded to an accurate prediction performance of the intraparticle diffusion model. At the same time, as the adsorption time progressed, the specific gravity of the diffusion resistance of SO₂ in the particle increased in the total process resistance of the chemisorption reaction, and the proportion of the catalytic oxidation reaction resistance has to overcome the activation energy to generate a new chemical bond in total resistance. The decline increased the predictive power of several diffusion-type apparent adsorption kinetic models as the SO₂ adsorption time progressed. This result indicates that the catalytic oxidation reaction of SO₂ occurring on the surface of microspores in C may be a quick-control step at the early stage of adsorption, which had a considerable influence on the chemical adsorption of SO₂ and may gradually transition to surface reaction and microporous diffusion at the late stage of adsorption. Hence, the combined control is the mass transfer rate control step of the adsorption reaction.

4.2 Calculation and analysis of effective internal diffusion coefficient of particles

The diffusion resistance in the particle is closely related to the diffusion coefficient. In this system, the diffusion effect was described by the effective internal diffusion coefficient of the particle, and the experimental instantaneous value and the simulated average value were investigated. Herein, the particles were assumed to be spherical; and given that the particle size ranged from 10 to 30 μm, the average diameter of the particles was 0.02 mm. The

method of obtaining the effective internal diffusion coefficient of the particles is shown in Table 5.

The effective diffusion coefficient of SO₂ in the sample should be composed of molecular, Kundsens, and configurational diffusion, which can be expressed by equations (10) and (11). The diffusion resistance was dominant, followed by the Kundsens diffusion resistance, and the molecular diffusion resistance contribution was the smallest. The different diffusion resistances varied with the adsorption time and the SO₂ volume fraction and were reflected by the change in the effective diffusion coefficient of SO₂.

$$\frac{1}{D_{\text{SO}_2}} = \sum_{j \neq \text{SO}_2}^n \frac{\varphi_j - \varphi_{\text{SO}_2} N_j / N_{\text{SO}_2}}{D_{\text{SO}_2, j}} + \frac{\alpha}{D_{k, \text{SO}_2}} + \frac{\beta}{D_{c, \text{SO}_2}} \quad (10)$$

$$D_{e, \text{SO}_2} = D_{\text{SO}_2} \frac{\varepsilon_p}{\tau} \quad (11)$$

where D_{c, SO_2} and D_{k, SO_2} are the Kundsens diffusion coefficient and the configuration diffusion coefficient of SO₂, respectively; α and β are the Kundsens and configuration diffusion coefficient contribution rates, respectively; ε_p is the particle porosity; and N_j and N_{SO_2} are the diffusion flux of SO₂ and other components, respectively. The reciprocal of the diffusion coefficient reflected the corresponding diffusion resistance. Figure 6 shows the effective intraparticle diffusion coefficients for different SO₂ volume fractions in flue gas.

Figure 6 shows that with the increase in SO₂ volume fraction and adsorption time, the effective internal diffusion coefficient of SO₂ also showed an increment. As the adsorption time elapsed, the sample microspores was continuously filled with H₂SO₄ molecules, the specific gravity of the configuration diffusion decreased, and the specific gravity of the Kundsens diffusion increased. This condition was manifested by a decrease in the total diffusion resistance and an increase in the effective internal diffusion coefficient. Meanwhile, the increase in SO₂ content also results in an increment in the diffusion force, and the diffusion of molecular diffusion and the contribution of the Kundsens diffusion increased faster than the configuration diffusion. This phenomenon resulted in the effective internal diffusion coefficient, increasing with the increase in the SO₂ volume fraction. Figure 6 shows that the instantaneous effective internal diffusion coefficient of SO₂ ranged from 10⁻¹⁶ to 10⁻¹⁴ m² s⁻¹. The SO₂ diffusion in the sample was dominated by configuration diffusion. The microporous distribution probability of the sample was 0.8 nm at the maximum; and the molecular diameters of O₂, H₂O, and SO₂ were in the range of 0.2–0.5 nm. This result was consistent with the theory of adsorption reaction space of SO₂ on C-based adsorbents [21]. Figure 6 shows the average effective

Table 4: Modeling results of diffusion-controlled apparent adsorption kinetics under different inlet SO₂ volume fraction of flue gas for MWCNT/TiO₂ + Zn

Kinetic models		Model parameters corresponding to inlet SO ₂ volume fraction		
		500 × 10 ⁻⁶	1,000 × 10 ⁻⁶	2,000 × 10 ⁻⁶
Weber and Morris I intraparticle diffusion model (60 min)	$k_{i,WMI}/\text{mg g}^{-1} \text{min}^{-0.5}$	0.531	0.718	0.925
	R^2	0.9344	0.9412	0.9519
Weber and Morris I intraparticle diffusion model	$k_{i,WMI}/\text{mg g}^{-1} \text{min}^{-0.5}$	0.487	0.669	0.819
	R^2	0.9789	0.9806	0.9862
Weber and Morris II intraparticle diffusion model (60 min)	$k_{i,WMI}/\text{mg g}^{-1} \text{min}^{-0.5}$	0.655	0.876	1.156
	$c/\text{mg g}^{-1}$	1.114	1.4093	2.060
	R^2	0.9887	0.9895	0.9960
Weber and Morris II intraparticle diffusion model	$k_{i,WMI}/\text{mg g}^{-1} \text{min}^{-0.5}$	0.707	0.856	1.414
	$c/\text{mg g}^{-1}$	-1.263	-1.245	-3.165
	R^2	0.9914	0.9926	0.9937
Dumwald–Wagner intraparticle diffusion model	$k_{i,DW}/\text{mg g}^{-1} \text{min}^{-0.5}$	-2.426	-1.658	-2.608
	R^2	0.984	0.987	0.992
Boyd–Crank–Ruthven intraparticle diffusion model	$k_{i,BCK}/\text{mg g}^{-1} \text{min}^{-0.5}$	0.669	0.889	1.321
	R^2	0.9062	0.9762	0.9802
Boyd pseudo first model	$k_{i,B}/\text{mg g}^{-1} \text{min}^{-0.5}$	9.996	8.993	8.327
	R^2	0.9606	0.9578	0.9542

Table 5: Solution methods of effective intraparticle diffusion coefficients

Methods	Theoretical expression	Coefficient equation
Transient Boyd experimental method	$q_t \approx \frac{6}{\sqrt{\pi}} \left(\frac{D_e t}{R^2} \right)^{\frac{1}{2}} q_e$	$D_e \approx \frac{\pi R^2}{36t} \left(\frac{q_t}{q_e} \right)^2$
Boyd, Crank, and Ruthven method	$\frac{q_t}{q_e} \approx \frac{6}{\sqrt{\pi}} \left(\frac{D_e t}{R^2} \right)^{\frac{1}{2}} = k_{i,BCK} t^{\frac{1}{2}}$	$D_e \approx \frac{\pi R^2 k_{i,BCK}^2}{36}$
Weber and Morris I method	$q_t \approx \frac{6}{\sqrt{\pi}} \left(\frac{D_e t}{R^2} \right)^{\frac{1}{2}} q_e = k_{i,WMI} t^{\frac{1}{2}}$	$D_e \approx \frac{\pi R^2 k_{i,WMI}^2}{36 q_e^2}$
Weber and Morris II method	$q_t \approx \frac{6}{\sqrt{\pi}} \left(\frac{D_e t}{R^2} \right)^{\frac{1}{2}} q_e + c = k_{i,WMI} t^{\frac{1}{2}} + c$	$D_e \approx \frac{\pi R^2 k_{i,WMI}^2}{36 q_e^2}$
Dumwald–Wagner method	$\frac{q_t}{q_e} \approx \left[1 - \exp \left(-\pi^2 \frac{D_e t}{R^2} \right) \right]^{\frac{1}{2}} = [1 - \exp(-k_{i,DW} t)]^{\frac{1}{2}}$	$D_e \approx \frac{k_{i,DW} R^2}{\pi^2}$

Table 6: Error analysis of modeling results

Kinetic models		Values of SSE under different SO ₂ volume fractions		
		500 × 10 ⁻⁶	1,000 × 10 ⁻⁶	2,000 × 10 ⁻⁶
Weber and Morris II intraparticle diffusion model	MWCNT/TiO ₂ + Cr	154.3	104.7	44.8
	MWCNT/TiO ₂ + Cu	173.7	130.8	49.9
	MWCNT/TiO ₂ + Zn	189.8	147.8	59.7
Weber and Morris I intraparticle diffusion model	MWCNT/TiO ₂ + Cr	386.8	170.1	39.8
	MWCNT/TiO ₂ + Cu	409.8	192.4	42.7
	MWCNT/TiO ₂ + Zn	411.6	209.5	55.6
Dumwald–Wagner intraparticle diffusion model	MWCNT/TiO ₂ + Cr	478.3	187.8	94.5
	MWCNT/TiO ₂ + Cu	541.7	234.7	127.5
	MWCNT/TiO ₂ + Zn	579.8	284.6	148.8
Boyd–Crank–Ruthven intraparticle diffusion model	MWCNT/TiO ₂ + Cr	312.5	134.5	51.8
	MWCNT/TiO ₂ + Cu	342.7	168.8	60.9
	MWCNT/TiO ₂ + Zn	349.9	172.5	65.8
Boyd pseudo first model	MWCNT/TiO ₂ + Cr	0.6398	3.89	5.89
	MWCNT/TiO ₂ + Cu	1.36	4.56	7.65
	MWCNT/TiO ₂ + Zn	1.78	5.23	7.98

Figure 6: Effective intraparticle diffusion coefficients under different inlet SO_2 volume fractions of flue gas. (a) MNCNT/ TiO_2 + Cr, (b) MNCNT/ TiO_2 + Cu, (c) MNCNT/ TiO_2 + Zn.

internal diffusion coefficient of SO_2 calculated by the model. The value was in the range of 10^{-16} – $10^{-14} \text{ m}^2 \text{ s}^{-1}$, which was also dominated by configuration diffusion.

4.3 Model error and applicability analysis

The simulation results of different adsorption kinetic models were analyzed by the sum of squared errors (SSEs) [28]. The SSE expression is shown in equation (12), and the SSE analysis results are listed in Table 6. Small SSEs indicated that the analog value was close to the experimental value, and the small error between the two indicates high prediction ability and prediction accuracy of the adsorption kinetic model.

$$\text{SSE} = \sum \left[\frac{(q_{t,\text{exp}} - q_{t,\text{theo}})^2}{q_{t,\text{exp}}^2} \right] \quad (12)$$

5 Adsorption thermodynamics of SO_2 on the sample

The feasibility, trend, and driving force of the adsorption can be obtained from adsorption thermodynamics

studies. Adsorption thermodynamic analysis is important in explaining the adsorption characteristics, laws, and adsorption mechanism. The thermodynamic parameters are useful in determining the adsorption temperature and adsorption properties of the adsorption. Experiments were carried out at 333.15, 353.15, 373.15, and 393.15 K to determine the most favorable adsorption temperature. The changes in the thermodynamic parameters of the adsorption process were generally calculated from the Gibbs equation and the Van't Hoff equation [34], as follows:

$$\Delta G = -RT \ln K \quad (13)$$

$$\ln K = \ln K - \frac{\Delta H}{RT} \quad (14)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (15)$$

where R is the gas constant ($8.314 \text{ J}/[\text{mol K}]$), T is the thermodynamic temperature (K), ΔG is the adsorption-free change in energy (kJ/mol), ΔH is the change in adsorption enthalpy (kJ/mol), ΔS is the change in adsorption entropy ($\text{J}/[\text{mol K}]$), and K is the equilibrium constant. The plot was plotted as $1/T$ with $\ln K$, and the results are shown in Figure 7. The calculation results of the adsorption thermodynamic parameters of SO_2 for these samples are shown in Table 7.

Figure 7: The relationship between $\ln K$ and $1/T$ for SO₂ adsorption on samples. (a) MNCNT/TiO₂ + Cr, (b) MNCNT/TiO₂ + Cu, (c) MNCNT/TiO₂ + Zn.

The table shows that the adsorption-free energy changes ΔG to a negative value, thereby indicating that the SO₂ adsorption on the sample was a spontaneous process, and the absolute value of ΔG decreased with the increase in temperature. This finding indicated that the adsorption process spontaneously increased with the increasing temperature. The trend was low, and the temperature rise was inconducive to the adsorption. The ΔH was negative, indicating that the adsorption process

was exothermic, which indicated that there must be a physical adsorption process in the adsorption and removal process of SO₂ in flue gas by activated carbon. The ΔS was negative, thereby indicating that the SO₂ adsorption on the sample reduced the degree of freedom of the adsorbate molecules and decreased the entropy of the adsorption process.

6 Conclusion

Table 7: Thermodynamic parameters of SO₂ adsorption on samples

Samples	Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/(mol K))
MWCNT/TiO ₂ + Cr	333.15	-6.67	-20.93	-42.81
	353.15	-5.73	-20.93	-43.04
	373.15	-4.96	-20.93	-42.79
	393.15	-4.07	-20.93	-42.88
MWCNT/TiO ₂ + Cu	333.15	-2.86	-12.56	-29.12
	353.15	-2.17	-12.56	-29.42
	373.15	-1.86	-12.56	-28.67
	393.15	-1.79	-12.56	-27.39
MWCNT/TiO ₂ + Zn	333.15	-2.39	-9.51	-21.37
	353.15	-1.82	-9.51	-21.77
	373.15	-1.17	-9.51	-22.35
	393.15	-1.15	-9.51	-21.26

- (1) The diffusion-based intraparticle diffusion model had poor prediction ability, and the prediction accuracy increased with the increase in SO₂ volume fraction. According to the SSE values, the overall predictive power of the model for these samples was in descending order as follows: the Weber and Morris I model (60 min) > Weber and Morris II model (60 min) > Boyd–Crank–Ruthven model > Weber and Morris I model > Dumwald–Wagner Model > Weber and Morris II model.
- (2) The simulation results of the Weber and Morris I, the Weber and Morris II, and the Boyd–Crank–Ruthven models deviated significantly from the initial stage of adsorption, and the line obtained by the Weber and

Morris II model, including the boundary layer parameters, did not pass the coordinate origin. This result indicated that intragranular pore diffusion (mesoporous and microspore diffusion) was not the only chemical adsorption rate control step. The Weber and Morris I and Weber and Morris II models had better simulation effects at the early stage of adsorption than at the later stage of adsorption.

- (3) Compared with MWCNT/TiO₂ + Zn, the Dumwald–Wagner model had lower prediction accuracy for MWCNT/TiO₂ + Cr and MWCNT/TiO₂ + Cu, but the prediction performance increased with the increase in SO₂ volume fraction, which was predicted at the late stage of adsorption. The increase in the SO₂ volume fraction and the decrease in adsorption time shift activity resulted in the diffusion resistance of SO₂ in the particles and in mesopores and microspores, respectively, which overcame more activation energy barrier resistance than in the catalytic oxidation reaction at the active sites. The increase was fast, and the proportion of diffusion resistance in total resistance of the diffusion reaction increased. One possible mechanism of the SO₂ adsorption process was the transition from the surface reaction control in the early stage of adsorption to the joint control of diffusion and surface reaction at a later stage.
- (4) Adsorption thermodynamics studies showed that the ΔG , ΔH , and ΔS values were negative. The adsorption process on the sample was a spontaneous, exothermic, and entropic reduction process, and the temperature rise was inconducive to SO₂ adsorption.

Nomenclature

B_t	Boyd–Ruthven–Ho model rate constant (min ⁻¹)
c	Weber and Morris II intraparticle diffusion model parameters (mg g ⁻¹)
D_{c,SO_2}	configuration diffusion coefficient of SO ₂ (m ² s ⁻¹)
D_e	effective intraparticle diffusion coefficient (m ² s ⁻¹)
D_{e,SO_2}	effective intraparticle diffusion coefficient of SO ₂ (m ² s ⁻¹)
D_{k,SO_2}	Knudsen diffusion coefficient of SO ₂ (m ² s ⁻¹)
D_{SO_2}	integrated intraparticle diffusion coefficient of SO ₂ (m ² s ⁻¹)
$D_{SO_2,j}$	integrated intraparticle diffusion coefficient of SO ₂ and components j (m ² s ⁻¹)
F	Boyd dimensionless adsorption

G	adsorption-free change in energy (kJ/mol)
H	change in adsorption enthalpy (kJ/mol)
K	equilibrium constant
$k_{i,B}$	Boyd pseudo first model rate constant (mg g ⁻¹ min ^{-0.5})
$k_{i,BCR}$	Boyd–Crank–Ruthven intraparticle diffusion model rate constant (mg g ⁻¹ min ^{-0.5})
$k_{i,DW}$	Dumwald–Wagner intraparticle diffusion model rate constant (min ⁻¹)
$k_{i,WMI}$	Weber and Morris intraparticle diffusion model I parameters (mg g ⁻¹ min ^{-0.5})
$k_{i,WMI}$	Weber and Morris intraparticle diffusion model II parameters (mg g ⁻¹ min ^{-0.5})
N_j	diffusion flux of other components (mol m ⁻² s ⁻¹)
N_{SO_2}	diffusion flux of SO ₂ (mol m ⁻² s ⁻¹)
q_e	equilibrium adsorption capacity (mg g ⁻¹)
q_t	adsorption capacity (mg g ⁻¹)
R	gas constant (8.314 J/[mol K]) or the particle of adsorbent (m)
S	change in adsorption entropy (J/[mol K])
T	thermodynamic temperature (K)
t	adsorption time (min)

Greek alphabet

α	Knudsen diffusion coefficient contribution rate
β	configuration diffusion coefficient contribution fraction
ε_p	particle porosity
τ	
φ_j	volume fraction of other components
φ_{SO_2}	volume fraction of SO ₂

Subscript

e	effective diffusion, adsorption equilibrium
exp	experimental value
i	intraparticle diffusion
$theo$	calculated value
t	time

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