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A numerical modelling study of SO_2 adsorption on activated carbons with new rate equations

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HIGHLIGHTS

- SO_2 adsorption on activated carbons were studied experimentally and numerically.
- Varying effects of intraparticle diffusion on SO_2 adsorption rate with particle size.
- Introduction of Vermeulen rate law in predicting SO_2 adsorption on large particles.
- Improved the linear driving force rate law for SO_2 adsorption on small particles.

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ABSTRACT

Modelling dynamic adsorption of sulfur dioxide (SO_2) on activated carbons (ACs) is significant in guiding practical desulphurization processes and making highly efficient use of adsorbents in terms of the adsorption rate which largely depends on particle size. In this work, models derived from the Vermeulen and an improved linear driving force (LDF) rate equation were studied for the first time on SO_2 adsorption over AC particles with different sizes. For larger particles (≥ 3 mm), breakthrough curves predicted by the Vermeulen equation showed good agreement with experimental data, demonstrating that intraparticle diffusion resistance varied with particle size, feed concentration, adsorption time and location. For smaller particles (1 mm), a correction on the volume-averaged adsorption capacity as a function of adsorption time and saturation in the rate equation was developed to avoid the underestimation of adsorption rate due to the inappropriate parabolic concentration profile inherent in the conventional LDF model. By providing a concentration gradient and adsorption rate closer to actual values, the improved LDF equation was confirmed to provide excellent prediction results on 1-mm particles. Different modelling characteristics of the two models indicates varying effects of intraparticle diffusion on adsorption rate with particle size regarding the specificity of SO_2 physisorption on ACs.

1. Introduction

The problem of air pollution caused by sulfur dioxide (SO_2) emissions have been a great concern in recent decades, owing to its great contributions to acid rain as well as the formation of secondary particulate matters [1,2]. Flue gas desulfurization using the adsorption method with activated carbons (ACs) has been widely adopted in various industrial processes [3]. To develop an SO_2 removal system, a comprehensive understanding of SO_2 adsorption fundamentals over ACs is required. Some significant studies have been conducted previously. Martin et al. demonstrated the mechanism of reversible and irreversible adsorption of SO_2 by ACs, and the effect of water present in the microporosity on SO_2 adsorption via an initial physisorption step [4]. Przepiórski J. et al. provided experimental and mathematical

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Nomenclature

α	external surface area per unit volume of the AC particle ($3/R_p$), m^{-1}
C_i	SO_2 concentration in the gas phase, mg/L
C_{fi}	SO_2 concentration at the AC particle external surface, mg/L
C_{in}	SO_2 feed concentration, mg/L
C_{out}	SO_2 concentration in the outlet gas stream, mg/L
D_e	effective diffusivity of SO_2 inside the pores of the AC particle, $m^2\,s^{-1}$
D_m	SO_2 molecular diffusivity, $m^2\,s^{-1}$
D_Z	axial dispersion coefficient in the bed, $m^2\,s^{-1}$
ε	void fraction in the bed, %
k_1	Lagergren rate constant, min^{-1}
k_2	Dumwald and Wagner rate constant, min^{-1}
k_3	Ho and Mckay rate constant, min^{-1}
k_l	Lanmuir constant, $L{\cdot}mg^{-1}$

k_m	average film mass transfer coefficient, $m{\cdot}s^{-1}$
M	total adsorbent mass in specific packing length, g
q	SO_2 adsorption capacity on AC particle per unit mass, $mg\,g^{-1}$
q_e	SO_2 equilibrium adsorption capacity, $mg\,g^{-1}$
q_i	solid-phase SO_2 concentration at a location inside the particle, $mg\,g^{-1}$
$\underline{q}_m$	SO_2 saturated adsorption capacity, $mg\,g^{-1}$
q	volume averaged concentration of SO_2 in the solid phase, $mg\,g^{-1}$
Q	gas flow rate, $m^3\,min^{-1}$
r_i	radius of a location i inside the particle, m
R	radius of the AC particle, m
Re	Reynolds number
Sc	Schmidt number
t	adsorption time, s
t_m	the adsorption time when the C_{out} reaches 95% of C_{in}, s

studies on SO_2 adsorption kinetics over AC adsorbents [5]. Liu et al. give new insights into the interactions between the SO_2 molecule and the carbon surface and the effect of acidic oxygen-containing groups [6].

Among the fundamental work, the study of SO_2 adsorption kinetics is an important part, and is generally conducted with a fixed-bed adsorption experiment and corresponding mathematical modelling for data interpretation and prediction [7]. As an essential parameter in adsorption kinetic models, intraparticle diffusion resistance on ACs could be influenced by several factors such as particle size, pore size distribution and tortuosity. However, for adsorption processes using relatively large sized AC in engineering applications, intraparticle diffusion is more likely to be the rate limiting step, playing a key role in efficient use of an adsorbent bed [8,9]. Specifically, AC is a carbon adsorbent with abundant oxygen-containing groups which are likely to enhance the physisorption of SO_2 as a high-polarity adsorbate via hydrogen bonding and dipole–dipole interactions [3,10], leading to a greater interaction and correspondingly a larger resistance for SO_2 diffusion through interior pores. This highlights the importance of predicting the rate in which SO_2 adsorption takes place for a given system and the rate largely depends on the validation and utilization of adsorption kinetic models as expressed by a variety of rate equations. Several kinetic models have described the reaction order of adsorption systems based on adsorbed-phase concentration, such as Lagergren's first-order equation, Vermeulen's model, and Ho's second-order expression [11,12].

As a lumped-parameter model proposed by Glueckauf [13], the linear driving force (LDF) equation as a typical form of Lagergren's first-order equation relates the average adsorbate concentration inside the particle with the concentration in the fluid phase, and has been extensively applied for studying fixed-bed adsorption systems [14–17]. However, it could underestimate adsorption uptake at early adsorption stage, resulting from the large adsorption uptake difference because the LDF model deals with the average concentrations of the adsorbate within the adsorbent particle and the initial unreal parabolic concentration profile leads to discrepancy [18–20]. Several factors affect the LDF adsorption rate in terms of the varying rate-controlling step originating from the dominance of the intraparticle diffusion. This largely depends on the particle size which is one of the most variable factors in practical use based on a frequently-used coal-based AC with similar texture properties for SO_2 adsorption around China. When the particle size decreases, the external particle surface contacting with the gas increases and the diffusion distance of SO_2 in the pores of the adsorbent decreases, resulting in lower intraparticle resistance and thus larger SO_2 adsorption rate [21]. Even though many studies have dealt with modeling the adsorption process of SO_2, a quantitative discussion for the selection of the appropriate adsorption rate equation regarding adsorbents with different sizes is still lacking.

This work aims to explore the relationship between the particle size and the applicability of the rate equation using a frequently-used coal-based AC adsorbent, and address the utilization of the Vermeulen equation and an improved LDF equation for SO_2 adsorption regarding different particle sizes. A kinetic study is conducted to select the appropriate kinetic model for each particle size. The Vermeulen equation based on the intraparticle diffusion model is firstly introduced for larger AC particles, while an improved LDF equation is developed for smaller AC particles. Validations of the newly-introduced model predictions are demonstrated through comparisons with experimental results.

2. Mathematical models

2.1. Overall mass balance in the fixed bed

Adsorption in a fixed bed is a process of unsteady-state mass transfer between the gas phase and the solid phase of the adsorbate. The concentrations of adsorbate in both phases are functions of time and location in the bed. Considering a plug flow under the assumption of negligible pressure drop and uniform distribution radial with no variation in the superficial flow velocity throughout the bed (valid for trace component removal), the mass balance can be described by the following partial differential equation: [22]

$$\frac{\partial C_i}{\partial t} - D_Z\frac{\partial^2 C_i}{\partial Z^2} + \frac{u}{\varepsilon}\frac{\partial C_i}{\partial Z} + \frac{1-\varepsilon}{\varepsilon}k_m\alpha(C_i - C_{fi}) = 0 \tag{1}$$

The terms on the left-hand side of Eq. (1) are the transient term for the SO_2 as adsorbate in the gas phase, the axial dispersion term, the convection flow term, and the sink term dealing with the adsorption rate of SO_2 from the bulk gas to the external surface of the ACs, respectively. D_Z is axial dispersion coefficient in the bed, which can be estimated using the following correlation [23]:

$$D_Z = \frac{D_m}{\varepsilon}(20 + 0.5ReSc) \tag{2}$$

where D_m, Re and Sc are SO_2 molecular diffusivity, Reynolds number and Schmidt number, respectively. By equating the flux of the SO_2 adsorbate across the AC particle external surface to the increase in adsorption amount, a mass balance between gas and solid phases can be established as:

$$\frac{3}{R}k_m(C - C_{fi}) = \frac{\partial q}{\partial t} \tag{3}$$