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Thermodynamics for the adsorption of SO_2, NO and CO_2 from flue gas on activated carbon fiber

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HIGHLIGHTS

- ▶ The adsorption isotherm of SO_2, NO and CO_2 was constructed to characterize isotherms.
- ▶ Thermodynamic parameters were used to understand adsorption behavior.
- ▶ The Extended Langmuir model was used to simulate competition adsorption.

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ABSTRACT

For researching the co-adsorption behavior of SO_2, NO and CO_2 in flue gas, the adsorption characteristics of pure component on activated carbon fiber (ACF) at temperatures ranging from 323.15 K to 363.15 K have been experimentally measured by a volumetric apparatus. The equilibrium data were analyzed by the Langmuir and Freundlich model, which revealed that Freundlich model was more suitable to describe the three gases adsorption than Langmuir model. The Henry's Constant was investigated based on the adsorption isotherms. The results showed that adsorption affinity follows the order $SO_2 > NO > CO_2$ on ACF. Thermodynamic functions integral Gibbs' free energy, enthalpy and entropy were calculated to characterize adsorption behavior. Finally, The Extended Langmuir (EL) Model was used to predicted multicomponent competed adsorption. We compared the experimental data both for the individual adsorption and for the mixture adsorption in our research. This work can provide helpful information to understanding the removal SO_2, NO and CO_2 via simultaneous adsorption on ACF in further studies.

1. Introduction

SO_2, NO and CO_2 are major pollutants in the atmosphere, which contribute to acid rain, photochemical smog, ozone depletion and greenhouse effects [1–3]. It was estimated that SO_2 and NO_x emission of China in 2020 will be 30.6 and 26.6 Mt, respectively. CO_2 emission may be at peak between 2020 and 2035 [4]. Hitherto, many methods for protecting SO_2 and NO have been proposed and applied such as wet scrubbing, spray-dry scrubbing, and dry scrubbing using lime or limestone as absorbents, NO_x selective catalytic reduction (SCR). A lot of technologies such as membrane separation, the conventional temperature swing adsorption (TSA) or pressure swing adsorption (PSA) have been proposed to sequester CO_2 from the flue gases. However, removal techniques of the three gases alone have some disadvantages. Wet scrubbing was highly efficient but it tended to generate wastewater. Spray-dry scrubbing was suffering from many shortcomings such as the blockage of the spray nozzle and production of sludge. The main disadvantage of dry scrubbing was its low removal efficiency of SO_2 [5]. But the adsorption was considered as one of the most promising technologies in the commercial and industrial applications because of the low energy requirement, cost advantage, and ease of applicability over a relatively wide range of temperatures and pressures [6–8]. Active carbons fibers (ACFs) had been actually used in removal apparatus for noxious gas because of their extended specific surface area, high adsorption capacity, well-developed microspores, safety, reproducibility, process ability, and so on [9]. At present, research in the field of adsorbents had made rapid progress for adsorbing single pollutant in flue gas. Gaur [10] had performed lots of experiments to investigate the adsorption properties for SO_2 on ACF in the presence of O_2 and H_2O. Shirahama et al. [11] had tested the adsorption of NO_2 on ACF at different NO_2 concentrations. Liu [12] had researched modified ACF for adsorption of SO_2 and NO.

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Carbon capture by adsorption technology had drawn much research effort recently. An [13,14] had done lots of work to improve capture performance. However, there were few studies about adsorption for SO_2, NO, CO_2 simultaneously removal. For testing SO_2, NO and CO_2 co-adsorption on ACF, we had to understand the adsorption characteristics of single component.

From the above perspectives, the motivation for this work was to investigate experimentally adsorption properties for SO_2, NO and CO_2 on ACF in flue gases. The adsorption isotherms of SO_2, NO and CO_2 by ACF were investigated. The adsorption parameters (Gibbs' free energy, enthalpy and entropy), the heat of adsorption data and Henry's law constant were calculated to characterize adsorption behavior and understand the affinity of adsorbent and adsorbate.

2. Materials and method

2.1. Materials

ACF samples in this work were gotten from the Senyou Carbon Fiber Co. Ltd., Jiangsu, and China. The adsorbent materials were washed three times by distilled water, and dried at 373 K in a drying oven. Then the samples were kept in a desiccator. CO_2 was obtained from Foshan Kodi Gas Chemical Industry Co. Ltd. SO_2 and NO were gain from Dalian Special gases Co. Ltd., Liaoning, China. Adsorbate purities were 99.9%, 99.5% and 99.9% (wt.%) for SO_2, NO and CO_2, respectively.

2.2. Method

2.2.1. Adsorption isotherms

Equilibrium isotherms of SO_2, NO and CO_2 were measured by using a static volumetric adsorption instrument. The details about the experimental set-up and operational conditions were presented elsewhere [15]. This was capable of operating in the temperature range from 323.15 to 363.15 K and at pressure up to 70 kPa. Equilibrium isotherm data of SO_2, NO, and CO_2 on the ACF was obtained at 323.15 K, 343.15 K, 363.15 K, respectively.

The dynamic adsorption experiments were carried out in a fixed bed reactor using 0.5 g of sample at 323.15 K. The details about the experimental set-up were presented elsewhere [16]. Concentration for SO_2, NO, CO_2 and N_2 cylinder were 1%, 1%, 99.9% and 99.99% (v%) respectively. In all experiments, the volumetric flow rate of the gas was kept at 400 mL/min.

2.2.2. Adsorption isotherm simulation

Adsorptive capacity was described by adsorption isotherms which characterized by certain constants whose values could express the surface properties and affinity of the adsorbent [17]. In order to describe the SO_2, NO and CO_2 adsorption behavior on the ACF clearly, the Langmuir and Freundlich equations were used to fit the isotherms. The Langmuir model [8] originally developed for the adsorption of gases onto solids assumes that adsorption occurred in a monolayer or that adsorption may only occur at a fixed number of localized sites, on the surface with all adsorption sites identical and energetically equivalent. Therefore, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent. The model can be represented as follows [18]:

$$q = q_m \frac{bp}{1+bp} \tag{1}$$

where q is the amount adsorbed in equilibrium with the concentration of adsorbate in gas phase (mmol tg^{-1}), q_m is the maximum adsorption amount (mmol g^{-1}), P (kPa) is the equilibrium pressure of the adsorbate in gas phase, and b (kPa^{-1}) is the equilibrium constant of adsorption.

The Freundlich isotherm model [19] was the earliest known equation describing the adsorption process. It is an empirical equation used for nonideal sorption that involves heterogeneous sorption. The Freundlich isotherm is commonly given by the following nonlinear equation:

$$q = kp^{1/n} \tag{2}$$

where k is Freundlich constants, whereas $1/n$ is the heterogeneity factor and an indicator of adsorption capacity, becoming more heterogeneous as its value gets farther to one.

To compare the fitting results, r^2 is constructed which is calculated from the following relationship:

$$r^2 = \frac{\sum_{i-1}^{N} (\hat{y}_i - \bar{y})^2}{\sum_{i-1}^{N} (y_i - \bar{y})^2} \tag{3}$$

where y_i is the corresponding adsorbed amounts of each experimental points, while$\bar{y}$ is the amount calculated by equation, $\bar{y}$ is the average value, $N$is the number of experimental points. Parameters of each equation were given by ORIGIN 8.0.

2.2.3. Henry's law constant

In order to evaluate adsorption affinity between adsorbate and adsorbent, Henry's constant was investigated. The constant was directly related to the interaction of molecules with the surface of the adsorbent since at low pressure, molecule-surface forces predominated [20,21]. The higher value of the constant was, the stronger affinity between adsorption pair would be. This expression can reduce to Henry's law at low adsorbate pressure, in other words:

$$\frac{P}{q} = \frac{1}{K_H} \exp\left(2A_1 q + \frac{3}{2}A_2 q^2 + \frac{4}{3}A_3 q^3 + \ldots\right) \tag{4}$$

where A_1, A_2, A_3 are the virial coefficients. A plot of $\ln(P/q)$ vs the loading q, should approach the axis linearly as q close to 0 with slope $2A_1$ and intercept $-\ln(K_H)$.

2.2.4. Thermodynamics of adsorption

The thermodynamic parameters could provide very useful information that elucidated the behavior of adsorption. The enthalpy change (ΔH), the free energy (ΔG) and entropy (ΔS) were the main thermodynamic parameters for adsorption. These forms always exhibit singularity and thus integral functions including free energy (ΔG) were calculated in this study to understand the adsorption.

The change in the integral molar Gibbs' energy (ΔG) can be obtained in the following ways [22,23]:

$$\Delta G = \frac{\Omega}{q} = -\frac{RT \int_0^P q \, d \ln p}{q} \tag{5}$$

where Ω is the surface potential (kJ mol^{-1}), q is the adsorption amount (mmol tg^{-1}) R is the gas universal constant(J mol^{-1} K^{-1}), T is the absolute temperature (K).

The integral molar enthalpy change (ΔH) can be derived from the fundamental thermodynamic relationships:

$$\Delta H = \frac{\left[\frac{\partial(\Omega/T)}{\partial(1/T)}\right]_p}{q} \tag{6}$$

The integral molar entropy change (ΔS) can be calculated as follows:

$$\Delta S = \frac{-\left(\frac{\partial \Omega}{\partial T}\right)_p}{q} \tag{7}$$