# Equilibrium and Kinetics Analysis of $CO_2$ Adsorption on Waste Ion-exchange Resin-based Activated Carbon

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## ABSTRACT

The equilibrium and kinetics of $CO_2$ adsorption on waste ion-exchange resin-based activated carbon were investigated. Three adsorption isotherm models and four kinetic models were utilized to analyze the equilibrium and kinetic data. Sips model and Avrami model are the best ones to describe the equilibrium and kinetics, respectively. The isosteric heats of adsorption of $CO_2$ and $N_2$ were calculated according to the Sips model. The separation factor of $CO_2/N_2$, calculated by IAST-Sips model, decreases with the surface coverage increasing. The adsorption rate constant of Avrami model increases with the $CO_2$ concentration increasing and reduces with the temperature increasing. The activation energies of $CO_2$ adsorption are negative, due to the decrease of the reaction rate with the temperature increasing. And the activation energies of $CO_2$ adsorption on CA are a bit smaller than that of PA, but the difference is not obvious.

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## 1. Introduction

A large amount of $CO_2$ emission is the main reason of global warming in recent years, which has been a serious environment crisis all over the world. In response to the global warming crisis, many countries have paid a great deal of attention to energy conservation and low-carbon economy. In such circumstances, carbon capture and storage (CCS) has been put forward to reduce the emissions of $CO_2$ against global warming. Among all CCS technologies, adsorption has been considered to be a promising carbon mitigation technology. It is generally known that the adsorbent is the most important part of adsorption, and there are many kinds of adsorbents such as metallic oxides [1,2], zeolites [3,4], mesoporous silicas [3,5], metal-organic frameworks (MOFs) [3,6] and porous carbonaceous materials [7,8]. The way to get the excellent performance and low cost of $CO_2$ adsorbent is a major problem which has been a puzzle for the scientists around the world.

For the design of an adsorption equipment, the evaluation of properties of adsorbent in both equilibrium and kinetics plays an important role. Álvarez-Gutiérrez [9] studied the adsorption characteristics of $CO_2/CH_4$ separation by biomass-based activated carbons. Sips and Toth models were used to describe $CO_2$ and $CH_4$ adsorption. Monazam [10] studied the equilibrium and kinetics of $CO_2$ adsorption using immobilized amine on a meso-

porous silica. Four kinds of isotherm models were used to describe $CO_2$ adsorption isotherms. The JMA model and CDF were applied to analyze $CO_2$ adsorption kinetics. Heydari-Gorji [11] developed a new semi-empirical kinetic model on $CO_2$ capture by PEI-impregnated pore-expanded MCM-41, and the model well describes $CO_2$ adsorption. Liu [12] studied the kinetics of $CO_2$ adsorption/desorption on amine-functionalized multiwalled carbon nanotubes through four kinds of kinetic models.

Waste ion-exchange resin-based activated carbons (WIRACs), a kind of low-cost adsorbent derived from waste ion-exchange resins, have been utilized for sewage treatment [13], naphthalene adsorption [14] and high performance super-capacitor [15], rarely for $CO_2$ capture. In our previous work [16], the WIRACs were produced by waste ion-exchange resins for $CO_2$ adsorption. The results suggested that WIRACs possess great potential as adsorbents for post-combustion $CO_2$ capture. The performance of adsorbent can influence the equilibrium and kinetics of the adsorption. To the best of our knowledge, there are limited reports on the equilibrium and kinetics of $CO_2$ adsorption on WIRACs.

Herein, in this paper, Langmuir, Freundlich and Sips models were used to describe $CO_2$ and $N_2$ adsorption isotherms. Pseudo-first order, pseudo-second order, Avrami and fractional order kinetic models were utilized to describe $CO_2$ adsorption process. The investigation of equilibrium and kinetics of $CO_2$ adsorption is advantageous to design and improve the adsorption equipment, which promotes $CO_2$ adsorption process and adsorption capacity per unit time.

**Table 1.**
The theoretical models of adsorption isotherm and kinetics used in this paper.

| Models | | Equation | | Ref. |
|---|---|---|---|---|
| Adsorption isotherm models | Langmuir isotherm model | $q = q_m \frac{K_L P}{1 + K_L P}$ | | [9,17–20] |
| | Freundlich isotherm model | $q = K_F P^{1/n}$ | | [18,20,21] |
| | Sips isotherm model | $q = \frac{q_s (bP)^{1/n}}{1 + (bP)^{1/n}}$ | | [10,20,22,23] |
| Adsorption kinetic models | | Differential Form | Integral Form | |
| | Pseudo-first order kinetic model | $\frac{dq_t}{dt} = k_1(q_e - q_t)$ | $q_t = q_e(1 - e^{-k_1 t})$ | [24] |
| | Pseudo-second order kinetic model | $\frac{dq_t}{dt} = k_2(q_e - q_t)^2$ | $q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$ | [26] |
| | Avrami kinetic model | $\frac{dq_t}{dt} = k_A^{n_A} t^{n_A - 1}(q_e - q_t)$ | $q_t = q_e[1 - \exp(-(k_A t)^{n_A})]$ | [11,12,25] |
| | Fractional order kinetic model | $\frac{dq_t}{dt} = k_n t^{m-1}(q_e - q_t)^n$ | $q_t = q_e - \frac{1}{[((n-1)k_n/m)t^m + (1/q_e^{n-1})]^{1/n-1}}$ | [11] |

## 2. Experimental

### 2.1. Materials

The activated carbons (ACs) were produced by waste ion-exchange resins. Meanwhile, according to the different activation agents, the ACs were classified into two categories, namely, chemically activated carbon (CA) (The activation agent is KOH; the activation temperature is 1173 K; the activation time is 2 h and the impregnation ratio is 1.5.) and physically activated carbon (PA) (The activation agent is $CO_2$; the activation temperature is 1073 K; the activation time is 1 h and the gas flow is 200 ml/min.).

### 2.2. Adsorption isotherm

The adsorption isotherms of $CO_2$ and $N_2$ were tested by a specific surface area and pore size analyzer named NOVA 1200e at 273 K, 303 K, 323 K and 348 K and the pressure was 0–100 kPa. The temperatures of experiments were provided by ice water mixture and a constant temperature bath. Before the experiments, ACs were pretreated at 473 K under vacuum conditions for 10 h until the mass of ACs did not change.

### 2.3. Adsorption kinetics

$CO_2$ adsorption was investigated by a STA 409C thermogravimetric analyzer (TGA) at different temperatures and $CO_2$ concentrations. About 10 mg ACs were placed into a corundum crucible in TGA and heated to 393 K before adsorption. When the temperature decreased to adsorption temperature, $N_2$ was changed to required gas components and kept for 30 min.

### 2.4. Theoretical models

The theoretical models of adsorption isotherm and kinetics used in this paper can be seen in Table 1.

## 3. Results and discussion

### 3.1. Adsorption isotherms of $CO_2$ and $N_2$

To optimize the design of $CO_2$ adsorption system, it is crucial to establish the applicable mechanism to describe the thermodynamic equilibrium [10]. Hence, the analysis of the equilibrium data is essential to predict the adsorption behavior.

The adsorption data were analyzed according to nonlinear regression of three isotherm models with least square method. The adsorption isotherms of $CO_2$ and $N_2$ of ACs are shown in Fig. 1 and Fig. 2, and the fitting constants are shown in Table S1 and Table S2. As revealed in Fig. 1 and Fig. 2, for both $CO_2$ and $N_2$, the adsorption capacities of CA are greater than those of PA at the same conditions. From Fig. 1(a) and Fig. 2(a), $CO_2$ adsorption capacities increase with the pressure increasing, which indicates that
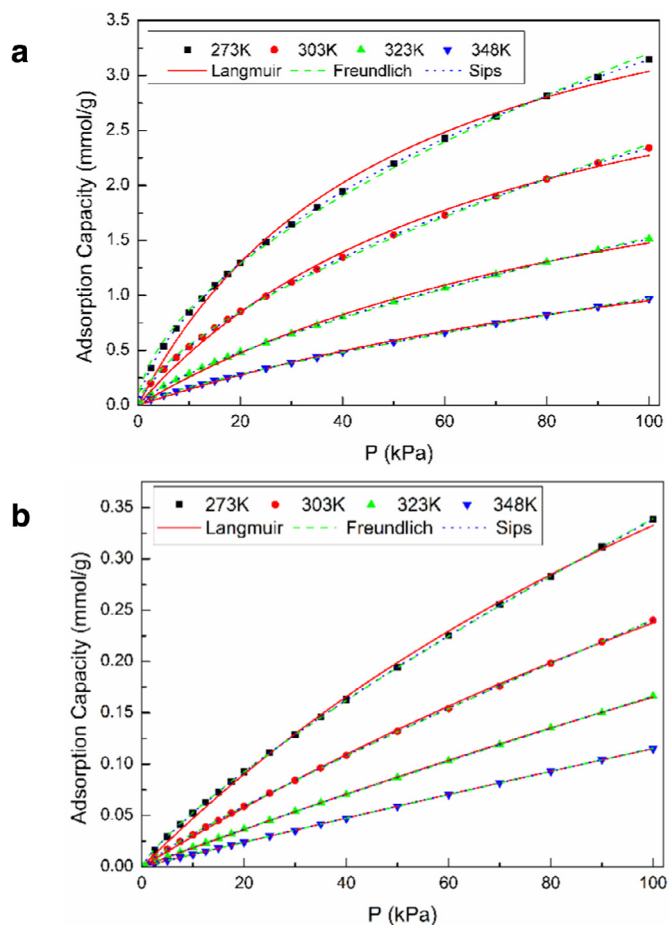


**Fig. 1.** The adsorption isotherms of $CO_2$ and $N_2$ on CA (a) $CO_2$; (b) $N_2$.

high pressure is conducive to $CO_2$ adsorption. However, the rise of flue gas pressure leads to more additional energy consumption. The increased $CO_2$ adsorption capacity is at the expense of more energy consumption. Hence, in actual operation, the increase of $CO_2$ adsorption capacity and more consumption of energy should be considered together. With the temperature increasing, $CO_2$ adsorption capacities reduce, which indicates that high temperature is disadvantageous to $CO_2$ adsorption by ACs. Fig. 1(b) and Fig. 2(b) describe $N_2$ adsorption isotherms on CA and PA. The laws of $N_2$ adsorption capacity are similar to those of $CO_2$ adsorption capacity with the change of pressure and temperature. In flue gas, $N_2$ accounts for the largest amount, and the increase of $N_2$ adsorption is negative and limits $CO_2$ adsorption. As a result, an excellent adsorbent for $CO_2$ adsorption should have a good capacity to $CO_2$ rather than $N_2$.