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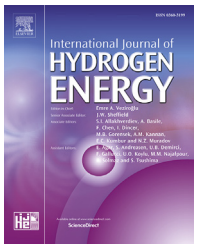

# Kinetics studies of $CO_2$ adsorption and desorption on waste ion-exchange resin-based activated carbon

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ABSTRACT

This paper is first to investigate the kinetics of $CO_2$ adsorption and desorption on waste ion-exchange resin-based activated carbons by the isothermal thermal analysis method. Not only the application of isothermal thermal analysis is expanded, but also a new method for study the kinetics of $CO_2$ adsorption and desorption is provided in this paper. $CO_2$ adsorption kinetics following Avrami-Eroféev model is A3/2 on chemically activated carbon (CA) and physically activated carbon (PA). The values of activation energy ($E$) of CA and PA are negative, and the absolute values of activation energy ($E$) reduce with the increase of $CO_2$ concentration. Desorption kinetics also follow Avrami-Eroféev model, and CA is A3/2 while PA is A1. The values of activation energy are positive, which is opposite to adsorption. $CO_2$ adsorption and desorption processes are similar to the nucleation and growth of the crystal, which starts from a point, then spreads to the surrounding.



## Introduction

The global warming, which is a universal crucial problem faced by all countries and severely constrains the sustainable development of human, should be solved imperatively. Global warming per se is not really the problem; the catastrophic climate changes which might be caused by it are. A considerable amount of $CO_2$ emissions cause global warming and change world climates. Therefore, it is of great necessity to decrease greenhouse like $CO_2$ emissions into the atmosphere to protect the living and development of human selves. Adsorption as a kind of carbon capture and storage (CCS) technology has been put forward to reduce the emissions of $CO_2$ against global warming.

The adsorbent is the most important to adsorption technology. Yong [1] talked about the adsorbent application of high temperature. Wang [2] and Samanta [3] reviewed different adsorbents in $CO_2$ capture and discussed their new trends. The commonly used adsorbents are metal-organic frameworks (MOFs) [4,5], carbon-based porous adsorbents [6–14], metallic oxides [15–17], zeolite [5,18] and mesoporous silicas [19,20] and some other adsorbents [21]. In addition, the kinetics of adsorption and desorption is another vital factor to

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be taken into account in the adsorption process. Monazam [22] studied the equilibrium and kinetics of $CO_2$ adsorption using immobilized amine on a mesoporous silica. The JMA model and CDF were implemented to $CO_2$ adsorption kinetic analysis. Heydari-Gorji [23] developed a novel semi-empirical kinetic model on $CO_2$ capture by PEI-impregnated pore-expanded MCM-41, and the model can describe $CO_2$ adsorption well. Liu [24] studied the kinetics of $CO_2$ adsorption/desorption on amine-functionalized multiwalled carbon nanotubes by four kinds of kinetic models using a fixed bed. The investigations of researchers on $CO_2$ adsorption main focus on the kinetics of $CO_2$ adsorption [22–25], however, there are a few researchers studying the $CO_2$ desorption mechanism and kinetic parameters, which is a barrier to apply and popularize the $CO_2$ adsorption technology in industry. Monazam [26] is the first person to study $CO_2$ desorption kinetics for immobilized polyethylenimine using the non-isothermal thermal analysis by a fluidized bed vessel.

The performance of adsorbent can influence the kinetics of adsorption and desorption. Waste ion-exchange resin-based activated carbons (WIRACs), which are a kind of low-cost adsorbent derived from waste ion-exchange resins, have been utilized for sewage treatment [27], naphthalene adsorption [28] and high performance super-capacitor [29], rarely for $CO_2$ capture. In our previous work [30], the WIRACs have been prepared by waste ion-exchange resins for $CO_2$ adsorption. The results suggested that WIRACs possess great potential as a kind of adsorbent for post-combustion $CO_2$ capture. To the best of our knowledge, there are no reports on the isothermal thermal analysis method (the reaction occurs at the isothermal condition, and the temperature does not change from the beginning to the ending of the reaction) by the kinetics of $CO_2$ adsorption and desorption. Thus, not much literature of the isothermal thermal analysis kinetics from the field of $CO_2$ adsorption and desorption can be learn from, but it can learn from the other fields [31,32]. In this investigation, the kinetics of $CO_2$ adsorption and desorption on WIRACs have been investigated by application of isothermal thermal analysis method to obtain a deeper understanding of the intrinsic reaction mechanisms.

## Experimental

### Materials

The activated carbons (ACs) were prepared by waste ion-exchange resins, which have been talked about in our previous work [23]. And due to the different activation agents, the WIRACs were named chemically activated carbon (CA) when activated by KOH, and physically activated carbon (PA) when activated by $CO_2$.

### Adsorption kinetics

The $CO_2$ adsorption was investigated by the thermogravimetric analyzer (TGA) (STA 409C) at different temperatures and $CO_2$ concentrations. Before used in $CO_2$ adsorption experiment, the WIRACs were heated to 393 K while $N_2$ was utilized to remove $CO_2$, $H_2O$ and some other impurities adsorbed on the surface of the WIRACs. When the temperature was decreased to the adsorption temperature (303 K, 323 K and 348 K), the $N_2$ gas flow was changed to the required gas components (15%, 50% and 100% $CO_2$ concentrations) and was maintained for 30 min.

### Desorption kinetics

Before $CO_2$ desorption, the previous process needed to be done to remove the impurities. When the temperature was decreased to 303 K, the $N_2$ gas flow was changed to the required gas components (50% and 100% $CO_2$ concentrations) and the gas flow was maintained for 30 min. Then the $CO_2$ saturated WIRACs were heated to different temperatures (373 K, 398 K and 423 K) until all adsorbed $CO_2$ desorbed from the WIRACs.

## Kinetic models

In kinetic analysis of solid state reaction, the extent of conversion can be defined as the ratio of actual mass loss dividing the total mass loss. In this paper, the extent of conversion means the conversion of $CO_2$ adsorption or desorption:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{1}$$

where $\alpha$ is the extent of conversion of $CO_2$ adsorption or desorption, $m_0$ is the initial mass of $CO_2$ adsorption or desorption of ACs, $m_t$ is the actual mass of ACs at the time t, $m_f$ is the final mass of ACs.

The kinetic process of $CO_2$ adsorption and desorption can be described by the following equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

where $k(T)$ is the reaction rate constant depending on temperature, $f(\alpha)$ is the dependent kinetic model function.

$k(T)$ is dependent on temperature, and can be calculated by the following equation:

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{3}$$

where $A$ is the pre-exponential factor which is assumed to be independent of temperature, $E$ is the apparent activation energy, $T$ is the absolute temperature, $R$ is the universal ideal gas constant.

To change Eq. (2), it can be modified as follows:

$$\frac{d\alpha}{f(\alpha)} = k(T)dt \tag{4}$$

Integrating both sides of Eq. (4), the following equation can be obtained:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \int_0^t k(T)dt \tag{5}$$

$$g(\alpha) = k(T)t \tag{6}$$

where $g(\alpha)$ is the integral form of the reaction model. From Eq.