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The heat and mass transfer performance of facile synthesized silica gel/carbon-fiber based consolidated composite adsorbents developed by freeze-drying method

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ABSTRACT

A series of experimental investigations had been performed to analyze the heat and mass transfer performance for two novel types of silica-based consolidated composite adsorbents developed by the freeze-drying method. The first type of adsorbent is silica gel consolidated with carboxymethyl cellulose (CMC) (SC), while the other is silica gel consolidated with CMC and carbon fiber powder (SCC). Results indicate that the thermal conductivity of consolidated composite adsorbents increases with the mass proportion of carbon fiber powder, while it decreases with the increasing moisture content in the preparation process of the adsorbents. When the mass ratio of silica gel, CMC, and carbon fiber powder is 4:1:4, the highest thermal conductivity of consolidated composite adsorbent obtained from experiments reaches $1.66 \text{ W m}^{-1} \text{ K}^{-1}$, which is 13.4 times greater than that of pure silica gel. Furthermore, the results of macroporous properties analysis of typical samples including SC20 and SCC20 (where the 20 means that the undried samples have a water content of 20% by mass during the preparation process) show that heat transfer additives effectively improve the macroporous porosity and permeability of the consolidated composite adsorbents. The study on adsorption dynamic performance indicates that the freeze-drying method helps to improve the adsorption performance including adsorption rate and equilibrium water uptake. The experimental results also show that the mass transfer coefficient K of the two typical samples are approximately stable at $5 \times 10^{-3} \text{ s}^{-1}$ when the adsorption temperature is ranged between 30 and 40°C, which are almost twice the corresponding values of the samples developed by heating-drying method. Therefore, the proposed approach which is the consolidation with heat transfer additives combined with freeze-drying method is effective for simultaneously enhancing the heat and mass transfer performance of the silica gel adsorbents.

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Introduction

Issues about enormous energy consumption in air conditioning have been challenging the current air conditioning industry. Hence, novel energy-saving cooling technologies that can assist or even

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replace the conventional vapor compression system are desired [1]. Solid adsorption cooling technology is considered as a benign alternative to the conventional compression cooling technology [2]. It takes full advantages of the low grade heat sources such as solar energy, waste heat in industrial settings, geothermal energy, etc. Moreover, the technology of adsorption cooling utilizes environment-friendly refrigerants instead of chlorofluorocarbons. At present, increasing attentions on this promising technology have been received in many countries [3–5].

However, drawbacks still exist for solid adsorption cooling technology. One of the main problems is that heat transfer performance of adsorption bed is too weak to lower the adsorption capacity of the system in a fixed operation cycle. It is reported that the enhancement of heat transfer performance of adsorbents is one of the most effective ways to improve the cooling capacity of adsorption units [6,7]. Intensive research efforts have been made to develop some promising adsorbents materials with high thermal conductivity both in chemical sorbents and physical adsorbents by introducing expanded graphite [8,9], carbon fiber [10,11], activated carbon (AC) [12,13], polymer [14,15], metal [14,16], etc. as thermal conductive materials. As one of the most common thermal conductive additives, carbon-based matrices are widely utilized to develop composite adsorbents due to its high thermal conductivity, porosity, and chemical inertness [9,10,17]. Chemical sorbents including metal chlorides and metal bromides usually possess higher sorption capacity than physical adsorbents, but the agglomeration of hygroscopic salts may cause a reduction of adsorption capacity and heat and mass transfer performances [18]. In order to solve this problem, carbon-based matrices have been extensively investigated to fabricate composite adsorbents. Oliveira et al. [8] developed CaCl_2 /expanded graphite consolidated composite adsorbents. By adding the expanded graphite as thermal conductive additive help to improve the heat transfer performance. Ye et al. [19] and Wang et al. [11] applied AC fiber (ACF) cloth as matrix to synthesize CaCl_2 /ACF composite adsorbents. The agglomeration of CaCl_2 can be eliminated to a great extent due to CaCl_2 well dispersed inside within pores of ACF, which improves the adsorption capacity and heat transfer properties of chemical adsorbents. Tso and Chao [13] synthesized composite adsorbents by impregnating Na_2SiO_3 and CaCl_2 into the pores of AC, and the composite adsorbents show favorable adsorption capacity and regeneration performance. In contrast, physical adsorbents such as silica gels, mesoporous aluminosilicate, AC, and so forth have the advantages of stable characteristics and low cost. Moreover, there is no lyolysis and agglomeration phenomenon compared with chemical sorbents. Therefore, it has been extensively applied in the adsorption system [10,20]. In the previous studies, using carbon-based matrices as thermal transfer additives to consolidate physical adsorbents was considered as a highly effective solution to enhance heat transfer performance. Dellero et al. [21,22] used carbon fibers as thermal transfer additive in a chemical heat pump. By adding carbon fibers, the thermal conductivity of the reagent bed was enhanced. The heat exchange coefficient of heat pump reached $110 \text{ W m}^{-2} \text{ K}^{-1}$ because of the good contact between reagent bed and reactor wall with the presence of carbon fibers. Eun et al. [23] experimentally measured the amount of adsorption and specific cooling power of the cooling system that utilized expanded graphite/silica gel composite blocks. The permeability of composite blocks increases with graphite fraction at 8 MPa molding pressure, and high molding pressure could reduce the permeability. The composite blocks show good thermal conductivity of $10\text{--}20 \text{ W m}^{-1} \text{ K}^{-1}$ and permeability of $3\text{--}40 \times 10^{-12} \text{ m}^2$. Jin et al. [24] investigated thermal conductivity and permeability of granular AC, consolidated AC with chemical binder, and consolidated AC with expanded natural graphite (ENG). It was reported that thermal conductivity of granular AC and consolidated AC with chemical binder are about 0.36 and $0.4 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. The highest thermal conductivity of consolidated AC with ENG ranges from 2.08 to $2.61 \text{ W m}^{-1} \text{ K}^{-1}$ according to its fraction of AC; however, its permeability is lower than that of the granular AC and consolidated AC with chemical binder. Zhao et al. [25] developed three types of adsorbents including consolidated AC with ENG treated with sulfuric acid (TSA) (ENG-TSA), consolidated AC with ENG, and granular AC. It was found that consolidated adsorbents with ENG-TSA have preferable heat transfer and mass transfer performances than consolidated

adsorbents with ENG, but the permeability of consolidated adsorbents decreased at least three orders of magnitude compared to that of granular AC.

Simple consolidation usually leads to the decrease of permeability in adsorbents and finally reduces the performance of mass transfer. For the sake of developing consolidated adsorbents with favorable heat and mass transfer performance simultaneously, extensive researches have been carried out on this issue. The particle diameter of adsorbent is considered as an influential parameter on the mass transfer performance since it affects both inter- and intraparticle mass transfer resistances [26]. Tamainot-Telto and Critoph [27] performed a series of experimental investigations on the thermophysical property of two types of monolithic carbons which were made up of coarse and fine powder. Typical value of the thermal conductivity of the tested samples is up to $0.44 \text{ W m}^{-1} \text{ K}^{-1}$. It was also reported that the sample prepared by coarse powder has an axial permeability ($3.6 \times 10^{-14} \text{ m}^2$) that is about 6 times higher than the sample prepared by fine powder. Therefore, an optimum particle diameter of adsorbent is desirable for enhancing mass transfer performance. Maintaining some mass transfer channels in the consolidated adsorbent layers is also one of the effective ways to enhance the mass transfer performance of the adsorbent. Wang et al. [28] used consolidated AC with mass flow channels to reduce mass transfer resistance in adsorbent beds. Chen et al. [29] investigated the adsorption performance of silica gel/polymer consolidated adsorbents with air channels. The research work showed that the desiccant wheel manufactured by silica gel/polymer consolidated adsorbents has high adsorption rate and low airflow pressure drop. Lately, Zhao et al. [25] and Wang et al. [30] utilized ENG-TSA as thermal transfer additive to synthesize a new type of consolidated AC adsorbents. The consolidated adsorbents have higher thermal conductivity than consolidated AC adsorbents with ENG. Moreover, it was found that consolidated AC adsorbents with ENG-TSA have preferable mass transfer performances than consolidated adsorbents with ENG when the density of consolidated adsorbents is between 350 and 450 kg m^3 in Ref. [25].

A new approach that simultaneously improves the heat and mass transfer performance of the adsorbent was introduced in this study to develop the consolidated composite adsorbents. Silica gel was consolidated with binder and heat transfer additive (carbon fiber powder) to enhance the heat transfer performance, and then the consolidated adsorbent samples were freeze-dried by freeze-drying method to improve the mass transfer performance. A series of comparative analysis of experimental results shed light on the heat and mass transfer performance of the consolidated composite adsorbents. First, the thermal conductivity and porous properties of the consolidated composite adsorbents and silica gel were discussed. Second, the adsorption performance and mass transfer performance of the consolidated composite adsorbents prepared by two different methods, i.e., freeze-drying method and heating-drying method, were evaluated and compared by using the laboratory-built volumetric testing device, and the linear driving force (LDF) model was employed to obtain the mass transfer coefficients of the adsorbents under three various adsorption temperatures.

Experiments

Development of consolidated composite adsorbents

The utilized materials for the development of consolidated composite adsorbents mainly include mesoporous silica gel, carbon fiber powder, and CMC, which were purchased from Qingdao Haiyang Chemical Co., Ltd., China; Jiangsu Elda Composite Materials Co., Ltd., China; and

Table 1. Surface area and pore characteristics of silica gel and carbon fiber power.

Material	D_p (mesh)	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	V_t ($\text{cm}^3 \text{ g}^{-1}$)	D_{av} (nm)
Silica gel	100–200	508.0	0.25	2.3
Carbon fiber powder	100–500	56.9	0.19	6.6

Table 2. The composition and preparation parameters of consolidated composite adsorbents.

Samples	Mass ratio ($M_{\text{silica}}:M_{\text{CMC}}:M_{\text{carbon fiber}}$)	Moisture content (wt%)	Abbreviation
Prepared by freeze-drying method	4:1:0	20	SC20
		30	SC30
		40	SC40
		50	SC50
	4:1:1	20	SCC20
		30	SCC30
		40	SCC40
		50	SCC50
	4:1:2	20	SCC220
	4:1:4	20	SCC420
Prepared by heating-drying method	4:1:0	20	SC20H
	4:1:1	20	SCC20H

Tianjin Kemiou Chemical Reagent Co., Ltd., China, respectively. The surface area and pore characteristics of silica gel and carbon fiber powder were listed in Table 1.

Two types of consolidated composite adsorbents were prepared by freeze-drying method. The first type is the consolidated silica gel/CMC with mass ratio of 4:1. The second type of consolidated composite adsorbents are made up of silica gel, CMC, and carbon fiber powder with three various mass ratios of 4:1:1, 4:1:2, and 4:1:4.

The detailed procedures for the adsorbent preparation are as follows. First, fixed amount of water according to the mass ratios listed by Table 2 was added to the component materials and stirred evenly to form wet mixture. Second, 1 g wet mixture was put into the metal compression mold. By this way, the thickness and density of the adsorbents were guaranteed to be identical under same pressure (10 MPa). Third, the adsorbent samples were placed in a low temperature refrigerator (-26°C) for 24 h, then the samples were moved into a vacuum freeze-drying oven for freeze-drying for 24 h. Finally, the obtained samples were heated at 200°C in muffle furnace in order to partially volatilize the CMC and form interlayer porosity inside the adsorbent samples.

It is found that when the water content accounts for 20 wt% of the total mass of wet mixture in the preparation process of the consolidated composite adsorbents, the mixed powder are fully wetted and desirable consolidation effects can be obtained. However, when the water content exceeds 50 wt%, the wet mixture turns into paste-like substance and the consolidation is difficult to proceed. Therefore, the wet mixture with 20 wt%, 30 wt%, 40 wt%, and 50 wt% moisture content were chosen to prepare the first type of consolidated composite adsorbents and the second type of adsorbents with mass ratio of 4:1:1. For the second type of consolidated composite adsorbents with the mass ratios of 4:1:2 and 4:1:4, the moisture content of wet mixture was fixed at 20 wt%. Table 2 listed the composition and preparation parameters of consolidated composite adsorbents.

The consolidated composite adsorbents, i.e., consolidated silica gel and CMC with mass ratio of 4:1 and consolidated silica gel, CMC and carbon fiber powder with mass ratio of 4:1:1 were developed by heating-drying method. The moisture content of wet mixture in the preparation process was 20 wt%. The preparation procedures of these two kinds of consolidated composite adsorbents are similar to the aforementioned procedures. The only difference is the third step of the aforementioned preparation procedures where the adsorbents are directly dried by the heat-drying method. All other preparation processes and conditions are the same. The composition parameters for these two types of composite adsorbents developed by heating-drying method were also listed in Table 2.

Experimental procedures

The thermal conductivity of consolidated composite adsorbents was tested in the DRL-II system (Xiangtan xiangyi instrument Co., Ltd., China) by utilizing the steady heat flow method under ambient conditions. The test unit was depicted as Figure 1. The test sample was located

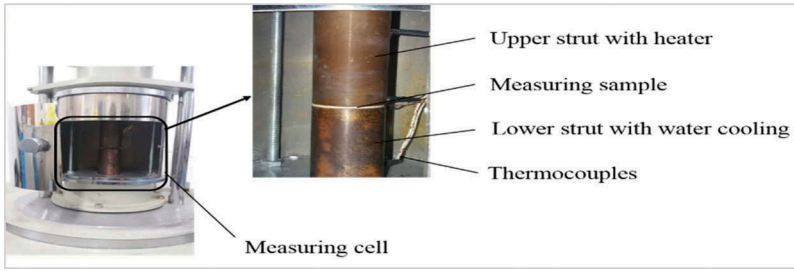


Figure 1. The schematic diagram of measuring cell of DRL-II system based on steady heat flow method.

between the upper and lower struts which provide a clamping force on the sample. The effective thermal conductivity λ was determined according to the measured average temperature gradient ΔT generated through the consolidated sample by a known axial heat flux Q under steady-state conditions. The effective thermal conductivity λ could be calculated by the following expression:

$$\lambda = \frac{Q \times \Delta z}{S \Delta T} \quad (1)$$

where Q is the measured average heat flux through test sample, Δz is the thickness of test sample, ΔT is the temperature difference across test sample, and S is the area of the cross section of the test sample. The test range and test accuracy of thermal conductivity in the DRL-II system supplied by instrument company were $0.1 \sim 300 \text{ W m}^{-1}\text{K}^{-1}$ and $\pm 3\%$, respectively.

The micro-mesoporous parameters such as specific surface area, average pore size, pore volume, and pore size distribution were estimated by using nitrogen adsorption in gas adsorption analyzer (Autosorb iQ-2). The specific surface area was obtained by the BET equations. The pore size distribution was evaluated by the utilization of the nonlocal density functional theory [31]. The macroporous parameters of the absorbent samples including intraparticle and interparticle pores were measured by mercury intrusion porosimetry, which has been widely adopted for macropores measurement (pore size $> 0.5 \text{ }\mu\text{m}$) [32].

The volumetric testing system was established for the measurement of adsorption performance and mass transfer performance of the adsorbents. It mainly consists of the steam vessel, measuring cell, thermostat chamber, circulating water bath, steam generator, and vacuum pump, as depicted in Figure 2. The temperature of the measuring cell can be adjusted by circulating water bath. The dead volume of the whole test system is $V_0 = 2.527 \times 10^{-3} \text{ m}^3$. The measurement procedures are as follows. At first, the sample is weighted immediately after drying in a vacuum drying oven for about 8 h at 100°C . The weight of the sample is marked as m_0 . Then, the sample is placed into the measuring cell which is heated by a constant temperature water bath at 90°C . The measuring cell is evacuated for 10 h by a vacuum pump in order to activate the adsorbent sample. When the activation process is finished, close the valves V1 and V2, and open the valves V3 and V4. The steam generator is evacuated for 40 min for removing the residual air. At the same time, the temperature of the measuring cell and thermostat chamber are adjusted to the required testing temperature. Subsequently, close the valve V4 and turn off vacuum pump. The valve V3 is opened and the valve V2 is opened slowly. Hence, water vapor goes into the vapor vessel until the pressure reaches the required adsorption pressure (3.37 kPa). When the pressure and temperature in the test cell become stable, open the valve V1 and the adsorption process begins. The pressure variations in the measuring cell are recorded by the computer.

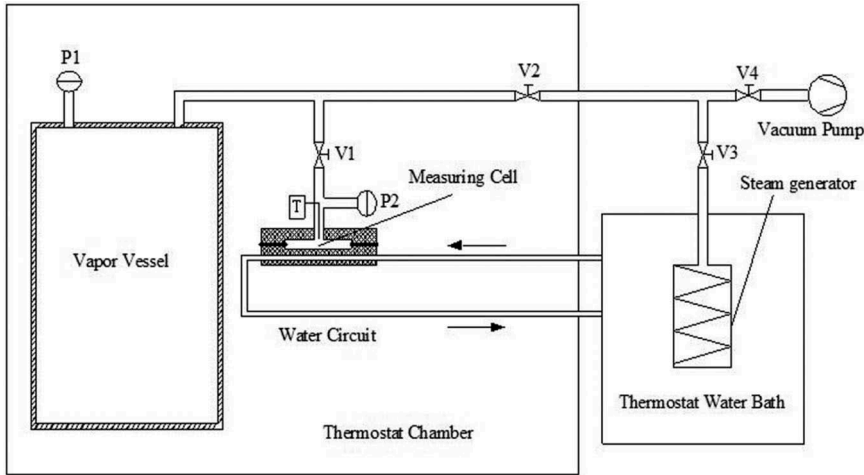


Figure 2. Schematic diagram of the volumetric testing device.

During the adsorption process, the water vapor is assumed as ideal gas. Therefore, the time variations of adsorption rate can be calculated by the variation of pressure value. The adsorption rate equation is

$$\left| \frac{dx}{dt} \right|_i = \frac{(P_i - P_{i+1})M_0 V_0}{RT\Delta t m_0} \quad (2)$$

where $\left| \frac{dx}{dt} \right|_i$ and P_i are the adsorption rate and pressure value at the time sequence i , respectively. M_0 is the molar mass of H_2O , R stands for gas constant, Δt and t are time intervals and adsorption time, respectively.

The amount of the adsorbed water vapor on the adsorbent sample at the time sequence i can be obtained by integrating Eq. (1) as follows:

$$x_i = \frac{(P_0 - P_i)M_0 V_0}{RTm_0} \quad (3)$$

where x_i is the amount of adsorbed water vapor on per unit mass of adsorbent sample and its unit is g/g.

Results and discussion

Thermal conductivity

Figure 3 shows that the thermal conductivity of both the samples of SC and SCC series developed by freeze-drying method decreases with the increasing moisture content in the preparation process. The higher the moisture content, the richer the pores in the samples after the process of freeze-drying. Thereby, the thermal conductivity of the adsorbents is decreased. Compared with the SC series samples, the SCC series samples have higher thermal conductivity because carbon fiber powder serves as heat transfer additive. The thermal conductivities of SC series samples are 3.5–4.75 times higher than that of pure silica gel ($0.12 \text{ W m}^{-1} \text{ K}^{-1}$), while the SCC series samples can reach 4.33–6.92 times. The SEM images of silica gel powder, carbon fiber powder, SC20, and SCC20 also were observed, and the results are shown in Figure 4. For the consolidated composite adsorbents, the voids between silica gel particles are greatly reduced due to the compressed consolidation. The consolidation with polymer binder enhances the contact of silica gel particles, which improves the heat transfer property to some

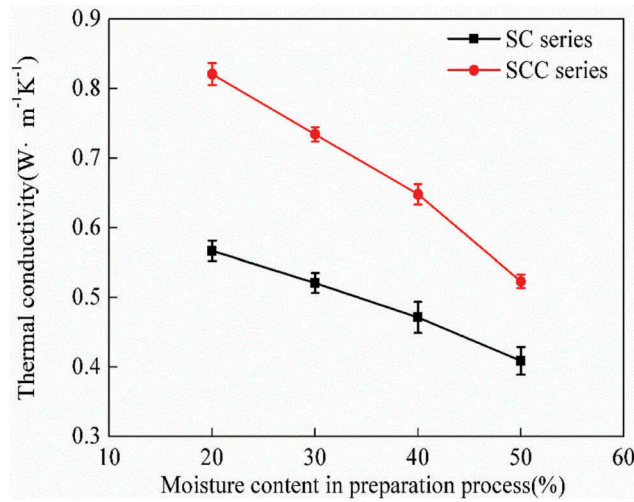


Figure 3. The thermal conductivity of consolidated composite adsorbents prepared by freeze-drying method with different moisture content mixture in preparation process.

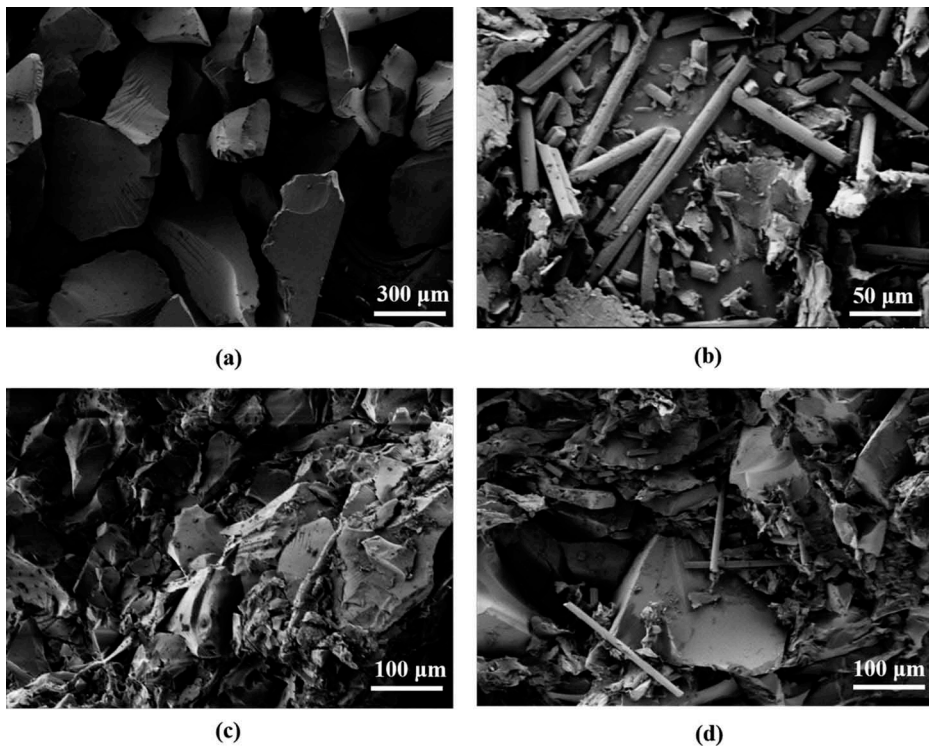


Figure 4. SEM images. (a) Silica gel powder; (b) carbon fiber powder; (c) the cross section of SC 20 sample; (d) the cross section of SCC 20 sample.

extent. It can be seen from [Figure 4\(d\)](#) that the voids between silica gel particles in SCC20 adsorbent layer are filled with carbon fiber powder, which further enhances the heat transfer property of consolidated composite adsorbents.

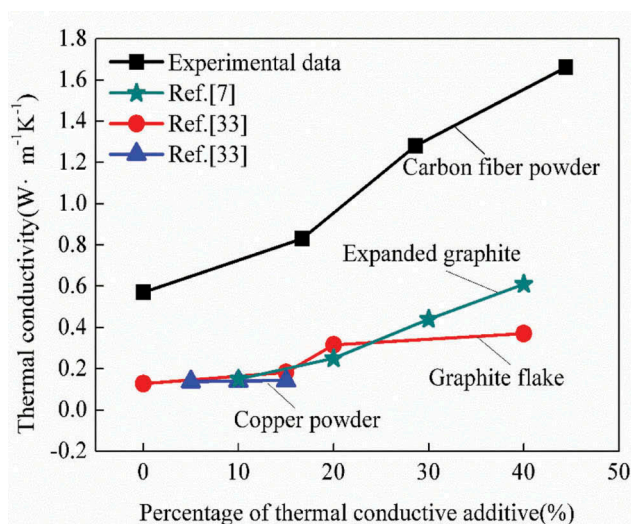


Figure 5. The comparison of thermal conductivity of consolidated composite adsorbents with different kinds of thermal conductive additives under various mass percentages.

The variation of the thermal conductivity of consolidated composite adsorbents with the increasing mass ratios of thermal conductive additive both in the literature [7,33] and our study were described in Figure 5. In our study, the consolidated composite adsorbents with different mass ratios of thermal conductive additive were developed by freeze-drying method, and the moisture content of wet mixture in the preparation process was 20% wt. Two kinds of consolidated silica gel adsorbents developed by using flake graphite and copper powder as heat transfer additives were reported in reference [33], and AC consolidated adsorbent was developed by using expanded graphite as heat transfer additive in literature [7]. Obviously, the consolidated composite adsorbents prepared by freeze-drying method in our study have higher thermal conductivity, and the thermal conductivity of the samples increases as the mass ratio of heat transfer additive, i.e., carbon fiber powder. The effect of adding thermal conductive additive on thermal conductivity of consolidated composite adsorbents in our study is similar to the results reported in the Refs. [7,9,33]. The thermal conductivity of sample is $1.66 \text{ W m}^{-1}\text{K}^{-1}$ when the mass ratio of silica gel, CMC, and carbon fiber powder is 4:1:4, which is 13.8 times higher than that of pure silica gel, while it reduces to $0.57 \text{ W m}^{-1}\text{K}^{-1}$ for the sample without carbon fiber powder. Even though a high proportion of heat transfer additive could improve the thermal conductivity of consolidated composite adsorbent, it should be pointed out that the increasing proportion of carbon fiber powder will decrease the adsorption capacity per unit mass of adsorbent due to the decline of the relative content of silica gel.

Porous properties

As described in Figure 6 that all the tested samples meet the Type I isotherms with hysteresis loop, which is suggested that mesoporous adsorption has occurred in the absorption process [22]. The nitrogen adsorption amount rapidly rises in the range of relative pressure (P/P_0) of 0–0.4, which is the result of micropore volume filling. The hysteresis loops corresponding to mesoporous adsorption mainly distribute in the range of relative pressure (P/P_0) of 0.4–0.8. The rapid increase of nitrogen adsorption amount is not observed at high relative pressure, indicating that there is no obvious macroporous adsorption. This also can be illustrated by the fact that the pore size distributions of the three samples in Figure 7 are mainly concentrated at 0.5–6 nm. Therefore, the adsorption phenomenon of the adsorbents is mainly micro-mesoporous adsorption. Note that in contrast to the silica

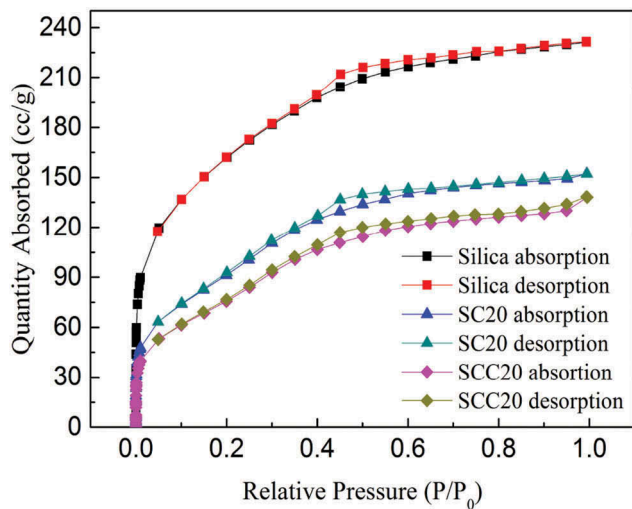


Figure 6. Nitrogen absorption–desorption isotherms of adsorbent samples in 77 K.

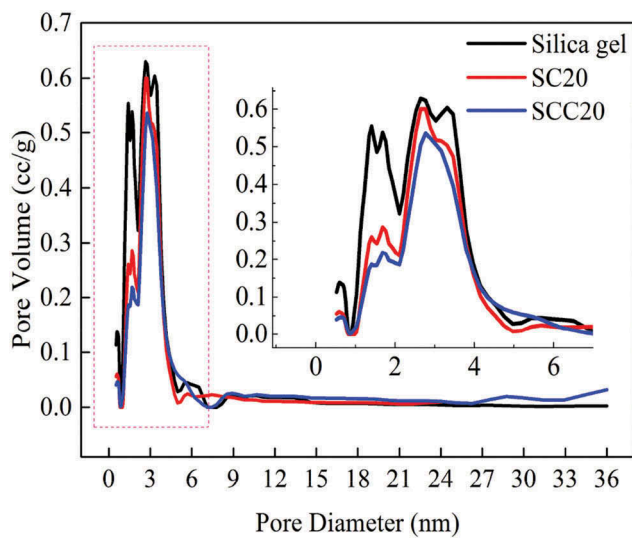


Figure 7. The micro-mesoporous size distributions of the adsorbents evaluated by NLDF method.

Table 3. Surface area and pore parameters of adsorbents obtained by N₂ adsorption method.

Sample	Specific surface area (m ² /g)	Specific pore volume (m ³ /g)	Average pore diameter (nm)
Silica gel	507.97	0.25	2.32
SC20	314.73	0.19	2.46
SCC20	249.38	0.18	2.82

gel, the consolidated composite adsorbents (SC20 and SCC20) have the less nitrogen adsorption capacity. It is ascribed to the fact that the consolidation with binder results in the partial blockage of pores inside the silica gel. Hence, the specific surface area and total pore volume reduce, as shown in Table 3. The obtained value of specific surface area of SCC20 is lower of about 20.7% than the SC20, as result of the presence of the heat transfer additive, which is almost coherent with the reduced

percentage amount of silica gel in SCC20. Moreover, the specific pore volume of SCC20 is nearly equal to that of SC20. These facts indicate that the adsorbents consolidated by the addition of heat transfer additive does not sacrifice the good porous property of silica gel compared to that of the consolidated adsorbents developed by only using binder.

The three samples have similar pore size distribution curves, as shown in Figure 7. It agrees well with the pore size distributions of consolidated composite adsorbents found by Zheng et al. [17]. This phenomenon indicates that simple mixture and consolidation of silica gel with CMC and carbon fiber powder has not led to the destruction of the morphology of silica gel. The peaks of pore size distributions are observed in the range between 0.5 and 6 nm. Such a narrow range of distribution illustrates that the adsorbents have uniform pore size.

As can be seen from Table 4, the macroporous porosity and permeability of SC20 and SCC20 are greatly less than those of silica gel. The permeability of silica gel is 199 times higher than that of SC20 and 22 times higher than that of SCC20. It should be highlighted that the porosity and permeability of SCC20 are higher than those of SC20. It can be surmised that SCC20 is developed by adding carbon fiber powder with different particle size from silica gel. Therefore, the contact between the neighboring particles for SCC20 is not as close as that for SC20 in the process of mixing and consolidation, which can be illustrated by Figure 4(c) and Figure 4(d) that the carbon fiber powder is well distributed in the voids between the silica gel particles, avoiding the compact contact between the silica gel particles due to the consolidation with binder.

The macropores of the adsorbents can be divided into intraparticle and interparticle pores. Figure 8 depicts that the shape of pore size distribution curves of silica gel, SC20, and SCC20 are similar in the range of pore size less than 110 μm . It implies that the macropores in this range are interparticle pores. The pore size of silica gel is concentrated in the range of 15–60 μm , while the pore size of SC20 and SCC20 distribute mainly in the range of 0–30 μm . The reason for this phenomenon is that the intraparticle pores of SC20 and SCC20 are blocked partially. It consequently causes the change of pore size and the decrease of the pore volume. The pores of silica gel in the

Table 4. Surface area and pore parameters of adsorbents measured by MIP.

Sample	Total porosity (%)	Permeability (nm^2)	Specific surface area (m^2/g)	Specific pore volume (m^3/g)
Silica	30.96	173.12	0.19	0.61
SC20	8.02	0.87	0.42	0.20
SCC20	19.68	7.86	0.50	0.45

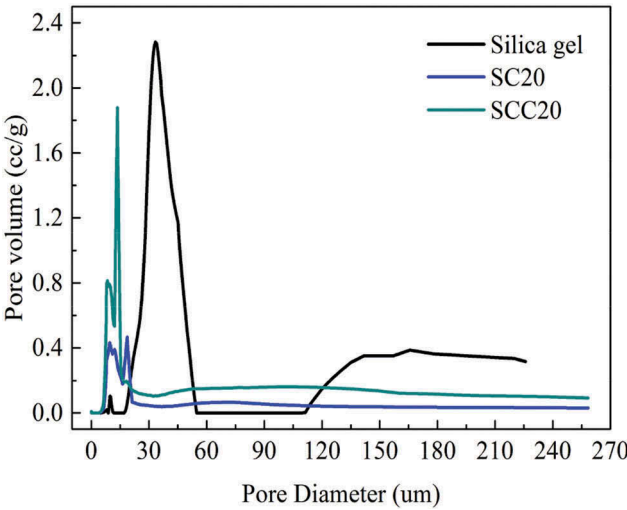


Figure 8. The macroporous size distributions of the adsorbents obtained by MIP.

range of 110–230 μm are considered to be interparticle pores formed in natural bulk density. They are greatly reduced after the consolidation. Especially, there is pore volume in the range of pore size greater than 30 μm for SCC20, but almost not for SC20, which results in SCC20 possessing higher porosity and permeability than SC20.

Adsorption kinetic performances

Figure 9 shows the adsorption kinetic curves of silica gel, SC20, SCC20, SC20H, and SCC20H under adsorption initial pressure of $P_0 = 3.37$ kPa and adsorption temperature of $T = 30, 35$, and 40°C , respectively. The pressure $P_0 = 3.37$ kPa is 60% of the saturated vapor pressure of water at 35°C . Experimental results indicate that the adsorption equilibrium times of all samples under the three adsorption temperatures are less than 1 h. Hence, the adsorption kinetic curves are only shown within an hour in Figure 9. The dynamic water uptakes of the five adsorbent samples increase rapidly during the initial sorption stage and then slow down gradually until they reach the equilibrium water uptake. For the same adsorption temperature, silica gel has higher equilibrium water uptake than the other samples. The reduction of adsorption capacity can be ascribed to the decreased specific surface area, pore volume, porosity, and relative content of silica gel in consolidated adsorbents. When the adsorption temperature is 30°C , the equilibrium water uptakes of SC20 and SC20H, SCC20 and SCC20H are almost equal with each other. However, the adsorption processes of SC20H and SCC20H spend longer time to reach the equilibrium state. Even though the equilibrium adsorption capacities of SC20H and SCC20H are significantly lower than that of SC20 and SCC20 when the adsorption temperature increases, the adsorption processes of SC20H and SCC20H still spend longer time to reach the adsorption equilibrium. It means that the enhanced mass transfer performance of the consolidated composite adsorbents in freeze-drying method outweighs that of heating–drying method. Therefore, the adsorption performance including adsorption rate and equilibrium water uptake are improved. The equilibrium adsorption times of SC20 at three different adsorption temperatures of 30, 35, and 40°C are 26, 27, and 23 min, respectively, while those of SCC20 are 17, 19, and 22 min. SCC20 has a shorter equilibrium adsorption time than SC20 at the various adsorption temperatures, which can be attributed to the higher porosity, permeability, and heat transfer property of SCC20. The half-time of water adsorption (the adsorption time when the adsorption uptake reaches 50% of the equilibrium uptake) for SC20 and SCC20 at the three different adsorption temperatures is all less than 2 min, which can be deemed to quite suitable for designing adsorption cooling system with a short working cycle.

The increasing adsorption temperature reduces the equilibrium water uptakes of the adsorbents as described in Figure 10. For example, the equilibrium water uptakes of the five samples are 0.223, 0.197, 0.166, 0.198, and 0.167 g/g at the adsorption temperature of 30°C , while they reduce to 0.138, 0.127, 0.106, 0.109, and 0.086 g/g at the adsorption temperature of 40°C , which declines by

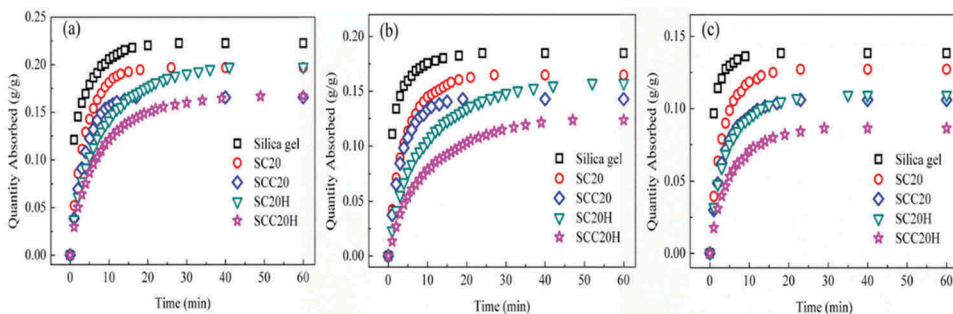


Figure 9. The comparison of the sorption kinetics of water vapor among the five samples at a starting pressure of 3.37 kPa. (a) sorption temperature of 30°C , (b) sorption temperature of 35°C , (c) sorption temperature of 40°C .

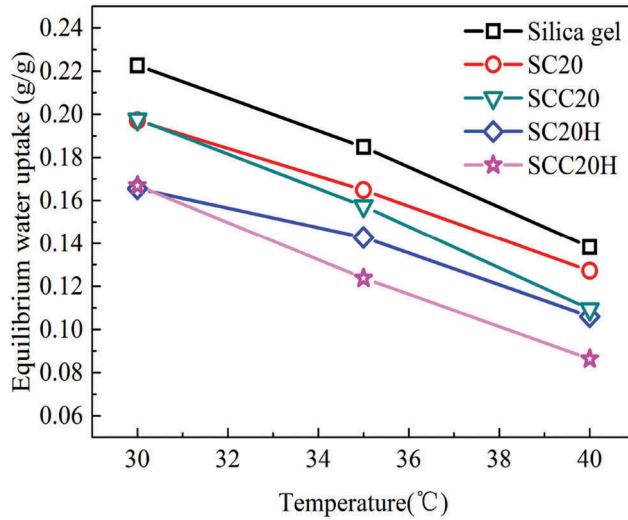


Figure 10. The comparison of equilibrium water uptakes of silica gel, SC20, SCC20, SC20H, and SCC20H at sorption temperature of 30, 35, and 40°C.

38%, 35%, 36%, 45%, and 49%, respectively. Obviously, the temperature has a significant influence on the adsorption capacity. In the practical adsorption system, the temperature of adsorbents goes up significantly due to the phenomenon that the water sorption process is accompanied by a considerable heat release. As the measurement results by Freni et al. [34], the increase of the SWS-pellet temperature can reach 15–40°C because of the dissipation of the sorption heat under vacuum condition. Therefore, reducing the temperature of adsorbents in sorption process is of great importance to improve adsorption capacity.

In order to better understand the dynamic characteristics of adsorbents and evaluate the mass transfer performance, the LDF model is employed for fitting adsorption kinetic curves. The LDF model equation is given as below [35]:

$$\frac{dx}{dt} = K(x^* - x) \quad (4)$$

where $\frac{dx}{dt}$ is the adsorption rate, x^* is the equilibrium adsorption quantity, and K is the rate coefficient.

The following form is obtained by integrating Eq. (3):

$$\ln(x^* - x) = -Kt + \ln A_2 \quad (5)$$

Rearranging Eq. (4) and using Napierian logarithm, the dynamic adsorption quantity is calculated by the following expression:

$$x = x^* - A_2 e^{-Kt} \quad (6)$$

Assuming $x^* = A_1$, then

$$x = A_1 - A_2 e^{-Kt} \quad (7)$$

In Eq. (6), if $t = 0$, then $x = A_1 - A_2$, this is the initial quantity of adsorption. If $t = \infty$, then $x = A_1 = x^*$, this is the equilibrium adsorption quantity.

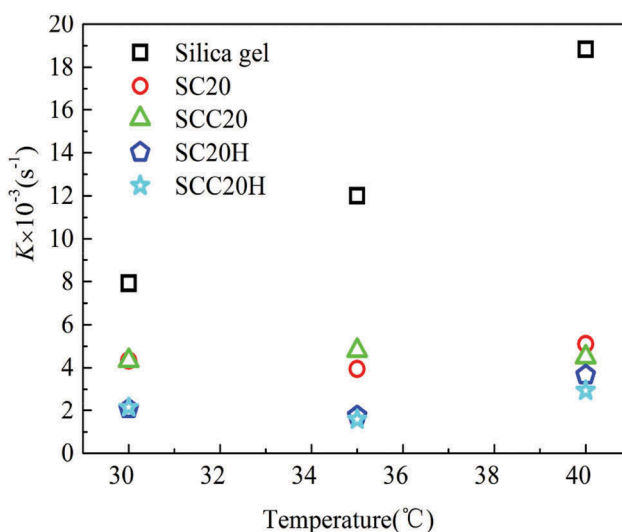


Figure 11. The comparison of adsorption rate coefficients K of silica gel, SC20, SCC20, SC20H, and SCC20H at sorption temperature of 30, 35, and 40°C.

Figure 11 indicates the mass transfer coefficients K obtained by LDF model. It is found that the mass transfer coefficients of silica gel increase with the adsorption temperature, which ranges from 7.913×10^{-3} to $18.817 \times 10^{-3} \text{ s}^{-1}$. Moreover, the mass transfer coefficient of silica gel is significantly larger than that of the consolidated composite adsorbents. It is due to the fact that the mass transfer performance of adsorbents are the main factor affecting the adsorption rate in the adsorption process, thus silica gel with higher porosity and permeability results in a faster adsorption rate as shown in Figure 9. Although the mass transfer performance of consolidated composite adsorbents is not as good as silica gel, the thermal conductivity of the consolidated composite adsorbents is enhanced considerably. The abundant pores are formed in the consolidated composite adsorbents after freeze-drying, which significantly enhance the mass transfer. Meanwhile, the consolidated composite adsorbents are heated and dried at 200°C thoroughly after the process of freeze-drying, which leads to partial decomposition and volatilization of CMC. As a result, certain interparticle pores are formed, and the mass transfer performance is further strengthened. The mass transfer coefficient K of SC20 and SCC20 are approximately stable at $5 \times 10^{-3} \text{ s}^{-1}$ as the change of adsorption temperature, which are greater than the corresponding values of SC20H and SCC20H. It is demonstrated that the samples prepared by freeze-drying method have better mass transfer performance.

Conclusions

A new approach that simultaneously improves the heat and mass transfer performance of adsorbent was introduced in this study to develop the consolidated composite adsorbents. The heat and mass transfer performance of the consolidated composite adsorbents were experimentally investigated. It was found that the thermal conductivity of the adsorbents decreases as the increasing moisture content of wet mixtures during the preparation process, whereas it increases as the increasing mass ratio of heat transfer additive (carbon fiber powder). The thermal conductivities of the two types of adsorbents developed by freeze-drying method, i.e., consolidated silica gel with CMC and consolidated silica gel, CMC and carbon fiber powder, are between 0.42–0.57 and 0.52–0.83 $\text{W m}^{-1} \text{ K}^{-1}$, respectively, when the moisture content of wet mixture in the preparation process is ranged between 20 and 50 wt%. The thermal conductivity of the adsorbents with increasing mass ratio of carbon fiber powder are between 0.57 and 1.66 $\text{W m}^{-1} \text{ K}^{-1}$, when the moisture content of wet mixture in the

preparation process fixed at 20 wt%. Comparing the pore structure properties of typical samples including SC20 and SCC20, it is found that heat transfer additive effectively improve the macroporous porosity and permeability of the consolidated composite adsorbents. The study on adsorption dynamic performance indicates that the freeze-drying method helps to improve the adsorption performance including adsorption rate and equilibrium water uptake. The experimental results also show that the mass transfer coefficient K of the two typical samples are approximately stable at $5 \times 10^{-3} \text{ s}^{-1}$ when the adsorption temperature is ranged between 30 and 40°C, which are almost twice the corresponding values of the samples developed by heating-drying method. Therefore, the proposed approach in our study is effective for simultaneously enhancing the heat and mass transfer performance of the silica gel adsorbents.

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