

# Evaluation of CO<sub>2</sub> adsorption capacity of solid sorbents

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**Abstract** The CO<sub>2</sub> adsorption capacity of the low-cost solid sorbents of waste tire char (TC) and chicken waste char (CW) was compared with commercial active carbon (AC) and 5 Å zeolite (ZA) using thermogravimetric analysis (TG), pressurized TG, and differential scanning calorimetry (DSC). The sorbents were degassed in a TG up to 150 °C to release all gases on the surface of the sample, then cooled down to the designed temperature for adsorption. TG results indicated that the CO<sub>2</sub> adsorption capacity of TC was higher than that of CW, but lower than those of AC and ZA. The maximum adsorption rate of TC at 50 °C was 0.61% min<sup>-1</sup>, lower than that of AC, but higher than that of CW, 0.44% min<sup>-1</sup>. The maximum adsorption rate of ZA at 50 °C was 3.1% min<sup>-1</sup>. When the pressure was over 4 bar, the adsorption rate of ZA was lower than that of TC and AC. At 30 bar, the total CO<sub>2</sub> uptake of TC was 20 wt%, higher than that of CW and ZA but lower than that of AC. The temperature, nitrogen concentration, and water content also influenced the CO<sub>2</sub> adsorption capacity of sorbents to some extent. DSC results showed that adsorption was an exothermic process. The heat of CO<sub>2</sub> adsorption per mole of CO<sub>2</sub> of TC at 50 °C was 24 kJ mol<sup>-1</sup> while the ZA had the largest heat of adsorption at 38 kJ mol<sup>-1</sup>. Comparing the characteristics of TC and CW, TC may be a promising sorbent for removal of CO<sub>2</sub>.

**Keywords** Waste tire · Chicken waste ·  
CO<sub>2</sub> adsorption capacity · Thermal analysis

## Introduction

The increased CO<sub>2</sub> concentration in the atmosphere has been paid more and more attention since CO<sub>2</sub> is one of the major gases which cause greenhouse effect. Research shows that most CO<sub>2</sub> comes from combustion of fossil fuels, so CO<sub>2</sub> capture and storage has been explored. Various methods, such as solvent absorption, adsorption, cryogenics, membranes, microbial, and denitrogenation (i.e., oxy-fuel combustion and chemical looping combustion) are used to capture more CO<sub>2</sub> [1]. Solvent absorption has been widely used and the technology has matured, but regeneration of the solvent is expensive. Cryogenics, membrane, microbial capture, and denitrogenation are under development and have shown considerable promise recently. At present, adsorption is one of the promising methods for CO<sub>2</sub> capture from flue gas. Many solid sorbents have been, or are currently being, investigated, such as activated carbons [2–4], zeolites [3–7], coal [8], fly ash [9], carbonates [10], hydrotalcite-like compounds [11], and metal organic frameworks [12, 13]. Comparing these sorbents, activated carbon presents a series of advantages for CO<sub>2</sub> adsorption, such as low cost, high capacity and selectivity. It has been utilized in pilot-scale power plants, but not yet in large-scale power plants, so it is necessary to develop low-cost sorbents for large-scale plants [14]. Activated carbons can be produced from any type of carbonaceous materials, such as waste tire [15], fly ash [9], biomass [16, 17], and chicken waste [18]. Waste tire and chicken waste have been considered to be a profitable way for generating activated carbon [13, 15], but few studies on evaluating the adsorption capacity of activated carbon from waste tire and chicken waste have been conducted. This paper evaluates the CO<sub>2</sub> adsorption capacity of activated carbon from waste tire char (TC), chicken waste (CW) and

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compares them with commercial activated carbon (AC) and 5 Å zeolite (ZA) using thermogravimetric analysis (TG), differential scanning calorimetry (DSC), and pressurized TG. The specific factors examined were temperature, nitrogen interference, and water content.

## Materials and methods

### Materials

Commercially available 5 Å zeolite (TA Instruments, USA, CAS 69912-79-4), Activated carbon (Fisher, USA, CAS 7440-44-0) were used as-received. The original waste tire and chicken waste were first crushed, dried, sieved, and then pyrolyzed at 650 °C in a nitrogen atmosphere with a flow rate of 100 mL min<sup>-1</sup>. Then 0.1 mL min<sup>-1</sup> water was injected for 60 min to complete the process.

### Methods

#### *Textural characterization*

The textural properties of the sorbents were characterized by a Micromeritics ASAP 2020, (accelerated surface area and porosity analyzer). Prior to the adsorption measurement, the sorbents were first degassed at 150 °C under a vacuum of 30 μmHg (4 Pa) for 120 min. The apparent surface area of the samples was evaluated from the N<sub>2</sub> adsorption isotherms by applying the BET equation in the relative pressure range of 0.05–0.35. The pore size distribution and the micropore volume were determined by *t*-plot method. BJH method was used to determine mesoporosity. The porosity type is based on IUPAC classification.

#### *Adsorption–desorption isotherms*

In the experiment, the temperature range was set in the 40–75 °C range to cover the typical temperature of 50–77 °C that is seen after the flue gas desulfurization (FGD) system.

The CO<sub>2</sub> adsorption and desorption performance of the solid sorbents were measured using a TA Instruments Q600 SDT. Approximately 10 mg sample was placed in an alumina crucible and outgassed at 150 °C for 30 min under N<sub>2</sub> gas flowing at 100 mL min<sup>-1</sup>. Subsequently the temperature was decreased to 40, 50, and 75 °C, respectively, and then either CO<sub>2</sub> or the simple simulated flue gas consisting of 15% CO<sub>2</sub> in N<sub>2</sub> was introduced with a flow rate of 100 mL min<sup>-1</sup>. After 60 min of adsorption, the gas was switched back to pure N<sub>2</sub> at 100 mL min<sup>-1</sup> to perform desorption at the same temperature.

The CO<sub>2</sub> adsorption/desorption with 10% H<sub>2</sub>O experiment was performed using a Dupont 951 TGA. Approximately 10 mg sample was placed in a platinum pan and outgassed at 150 °C for 30 min under N<sub>2</sub> gas at 50 mL min<sup>-1</sup>. Subsequently the temperature was decreased to 50 °C, and CO<sub>2</sub> and 10% H<sub>2</sub>O were introduced with a flow rate of 50 mL min<sup>-1</sup>. The water was injected by a syringe. After the CO<sub>2</sub> adsorption reached equilibrium, the CO<sub>2</sub> and 10% H<sub>2</sub>O were stopped and 50 mL min<sup>-1</sup> nitrogen was introduced again for desorption for 60 min.

The pressure swing adsorption/desorption was conducted on TA Instruments TGA-HP150s. The system consists of Rubotherm magnetic suspension balance and a reaction chamber. The magnetic suspension balance with an accuracy of 0.01 mg is isolated from the reaction chamber and the aggressive purge gas, which allows the chamber to be completely sealed. Approximately 200 mg sample was placed in the alumina holder and outgassed at 150 °C for 30 min under N<sub>2</sub> at 500 mL min<sup>-1</sup>. Subsequently the temperature was decreased to 75 °C and the CO<sub>2</sub> adsorbate was introduced with a flow rate of 500 mL min<sup>-1</sup>. Then the pressure was increased from 1 to 30 bar, and held isothermal for 60 min. The volume of the furnace is too big to keep the temperature at 50 °C, so the experiment was done at 75 °C. Desorption at the same temperature was conducted by gradually decreasing the pressure from 30 to 1 bar after the adsorption. In this system, the balance is non-symmetrical, so the buoyancy correction is important, which includes magnet assembly, sample holder and sample.

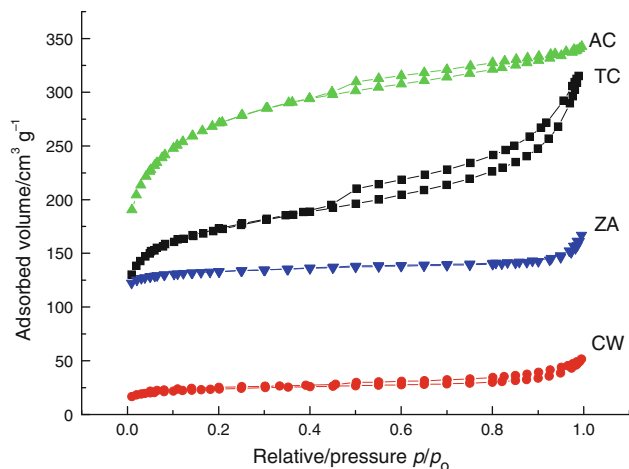
#### *Heat of adsorption–desorption*

The heat of adsorption was measured using a TA Instruments Q2000 DSC. About 3–5 mg sorbents was placed in an open aluminum pan and outgassed at 150 °C for 30 min under N<sub>2</sub> at 50 mL min<sup>-1</sup>. Subsequently the temperature was decreased to 40, 50, and 75 °C, respectively, and the CO<sub>2</sub> gas flow was introduced at 50 mL min<sup>-1</sup>. After 60 min adsorption, the gas was switched back to pure N<sub>2</sub> at 50 mL min<sup>-1</sup> for 60 min for desorption at the same temperature.

## Results and discussion

### Textural characterization

The textural properties of the sorbents were determined by the adsorption of N<sub>2</sub> at -196 °C. The N<sub>2</sub> adsorption isotherms showed that AC was a microporous material with a type I adsorption isotherm while TC, CW, and ZA had type II adsorption isotherms based on IUPAC classification



**Fig. 1** Adsorption–desorption isotherms of solid sorbents at  $-196\text{ }^{\circ}\text{C}$

**Table 1** Physical properties of sorbents

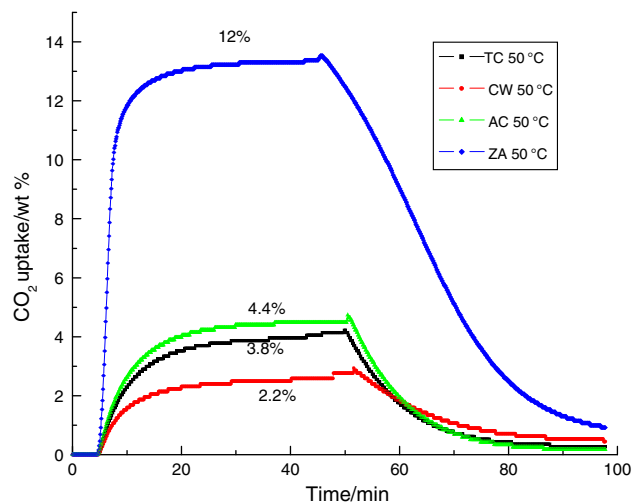
Sample ID	BET surface area/ $\text{m}^2\text{ g}^{-1}$	Microporosity/ $\text{cm}^3\text{ g}^{-1}$	Mesoporosity/ $\text{cm}^3\text{ g}^{-1}$
TC	523	0.15	0.33
CW	72	0.02	0.05
AC	817	0.21	0.29
ZA	384	0.18	0.07

(Fig. 1). Table 1 shows that for carbon-based sorbents (TC, CW and AC), the higher the microporosity, the higher the surface area, which is because the micropores contribute 95% to the total surface area. Although the microporosity of ZA was  $0.18\text{ cm}^3\text{ g}^{-1}$ , the surface area was only  $384\text{ m}^2\text{ g}^{-1}$ , less than that of TC and AC, indicating that the structure of ZA was different from the carbon-based sorbents. It can also be noticed that even though the mesoporosity of the TC was  $0.33\text{ cm}^3\text{ g}^{-1}$ , the surface area was less than that of AC.

#### Adsorption isotherms

The ideal solid sorbent candidate for CO<sub>2</sub> capture should have high CO<sub>2</sub> selectivity and adsorption capacity, high pressure loading, and ease of regeneration. So the following factors were taken into account when evaluating the sorbents: weight uptake during adsorption, adsorption rate and desorption that related to regeneration of the sorbents, CO<sub>2</sub>/N<sub>2</sub> selectivity as well as the effects of H<sub>2</sub>O and pressure.

The CO<sub>2</sub> adsorption capacity of the four sorbents at 50 °C under a CO<sub>2</sub> atmosphere is given in Fig. 2. The CO<sub>2</sub> uptake of TC at 50 °C was similar to that of AC, 3–4 wt%, while the CW had the least at 2.2 wt%. The CO<sub>2</sub> uptake of



**Fig. 2** Adsorption isotherms of TC, CW, AC, and ZA at  $50\text{ }^{\circ}\text{C}$  under CO<sub>2</sub> flow

ZA was the largest at 12 wt%. Although the surface area of AC was larger than that of ZA, the CO<sub>2</sub> adsorption capacity of AC was less than that of ZA, indicating that surface area was not the determining factor, consistent with other researcher [3] that found bulk density was a determining factor when adsorption was denoted in moles on mass adsorbent. For carbonaceous sorbents, the higher the surface area, the higher the adsorption capacity.

The absorbing rate is one of the important parameters for evaluating the adsorption capacity of CO<sub>2</sub>. With a higher adsorbing rate, the time to reach equilibrium is shorter. Table 2 shows that the maximum adsorbing rate of the ZA at 50 °C was the highest at  $4.97\%\text{ min}^{-1}$ . The maximum adsorbing rate of TC at 50 °C was  $0.61\%\text{ min}^{-1}$  and for CW it was  $0.44\%\text{ min}^{-1}$ , less than that of ZA and AC.

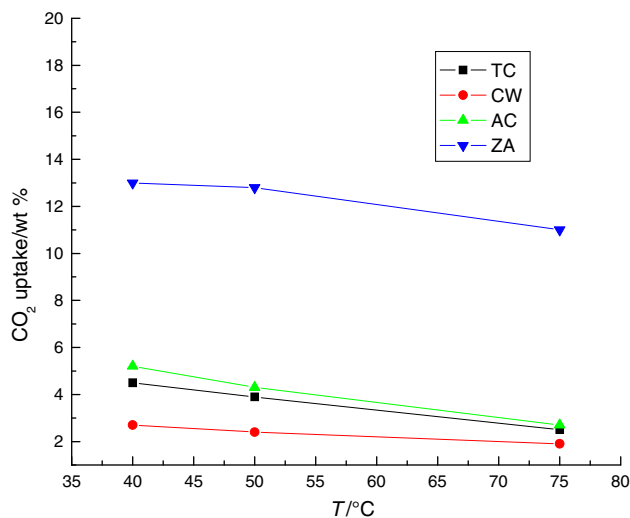
The desorption results show that the weight loss of all sorbents in CO<sub>2</sub> was similar to that of the weight gain during adsorption (Table 2), indicating that the CO<sub>2</sub> adsorption for the samples was nearly completely reversible under a pure CO<sub>2</sub> atmosphere.

#### Effect of temperature

Temperature is an important parameter for evaluating CO<sub>2</sub> adsorption capacity of sorbents. Figure 3 shows that all solid sorbents had a similar trend, where the adsorption capacity decreased significantly with increasing adsorption temperature. Similar observations on the relationship between the sorption capacity and temperature have been reported in other studies of carbon-based sorbents and zeolite sorbents [2–6]. This is because adsorption is a physical process, where both the surface adsorption energy and molecule diffusion rate increase with increasing temperature [5]. As a result, the adsorbed CO<sub>2</sub> in the sorbents

**Table 2** Summarized TGA result for sorbents under pure CO<sub>2</sub> flow

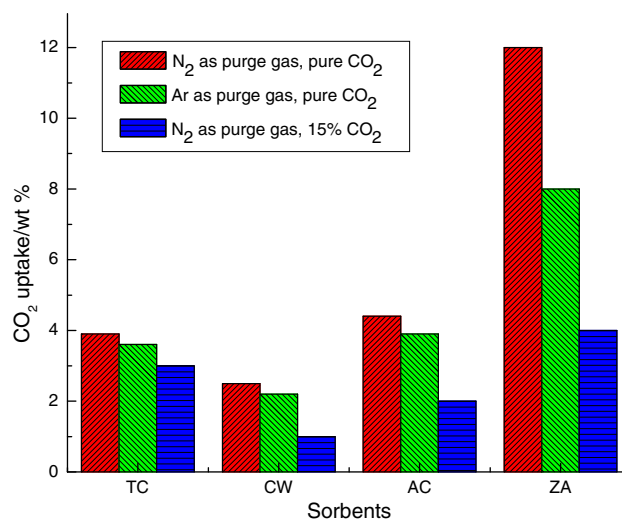
Sample ID	Adsorption weight at 50 °C/%	Desorption weight at 50 °C/%	Adsorption rate at 40 °C/ % min <sup>-1</sup>	Adsorption rate at 50 °C/ % min <sup>-1</sup>	Adsorption rate at 75 °C/ % min <sup>-1</sup>
TC	3.9	3.8	0.77	0.61	0.35
CW	2.5	2.2	0.53	0.44	0.26
AC	4.4	4.3	0.91	0.71	0.38
ZA	12.7	12.5	5.54	4.97	3.29

**Fig. 3** Adsorption isotherms for sorbents at 40, 50, and 75 °C

desorbed. For carbon-based adsorbents, the CO<sub>2</sub> adsorption capacity at 40 °C was two times higher than that at 75 °C, while for ZA there was no obvious difference, indicating the adsorption mechanism of ZA was different that for carbon-based sorbents. The adsorption rate also decreased with increasing temperature (Table 2). From a practical point of view, 40–50 °C may be a suitable temperature for the sorbent since even the adsorption capacity increased at lower temperatures, the lower temperature needs more energy or time.

#### Effect of N<sub>2</sub>

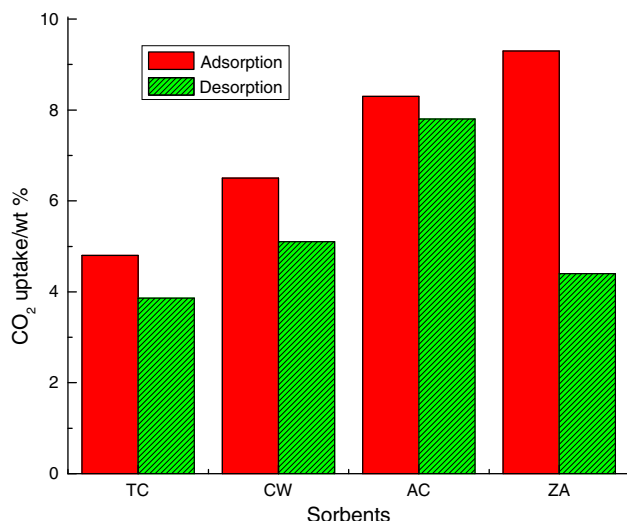
The effect of N<sub>2</sub> on CO<sub>2</sub> adsorption capacity of sorbents was studied by comparing the CO<sub>2</sub> adsorption capacity using argon and N<sub>2</sub> as purge gasses, respectively. Figure 4 shows that when the purge gas was argon, the CO<sub>2</sub> uptake of carbon-based sorbents and ZA decreased by 0.3 and 4 wt%, respectively, indicating that N<sub>2</sub> has more influence on ZA. These findings agree with Siriwardane et al.'s observation [2]. The simple simulated flue gas of 15% CO<sub>2</sub> in N<sub>2</sub> was also used to investigate the CO<sub>2</sub> adsorption capacity of the sorbents. From Fig. 4, it can be seen that under the simulated flue gas condition, the adsorption

**Fig. 4** CO<sub>2</sub> adsorption capacity for sorbents at 50 °C under different purge gas

capacity of all sorbents decreased by 2/3, indicating that the sorbents had the priority of adsorbing the CO<sub>2</sub>, which was different from the calculated result of Mao et al. [19]. So the priority of N<sub>2</sub> and CO<sub>2</sub> for the sorbents needs to be further studied.

#### Effect of H<sub>2</sub>O

Most flue gas from post-combustion is very humid, which will poison the sorbents for adsorbing CO<sub>2</sub> because some sorbents have a higher affinity for H<sub>2</sub>O than CO<sub>2</sub> [6, 19]. 10% H<sub>2</sub>O in CO<sub>2</sub> was used to study the effect of H<sub>2</sub>O on the CO<sub>2</sub> adsorption capacity of sorbents. The CO<sub>2</sub> adsorption for all sorbents changed considerably since it not only adsorbed water but also adsorbed CO<sub>2</sub>. The adsorption–desorption results show that the H<sub>2</sub>O adsorption of carbon-based was nearly reversible, but for ZA, it was not because the difference between adsorption and desorption was about 4 wt%, which was caused by H<sub>2</sub>O adsorption (Fig. 5). This also indicates that CO<sub>2</sub> molecule and H<sub>2</sub>O molecule do not have noticeable effect on each other in the adsorption–desorption process for carbon-based sorbents. For ZA sample, the irreversible may be

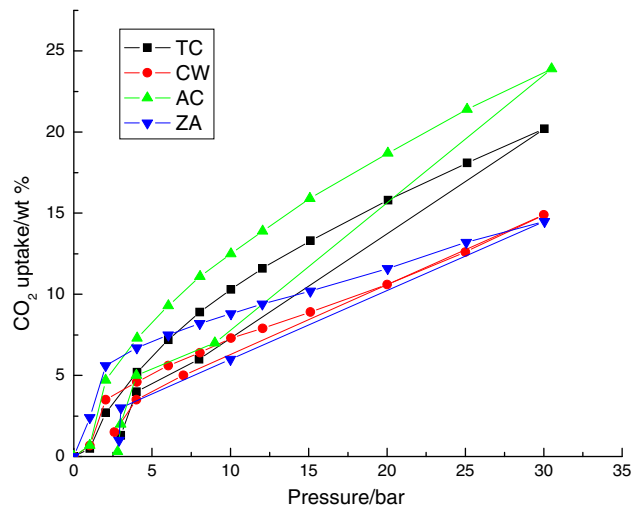


**Fig. 5** Adsorption–desorption isotherms of sorbents under 10% H<sub>2</sub>O balanced CO<sub>2</sub> flow at 75 °C

because ZA has polar function groups, which prefer to adsorb polar compounds such as H<sub>2</sub>O. So when ZA is used as a solid sorbent, drying the adsorbates is very important, while for TC, CW, and AC, the influence of water was negligible. But the CO<sub>2</sub> adsorption capacity and H<sub>2</sub>O adsorption capacity of the sorbents needs to be further studied.

#### Effect of pressure

Pressure swing adsorption (PSA) and temperature swing adsorption (TSA) are commercially practiced technologies for regenerating sorbents. Usually the target gas is adsorbed at high pressure/low temperature and swung to low pressure/high temperature for desorption. Compared to TSA, PSA has many advantages; for example, dry operation, system simplicity, and low energy consumption, as well as no corrosion. PSA also has more challenges because it is based on preferential adsorption of the desired gas on a porous adsorbent, so the purity of CO<sub>2</sub> should be very high. Also the sorbent needs to have a high capture capacity [2]. The adsorption–desorption isotherms of CO<sub>2</sub> are shown in Fig. 6. With increasing pressure, the CO<sub>2</sub> adsorption capacity of the four sorbents increased. When the pressure increased to 30 bar, the total CO<sub>2</sub> uptake weight of AC was the highest at 23 wt%, followed by TC at 20 wt%, and CW and ZA at 15 wt%. It also can be noticed that when the pressure was less than 2 bar, the adsorption rate of ZA was the highest of the four samples, corresponding to the result at atmospheric pressure. Beyond 2 bar, the CO<sub>2</sub> adsorption capacity of ZA increased slowly and when the pressure was more than 4 bar, the CO<sub>2</sub> uptake weight was less than AC and TC,

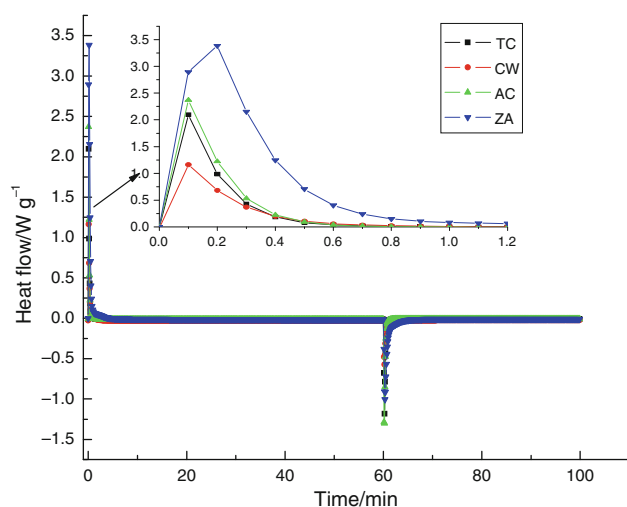


**Fig. 6** Adsorption–desorption isotherms of CO<sub>2</sub> on samples at 75 °C

suggesting that ZA may be not suitable for PSA. This is also confirmed by Mario et al. [3] that reported that ZA was a good adsorbent at atmospheric pressure. The CO<sub>2</sub> adsorption weight of TC and AC increased quickly after 2 bar. The adsorption capacity of CW was the lowest of the four samples, which is likely due to its low surface area. The desorption isotherm showed that the desorption of CO<sub>2</sub> was similar to the adsorption isotherms, indicating that the adsorbed CO<sub>2</sub> can be recovered by lowering the pressure.

#### Heat of adsorption

The heat of adsorption of sorbents represents the strength of adsorbate–sorbent interaction. Quantification of the heat of adsorption is very important for kinetic studies of the adsorption process because the heat released or absorbed upon adsorption influences sorbent temperature and thus the rate of adsorption [20]. Lu et al. [21] obtained the heat of adsorption based on the Clausius–Clapyron equation. Siriwardane et al. [5] measured the heat of adsorption between CO<sub>2</sub> and sorbent using DSC. DSC is a very useful tool for measuring the heat of adsorption and desorption. Figure 7 shows that CO<sub>2</sub> adsorption on TC, CW, AC, and ZA is an exothermic process while the desorption is an endothermic process. It also shows that the heat of adsorption per mole of CO<sub>2</sub> of ZA was the largest, which was two times of that of AC, and followed by TC and CW. Moreover, the heat of adsorption of the sorbents showed the same trend, i.e., the heat of adsorption decreased with increasing temperature (Table 3). The heat of adsorption per mole of CO<sub>2</sub> was 25–40 kJ mol<sup>-1</sup> for sorbents, indicating a weak physical interaction (in range of weak physical interaction of ~20–48 kJ mol<sup>-1</sup>), which is caused by van der Waals forces. Combining the TG and



**Fig. 7** Heat adsorption of four sorbents at 50 °C

**Table 3** Heat of CO<sub>2</sub> adsorption of sorbents at 50 °C

Sample ID	Heat of adsorption at 50 °C/kJ mol <sup>-1</sup>
TC	-24
CW	-31
AC	-22
ZA	-38

DSC results of sorbents, TC may be a good sorbent for CO<sub>2</sub> capture in power plant.

## Conclusions

The CO<sub>2</sub> adsorption behavior of TC, CW, AC, and ZA have been investigated at various temperatures, pressures, N<sub>2</sub> levels, and water contents via thermogravimetric analysis, differential scanning calorimetry, and pressurized thermogravimetric analysis. TG results showed that the CO<sub>2</sub> adsorption capacity of TC was similar to that of AC while CW had the least. ZA has the largest CO<sub>2</sub> adsorption capacity. The surface area is not the determining factor for evaluating the CO<sub>2</sub> adsorption capacity. H<sub>2</sub>O had less influence on the CO<sub>2</sub> adsorption capacity of carbon-based sorbents, while it seriously influences the CO<sub>2</sub> capacity of ZA, whose adsorption weight decreased by 5% at 50 °C. When the pressure was less than 2 bar, the adsorption rate of ZA was the largest, but as the pressure went over 2 bar, the CO<sub>2</sub> adsorption rate of carbon-based sorbents became larger. The total CO<sub>2</sub> uptake weight of TC was 20 wt%. The heat of adsorption per mole of CO<sub>2</sub> of TC was

24 kJ mol<sup>-1</sup>, suggesting TC is a good adsorbent candidate, not only because of high uptake adsorption weight, but also it is a reused material. Since TC is sensitive to the temperature, the next step is to eliminate the influence of temperature and improve the adsorption weight.

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