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CO₂ capture by kaolinite and its adsorption mechanismYen-Hua Chen ^{*}, De-Long Lu

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ABSTRACT

The low-cost and naturally abundant clay mineral kaolinite was studied for use as an adsorbent for CO₂ capture. Samples of kaolinite were subjected to acid treatments to improve their textural properties, namely, its surface area and pore volume. It was found that the kaolinite sample treated with 3 M H₂SO₄ for 10 h reaction exhibited the highest Brunauer–Emmett–Teller (BET) surface area (18.9–74.3 m²/g) and pore volume (0.11–0.31 cm³/g). The CO₂ adsorption capacity of kaolinite, which was ~0 mg-CO₂/g-sorbent at 25 °C, increased to 3.4 mg-CO₂/g-sorbent after the acid treatment. Moreover, it was found that the CO₂ adsorption capacity of kaolinite was greater at room temperature than at higher temperatures. The CO₂ adsorption by kaolinite, which was investigated using X-ray diffraction analysis, Fourier transform infrared spectroscopy, and CO₂ adsorption isotherm measurements, was found to be mainly attributable to physical adsorption.

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1. Introduction

Global warming due to CO₂ emissions into the atmosphere has become a public concern and an important environmental challenge facing the world (Rosa and Ribeiro, 2001; Damen et al., 2006; Gibbins and Chalmers, 2008). One potential solution is to develop and implement CO₂ capture and storage (CCS) technologies. Adsorption is considered to be a promising CCS technology for separating CO₂ from gas mixtures owing to its low energy requirement, ease of implementation, and low maintenance. A number of novel CO₂ adsorbents are being studied, and considerable attention is being paid to mesoporous silicas because of their large surface areas, uniform mesopores, and tunable pore size (Peter and Sayari, 2006; Son et al., 2008; Du et al., 2013). Mello et al. (2011) reported that MCM-41 exhibits a CO₂ adsorption capacity of 5.3 mg/g. Sanz et al. (2012) studied the adsorption and desorption of CO₂ on SBA-15 and reported that its CO₂ adsorption capacity was 19.4 mg/g at 298 K. Xu et al. (2002) developed a functional MCM-41 material that exhibited a CO₂ adsorption capacity as high as 133 mg/g. However, the above-mentioned materials are expensive and therefore hard to adopt on an industrial scale.

A number of alternatives, including basic liquid-form sorbents and supported amines (MacDowell et al., 2010; Choi et al., 2011; Nuchitprasittichai and Cremaschi, 2011; Brilman et al., 2013), are being considered. Nonetheless, the need for the thermal regeneration of the adsorbent results in issues such as adsorbent decomposition and increased energy consumption. A new approach should consist in the preparation of regenerable materials with lower basicities, able to achieve simultaneous retention of large amounts of CO₂ with easy

release upon slight heating. In this regard, clay minerals (Venaruzzo et al., 2002; Rodlert et al., 2004; Gil et al., 2009) appear to be the most suitable materials owing to their low basicities. Clay mineral is one of the most abundant natural materials and is thus available at a low cost. For example, kaolinite, a clay mineral, consists of tetrahedral silicate sheets and octahedral hydroxide sheets in a 1:1 ratio (Deng et al., 2002; Sperinck et al., 2011). Thus, clay mineral can be a potential CO₂ adsorbent owing to its low cost, rich natural abundance, and high mechanical and chemical stability. Consequently, clay mineral should exhibit significant potential for use in the adsorption and separation of CO₂. Yet few studies have investigated the suitability of acid-treated clay minerals for CO₂ capture or their adsorption mechanism.

From an industrial point of view, most research efforts have focused on clay minerals. In this study, the commonly available and cheap clay mineral kaolinite was investigated for use as a CO₂ adsorbent. It was treated with H₂SO₄ in order to improve its textural properties, namely, its pore volume and surface area, for CO₂ capture. The acid-treated adsorbent sample was compared with the untreated one. Next, the acid-treated sample was used for CO₂ adsorption, which was characterized using thermogravimetric analysis (TGA). The crystal structure, textural properties, and morphology of the adsorbent were characterized using X-ray diffraction (XRD) analysis, N₂ adsorption tests (i.e., Brunauer–Emmett–Teller or BET measurements), and scanning electron microscopy (SEM). The effects of the pretreatment temperature and time (i.e., of the treatment before CO₂ adsorption), the adsorption temperature, and the desorption temperature on the CO₂ adsorption–desorption process as well as the thermal stability of kaolinite were investigated. Further, we attempted to determine whether acid-treated kaolinite exhibited a higher CO₂ adsorption capacity than did untreated kaolinite. We also investigated whether the adsorption of CO₂ onto kaolinite was owing to physical adsorption or whether it also involved chemical adsorption.

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Therefore, the adsorption mechanism of kaolinite was studied in depth using XRD analysis, Fourier transform infrared (FTIR) spectroscopy, and CO₂ adsorption isotherm measurement.

2. Materials and methods

2.1. Preparation of acid-treated kaolinite

In order to improve the textural properties, pore volume, and surface area of kaolinite, kaolinite samples purchased from San-Lin company (Taipei, Taiwan) were treated with H₂SO₄ solutions of different concentrations (0.5, 1, 2, and 3 M). Kaolinite was added to the acid solution in a fixed ratio of 1 g of kaolinite per 10 ml of acid. Next, the mixtures were heated in a bath at 95 °C for the acid treatment, while being stirred at 300 rpm for 3, 5, 10, and 15 h. Next, the dispersions were filtered and the precipitates were washed with large amounts of deionized water and dried in an oven overnight at 60 °C. The H₂SO₄ solution concentration of 3 M was found to be the most suitable one, as it resulted in the highest pore volume and surface area. The textural properties of the various kaolinite samples treated with the H₂SO₄ solutions of different concentrations and for various reaction times are listed in the Tables 1 and 2, respectively.

2.2. Characterization of acid-treated kaolinite

The crystal structure of kaolinite was identified using XRD analysis. The morphology and the grain distribution of kaolinite were observed using SEM. To study the thermal stability of the kaolinite, TGA was performed using a NETZSCH analyzer. The sample was ground into a powder and analyzed over temperatures of 25–1000 °C at a heating rate of 10 °C/min in a N₂ atmosphere. The textural properties of kaolinite were characterized on the basis of physical adsorption of N₂ at 77 K. A Micromeritics ASAP 2020 analyzer was employed for the purpose. The acid-treated kaolinite sample was degassed at 150 °C under vacuum for 24 h before the measurement. The surface area was determined from the N₂ adsorption isotherm using the BET equation. The total pore volume was calculated on the basis of the amount of N₂ absorbed after the completion of pore condensation; the relative pressure (P/P₀) was 0.995. The pore sizes were determined from the Barrett–Joyner–Halenda (BJH) pore size distribution curve.

2.3. Determination of CO₂ adsorption capacity

The CO₂ adsorption–desorption performance of the acid-treated kaolinite sample was assessed on the basis of the changes in its weight resulting from the adsorption and desorption of pure CO₂; the changes were determined from the results of TGA. Approximately 10 mg of the sorbent was placed in the measuring pan, and the temperature was increased from 25 °C to the desired temperature (150, 200, and 250 °C) at a rate of 10 °C/min. The sample was then heated at the desired temperature for 40, 80, 120, and 180 min in pure N₂ (99.9%), whose flow rate was 100 ml/min, in order to remove moisture and other impurities from the sample. The temperature was then dropped to the desired adsorption temperature (25, 50, 100, and 150 °C), and the flowing gas was changed from N₂ to pure CO₂ (99.5%). The adsorption temperature

Table 2

The BET surface area, pore volume, and pore size of the kaolinites treated with 3 M H₂SO₄ for different treatment times.

Reaction time (h)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
3	42.4	0.139	13.7
5	61.0	0.164	11.9
10	74.3	0.305	15.3
15	77.6	0.290	17.8

was maintained for 1 h to allow for CO₂ adsorption. Finally, the temperature was increased to 100 or 150 °C, and the flowing gas was changed back to N₂ to allow for CO₂ desorption. Then, on the basis of the change in the weight of the sample, measured using TGA, the CO₂ adsorption capacity (mg-CO₂/g-adsorbent) of the sample was calculated. It should be pointed out that the adsorption capacity as determined from the TGA results in this study is not the equilibrium adsorption capacity, as the weight of the sample kept slowly increasing even after 1 h of adsorption, most likely owing to the adsorption rate being low.

In order to elucidate the CO₂ adsorption mechanism of kaolinite (i.e., to determine the ratio of the amounts of CO₂ adsorbed physically and chemically), its CO₂ adsorption isotherm at 298 K was also determined using an ASAP 2020c (Micromeritics) static volumetric apparatus. As the CO₂ adsorption isotherm was measured (this curve included physical and chemical adsorption of CO₂), desorption was performed on the sample at 25 °C for 1 h in a vacuum generated using a turbomolecular pump (to desorb the CO₂ molecules with the physical adsorption). Then the CO₂ adsorption isotherm was measured again to obtain the solely physical adsorption curve by using the ASAP 2020 analyzer. After the CO₂ adsorption experiment, the resultant was examined using XRD and FTIR analyses.

3. Results and discussion

3.1. Characteristics of untreated kaolinites

The XRD pattern of the untreated kaolinite sample is shown in Fig. 1(a). The diffraction peaks could be attributed as belonging to kaolinite with a triclinic structure and were in agreement with the standard data given in its ICDD card (58–2001). No impurity peaks were observed. Further, the intensity of the diffraction peaks was high and the peaks were sharp. This indicated that the starting sample was highly crystalline and consisted entirely of kaolinite. Moreover, the XRD pattern of acid-treated kaolinite kept unchanged after acid treatment (Fig. 1(b)), which suggested the structure of kaolinites would not be affected with acid treatment.

The morphology of the kaolinite sample was investigated using SEM; the resulting image is shown in Fig. 2(a). It can be seen that the kaolinite sample was composed of large as well as small grains. The former

Table 1

The BET surface area, pore volume, and pore size of the kaolinites treated with H₂SO₄ solutions of different concentrations.

Concentration of H ₂ SO ₄ (M)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
0 (untreated kaolinite)	18.9	0.110	21.0
0.5	24.7	0.097	16.5
1	33.7	0.117	16.1
2	43.3	0.120	12.8
3	42.4	0.139	13.7

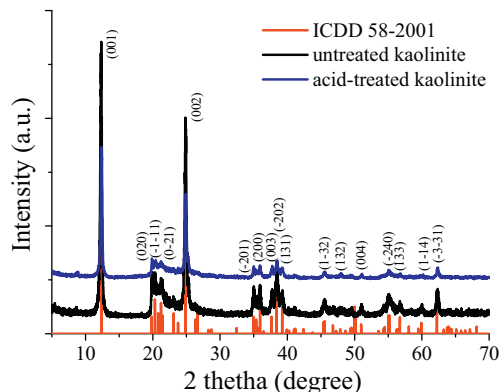


Fig. 1. The XRD pattern of the untreated and acid-treated kaolinites.

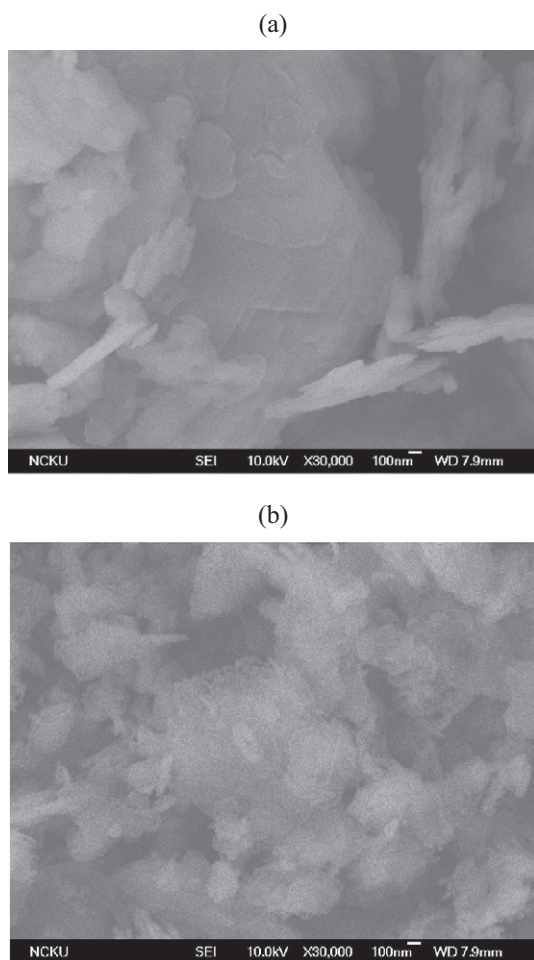


Fig. 2. The SEM morphologies of the (a) untreated and (b) acid-treated kaolinites.

had a hexagonal shape with a layered-stacking structure and their size was approximately 5 μm , while the latter had a fracture-like shape. The smaller grains formed aggregates that had a diameter of approximately 1 μm . The SEM image of acid-treated kaolinite showed an uneven and cracked surface (Fig. 2(b)); it indicated a more rough and fractured surface made the acid-treated kaolinite along with a higher surface area after acid treatment.

The specific surface area, pore volume, and pore diameter of the kaolinite sample were 18.9 m^2/g , 0.11 cm^3/g , and 21.0 nm, respectively. The N_2 adsorption–desorption isotherm curve for the kaolinite sample is shown in Fig. 3(a). On the basis of the IUPAC classification, the isotherm could be labeled as a typical type-IV isotherm (Miller et al., 1987) because it exhibited a hysteresis loop between the adsorption and desorption curves. Moreover, the shapes of the adsorption and desorption curves were similar to that of an H3 hysteresis loop (Leslie-Pelecky and Rieke, 1996). This type of an isotherm is usually noticed in the case of aggregates of tabular or sheet-like materials and was thus indicative of the layer-like structure of the kaolinite sample.

3.2. Characterization of acid-treated kaolinite

3.2.1. Effects of acid treatment on the textural properties of kaolinite

To improve the textural properties of kaolinite, samples of the adsorbent were treated with H_2SO_4 solutions with concentrations of 0.5, 1, 2, and 3 M. Table 1 lists the textural properties, including the BET surface areas, pore volumes, and pore sizes, of the untreated and treated kaolinite samples. The surface area and pore volume of the untreated kaolinite sample were 18.9 m^2/g and 0.11 cm^3/g , respectively, indicating that the

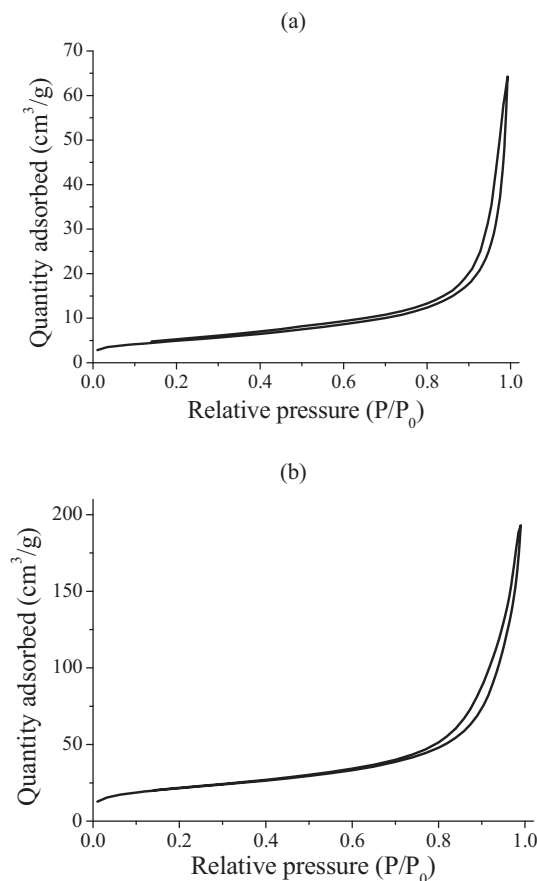


Fig. 3. The nitrogen adsorption–desorption isotherm curves for the (a) untreated and (b) acid-treated kaolinites.

original kaolinite exhibited low porosity. After the acid treatment, the values increased to 42.4 m^2/g and 0.139 cm^3/g , respectively. This suggested that an acid treatment can effectively improve the textural properties of kaolinite. This is probably owing to the dissolution of the metal ions present in the kaolinite and the rearrangement of its crystal structure, as a result of a reaction between the acid and the clay mineral.

Of the various acid-treated kaolinite samples, the one treated with the 3 M solution of H_2SO_4 exhibited the highest pore volume and surface area and was thus selected to study the effects of the treatment time (3, 5, 10, and 15 h) on the textural properties. Table 2 lists the textural properties of the kaolinite samples treated with the 3 M solution of H_2SO_4 for different treatment times. It can be seen that the surface area and pore volume of the kaolinite sample increased with an increase in the reaction time. For reaction times of 10 and 15 h, the surface areas were 74.3 and 77.6 m^2/g , respectively, while the pore volumes were 0.305 and 0.290 cm^3/g , respectively. Thus, because of energy and cost considerations, we used the kaolinite sample treated with the 3 M solution of H_2SO_4 for 10 h for CO_2 capture and its N_2 adsorption–desorption isotherm curve was shown in Fig. 3(b). The isotherm curve could be labeled as a typical type-IV isotherm and an H3 hysteresis loop.

3.2.2. Thermal stability of acid-treated kaolinite

The thermal stability of acid-treated kaolinite was measured through TGA and differential thermal analysis (DTA). The variation of weight for the kaolinite sample and the corresponding derivative thermogravimetric (DTG) and DTA curves are shown in the Fig. 4. The acid-treated kaolinite sample exhibited a weight loss of 4.5% at 455 $^{\circ}\text{C}$, as evidenced by the DTG curve peak at 500 $^{\circ}\text{C}$, while the DTA curve showed an endothermic peak at approximately 575 $^{\circ}\text{C}$. This weight loss was related to the dehydroxylation of the kaolinite layers. This

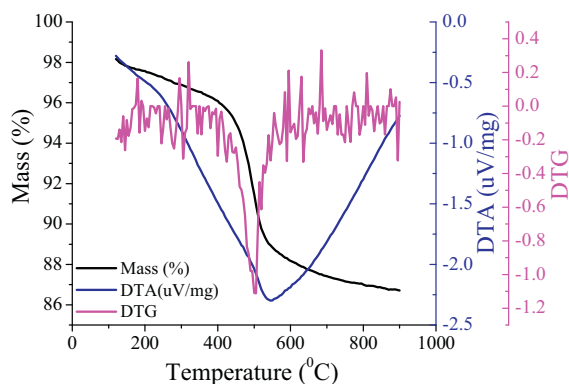


Fig. 4. The weight loss and corresponding first derivative DTG curve and DTA curve of acid-treated kaolinite.

result was in keeping with those reported previously (Piga, 1995; Cheng et al., 2010; Ptáček et al., 2010). On the basis of these results, the temperature was kept at less than 455 °C when investigating the CO₂ adsorption–desorption mechanism of kaolinite.

3.3. Results of CO₂ adsorption analysis

The CO₂ adsorption capacities of the untreated and acid-treated kaolinite samples were examined. However, because the CO₂ adsorption capacity of the untreated samples was lower than the detection limit of the TGA system employed, we will focus on the kaolinite sample treated with 3 M H₂SO₄ for 10 h. It is known that the pretreatment temperature and time as well as the adsorption and desorption temperatures have significant effects on the adsorption capacity of an adsorbent. We now discuss how these factors affected the adsorption of CO₂ by kaolinite.

3.3.1. Effect of the pretreatment temperature

Before determining the CO₂ adsorption capacity, the pretreatment temperature of the kaolinite sample was increased from 25 °C to the desired level (150, 200, and 250 °C). The results of the CO₂ adsorption capacity measurement are shown in Fig. 5. It can be seen that a weight loss of approximately 2% occurred during the pretreatment process, owing to the desorption of the physically adsorbed water. This was followed by an increase in weight because of the adsorption of CO₂. The CO₂ adsorption capacity of kaolinite was determined using the following formula: Q (capacity in mg/g) = ((the weight of the sample after CO₂ adsorption) – (the weight of the sample before CO₂ adsorption)) / (the weight of the sample before CO₂ adsorption). From the TG curve, the CO₂ adsorption capacities for pretreatment temperatures of 150, 200, and 250 °C were found to be 2.8, 2.7, and 2.5 mg/g, respectively. The CO₂ adsorption capacities at the three temperatures were almost the same. Therefore, in order to save time and energy, we chose 150 °C as the pretreatment temperature for the rest of the study.

3.3.2. Effect of pretreatment time

Next, before determining the CO₂ adsorption capacity, the sample was heated to 150 °C and held at this temperature for 40, 80, 120, and 180 min in a flow of pure N₂. The results of the CO₂ adsorption capacity measurement are shown in Fig. 6. It can be seen that the curve is unstable in the high-temperature region; this was owing to deviations in the TGA system used for the measurements. From the TG curve, the CO₂ adsorption capacities were calculated to be 3.3, 3.2, 3.0, and 3.5 mg/g for pretreatment times of 40, 80, 120, and 180 min, respectively. Thus, the CO₂ adsorption capacities corresponding to the different pretreatment times were almost the same, suggesting that the pretreatment times investigated were enough to allow all the physically adsorbed

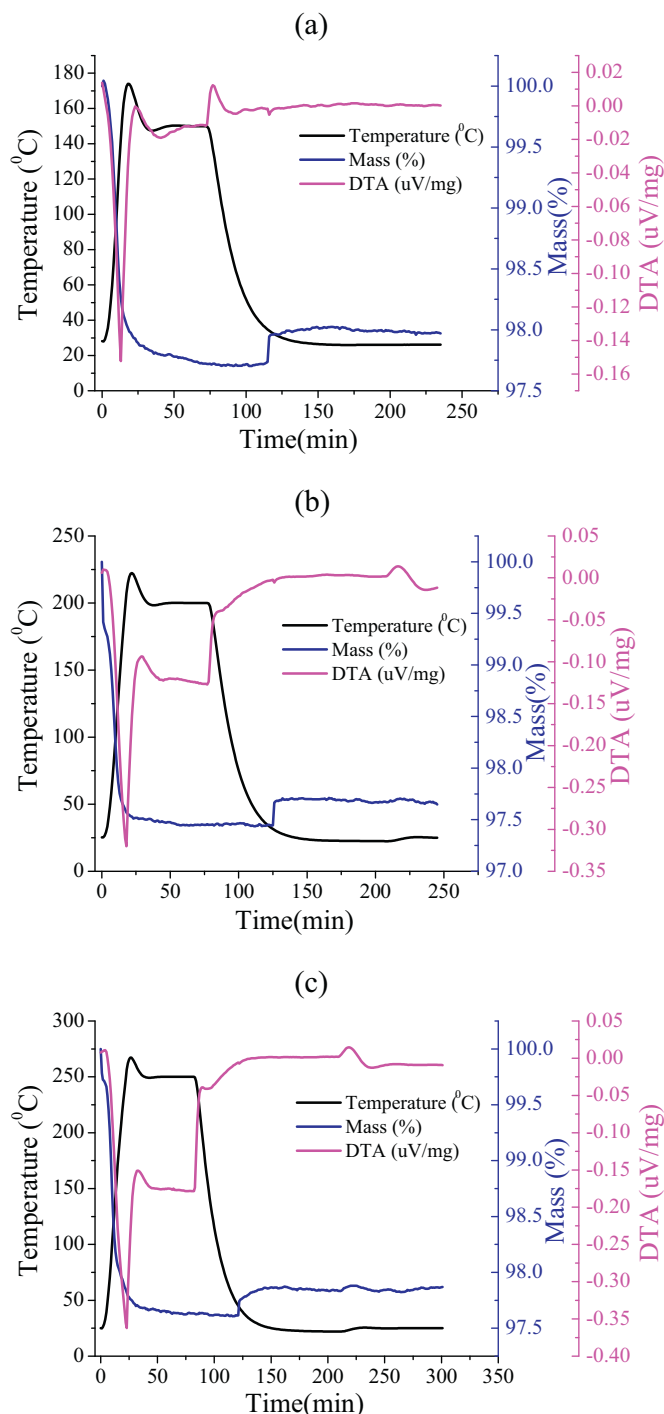


Fig. 5. The CO₂ adsorption capacity in relation to the pre-treated temperature of acid-treated kaolinite from the TG measurement at (a) 150, (b) 200, and (c) 250 °C.

water to be fully desorbed. Therefore, in order to save time and energy, the pretreatment time was set at 40 min.

3.3.3. Effect of temperature during adsorption

In order to evaluate the temperature effect during CO₂ adsorption, the sample was held at the temperatures of 25, 50, 100, and 150 °C for 2 h to allow for CO₂ adsorption. The results of the CO₂ adsorption capacity measurement are shown in Fig. 7. It can be seen that the CO₂ adsorption capacity of kaolinite decreased with an increase in the adsorption temperature. The CO₂ adsorption capacities were 3.3, 2.4, 0, and 0 mg/g for adsorption temperatures of 25, 50, 100, and 150 °C, respectively. Thus,

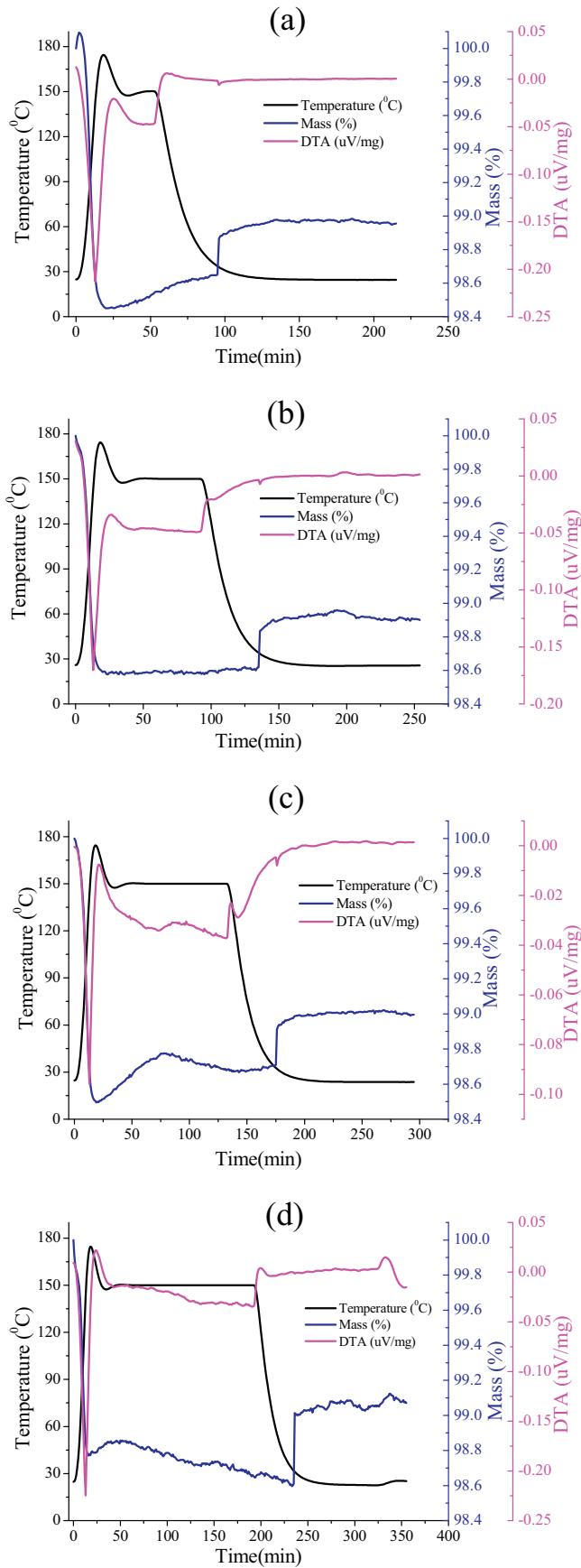


Fig. 6. The CO₂ adsorption ability and the pre-treated time of (a) 40, (b) 80, (c) 120, and (d) 180 min for the acid-treated kaolinite from the TG measurement.

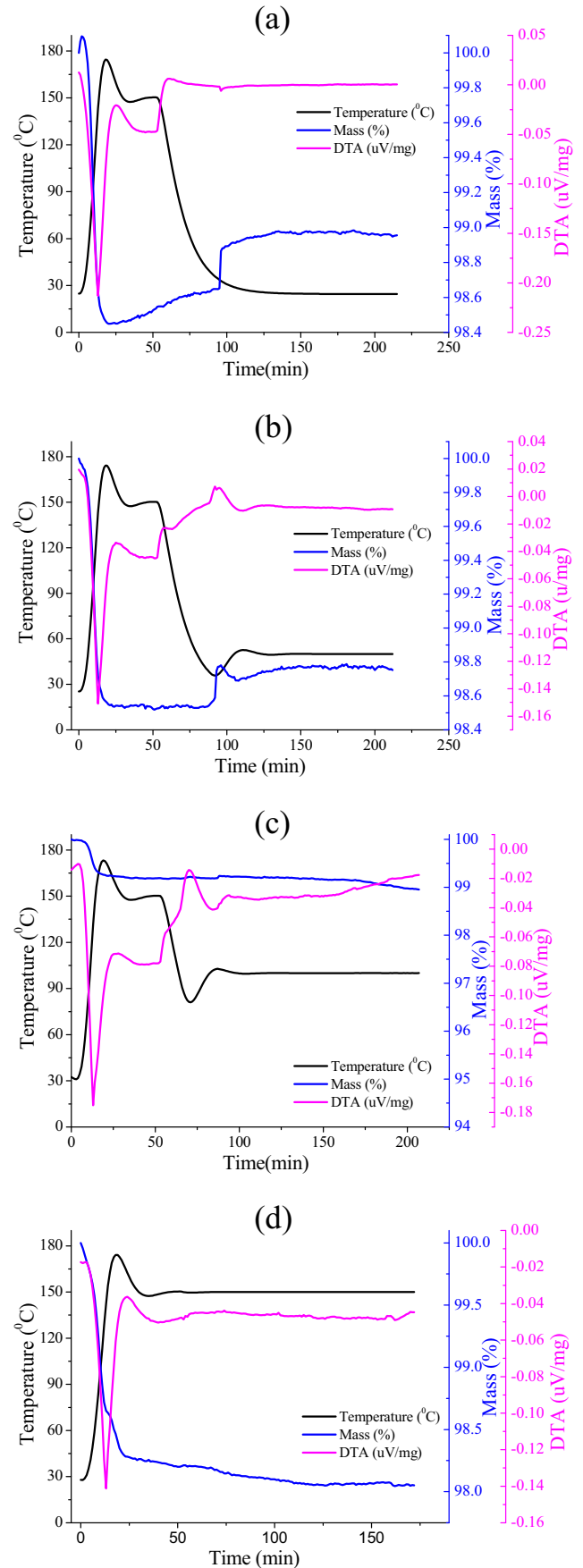


Fig. 7. The CO₂ adsorption capacity in relation to the adsorption temperatures of (a) 25, (b) 50, (c) 100, and (d) 150 °C by the TG measurement.

the ideal CO₂ adsorption temperature was determined to be 25 °C, as it resulted in the highest CO₂ adsorption capacity.

3.3.4. Effect of desorption temperature

CO₂ was made to desorb from the kaolinite sample using the following procedure. The temperature was kept at 100 or 150 °C, and the sample was held at the chosen temperature for 1 h in a flow of pure N₂ to allow for CO₂ desorption. The result is shown in Fig. 8. It can be observed that the sample still exhibited a little bit weight gain at the desorption temperature of 100 °C, as evidenced by the TG curve peak. This means the mass all the adsorbed CO₂ desorbed at 150 °C but not at 100 °C, which suggests the adsorbed CO₂ molecules cannot be completely desorbed at the temperature of 100 °C. Therefore, the ideal desorption temperature for completely removing the adsorbed CO₂ gas was determined to 150 °C.

3.4. Analyses of kaolinite after CO₂ adsorption

3.4.1. XRD analysis

The XRD pattern of the acid-treated kaolinite sample obtained after CO₂ adsorption was the same as that before CO₂ adsorption, suggesting that no new diffraction peaks were noticed after the adsorption of CO₂. Usually, when CO₂ molecules enter the interlayer spaces of kaolinite, the d-spacing of the (001) plane should increase. However, the position of the (001) plane peak did not change, indicating that the interlayer spacing remained almost the same. We believe that this was because there may be no amount of CO₂ entering the interlayer spaces of the kaolinite sample, resulting in a negligible increase in the spacing.

3.4.2. FTIR analysis

The FTIR spectrum of the acid-treated kaolinite sample is shown in Fig. 9. The triclinic layer structure of the kaolinite sample resulted in

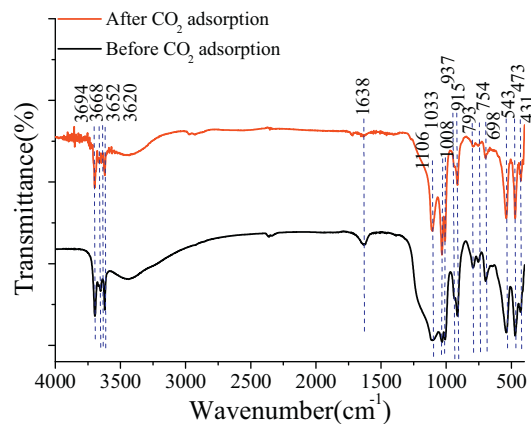


Fig. 9. The FTIR spectrum of acid-treated kaolinite before and after CO₂ adsorption.

four well-resolved (OH) bands. Three of these bands could be assigned to the stretching vibrations of the surface hydroxyl groups (3694, 3668, and 3652 cm⁻¹), while the fourth one (3620 cm⁻¹) was attributable to the vibration of the inner hydroxyl groups. The (Si-O) band exhibited three well-resolved bands in the 1000–1100 cm⁻¹ region. The OH-bending region of the acid-treated kaolinite sample exhibited peaks corresponding to vibrations of the inner-surface OH groups (at 937 cm⁻¹) as well of those corresponding to the inner OH groups (near 915 cm⁻¹). Absorption bands noticed at approximately 698 and 754 cm⁻¹ were associated with the Si-O vibrational modes; absorption bands due to Si-O-Al and Si-O-Si were also observed at 543 and 473 cm⁻¹, respectively. These were in agreement with the literatures (Madejova and Komadel, 2001; Georges-Ivo, 2005; Vaculikova et al., 2011; Spence and Kelleher, 2012; Aroke et al., 2013).

The FTIR spectrum of the acid-treated kaolinite sample obtained after CO₂ adsorption is also shown in Fig. 9. All the previously noticed peaks were present, and no new peaks were observed. The bands attributed to carbonates, located at 813 and 690 cm⁻¹ (Bhattacharyya, 1989; Christenson, 1993; Cole et al., 2010), were not observed, indicating that the adsorbed CO₂ molecules did not react with OH group to form carbonates. Because there was no strong evidence for chemical bonding (vibrational modes disappear or additional bands occur), it can be surmised that the adsorption of CO₂ onto kaolinite was mainly attributable to physical adsorption.

3.4.3. CO₂ adsorption isotherm

In order to confirm the CO₂ adsorption mechanism of kaolinite, the measurement of CO₂ adsorption isotherm was performed at 298 K by using the ASAP 2020c analyzer. The two resulting isotherm curves, which corresponded to physical and chemical adsorption, are shown in Fig. 10. The degree of chemical adsorption remained unchanged at zero for increases in the pressure. On the other hand, the degree of physical adsorption increased with an increase in the pressure, with the CO₂ adsorption capacity at a pressure of 765 mm Hg being 3.6 mg/g. This result was in keeping with those of the TG measurement (3.3 mg/g). Thus, it was confirmed again that the adsorption of CO₂ by the investigated kaolinite samples was exclusively because of physical adsorption.

3.5. CO₂ adsorption mechanism of kaolinite

Table 3 lists the CO₂ adsorption mechanisms of various clay minerals as reported in the literatures (Bhattacharyya, 1989; Christenson, 1993; Cole et al., 2010). Bhattacharyya (1989), Christenson (1993), and Cole et al. (2010) found that mica adsorbed CO₂ through the formation of a bicarbonate owing to the reaction between the CO₂ and OH groups; this bicarbonate reacts with the CO₂ and the cations of inner layers of mica. Giesting et al. (2012) reported that the CO₂ adsorption mechanism of montmorillonite was based on the reaction of CO₂ with the

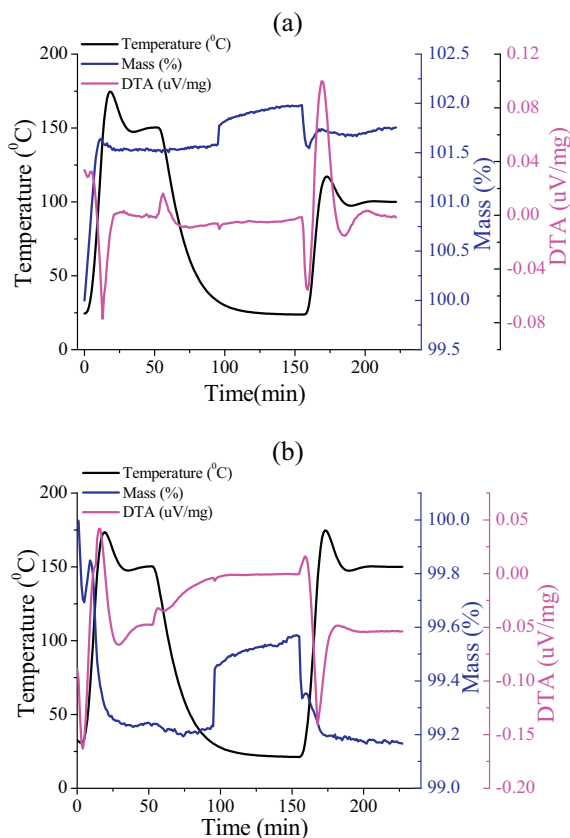


Fig. 8. The relationship between the CO₂ adsorption ability and the desorption temperatures of (a) 100 °C and (b) 150 °C from the TG measurement.

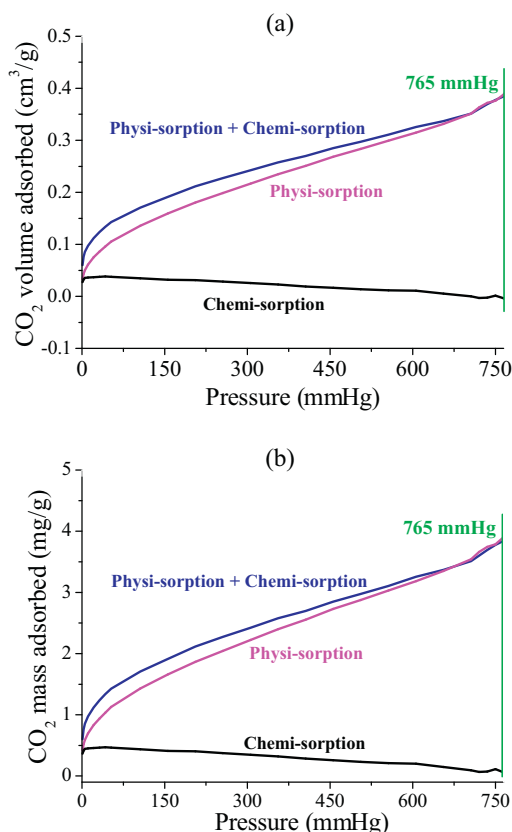


Fig. 10. The CO₂ adsorption isotherm curves of (a) untreated and (b) acid-treated kaolinites derived from the measurement by using ASAP 2020c analyzer at 25 °C.

H₂O present in montmorillonite. There are no cations present in the interlayer spaces in the kaolinite structure. Therefore, the CO₂ adsorption mechanism of kaolinite is based on the reaction of the OH group with the CO₂, resulting in the formation of a bicarbonate. However, the obtained results showed that bonds involving –HCO₃ were not present in the kaolinite sample that been used for CO₂ adsorption. This may have been because the amount of bicarbonate produced was very small and lower than the limited detection of the analyzers employed in the present study. To sum up, the XRD pattern, the FTIR spectrum, and the CO₂ adsorption isotherms suggested that kaolinite had not reacted with CO₂. Therefore, it was further confirmed that the adsorption of CO₂ by kaolinite is mainly owing to physical adsorption.

4. Conclusion

Kaolinite, a cheap and commonly available clay mineral, was modified by an acid (H₂SO₄) treatment. The surface area and the porosity of the acid-treated kaolinite sample were much higher than that of the untreated one. This suggested an acid treatment is an effective way of improving the textural properties of kaolinite. Moreover, the CO₂ adsorption capacity of kaolinite was also improved by the acid treatment. It was found that the adsorption of CO₂ by kaolinite is physical in nature; this conclusion was arrived at on the basis of the results of

XRD analysis, FTIR, and CO₂ adsorption isotherm measurements. Thus, kaolinite shows high potential as an adsorbent for CO₂ capture.

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Table 3

The list of the CO₂ adsorption mechanism of clay minerals from the literatures.

Reference	Adsorbent	Adsorption mechanism
Bhattacharyya (1989)	Mica	–OH + CO ₂ → –HCO ₃
Christenson (1993)	Mica	Cations + CO ₂ → –CO ₃
Cole et al. (2010)	Muscovite	–OH + CO ₂ → –HCO ₃
Giesting et al. (2012)	montmorillonite	–H ₂ O + CO ₂ → –H ₂ CO ₃

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