CO₂ Adsorption Performance and Kinetics of Ionic Liquid-Modified Calcined Magnesite

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Abstract: CO₂ is a major contributor to global warming, and considerable efforts have been undertaken to capture and utilise it. Herein, a nanomaterial based on ionic liquid (IL)-modified calcined magnesite was investigated for CO₂ capture. The synthesised nanomaterial (magnesite modified using [APMIM]Br) exhibited the best adsorption performance of 1.34 mmol/g at 30% IL loading amount, 50 °C, 0.4 MPa and 150 mL/min. In particular, the obtained nanomaterial could be regenerated at a low temperature of 90 °C for 3 h, and its CO₂ adsorption capacity of 0.81 mmol/g was retained after eight cycles. FT-IR results showed that the imidazole ring and C–N group are directly related to CO₂ adsorption capacity. Moreover, improving the conjugative effect of the imidazole ring enhanced the adsorption performance. Further, CO₂ was adsorbed on the adsorbent surface and incomplete desorption decreased the BET surface area and CO₂ adsorption capacity. Additionally, four models were selected to fit the adsorption kinetics. The results show that the adsorption mechanism fits the pseudo-first-order model well.

Keywords: ionic liquid; magnesite; CO₂ capture; kinetics; nanomaterial

1. Introduction

CO₂ emission reduction is crucial owing to the rapid increase in global warming. With the highest carbon emissions globally, China has pledged to stop the growth of CO₂ emissions by 2030, followed by a gradual decline, thereby realising carbon neutrality by 2060 [1]. Carbon Capture, Utilisation and Storage (CCUS) technology is regarded as the only effective technology for achieving zero CO₂ emissions in the aspect of the large-scale utilization of fossil energy [1]. Accelerating the research and development of CCUS technology and reducing costs and energy consumption are the main tasks at present [2]. CO₂ capture is the core of CCUS technology. Generally, the CO₂ adsorption capacity of liquid adsorbents is higher than solid adsorbents. However, high investment, corrosion of the equipment and high regeneration energy consumption are problems for liquid adsorbents applied in industry. Researchers across the globe have conducted studies on solid adsorbents, including layered double hydroxide-derived [3,4], CaO-based [5,6], MgO-based [7,8] and alkaline ceramic-based adsorbents [9,10] for pre-combustion CO₂ capture, and carbon-based [11,12], zeolite-silica-based [13,14], metal-organic framework-based [15,16] and alkali metal carbonate-based adsorbents [17–19] for post-combustion CO₂ capture. Furthermore, the adsorption process, such as two stage vacuum swing adsorption (VPSA), temperature swing adsorption (TSA), temperature/vacuum swing adsorption (TVSA) [20] and sound-assisted fluidized bed reactor [21], has also been investigated for implementation in industrial applications.

In China, magnesite has nearly no value in utilization and is almost abandoned. If the abundant magnesite can be applied in CO₂ capture, it will greatly reduce costs. In
our previous work, MgO obtained by calcining low-cost magnesite was investigated at low temperature for post-combustion CO$_2$ capture [22,23]. Although the CO$_2$ adsorption capacity of MgO was sufficiently high, its regeneration temperature was extremely high, which is the biggest problem for its industrial application. Ionic liquids (ILs) can address such a problem and exhibit superior CO$_2$ adsorption performance [24,25]; however, besides high cost, another drawback of pure ILs is their high viscosities causing strong gas diffusion resistances [26]. Therefore, for practical application, it will also be highly desirable to dispersely immobilize ILs into a support in order to overcome the gas diffusion limitation. Therefore, we propose to modify calcined magnesite using ILs for CO$_2$ capture. This approach can retain the benefits and solve the weakness of magnesite and ILs, respectively, designing an effective, cost efficient, easily achieved and low energy consumption adsorbent.

Herein, functionalised ILs with CO$_2$ adsorption groups of $-\text{OH}$ and $-\text{NH}_3$, 1-aminoethyl-3-methylimidazolium bromide ([AEMIM]Br), 1-aminoethyl-3-methylimidazolium tetrafluoroborate ([AEMIM]BF$_4$), 1-aminopropyl-3-methylimidazolium bromide ([APMIM]Br) and 1-aminopropyl-3-methylimidazolium tetrafluoroborate ([APMIM]BF$_4$) were selected for investigation. Different adsorption conditions, such as the adsorption temperature, flow rate and relative pressure, were optimised to achieve parameters suitable for industry applications. Additionally, the thermal stability of the adsorbent was determined using thermogravimetry (TG) and differential scanning calorimetry (DSC) (TG–DSC). The structure and properties of the adsorbent were analysed using Scanning Electron Microscope (SEM), Fourier transform infrared (FT-IR) spectroscopy and the Brunauer–Emmett–Teller (BET) method. The adsorption kinetics were also calculated.

2. Materials and Methods
2.1. Reagents and Instruments

[AEMIM]Br, [AEMIM]BF$_4$, [APMIM]Br and [APMIM]BF$_4$, were of AR grade and obtained from Shanghai Chengjie Chemical Co., Ltd. (Shanghais, China). Ethanol (AR grade) was obtained from Tianjin Fuyu Fine Chemical Co., Ltd. (Tianjin, China). Magnesite was received from Laizhou Magnesium Mine, Shandong Province (Laizhou, China). N$_2$ (99.999% purity) and 10% CO$_2$ were supplied by Jinan Deyang Gas Co., Ltd. (Jinan, China). The gas mass flow controllers (S4932/MT) were purchased from Beijing Huibolong Instruments Co., Ltd. (Beijing, China). A rotary evaporator (RE-52A) was purchased from Shanghai Yarong Biochemical Instrument Factory (Shanghai, China). An electric heater (DF-101S) was purchased from Henan Yuhua Instrument Co., Ltd. (Gongyi, China). A muffle furnace (XMT806) was purchased from Longkou Xianke Instrument Co., Ltd., Shandong Province (Longkou, China). A portable infrared CO$_2$ analyser (GXH-3010E), was supplied by Beijing HuaYun Instrument Co., Ltd. (Beijing, China). A counterbalance valve was purchased from Beijing Jiafa Instrument Co. Ltd. (Beijing, China). A powder compression machine (BJ-15) was purchased from Tianjin Bojun Technology Co., Ltd. (Tianjin, China). A magnetic stirrer, mortar and pestle, griddle and a fixed bed reactor as the adsorber were purchased from Jinan Bangen Instrument Co., Ltd. (Jinan, China).

2.2. Preparation of Adsorbents

The primary component of magnesite is MgCO$_3$, and the appropriate calcination condition is 550 °C for 4 h [22]. Therefore, the magnesite was calcined in a muffle furnace for 4 h at 550 °C to obtain MgO. A certain amount of IL was added to 100 mL of ethanol and stirred continuously for 15 min using a magnetic stirrer. Based on the loading amount, the calcined magnesite was added to the aforementioned solution and stirred for 3 h to obtain a homogeneous mixture. To remove the solvent, the resulting solution was heated to remove the solvent in a rotary evaporator under vacuum. The obtained sample was pressed using a compression machine and then ground using a mortar. The resulting sample was sieved to screen solid particles with sizes 0.2–0.4 mm as the adsorbent for the test.
2.3. CO₂ Adsorption-Regeneration Experiments

The CO₂ adsorption apparatus is shown in Figure 1, including gas cylinders, relief valves, gas mass flow controllers, a fixed bed reactor and a CO₂ analyser. Primarily, N₂ was introduced to blow the gas analyser for 15 min at a flow rate of 100 mL/min. Thereafter, 10% CO₂ simulated flue gas in the plant evacuated freely at a flow rate of 100 mL/min to stabilise the gas path. After attaining a steady state, 10% CO₂ flowed to the adsorber with 3 g adsorbent by adjusting the three-way valve, while the CO₂ analyser was turned on to perform the analysis. By changing IL loading amount, adsorption temperature, flow rate and relative pressure, the optimal adsorption conditions were determined. The temperature and flow rate were controlled using an electrical heating controller and a gas mass flow controller, respectively. The relative CO₂ pressure was adjusted using a counterbalance valve.

The adsorbent regeneration experiment was performed by heating the saturated adsorbent under vacuum in a rotary evaporator for 3 h at 90 °C.

The CO₂ adsorption capacity was calculated by the following equation:

\[
\text{CO₂ capacity} = \frac{A \times S \times M}{C \times m} \text{ mmol/g}
\]

where A is the integral area by adsorption curves in min, S is the CO₂ concentration, M is the CO₂ flow rate in mL/min, C is constant 22.4 L/mol, m is the quality of adsorbent in g.

2.4. Characterisation of Adsorbents

SEM images were obtained using a ZEISS MERLIN Compact microscope (Carl Zeiss AG, Jena, Germany). The sample was coated with platinum. Particle size and size distribution analyses were performed on a dynamic light scattering device.

TG-DSC analysis was conducted using an SDT Q600 Universal V4.1D TA instrument (Waters Corp., Milford, MA, USA). The experimental material (3 mg) was purged with N₂. The analysed temperature range was 25 °C to 750 °C and the heating rate was 10 °C/min. The thermal stability of the adsorbent was also tested.

FT-IR spectroscopic analysis was performed using a 5DXC IR spectrometer (Nicolet Instrument Corp., Madison, WI, USA). The wave scan ranged from 500–2000 cm⁻¹, with a
resolution of 2 cm$^{-1}$. The sample testing was performed using KBr, and the sample was pressed into a pellet.

The specific surface area and porosity analysis were performed using a Tristar 3020 physisorption apparatus (MICROMERITICS Corp., Norcross, GA, USA). For this analysis, the BET model was selected for calculating the specific surface area, and the Barrett–Joyner–Halenda (BJH) method was used to analyse the pore size and distribution.

3. Results and Discussion

3.1. Properties of the Adsorbents

Figure 2 shows the infrared spectra of the magnesite modified using different types of ILs. The characteristic peak of the imidazole ring of the ILs appears at 1168 cm$^{-1}$ and the C–N group peak is observed at 1334 cm$^{-1}$, which indicates that the IL loading on the magnesite materials is successful. The peaks of magnesite modified using [AEMIM]BF$_4$ and [APMIM]BF$_4$ at 1083 cm$^{-1}$ and 1126 cm$^{-1}$ are caused by the B-F bond [25]. Moreover, the strength of the imidazole rings are in the order of [APMIM]Br > [AEMIM]Br > [AEMIM]BF$_4$ > [APMIM]BF$_4$.

![Figure 2](image.png)

**Figure 2.** Infrared spectra of magnesite modified using different ILs ((1) [AEMIM]Br, (2) [APMIM]Br, (3) [AEMIM]BF$_4$ and (4) [APMIM]BF$_4$).

The morphology features of the calcined magnesite and ILs-modified magnesite were determined using the obtained SEM image. Figure 3a,b show the SEM images of calcined magnesite the magnifications of 300 nm and 1 μm. The particles of the calcined magnesite (main component MgO [22]) show irregularities, and many nanoscale particles are clustered. Figure 3c–f are the SEM images of different ILs-modified magnesite and show the ILs loading on the magnesite successfully. All ILs evenly distribute on the magnesite. The particle sizes of the [AEMIM]Br and [APMIM]Br modified magnesite are uniform. [AEMIM]BF$_4$ and [APMIM]BF$_4$ modified magnesite are still clustered.
Figure 3. SEM images of calcined magnesite and ILs-modified magnesite with different magnifications: ((a) calcined magnesite (300 nm); (b) calcined magnesite (1 μm); (c) [AEMIM]Br-modified magnesite (1 μm); (d) [APMIM]Br-modified magnesite (1 μm); (e) [AEMIM]BF$_4$-modified magnesite (1 μm) and (f) [APMIM]BF$_4$-modified magnesite (1 μm)).
3.2. Influence of Different ILs

Four types of nanomaterials were fabricated by loading different types of ILs, ([AEMIM]Br, [APMIM]Br, [AEMIM]BF₄, and [APMIM]BF₄), at the loading amount of 10% on the calcined magnesite. The influence of the type of IL on the CO₂ adsorption capacity was determined at the adsorption temperature of 50 °C and a gas flow rate of 100 mL/min. The adsorption curves of different modified magnesites are presented in Figure 4. This figure shows that the CO₂ adsorption performance of the bromide-based magnesite is better than that of the tetrafluoroborate-based magnesite, with an effective adsorption time of >10 min. The CO₂ effective adsorption times of the magnesite modified using [AEMIM]BF₄ and [APMIM]BF₄ are approximately 8 and 7 min, respectively. The CO₂ adsorption capacity (Table 1) of the [AEMIM]Br-modified magnesite is 0.29 mmol/g, lower than that achieved by the [APMIM]Br-modified magnesite, i.e., 0.34 mmol/g. These results may be due to the fact that the tetrafluoroborate-based magnesite is gathered, and the particle size of bromide-[APMIM]Br-modified magnesite, i.e., 0.34 mmol/g. These results may be due to the fact that the tetrafluoroborate-based magnesite is uniform, which can be seen in the SEM images. Thus, the magnesite modified using [APMIM]Br was selected as the adsorbent in the subsequent experiments.

![Figure 4. CO₂ adsorption curves and CO₂ capacity of different modified magnesites (3 g adsorbent, 10% loading amount, 100 mL/min flow rate, 50 °C and 0 MPa; c–CO₂ monitoring concentration, c₀–CO₂ initial concentration, the same in the following figures).](https://example.com/figure4.png)

Table 1. CO₂ adsorption capacity of magnesite modified under different conditions (10% CO₂).

| Ionic Liquid | Loading Amount | Adsorption Temperature (°C) | Flow Rate (mL/min) | Adsorption Pressure (MPa) | CO₂ Adsorption Capacity (mmol/g) |
|--------------|----------------|-----------------------------|--------------------|---------------------------|-------------------------------|
| [AEMIM]Br    | 10%            | 50                          | 100                | 0                         | 0.29                          |
| [APMIM]Br    | 10%            | 50                          | 100                | 0                         | 0.34                          |
| [AEMIM]BF₄   | 10%            | 50                          | 100                | 0                         | 0.27                          |
| [APMIM]BF₄   | 10%            | 50                          | 100                | 0                         | 0.20                          |
| [APMIM]Br    | 0              | 50                          | 100                | 0                         | 0.20                          |
| [APMIM]Br    | 20%            | 50                          | 100                | 0                         | 0.76                          |
| [APMIM]Br    | 30%            | 50                          | 100                | 0                         | 0.95                          |
| [APMIM]Br    | 30%            | 30                          | 100                | 0                         | 0.72                          |
| [APMIM]Br    | 30%            | 70                          | 100                | 0                         | 0.81                          |
| [APMIM]Br    | 30%            | 90                          | 100                | 0                         | 0.78                          |
| [APMIM]Br    | 30%            | 30                          | 150                | 0                         | 0.85                          |
| [APMIM]Br    | 30%            | 50                          | 150                | 0.2                       | 1.01                          |
| [APMIM]Br    | 30%            | 50                          | 150                | 0.4                       | 1.34                          |
3.3. Influence of IL Loading Amount

The loading amount is directly related to the cost of ILs and CO\textsubscript{2} adsorption performance. Therefore, the IL loading amount was investigated using the [APMIM]Br-modified magnesite as the adsorbent at the adsorption temperature of 50 °C and a gas flow rate of 100 mL/min. The results are presented in Figure 5 and Table 1. The CO\textsubscript{2} capacity of the calcined magnesite without IL modification is only 0.20 mmol/g. Introducing ILs can improve the CO\textsubscript{2} capacity of the calcined magnesite. With the loading amount increasing, the CO\textsubscript{2} adsorption performance of the modified magnesite also improves. The effective adsorption time with 20% and 30% loading amounts is about 18 min, longer than that achieved with a 10% loading amount. The CO\textsubscript{2} adsorption capacity of the modified calcined magnesite with 20% and 30% loading amounts can reach 0.76 and 0.95 mmol/g, respectively. Thus, ILs were important in capturing CO\textsubscript{2}. As the IL is too expensive, an extremely high loading amount implies a high cost, which is industrially inappropriate. Moreover, an excess IL amount might result in agglomeration, inhibiting CO\textsubscript{2} capture. The magnesite modified using [APMIM]Br with a 30% loading amount was selected for subsequent experiments.

![Figure 5. The CO\textsubscript{2} adsorption curves and CO\textsubscript{2} capacity of magnesite modified by [APMIM]Br with different loading amounts (3 g, 100 mL/min flow rate, 50 °C and 0 MPa).](image)

3.4. Influence of Adsorption Temperature

After desulphurisation, the temperature of the industrial flow gas can decrease from 100 °C to 50 °C; hence, the influence of temperature on the CO\textsubscript{2} adsorption performance was investigated at 30, 50, 70 and 90 °C using the [APMIM]Br-modified magnesite with the loading amount of 30% and a gas flow rate of 100 mL/min. The results are presented in Figure 6 and Table 1, showing that the CO\textsubscript{2} capacity is only 0.72 mmol/g at 30 °C and culminates to 0.95 mmol/g at 50 °C. As the temperature increases, the CO\textsubscript{2} adsorption capacity gradually decreases, i.e., 0.81 mmol/g at 70 °C and 0.78 mmol/g at 90 °C. The influence of the temperature on CO\textsubscript{2} capture is complex. In the temperature range of 30 °C to 50 °C, increasing temperature can improve the chemical adsorption on modified magnesite. However, when the temperature increases continuously, the CO\textsubscript{2} desorption happens, leading to the decline of the adsorption capacity. The results also imply that a low temperature can satisfactorily modify the magnesite regeneration.
3.5. Influence of Gas Flow Rate

The adsorption efficiency should also be improved to realize industrial applications. Therefore, the CO$_2$ adsorption performance of the magnesite modified by [APMIM]Br was studied at 50 °C and gas flow rates of 100, 150 and 200 mL/min. As shown in Figure 7 and Table 1, with the flow rate increasing, the effective adsorption time decreases and the CO$_2$ adsorption capacity gradually decreases. By comprehensively considering the CO$_2$ adsorption capacity and exhaust gas-pressing quantity, the gas flow rate of 150 mL/min was deemed to be appropriate for subsequent experiments, with an adsorption capacity of 0.85 mmol/g.

3.6. Influence of Relative Pressure

Our previous work reported that pressure can improve the CO$_2$ adsorption capacity of calcined magnesite [22]. The CO$_2$ adsorption performance of the magnesite modified by [APMIM]Br was also studied at 50 °C, a gas flow rate of 150 mL/min and relative pressures of 0, 0.2 and 0.4 MPa. The adsorption curves are presented in Figure 8, indicating that the effective adsorption time extends slightly as the relative pressure is increased, i.e., nearly
20 min at 0.4 MPa. When the relative pressure is increased from 0 to 0.4 MPa, the CO$_2$ adsorption capacity increases from 0.85 to 1.34 mmol/g (Table 1), proving that the relative pressure also has an obvious influence on CO$_2$ capacity.

![Adsorption curves and CO$_2$ capacity of magnesite modified by [APMIM]Br under different pressures](image)

**Figure 8.** Adsorption curves and CO$_2$ capacity of magnesite modified by [APMIM]Br under different pressures (3 g, 10% loading amount, 50 °C and 150 mL/min).

### 3.7. Cyclic Regenerative Performance

Except for CO$_2$ adsorption capacity, the regeneration of the adsorbent is also a key factor affecting industrial applications. The adsorption was performed using the magnesite modified by [APMIM]Br with 30% loading amount at 50 °C, 0.4 MPa and 150 mL/min, and desorption was performed at 90 °C for 3 h under vacuum in a rotary evaporator. Figure 9 shows that the CO$_2$ adsorption capacity decreases from 1.34 to 0.95 mmol/g for the first cycle, showing a slightly downward trend from the second to the fifth cycle, after which it remains steady until the eighth cycle.

![CO$_2$ adsorption capacity of [APMIM]Br-modified magnesite](image)

**Figure 9.** CO$_2$ adsorption capacity of [APMIM]Br-modified magnesite for eight cycles.

Compared with calcined magnesite and other MgO-based adsorbent in our previous work [22], the CO$_2$ adsorption capacity of the [APMIM]Br-modified magnesite is 1.34 mmol/g, slightly lower than the calcined magnesite in the presence of water, i.e.,
1.82 mmol/g. However, the advantage of the calcined magnesite modified by [APMIM]Br is that the regeneration temperature is decreased from 550 °C to 90 °C [22]. Both the adsorption temperature 50 °C and regeneration temperature 90 °C are in the range of flue gas temperature after desulphurisation (about 50–100 °C), so the flue gas energy can be used directly for CO₂ capture and regeneration, reducing the consumption. The CO₂ adsorption performance of other ILs-based adsorbents are shown in Table 2 [26–32]. By comparison, the 1.34 mmol/g CO₂ capacity we achieved is lower than 5.53 mmol/g by TEOS-APTES-EMIM(Tf₂N) and 4.49 mmol/g by [bmim][Ac]. However, the performance of [APMIM]Br-modified magnesite has little difference from the other ILs-based adsorbents listed in Table 2 in CO₂ capacity and regeneration conditions. [APMIM]Br-modified magnesite retains the benefits of ILs-based adsorbent and the material used is non-pollution. Furthermore, the low ILs consumption, the abundant magnesite and the simple production process reduce the cost greatly for industry application. MOFs and activated carbon have been reported to achieve high CO₂ adsorption capacity. However, the cost of production and raw materials are the significant challenging factors for industry application [33]. Activated carbons or porous carbons for CO₂ capture need chemical activation (chemical agents and temperatures from 400 °C to 900 °C), physical activation (temperatures about 700 °C to 1200 °C), or others. Both activation process and regeneration require much energy, and the production of activated carbons also incurs costs [34]. Therefore, the [APMIM]Br-modified magnesite is available and could potentially be adopted on an industrial scale.

### Table 2. Comparison of CO₂ capacity and regeneration condition of ILs-based adsorbent.

| Sample                                      | Adsorption Temperature (°C) | CO₂ Adsorption Capacity (mmol/g) | Regeneration Temperature (°C) | Reference |
|---------------------------------------------|----------------------------|---------------------------------|-------------------------------|-----------|
| TEOS a-APTES b-EMIM(Tf₂N)                  | -                          | 5.53                            | -                             | [27]      |
| [bmim][Ac] c                               | 30                         | 4.49                            | -                             | [28]      |
| [AEMIM][Lys] d-immobilized on PMMA e       | 30                         | 1.50                            | 100                           | [29]      |
| PSF f-[bmim][NTf₂]-Fe₂O₃                   | 45                         | 1.30                            | 70                            | [30]      |
| [DMAPAH][EOAc]                             | 30                         | 2.44                            | 30                            | [31]      |
| [TBMP][MeSO₄] g                            | 40                         | 1.13                            | -                             | [32]      |
| [EMIM][Lys]/PMMA                           | 30                         | 1.20                            | 100                           | [26]      |
| [APMIM]Br-modified magnesite               | 50                         | 1.34                            | 90                            | This work |

a TEOS represents tetraethyl orthosilicate. b APTES represents (3-Aminopropyl)triethoxysilane. c [Ac] represents acetate. d [Lys] represents L-lysine. e PMMA represents Poly(methyl methacrylate). f PSF represents Polysulfone. g [TBMP][MeSO₄] represents tributylmethylphosphonium methylsulfate.

### 3.8. Characterisation

The TG-DSC curve of pure magnesite has been reported in our previous work [22], showing that the decomposition of magnesite to MgO happens from 400 °C to 800 °C. The TG-DSC curve of the [APMIM]Br-modified magnesite is shown in Figure 10. As the temperature is increased from 30 °C to 100 °C, the mass loss rate is approximately 7.3%, which can be attributed to the desorption of micromolecules or impurities, including H₂O, CO₂ and others adsorbed by the sample in air and residual solvents from the preparation process. A peak is observed at 200–450 °C, corresponding to the mass loss rate of 28.5%, accompanied by a DSC endothermic peak, which is attributed to the decomposition of the [APMIM]Br-modified magnesite. Therefore, at 30–100 °C, the [APMIM]Br-modified magnesite exhibits excellent thermostability.
Figure 10. The TG-DSC curve of the magnesite modified by [APMIM]Br.

Figure 11 shows the infrared spectra of the magnesite modified by [APMIM]Br with different loading amounts and the 30% loading amount of the modified magnesite after adsorption. The strength of both the imidazole ring characteristic and C–N group peaks at 1168 and 1334 cm$^{-1}$, respectively, is in the order of the loading amounts of 30% > 20% > 10%. Moreover, the strength magnitudes of the peaks after CO$_2$ adsorption decrease. The CO$_2$ adsorption capacity determined experimentally of the different ILs and loading amounts are consistent with the strengthening of the imidazole ring and C–N groups (Figures 2 and 11), indicating that improving the conjugative effect of the imidazole ring can enhance the adsorption performance.

Figure 11. Infrared spectra of magnesite modified by [APMIM]Br with different loading amounts and 30% loading amount of the modified magnesite after adsorption ((1) 10% loading amount; (2) 20% loading amount; (3) 30% loading amount and (4) after adsorption).

The BET results are presented in Table 3. The N$_2$ adsorption-desorption isotherm and the pore size distributions of the magnesite modified by [APMIM]Br before adsorption and after the first cycle are presented in Figure 12. Before adsorption, the BET surface area is 128.5 m$^2$/g, the pore volume is 0.2 cm$^3$/g and the pore size is 62.5 Å. After the first cycle, the BET surface area is 105.6 m$^2$/g, the pore volume is 0.13 cm$^3$/g and the pore size is
51.0 Å. The results verify that the modified magnesite used in the experiments shows a good pore structure, which plays an essential role in CO₂ adsorption. The reduction in the BET surface area, pore volume and pore size after the first cycle may be attributed to CO₂ adsorption on the modified magnesite surface and incomplete desorption, thus decreasing the CO₂ adsorption capacity. By comparison with the BET surface area of the pure calcined magnesite, 118.6 m²/g [22], it indicates that the 30% IL loading amount has little influence on the pore structure of the calcined magnesite. According to the International Union of Pure and Applied Chemistry classification, the two samples belong to the type IV isotherm with an H3 hysteresis loop, coinciding with mesoporous materials (pore size 2–50 nm).

Table 3. Porous structure parameters determined from N₂ adsorption-desorption isotherms.

| Sample                        | BET Surface Area (m²/g) | Pore Volume (cm³/g) | Pore Size (Å) |
|-------------------------------|-------------------------|---------------------|---------------|
| Magnesite modified by [APMIM]Br | 128.5                   | 0.2                 | 62.5          |
| Magnesite modified by [APMIM]Br after the first cycle | 105.6                   | 0.13                | 51.0          |

![Diagram](a) Before adsorption
![Diagram](b) After the first cycle

Figure 12. N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of magnesite modified by [APMIM]Br before and after the first cycle.

3.9. Adsorption Kinetics

To study the adsorption kinetics of CO₂ on the magnesite modified by [APMIM]Br, the pseudo-first-order, pseudo-second-order, intraparticle diffusion and Bangham models were used to fit the adsorption curves [35,36].

The pseudo-first-order model is expressed as

$$q_t = q_e [1 - \exp(-k_1 t)]$$

where \( q_t \) is the CO₂ adsorption capacity at \( t \) min in mmol/g, \( q_e \) is the CO₂ adsorption capacity at the adsorption equilibrium in mmol/g and \( k_1 \) is the adsorption reaction rate in min⁻¹.

The pseudo-second-order model is expressed as

$$q_t = k_2 q_e^2 t / (1 + k_2 q_e t)$$

where \( k_2 \) is the adsorption reaction rate in g/mmol-min.

The intraparticle diffusion model is expressed as

$$q_t = k_i t^{0.5} + C$$

where \( k_i \) is the intraparticle diffusion rate constant in mmol/m²-min²/Å².
where \( k_i \) is the intragranular diffusion constant in mmol·g\(^{-1}\) min\(^{-0.5}\) and \( C \) is a constant in mmol/g.

The Bangham model is expressed as

\[
\log \log \left( \frac{q_t}{q_e - q_t} \right) = \log \left( k_b / 2.303 \right) + n \log t
\]  

(4)

and \( q_t \) can be expressed as

\[
q_t = q_e \left[ 1 - \exp(-k_b t^n) \right]
\]  

(5)

where \( k_b \) is the Bangham constant in min\(^{-n}\) and \( n \) is a constant.

The pseudo-first-order and pseudo-second-order indicate that the reaction rate is related to one or two reactants. The intraparticle diffusion model indicates that the overall adsorption process is controlled by several steps, film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, a combination of more than one step etc. The Bangham model indicates that the pore-diffusion is the only rate-controlling step [36,37].

The experimental dates and the non-linear fitting curves of the four adsorption kinetic models are shown in Figure 13. The kinetic parameters are listed in Table 4. The kinetic parameter \( R^2 \) value of the pseudo-first-order and Bangham models is 0.999. The concluded \( q_e \) values by pseudo-first-order 1.302 mmol/g and Bangham models 1.302 mmol/g are closed to the experimental date. The pseudo-second-order overestimates CO\(_2\) adsorption capacity (\( q_e \)) (Table 4) in the first few minutes (about <8 min) and underestimates in the following minutes (about 8 min~32 min), with \( R^2 \) value 0.988. The pseudo-first-order and Bangham models fit the experimental curves well. When the parameter \( n \) of Bangham is 1, the Bangham model is entirely the same as the pseudo-first-order model. Therefore, the adsorption mechanism fits the pseudo-first-order model excellently and the process should accord with the characteristics of the pseudo-first-order model. It can be concluded that the CO\(_2\) adsorption process involves reversible adsorbent surface interactions, and the rate is related to CO\(_2\) concentration directly.

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**Figure 13.** Adsorption kinetics of CO\(_2\) on magnesite modified by [APMIM]Br under the conditions of 50 °C, 0.4 MPa, gas flow rate 150 mL/min.
Table 4. Kinetics parameters for magnesite modified by [APMIM]Br under the conditions of 50 °C, 0.4 MPa and gas flow rate 150 mL/min.

| Models                  | Parameter | Value |
|-------------------------|-----------|-------|
| Pseudo-first-order      | $R^2$     | 0.999 |
|                         | $k_1$     | 0.224 |
|                         | $q_e$     | 1.302 |
| Pseudo-second-order     | $R^2$     | 0.988 |
|                         | $k_2$     | 0.312 |
|                         | $q_e$     | 1.386 |
| Intraparticle diffusion | $R^2$     | 0.624 |
|                         | $k_i$     | 0.131 |
|                         | $C$       | 0.491 |
|                         | $k_s$     | 0.221 |
|                         | $q_e$     | 1.302 |
|                         | $n$       | 1.010 |

4. Conclusions

Herein, an effective and easily achieved nanomaterial was prepared using calcined magnesite modified with [APMIM]Br, which had the benefits of cost efficiency, low energy consumption and non-pollution. By comparison, the particle sizes of [AEMIM]Br and [APMIM]Br modified magnesite were uniform and had higher CO$_2$ capacity. [AEMIM]BF$_4$ and [APMIM]BF$_4$ modified magnesite were clustered and had lower CO$_2$ capacity. Besides, the conjugative effect of the imidazole ring could affect the adsorption performance. By experiments, the optimal adsorption conditions of 30% IL loading amount, 50 °C, 0.4 MPa and 150 mL/min gas flow rate was achieved with a CO$_2$ adsorption capacity of 1.34 mmol/g. The regeneration temperature was reduced to 90 °C, saving considerable amounts of energy, which is beneficial for industrial applications. The adsorbent showed good thermostability in the experimental temperature range. However, the cyclic stability needs to be further improved. The investigation of the adsorption kinetics indicated that the adsorption mechanism fits the pseudo-first-order model well.

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References
1. Xian, Z. Carbon capture, utilization and sequestration in China under the carbon neutral target. Ke Chi Xu Fa Zhang Jing Ji Dao Kan 2020, 12, 22–24.
2. Wang, J.Y.; Huang, L.; Yang, R.; Zhang, Z.; Wu, J.; Gao, Y.; Wang, Q.; O’Hare, D.; Zhong, Z. Recent advances in solid sorbents for CO$_2$ capture and new development trends. Energy Environ. Sci. 2014, 7, 3478–3518. [CrossRef]
3. Wang, J.; Mei, X.; Huang, L.; Zheng, Q.; Qiao, Y.; Yang, R.; Zhang, Z.; Gao, Y.; et al. Synthesis of layered double hydroxides/graphene oxide nanocomposite as a novel high-temperature CO$_2$ adsorbent. J. Energy Chem. 2015, 24, 127–137. [CrossRef]
4. Wang, Q.; Tay, H.H.; Zhong, Z.; Luo, J.; Borgna, A. Synthesis of high-temperature CO$_2$ adsorbents from organo-layered double hydroxides with markedly improved CO$_2$ capture capacity. Energy Environ. Sci. 2012, 5, 7526–7530. [CrossRef]
5. Nawar, A.; Ali, M.; Khoja, A.H.; Waqas, A.; Anwar, M.; Mahmood, M. Enhanced CO$_2$ capture using organic acid structure modified waste eggshell derived CaO sorbent. J. Environ. Chem. Eng. 2021, 9, 104871. [CrossRef]
6. Dashtestani, F.; Nusheh, M.; Siriwongrungson, V.; Hongrapitap, J.; Materic, V.; Pang, S. Effect of H₂S and NH₃ in biomass gasification production gas on CO₂ capture performance of an innovative CaO and Fe₂O₃ based sorbent. *Fuel* 2021, 255, 120586. [CrossRef]

7. Li, P.; Chen, R.; Lin, Y.N. General approach to facile synthesis of MgO-based porous ultrathin nanosheets enabling high-efficiency CO₂ capture. *Chem. Eng. J.* 2021, 404, 126459. [CrossRef]

8. Iugai, I.A.; Steksova, Y.P.; Vedyagin, I.V.; Bauman, Y.I.; Belyy, V.A.; Danilovich, D.P.; Krivoshapkin, E.F.; Krivoshapkin, P.Y. MgO/carbon nanofibers composite coatings on porous ceramic surface for CO₂ capture. *Surf. Coat. Technol.* 2020, 400, 126208. [CrossRef]

9. Bernabe-Pablo, E.; Duan, Y.; Pfeiffer, H. Developing new alkaline ceramics as possible CO₂ chemisorbents at high temperatures: The lithium and sodium yttrates (Li₂O₂ and Na₂O₂) cases. *Chem. Eng. J.* 2020, 396, 125277. [CrossRef]

10. Wu, Y.; Liu, W. Element doped sodium-based sorbents with high attrition resistance and CO₂ capture capacity during CO₂ sorption / desorption processes. *Fuel* 2021, 201, 108165. [CrossRef]

11. Heo, Y.J.; Zhang, Y.; Rhee, K.Y.; Park, S.J. Synthesis of PAN/PVDF nanofiber composites-based carbon adsorbents for CO₂ capture. *Compos. Part B-Eng.* 2019, 156, 95–99. [CrossRef]

12. Kutorgle, E.M.; Hassouna, F.; Beltzung, A.; Kopecký, D.; Sedlářová, I.; Šoš, M. Nitrogen-rich hierarchically porous polyaniline-based adsorbents for carbon dioxide (CO₂) capture. *Chem. Eng. J.* 2019, 360, 1199–1212. [CrossRef]

13. Somklat, K.; Kingkaew, C.C.; Nuntaporn, K. Synthesis and characterization of NaX-type zeolites prepared by different silica and alumina sources and their CO₂ adsorption properties. *Micropor. Mesopor. Mater.* 2021, 310, 110632. [CrossRef]

14. Zagho, M.M.; Hassan, M.K.; Khraisheh, M.; Al-Maadeed, M.A.; Nazarenko, S. A review on recent advances in CO₂ Separation using zeolite and zeolite-like materials as adsorbents and fillers in mixed matrix membranes (MMMs). *Chem. Eng. J.* 2021, 6, 100091. [CrossRef]

15. Zhao, Y.; Ge, H.; Miao, Y.; Chen, J.; Cai, W. CO₂ capture ability of Cu-based metal-organic frameworks synergized with amino acid-functionalized layered materials. *Catal. Today* 2020, 356, 604–612. [CrossRef]

16. Liao, J.; Jin, B.; Zhao, Y.; Liang, Z. Highly efficient and durable metal-organic framework material derived Ca-based solid sorbents for CO₂ capture. *Chem. Eng. J.* 2019, 372, 1028–1037. [CrossRef]

17. Abdalazeez, A.; Li, T.; Wang, W.; Abuelgasim, S. A brief review of CO₂ utilization for alkali carbonate gasification and biomass/coal gasification: Reactivity, products and process. *J. CO₂ Util.* 2021, 43, 101370. [CrossRef]

18. Li, P.; Yang, M.; Chen, D.; Guo, H.; Yan, B. CO₂ fuel and LiAlO₂ production through alkali carbonate-assisted CO₂ splitting by reusing aluminum wastes. *J. CO₂ Util.* 2020, 39, 101168. [CrossRef]

19. Cimino, S.; Boccia, F.; Lisi, E. Effect of alkali promoters (Li, Na, K) on the performance of Ru/Al₂O₃ catalysts for CO₂ capture and hydrogenation to methane. *J. CO₂ Util.* 2020, 37, 195–203. [CrossRef]

20. Jiang, N.; Shen, Y.; Liu, B.; Zhang, D.; Tang, Z.; Li, G.; Fu, B. CO₂ capture from dry flue gas by means of VPSA, TSA and TVSA. *J. CO₂ Util.* 2020, 35, 153–168. [CrossRef]

21. Raganati, F.; Ammondola, P. Sound-assisted fluidization for temperature swing adsorption and calcium looping: A review. *Materials* 2021, 14, 672. [CrossRef]

22. Yang, N.; Ning, P.; Li, K.; Wang, J. MgO-based adsorbent achieved from magnesite for CO₂ capture in simulate wet flue gas. *J. Taiwan Inst. Chem. Eng.* 2018, 86, 73–80. [CrossRef]

23. Yang, N.; Ning, P.; Li, K.; Wang, J. A new method of processing CO₂ and magnesite slag simultaneously. *J. Serb. Chem. Soc.* 2018, 83, 1–15. [CrossRef]

24. Hospital-Benito, D.; Lemus, J.; Moya, C.; Santiago, R.; Ferro, V.R.; Palomar, J. Techno-economic feasibility of liquidiclic acids-based CO₂ chemical capture processes. *Chem. Eng. J.* 2021, 407, 127196. [CrossRef]

25. Yang, N.; Wang, R. Molecular sieve-supported liquidic acids as efficient adsorbents for CO₂ capture. *J. Serb. Chem. Soc.* 2015, 80, 265–275. [CrossRef]

26. Uehara, Y.; Karami, D.; Mahinpey, N. CO₂ adsorption using amino acid liquid-impregnated mesoporous silica sorbents with different textural properties. *Micropor. Mesopor. Mat.* 2019, 278, 378–386. [CrossRef]

27. Garip, M.; Gizili, N. Ionic liquid containing amin-based silica aerogels for CO₂ capture by fixed bed adsorption. *J. Mol. Liq.* 2020, 300, 113227. [CrossRef]

28. Orhan, O.Y. Effects of various anions in ionic liquids on CO₂ capture. *J. Mol. Liq.* 2021, 333, 115981. [CrossRef]

29. Huang, Z.; Karami, D.; Mahinpey, N. Study on the efficiency of multiple amino groups in ionic liquids on their sorbents performance for low-temperature CO₂ capture. *Chem. Eng. Res. Des.* 2021, 167, 198–206. [CrossRef]

30. Nisar, M.; Bernard, F.L.; Duarte, E.; Chaban, V.V.; Einloft, S. New polysulfone microcapsules containing metal oxides and [BMIM][NTf₂] ionic liquid for CO₂ capture. *Environ. Chem. Eng. J.* 2021, 9, 104781. [CrossRef]

31. Wei, L.; Guo, R.; Tang, Y. Properties of aqueous amine based protic ionic liquids and its application for CO₂ quick capture. *Sep. Purif. Technol.* 2020, 239, 116531. [CrossRef]

32. Ramdin, M.; Thijs, J.H.; Theo, W. Solubility of CO₂ in the ionic liquids [TBMN][MeSO₄] and [TBMP][MeSO₄]. *J. Chem. Eng. Data* 2021, 57, 2275–2280. [CrossRef]

33. Younas, M.; Rezakazemi, M.; Daud, M.; Wazir, M.B.; Ahmad, S.; Ullah, N.; Ramakrishna, S. Recent progress and remaining challenges in post-combustion CO₂ capture using metal-organic frameworks(MOFs). *Prog. Energy Combust. Sci.* 2020, 80, 100849. [CrossRef]
34. Abuelnoor, N.; AlHajaj, A.; Khaleel, M.; Vega, L.F.; Abu-Zahra, M.R. Activated carbon from biomass-based sources for CO₂ capture applications. *Chemosphere* **2021**, *283*, 131111. [CrossRef]

35. Kumar, K.V. Linear and non-linear regression analysis for the sorption kinetics of methylene blue on to activated carbon. *J. Hazard. Mater.* **2006**, *137*, 1538–1544. [CrossRef]

36. Bilgili, M.S. Adsorption of 4-chlorophenol from aqueous solutions by xad-4 resin: Isotherm, kinetic and thermodynamic analysis. *J. Hazard. Mater.* **2006**, *137*, 157–164. [CrossRef] [PubMed]

37. Ammendola, P.; Raganati, F.; Chirone, R.; Miccio, F. Fixed bed adsorption as affected by thermodynamics and kinetics: Yellow tuff for CO₂ capture. *Powder Technol.* **2020**, *373*, 446–458. [CrossRef]