Simultaneous Online Measurement of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) in the Humid \( \text{CO}_2 \) Adsorption/Desorption Process

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A dew point meter (DP) and an infrared (IR) \( \text{CO}_2 \) analyzer were assembled in a humid \( \text{CO}_2 \) adsorption/desorption system in series for simultaneous online measurements of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \), respectively. The humidifier, by using surface-flushing on a saturated brine solution was self-made for the generation of humid air flow. It was found that by this method it became relatively easy to obtain a low \( \text{H}_2\text{O} \) content in air flow and that its fluctuation could be reduced compared to the bubbling method. Water calibration for the DP-IR detector is necessary to be conducted for minimizing the measurement error of \( \text{H}_2\text{O} \). It demonstrated that the relative error (RA) for simultaneous online measurements \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) in the desorption process is lower than 0.1%. The high RA in the adsorption of \( \text{H}_2\text{O} \) is attributed to \( \text{H}_2\text{O} \) adsorption on the transfer pipe and amplification of the measurement error. The high accuracy of simultaneous online measurements of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) is promising for investigating their co-adsorption/desorption behaviors, especially for direct \( \text{CO}_2 \) capture from ambient air.

Keywords \( \text{CO}_2 \) capture, water calibration, co-adsorption, humidifier, dew point meter, infrared \( \text{CO}_2 \) analyzer

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Introduction

It is well known that anthropogenic \( \text{CO}_2 \) emissions are major contributors to climate change. The ever-increasing concentration of atmospheric \( \text{CO}_2 \) from 278 ppm to more than 390 ppm today is derived from increasing fuel consumption after the industrial revolution. Capturing \( \text{CO}_2 \) directly from ambient air, commonly referred to as direct air capture (DAC), can be used for \( \text{CO}_2 \) stabilization in the atmosphere. \( \text{CO}_2 \) removal is also conducted in the life-support systems (LSS) when \( \text{CO}_2 \) reaches a relatively high concentration, such as in submarines and space capsules, which would threaten the survival of humans in the enclosed spaces. An adsorption technology has been proven to be one of the most efficient ways for \( \text{CO}_2 \) capture or removal, because high-purity streams can be obtained with low energy consumption. Generally, the \( \text{H}_2\text{O} \) content is high in the DAC process and LSS due to the moist air. Therefore, it is crucial to accurately measure the \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) concentrations in order to conduct investigations of their corresponding adsorption behaviors, especially in the online way. An infrared \( \text{CO}_2 \) analyzer, gas chromatography (GC) and a gas chromatography-mass spectrometer (GC-MS) were common for online measurements of \( \text{CO}_2 \). However, they failed to achieve \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) elution curves simultaneously in the humid \( \text{CO}_2 \) co-adsorption/desorption process. In addition, thermogravimetric analysis (TGA) and TGA-MS were also used to study \( \text{CO}_2 \) adsorbent/desorption, which can provide a quantitative understanding of \( \text{CO}_2 \) uptake in the adsorption of dry \( \text{CO}_2 \). However, it is hard to collect the individual concentrations of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) in the co-adsorption/desorption process because the response of TGA is a result of the overall weight gain or loss. In particular, the adsorption behavior in the pan obtained from TGA was significantly different from that in adsorption-column reactors. Serna-Guerrero and coworker installed MS to the outlet of a fixed-bed reactor for collecting \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) breakthrough data and their elution curves. The concentrations of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) were determined using a single ion monitor (SIM) with \( m/z = 44 \) and \( m/z = 18 \), respectively. Since the gas flow rate in the practical reactor is much higher than that required by MS, the gas flow must be split before entering MS, which would result in measurement errors. In addition, MS is relatively expensive, and it would be easily contaminated if used as an online monitor.

The combination of the humidity sensor with the infrared (IR) \( \text{CO}_2 \) analyzer in series was a simple and practical way to obtain breakthrough and elution curves of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) simultaneously. However, the concentration difference between the real \( \text{H}_2\text{O} \) and the measured \( \text{H}_2\text{O} \) was up to 17% when the humidity sensor-IR \( \text{CO}_2 \) analyzer was used as the online monitor. Generally, the measurement errors of \( \text{H}_2\text{O} \) resulted from three sources: (a) the measurement error from meters, (b) the fluctuation of the \( \text{H}_2\text{O} \) content in the flow gas, and (c) the adsorbed capacity by the transfer pipe in the setup. Therefore, the objective of the present work is to develop a technique with the integration of a dew-point meter and an IR \( \text{CO}_2 \) analyzer as online monitors for simultaneous measurement of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \). The surface-flushing humidifier was used to

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reduce the fluctuation of H₂O content in humid air flow, and the measurement error of H₂O could be further minimized by the water calibration. The proposed technique on the simultaneous online measurement of H₂O and CO₂ would be promising for investigating the co-adsorption/desorption behavior of H₂O and CO₂, especially of direct CO₂ capture from ambient air.

Experimental

Materials

Branched polyethylenimine (PEI, $M_w = 600$) was purchased from Labo Co., Ltd. (Hangzhou, China). Polymethymethacrylate microspheres (mean diameter, ~0.45 mm) were obtained from Knowledge & Benefit Sphere Tech. Co., Ltd. (Suzhou, China). Ethanol purchased from JRDUN Biotechnology Co., Ltd. (Shanghai, China) was of AR grade. The adsorbent used in the work was prepared by physically immobilizing PEI into polymethymethacrylate microspheres, where ethanol was used as the solvent. PEI loadings of 20 wt% were obtained when the solvent was evaporated. The physical properties of the obtained adsorbent are shown in Table 1.

Table 1 Physical parameters of the obtained adsorbent used in experiment

| Surface area/m² g⁻¹ | Volume of pores/cm³ g⁻¹ | Average pore diameter/mm | Particle diameter/mm |
|----------------------|------------------------|--------------------------|----------------------|
| 20.1                 | 0.386                  | 75.40                    | 0.35 - 0.60          |

Fig. 1 Diagram of the co-adsorption/desorption experimental setup with simultaneous online measurements of H₂O and CO₂. (1) N₂, (2) CO₂, (3) compressed air, (4) mass flow controller, (5) humidifier, (6) thermostat, (7) tube reactor, (8) dew point meter, (9) gas dryer, (10) infrared gas analyzer, (11) check valve, (12) gas-mixer, (13) three-way valve.

In order to investigate the co-adsorption/desorption behavior of H₂O and CO₂, especially of direct CO₂ capture from ambient air, some adsorbents were packed in the tube reactor placed in the thermostat for the co-adsorption/desorption experiment. Prior to this measurement, the adsorbents were heated to 50 °C under the N₂ flow rate at 100 mL/min for two hours in order to remove the adsorbed CO₂ and H₂O. The CO₂ and H₂O concentrations from the inlet and outlet gas flows were also monitored.

Measurement procedure of H₂O and CO₂

Some adsorbents were packed in the tube reactor placed in the thermostat for the co-adsorption/desorption experiment. Prior to this measurement, the adsorbents were heated to 50 °C under the N₂ flow rate at 100 mL/min for two hours in order to remove the adsorbed CO₂ and H₂O. The CO₂ and H₂O concentrations in the outlet gas flow from the tube reactor were simultaneously monitored with a DP and an IR gas analyzer, respectively. The passing N₂ at a rate of 100 mL/min under the elevated temperature (usually at 30 °C) through the adsorbent was used for the desorption process. The co-desorption of H₂O and CO₂ would take place, and the corresponding concentrations of the outlet gas flow were also monitored.

The uptake of H₂O or CO₂ on the adsorbent over the adsorption time, $q_a$ (mg H₂O or CO₂/g adsorbent), was calculated by integrating the corresponding breakthrough curves:

$$q_a = \int_{t_0}^{t} \frac{Q_a(c_a - c_f)M}{m_s \times V_m} \, dt,$$  \hspace{1cm} (1)

where $t_0$ (min) is the adsorption time, $V_m = 22.4$ L/mol, $M$ (g/mol) is the molecular mass of CO₂ (or H₂O), $Q_a$ (mL/min) is the volumetric flow rate of the gas flow, $m_s$ (g) is 1.0011 g for the mass of the adsorbent in the tube reactor, and $c_0$ and $c_f$ (vol%) are the CO₂ (or H₂O) concentrations from the inlet and outlet gas flows, respectively.

Similarly, the amount of CO₂ (or H₂O) desorbed over desorption time, $q_d$ (mg CO₂ or H₂O/g adsorbent), was calculated by integrating the corresponding desorption curves:

$$q_d = \int_{t_0}^{t} \frac{Q_d M}{m_s \times V_m} \, dt,$$  \hspace{1cm} (2)

where $t_0$ (min) is the desorption time, $V_m = 22.4$ L/mol, $M$ (g/mol) is the molecular mass of CO₂ (or H₂O), $c$ (vol%) is the CO₂ or H₂O concentration in the outlet gas flow (the H₂O concentration was transferred from DP), and $Q_d$ (mL/min) is the
volumetric flow rate of N$_2$.

**Results and Discussion**

**Generation of humid air flow**

Humidification was usually obtained by bubbling air flow through water at a particular temperature. To reduce the fluctuation of H$_2$O content and to gain a low H$_2$O content of air flow, surface-flushing was used to humidify the air flow. Figure 2 shows the relationships between the humidity of the air flow and the temperature of the water bath for both the bubbling and surface-flushing methods. The polynomial fitting results are also given.

It was observed that the water concentration in the air flow increased with an increase of the water bath temperature in both cases. For the bubbling, the H$_2$O contents of 0.773 – 3.256 vol% were generated within the temperature range of –7 – 30°C. Whereas for the surface-flushing, 0.385 – 3.155 vol% were generated within –7 – 35°C. This reveals that the surface-flushing method generated air flow with a lower H$_2$O content than did the bubbling method within the experimental conditions.

On the basis of taking the derivative of polynomials (a) and (b) in Fig. 2, the corresponding derivations could be obtained as follows:

\[ c = 0.00143T + 0.02535 + 0.48496, \quad R^2 = 0.99965. \]

\[ c = 0.00143T + 0.48496, \quad R^2 = 0.99927. \]

The obtained value of $c'$ for the surface-flushing method was lower than that for bubbling at the given temperature, since the slope of Eq. (4) is smaller than that of Eq. (3). Accordingly, it indicates that the humidity of the air flow increased more smoothly with increasing bath temperature in the surface-flushing method. For instance, a humidity of 0.41% would be changed for the surface-flushing method when experiencing a 5°C increase or decrease at 20°C, whereas 0.49% would be changed for the bubbling method. This reveals that the control of the H$_2$O content in air flow for the surface-flushing method will be more stable and accurate and its fluctuation would be reduced.

**Deviation of measurement**

The single-component H$_2$O or CO$_2$ adsorption/desorption experiments were conducted in order to check the reliability of the measurement. The adsorption or desorption amounts could be calculated by Eqs. (1) and (2) based on the integration of the breakthrough or the elution curves, and the weight method of the adsorbents could also be determined. The obtained results and corresponding relative errors (RA) are presented in Table 2. It is observed that the adsorption amount of H$_2$O calculated by the integration is larger than that determined by the weight, especially for the case of the low H$_2$O content in the air gas. The values of RA are close to 1% either for the CO$_2$ adsorption or for the CO$_2$ desorption, indicating that the online measurement of CO$_2$ is reliable. The H$_2$O measurement in the desorption process can also be reliable, since the RA is close to 1%. Furthermore, the variations of the H$_2$O uptake at an H$_2$O content of 1% on the adsorbent against the adsorption time determined by the weight and calculated by the integration are presented in Fig. 3. It was observed that the differences of the obtained H$_2$O uptake between the integration and the weight increased with increasing the adsorption time. The H$_2$O uptake calculated by the integration is as high as 18% by weight at an operating time of 85 min. This means that the H$_2$O uptake integrated by Eq. (1) based on the breakthrough curve is higher than the actual value. It could be explained that some of H$_2$O was adsorbed on the transfer pipe before the DP monitor during the adsorption process, since the partial pressure of H$_2$O in the outlet gas flow gradually increased after H$_2$O broke though the adsorbent. Therefore, the breakthrough curve of H$_2$O generated would be lower than the real one. Due to the error-amplification in Eq. (1), the error of the H$_2$O measurement might be significant, even if only a little amount of H$_2$O was adsorbed by the transfer pipe. Herein, the online measurement of H$_2$O in the adsorption process should be corrected further, and water calibration would

![Fig. 2 Relationships between the humidity of air flow and temperature of (a) the bubbling approach, (b) the surface-flushing approach. Polynomial a (bubbling): $c = 0.00143T + 0.02535 + 0.86566$, $R^2 = 0.99965$. Polynomial b (surface-flushing): $c = 0.00143T + 0.48496$, $R^2 = 0.99927$.](image)

| q for 1.69% (vol) H$_2$O (mg/g adsorbent) | q for 1.37% H$_2$O (mg/g adsorbent) | q for 1% H$_2$O (mg/g adsorbent) | q for 0.4% dry CO$_2$ (mg/g adsorbent) |
|----------------------------------------|-----------------------------------|-------------------------------|--------------------------------------|
| $A_w$ | $A_t$ | RA, % | $A_w$ | $A_t$ | RA, % | $A_w$ | $A_t$ | RA, % | $A_w$ | $A_t$ | RA, % |
| Adsorption\(^a\) | 108.4 | 110.4 | +1.85 | 61.5 | 63.1 | +2.60 | 54.5 | 64.3 | +17.98 | 38.9 | 39.4 | +1.29 |
| Desorption\(^b\) | 108.3 | 107.7 | –0.55 | 61.6 | 62.1 | +0.81 | 54.7 | 54.1 | –1.10 | 38.5 | 38.9 | +1.04 |

\(^a\) 20°C, gas flow rate: 100 mL/min, \(^b\) 50°C, N$_2$ flow rate: 100 mL/min. $A_w$, the amount of adsorption/desorption was determined by the weight method, mg/g. $A_t$, the amount of adsorption/desorption was calculated by the integration of the breakthrough or elution curves, mg/g.
be conducted. In addition, it has been noticed that the effect of the H2O desorption can be ignored, since the transfer pipe was flushed by dry N2 in the desorption process.

Water calibration

The adsorption amount of H2O on the transfer pipe should be subtracted for the calculation of the adsorption amount on the adsorbents. Water calibration was conducted where no adsorbent was packed in the tube reactor, and the operating condition was the same as that of H2O adsorption. Figure 4 presents the H2O breakthrough curves at H2O contents of 1.00, 1.37 and 1.69% with and without adsorbents. The H2O uptake on the adsorbent with the water calibration would be revised according to the following equation:

$$q_1' = \int_{c_1}^{c_1'} Q_s (c_0 - c_1') M \frac{dt}{m \times V_a} - \int_{c_1}^{c_1''} Q_s (c_0 - c_1'') M \frac{dt}{m \times V_a},$$  \hspace{1cm} (5)

where $c_1'$ is the H2O concentration in the outlet gas flow in the water-calibration mode.

The obtained results with the water calibration on the basis of Eq. (5) in the adsorption of H2O are presented in Table 3. The relative errors were calculated compared with the weight method. It was observed that the RA were significantly reduced, especially in the case of a low H2O content. Although the RA of 4.04% at 1% H2O is higher than that at 1.37 or 1.69%, the accuracy of the H2O measurement can be acceptable since a
performances of dry CO2 (0.4 vol%) were also investigated in measured RA values of CO2 and H2O with water calibration in behavior.

It is as expected that the measurement error in the setup assembled with a DP and an IR CO2 analyzer in series was developed for simultaneous online measurements of CO2 and H2O in the humid CO2 co-adsorption/desorption process. Surface-flushing on a saturated brine solution was used to humidify the air flow, which can improve the controllability of the humidity in this air flow and reduce any fluctuation of the H2O content as well. The high RA in the adsorption of CO2 is attributed to H2O adsorption on the transfer pipe and amplification of the measurement error. The measurement accuracy in the setup is qualified for the investigation of co-adsorption/desorption behavior of H2O and CO2, especially for direct CO2 capture from ambient air in a confined space.

Simultaneous online measurements of CO2 and H2O

The resulting breakthrough of adsorption and the elution curves of desorption on the co-adsorption/desorption of H2O and CO2 are presented in Figs. 5 and 6, respectively, where the performances of dry CO2 (0.4 vol%) were also investigated in comparison. It can be observed that the online measurements of H2O and CO2 concentrations were successfully achieved in the co-adsorption/desorption system. The results obtained by simultaneous online measurements of CO2 and H2O with water calibration in the co-adsorption/desorption of humid CO2 process are presented in Table 4. Here the results determined by the weight are listed for comparison. It is as expected that the measured RA in the adsorption process at a low H2O content of H2O/CO2 = 1:0.4 is as high as 3.75% due to the H2O adsorption on the transfer pipe and amplification of the measurement error. Moreover, it has been shown that the measured RA values of CO2 and H2O with water calibration in the desorption process at an H2O content of H2O/CO2 = 1:0.4 is lower than 0.1%. Therefore, it demonstrated that the technique for the simultaneous online measurements of CO2 and H2O in the humid CO2 co-adsorption/desorption process was successfully conducted, and that the measurement accuracy was both reliable and acceptable for investigating the corresponding behavior.

Conclusions

The setup assembled with a DP and an IR CO2 analyzer in series was developed for simultaneous online measurements of CO2 and H2O in the humid CO2 co-adsorption/desorption process. Surface-flushing on a saturated brine solution was used to humidify the air flow, which can improve the controllability of the humidity in this air flow and reduce any fluctuation of the H2O content as well. The measurement error of H2O can be significantly reduced by the water calibration. It has been demonstrated that the RA for simultaneous measurements of CO2 and H2O are lower than 0.1% in the desorption process. The high RA in the adsorption of H2O is attributed to H2O adsorption on the transfer pipe and amplification of the measurement error. The measurement accuracy in the setup is qualified for the investigation of co-adsorption/desorption behavior of H2O and CO2, especially for direct CO2 capture from ambient air in a confined space.

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| Table 4 Measurement results of CO2 and H2O with water calibration in the adsorption/desorption of humid CO2 process |
| A1  | H2O | A1  | CO2 | A1  | H2O + CO2 | Awe | RA, % |
|-----|-----|-----|-----|-----|-----------|-----|-------|
| Adsorption | 69.4 | 41.2 | 110.6 | 106.6 | +3.75 |
| Desorption | 66.7 | 41.6 | 108.3 | 109.1 | -0.73 |