




# Carbon dioxide minimization using sodium and potassium impregnated calcium oxide sorbent derived from waste eggshell

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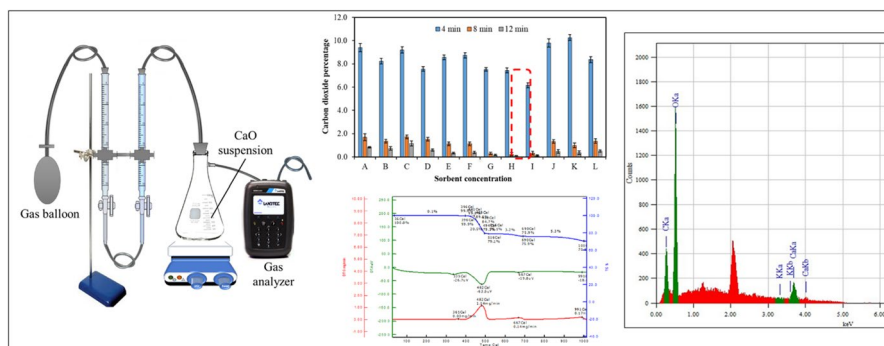
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## Abstract

In this study, we have investigated the effects of sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) impregnated calcium oxide ( $\text{CaO}$ ) on  $\text{CO}_2$  absorption from biogas.  $\text{Na}^+$  and  $\text{K}^+$  were impregnated on eggshell derived  $\text{CaO}$  by the incipient wetness impregnation method. A modified batch type reactor was used to conduct the absorption of  $\text{CO}_2$  to the sorbent. The sorbents were characterized using X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FESEM), and Thermogravimetric analysis (TGA) after absorption. Around 99.4%  $\text{CO}_2$  removal efficiency was obtained using 5%  $\text{KCl}$  with 4%  $\text{CaO}$  suspension at 8 min contact time which is the best absorption condition. The XRD pattern for 5%  $\text{K}^+$  impregnated  $\text{CaO}$  sorbent revealed the formation of crystalline  $\text{CaCO}_3$  with the highest intensity, indicating the highest absorption of  $\text{CO}_2$ . The more intensity of the FTIR spectra at 1795 and 1403  $\text{cm}^{-1}$  for the  $\text{K}^+$  impregnated  $\text{CaO}$  indicates  $\text{CO}_2$  absorption. From the TGA analysis it can be seen that the three step weight loss was occurred and the calcium carbonate formed during the  $\text{CO}_2$  absorption is completely decomposed at around 1000 °C. From the cost analysis of the sorbent preparation, it is observed that the net expense of the prepared sorbent in this study was about three times lesser than the commercially purchased one.

Extended author information available on the last page of the article

## Graphical abstract



**Keywords** Carbon dioxide · Environment · Absorption · Calcium oxide · Eggshell

## Introduction

Carbon dioxide (CO<sub>2</sub>) is one of the leading greenhouse gas which is responsible for global warming. On the other hand, in many ways including urbanization and industrialization, increasing use of petroleum fuel as well as the use of biogas as a green fuel which is unfortunately rich in CO<sub>2</sub> [1, 2] and this CO<sub>2</sub> lowering the fuel quality and increasing the global warming [3]. Therefore, research on the improvement of the quality of biogas by removing CO<sub>2</sub> and mitigating the adverse effects of CO<sub>2</sub> emissions on the environment is emerging at the present time.

Various strategies have been proposed to reduce CO<sub>2</sub> including the development of efficient carbon capture technologies [4–6]. Among these technologies, absorption-based approaches using various developed materials including activated carbon, zeolites, metal–organic frameworks (MOFs), and amine-based sorbents have gained substantial attention due to their promising potential for capturing and sequestering CO<sub>2</sub> from industrial flue gases and other emission sources [7–11]. These absorbents possess high surface areas and tailored pore structures that enhance the CO<sub>2</sub> capture capacity. Moreover, recent advancements in materials science have led to the development of novel sorbents with improved selectivity and efficiency.

Absorption process is the technique of moving a component from its gas phase to a liquid that is soluble in that liquid [12]. In the case of CO<sub>2</sub>, the solubility depends on the physical and chemical characteristics of the solvent. The absorption is referred to as physical absorption when the gaseous CO<sub>2</sub> molecules are joined to the liquid molecules by weak intermolecular interactions. The physical absorption process is often carried out at high pressure and low temperature to make CO<sub>2</sub> more soluble in the absorbing liquid. In order to perform the chemical absorption process, CO<sub>2</sub> from the biogas is covalently bonded with the molecules of the absorbing liquid [13]. Even at ambient temperature and pressure, the chemical absorption process is more effective at absorbing CO<sub>2</sub> due to the strong covalent bonds between the molecules

of the chemical solvent and the CO<sub>2</sub> molecules [14]. By choosing the ideal solvent the absorption process for removal of CO<sub>2</sub> from biogas can be optimized by controlling the other parameters such as contactor, gas and liquid flow rates, and stripping conditions. A perfect plug flow reactor, where mixing only occurs in the radial direction and not the axial direction, can be used to simulate the column in which the chemical absorption process is carried out [15]. The composition of the raw gas and the required composition of the treated gas determine the specific designs of the absorber, stripper, and solvent choice [14]. When employing a packed column to absorb CO<sub>2</sub> from biogas, the raw gas is typically fed from the bottom in a counter-current flow while a water solution made from the chosen absorbent is injected into the top of the packed column.

In recent years, the use of solid sorbents, particularly calcium oxide (CaO), has emerged as a highly effective and economically viable option for CO<sub>2</sub> capture [16, 17]. CaO (quicklime) possesses exceptional sorption capabilities, making it an ideal candidate for CO<sub>2</sub> absorption. The unique properties of CaO, such as high surface area, abundant active sites, and low cost, contribute to its superior performance as a CO<sub>2</sub> sorbent [18, 19]. Previously, some studies have been done to synthesize CaO from waste eggshell using various processes for carbon capturing application [20–22]. However, in-depth analysis of the synthesis methods of CaO sorbents with optimized properties, including their surface area, pore size distribution, and stability as well as the factors influencing the absorption performance of CaO sorbents, such as temperature, pressure, gas composition, absorption time, sorbent concentration and regeneration methods are very imperative.

CaO based sorbents can be the prominent candidate as the low-cost and efficient CO<sub>2</sub> absorber which can be easily derived from eggshell. Eggshell is the richest renewable source of CaO with 95% of CaO. Moreover, eggshells are the largest quantities of waste materials found in many sources such as poultries, kitchen waste, restaurants, and food manufacturing industries [23]. Approximately 70.4 million tons of chicken eggs were produced worldwide in 2015, and the Food and Agriculture Organization (FAO) of the United Nations projects that number to rise to 90 million tons by 2030 [24]. The production of chicken eggs in Malaysia amounts to roughly 642,600 tons per year, which results in about 70,686 tons of eggshell waste [25]. Currently, Bangladesh produces 23.35 billion eggs in the fiscal year 2021–22 [26] and if the average weight per eggshell is 5.60 g then the total approximate amount of eggshell will be 1.3 million tons [27]. This is a very large amount of poultry waste. So, it is a big challenge to manage the waste eggshell to protect the land and environment and also it is a great opportunity if possible to use this huge amount of eggshell as the source of CaO. Furthermore, the incorporation of alkali metal ions such as Na<sup>+</sup>, and K<sup>+</sup> improves the absorption capacity of CaO sorbent [28–31]. Incorporation of electropositive metal ions into the CaO improves the absorption capacity of CO<sub>2</sub> more than the pure CaO [32]. However, there have significant negative effects of other gases with mixed CO<sub>2</sub> gas to the absorption process and CO<sub>2</sub> exists with other gases of the environment as the mixture. However, the previous works used the pure CO<sub>2</sub> gas as the feed gas in CO<sub>2</sub> absorption process. So, it is vital to study the efficiency of CO<sub>2</sub> absorption with eggshell derived CaO sorbent using mixed gases. Therefore, this study aims to capture CO<sub>2</sub> from biogas as

the mixed gas using eggshell derived CaO as the sorbent with the impregnation of  $\text{Na}^+$ , and  $\text{K}^+$ .

## Experimental section

### Chemicals and equipment

The biogas produced by anaerobic digestion of cow dung in the biogas plant in IFRD, BCSIR, Dhaka 1205, Bangladesh was used as the source of  $\text{CO}_2$ . A 3–4 L capacity gas balloon made of vulcanized rubber was used to supply the biogas through the reactor. A portable gas analyzer (Geotech Biogas 5000) from Geotechnical Instruments (UK) Ltd. with the measuring levels of  $\text{CH}_4$  (0–100%);  $\text{CO}_2$  (0–100%);  $\text{O}_2$  (0–25%),  $\text{H}_2$  (0–1000 ppm);  $\text{NH}_3$  (0–1000 ppm);  $\text{H}_2\text{S}$  (0–50, 200, 500, 1000, 5000 or 10,000 ppm) was used to analyze the percentage  $\text{CO}_2$  before and after absorption process.  $\text{NaCl}$  (99.5%) and  $\text{KCl}$  (99.5%) were purchased from Merck, Germany. All chemicals were used without further purification. Deionized water was used for every purpose in this study.

### Preparation of CaO suspension

CaO suspensions were prepared from eggshell derived CaO as the absorption medium of  $\text{CO}_2$ . At first, CaO was produced from eggshell by calcination of eggshell powder. Raw eggshells were collected from nearby restaurants in Dhaka, Bangladesh. Then the eggshells were cleaned using DI water and dried in the oven (Universal oven UN55) at 95 °C for 4 h [33]. After drying, the eggshells were crushed into small pieces and were passed through a screen of mesh size 1 mm. The bigger pieces were crushed again. After that, the crushed pieces were taken to the ball mill to get a fine powder. The powdered eggshells were kept in the furnace (Linn High Thermo GmbH, LM 412.27, model DC021032 with a thermocouple type K, NiCr–Ni) at 900 °C for 5 h. After that, the finely powdered CaO was obtained. The CaO suspension with different concentrations was prepared by adding 500 mL of DI water with different amounts of CaO. Before the reaction,  $\text{Na}^+$  and  $\text{K}^+$  were impregnated in the form of  $\text{NaCl}$  and  $\text{KCl}$  using a wet process.

### Experimental setup

A special type of reactor was designed to carry out the absorption process with a cylindrical reactor which has a diameter of 53 mm and length of 20 cm. So the calculated volume of the reactant was 438  $\text{cm}^3$ . The biogas inlet and outlet pipe diameter was 9.41 mm.

When the screw valve of the reactor was rotated the inlet got opened and upon another rotation, the outlet of CaO suspension got opened. The tube reactor was filled with waste iron. The biogas pipe was connected to the inlet tube then the valve was kept open and let the gas flow. The valve was kept open until the balloon was

empty. The reading of gas composition was taken continuously by the biogas analyzer. The inlet pipe of the biogas analyzer was connected to the outlet of the reactor. Calcium hydroxide suspension with different concentrations of CaO such as 2%, 4%, and 6% was prepared for the reaction. The biogas was passed through the reactor and the outlet was kept closed for different times such as 4, 8, and 12 min. The system was kept on both continuous and periodic stirring.

## Characterization of materials

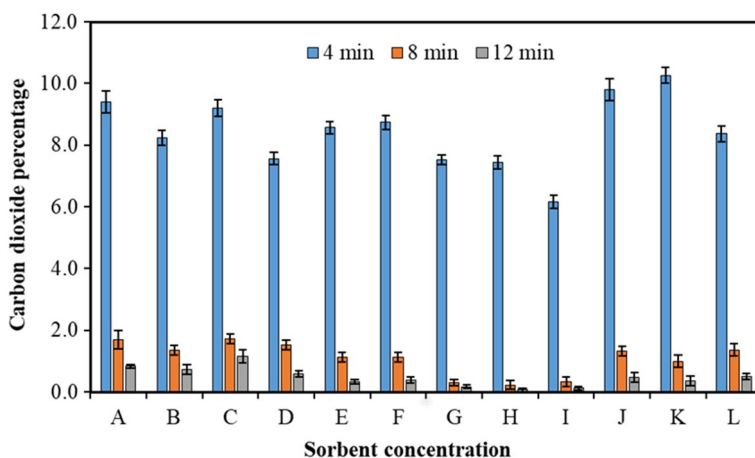
The synthesized CaO sorbents were characterized using various characterization techniques such as XRD, FESEM, and FTIR to study the structural and morphological properties. The XRD (XRD; Bruker D8 Advance, Germany) powders crystallographic information was characterized using XRD (Cu K $\alpha$  radiation,  $\lambda=0.15406$  nm, 40 kV and 60 mA, scanning range of 10°–80°, ARL Equinox 1000, Thermo Scientific TM, USA) to find the crystalline phases. FTIR spectroscopic (FTIR; Frontier, PerkinElmer, UK) study was performed to characterize various surface functionalities in samples, with wavenumbers ranging from 400 to 4000 cm<sup>-1</sup>. The surface morphology of CaO was observed by employing FESEM (FESEM; JSM-7610F, JEOL, Japan) with accelerating voltage: 15kv, magnification: 15000X. Thermo-gravimetric analysis (TGA) was used to determine the samples thermal stability and its fraction of volatile components by monitoring the weight change that occurred as a sample was heated at a constant rate.

## Results and discussion

### *Removal of CO<sub>2</sub> using CaO sorbent*

In this study, biogas was kept enclosed inside the reactor for different periods of time. Here the effect of time and concentration was observed to optimize the reaction condition. The mixture was on continuous agitation to keep the system homogeneous. For every run 300 mL of suspension was used. A significant change in carbon dioxide percentage was observed unlike the continuous process. Fig. 1 and Table S1 represent the change of CO<sub>2</sub> for different concentrations of sorbent (CaO) and contact time. CO<sub>2</sub> removal efficiency and CH<sub>4</sub> enrichment were determined using data collected from the gas analyzer after different duration of contact (by obtaining the CO<sub>2</sub> reading before it is saturated). All the experiments were done in triplicate and the data were represented as the average value.

From the analysis, it is clear that the absorption of CO<sub>2</sub> increased by increasing the absorption time and almost 99.4% of CO<sub>2</sub> was absorbed after 8 min of reaction. The impregnation of sodium ion (Na<sup>+</sup>), and potassium ion (K<sup>+</sup>) affects the absorption process of CO<sub>2</sub>. The impregnation of K<sup>+</sup> increased the absorption rate of CO<sub>2</sub> while the impregnation of Na<sup>+</sup> also increased the rate of absorption however, less than the K<sup>+</sup>. After 8 min of reaction only 0.2% of CO<sub>2</sub> were remains using 4% CaO sorbent with 5% K<sup>+</sup> while the percentage of CO<sub>2</sub> in the raw sample was 35%. This

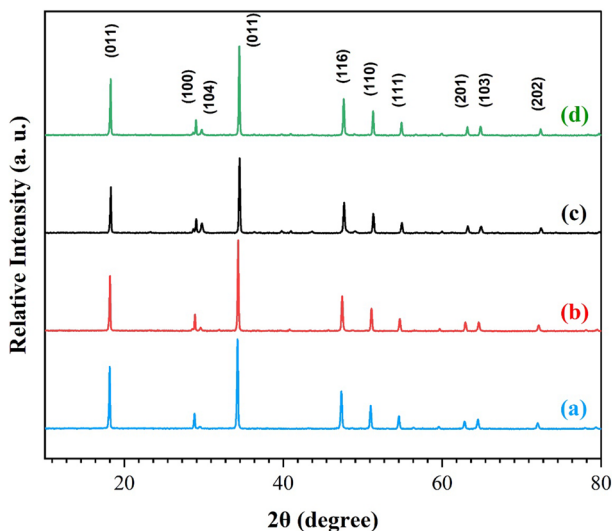


**Fig. 1** Absorption of  $\text{CO}_2$  using different concentrations of sorbent (A: 2% CaO, B: 4% CaO, C: 6% CaO, D: 2% CaO+5% NaCl, E: 4% CaO+5% NaCl, F: 6% CaO+5% NaCl, G: 2% CaO+5% KCl, H: 4% CaO+5% KCl, I: 6% CaO+5% KCl, J: 2% CaO+5% KCl+5% NaCl, K: 4% CaO+5% KCl+5% NaCl, L: 6% CaO+5% KCl+5% NaCl). <sup>a</sup>Raw gas composition:  $\text{CH}_4$  – 63%,  $\text{CO}_2$  – 35%

may be because the diffusion process of acidic  $\text{CO}_2$  is strongly affected by the  $\text{K}^+$  to the  $\text{CaCO}_3$  produced from the absorption reaction between CaO and  $\text{CO}_2$ . Furthermore, the impregnation of more electropositive  $\text{K}^+$  improves the absorption capacity of CaO than  $\text{Na}^+$  [32]. Previously, it [34] showed that the diffusion controlled carbonation process of CaO conversion increased by further accession of KCl or  $\text{K}_2\text{CO}_3$ . Moreover, the addition of KCl to the CaO media in the carbonation process may form bicarbonate or mixed bicarbonate [35]. NaCl also may act in the same way. Further studies should be needed to understand the mechanistic explanation in the depth of the affinity of the CaO to the  $\text{CO}_2$  as well as the electro-positivity and ionic radii of  $\text{K}^+$  ion.

### Characterization of the sorbent

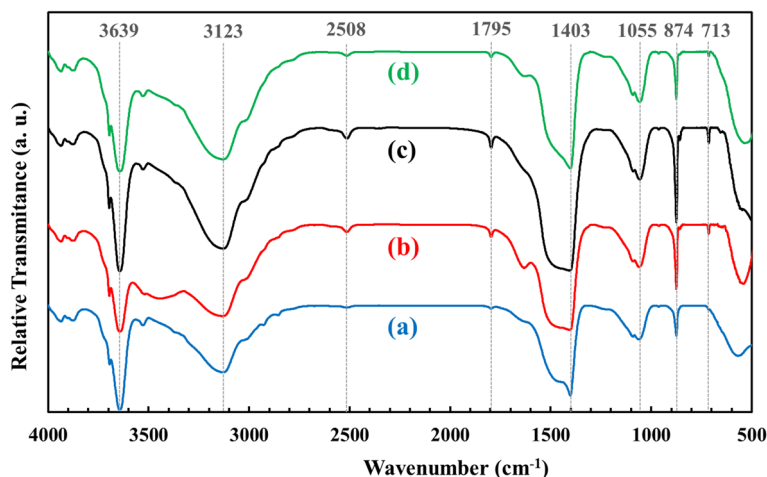
The XRD patterns of the pure CaO as well as  $\text{Na}^+$  and  $\text{K}^+$  impregnated CaO samples were shown in Fig. 2. It exhibited sharp and well-defined diffraction peaks, consistent with the known cubic crystal structure of CaO [36]. The prominent peaks at  $2\theta$  values of  $18.30^\circ$ ,  $28.99^\circ$ ,  $29.75^\circ$ ,  $34.49^\circ$ ,  $47.60^\circ$ ,  $51.31^\circ$ ,  $54.89^\circ$ ,  $63.17^\circ$ ,  $64.81^\circ$ , and  $72.39^\circ$  were attributed to the (001), (100), (104), (011), (012), (110), (111), (201), (103), and (202) crystallographic planes (JCPDS card number: 72-1652) which is in good agreement with the previous study [37]. Upon impregnation with  $\text{Na}^+$ , and  $\text{K}^+$ , the XRD patterns of the CaO samples displayed some noticeable changes. The characteristic diffraction peaks of CaO were still present, indicating the retention of the original cubic crystal structure. However, the  $\text{K}^+$ -impregnated CaO showed a clear difference at the peaks that emerged at  $2\theta$  values of  $28.99^\circ$ , and  $29.75^\circ$ , corresponding to the (100), and (104) planes of potassium oxide ( $\text{K}_2\text{O}$ ) crystals.



**Fig. 2** XRD pattern of different CaO sorbent after  $\text{CO}_2$  absorption (a) 4% CaO; (b) 4% CaO + 5% NaCl; (c) 4% CaO + 5% KCl; (d) 4% CaO + 5% KCl + 5% NaCl

The appearance of change to distinct  $\text{K}_2\text{O}$  peaks in the XRD pattern shown in Fig. 2c indicates the successful impregnation of  $\text{K}^+$  into the CaO lattice, leading to the formation of a new phase. The occurrence of  $\text{K}_2\text{O}$  suggests that  $\text{K}^+$  ions have integrated into the CaO crystal structure, likely occupying lattice sites and displacing calcium ions ( $\text{Ca}^{2+}$ ). This phenomenon may lead to lattice strain and affect the overall crystallinity of the material. Moreover, the presence of  $\text{K}_2\text{O}$  peaks alongside the dominant CaO peaks indicates the coexistence of both phases in the impregnated sample [36, 38]. The intensity of the  $\text{K}_2\text{O}$  peaks appeared to be relatively lower than that of CaO, suggesting that the impregnation process did not lead to a complete substitution of  $\text{Ca}^{2+}$  by  $\text{K}^+$  in the lattice. These findings are crucial for understanding the structural modifications and potential applications of  $\text{K}^+$ -impregnated CaO in sorption where the presence of  $\text{K}_2\text{O}$  may influence material properties and performance. Further investigations into the specific roles of  $\text{K}_2\text{O}$  in the modified CaO matrix are warranted to elucidate the impact of this impregnation on the functional properties of the material.

The FTIR spectrum of CaO as well as the  $\text{Na}^+$  and  $\text{K}^+$ -impregnated CaO were shown in Fig. 3. The sharp band stretching at  $3639$  and  $3123\text{ cm}^{-1}$  illustrated in the figure from FTIR analysis represented the O–H bond formed by absorption of moisture in CaO to form  $\text{Ca}(\text{OH})_2$  which is almost similar to the previous report [36, 39]. The band stretching vibration at  $2508\text{ cm}^{-1}$  denoted the stretching for atmospheric  $\text{CO}_2$ . The tinny peak at  $1795\text{ cm}^{-1}$  is due to the carbonate formation during the carbonation of CaO [38]. More intensity of the spectra at  $1795$  and  $1403\text{ cm}^{-1}$  for the  $\text{K}^+$  impregnated CaO in Fig. 3c indicates the larger amount of the carbonate formation using this sorbent and more  $\text{CO}_2$  absorption. The wide band at  $1403\text{ cm}^{-1}$  indicates the asymmetric stretching out of plane



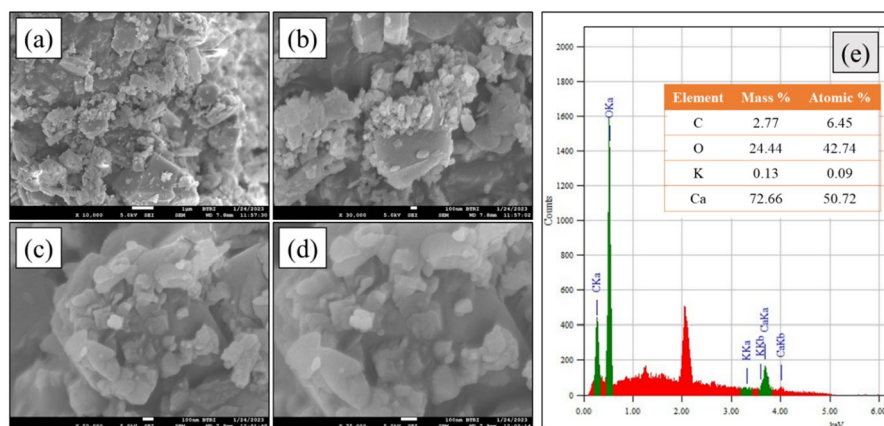
**Fig. 3** FTIR analysis of different CaO sorbent after CO<sub>2</sub> absorption (a) 4% CaO; (b) 4% CaO + 5% NaCl; (c) 4% CaO + 5% KCl; (d) 4% CaO + 5% KCl + 5% NaCl

vibration mode whereas the sharp absorption band at 874 and 713 cm<sup>-1</sup> indicates the asymmetric stretch in plane band vibration mode for CO<sub>3</sub><sup>2-</sup> ion formed in the absorption of CO<sub>2</sub> with Ca(OH)<sub>2</sub>. The stretching vibration at 1055 and 874 cm<sup>-1</sup> denoted the formation of mono and bidentate carbonate from CaO and CO<sub>2</sub> [38].

The FESEM-EDX analysis was conducted to investigate the morphological and elemental composition changes in CaO and metal ions impregnated CaO samples after CO<sub>2</sub> absorption. This analysis aimed to provide insights into the surface characteristics and chemical composition of the samples, which are crucial for understanding the CO<sub>2</sub> absorption behavior. From the absorption result and XRD, FTIR data it is clear that the K<sup>+</sup>-impregnated CaO showed better CO<sub>2</sub> absorption performance among the other sorbents. The FESEM images shown in Fig. 4 revealed important morphological changes in the K<sup>+</sup>-impregnated CaO samples after CO<sub>2</sub> absorption. The pristine CaO particles exhibited a relatively smooth and compact surface morphology, indicating a homogeneous structure (Fig. S1). However, after impregnation with K<sup>+</sup>, the surface morphology appeared to be slightly rougher and more porous. This change in morphology suggests that K<sup>+</sup> impregnation could lead to the formation of additional active sites for CO<sub>2</sub> absorption, potentially enhancing the absorption capacity.

EDX analysis provided valuable information regarding the elemental composition of the samples. The spectrum obtained from the pristine CaO sample showed the presence of calcium (Ca-72.66%) and oxygen (O-24.44%) as the major elements, which is expected for pure CaO (Fig. 4e). However, upon K<sup>+</sup> impregnation, the EDX spectrum exhibited the presence of additional potassium (K-0.13%) peaks, confirming the successful incorporation of K<sup>+</sup> into the CaO matrix. This suggests that K<sup>+</sup> impregnation was effective in modifying the elemental composition of CaO. Furthermore, the presence of carbon (C-2.77%) peak, indicates the





**Fig. 4** FESEM-EDX image of  $K^+$ -impregnated CaO sorbent after  $CO_2$  absorption **a–d** FESEM image of 4% CaO + 5% KCl sorbent; **e** EDX analysis of 4% CaO + 5% KCl sorbent

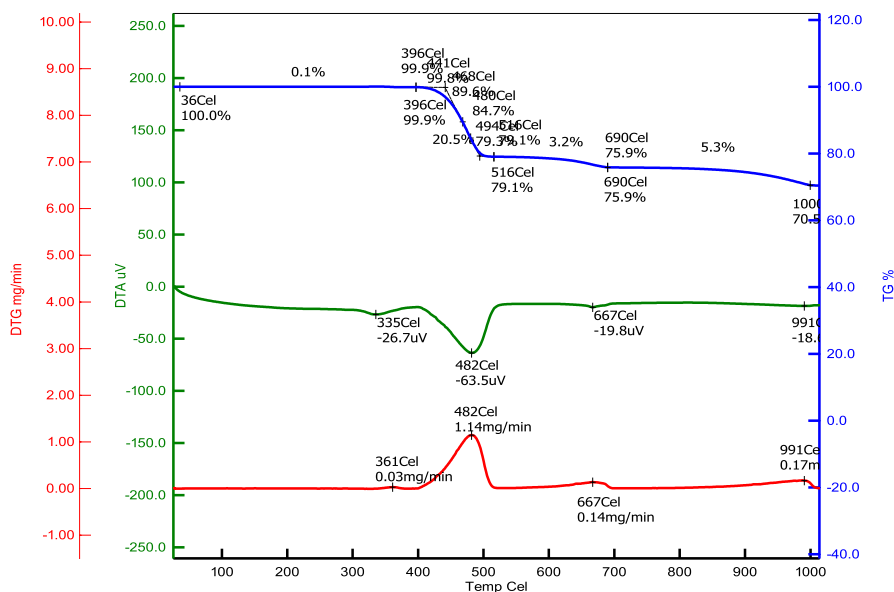
successful absorption of  $CO_2$  on the surface. The presence of the carbon peak further validates the capability of  $K^+$ -impregnated CaO for  $CO_2$  capture.

Overall, the FESEM-EDX analysis results suggest that  $K^+$  impregnation has led to morphological changes and modified the elemental composition of CaO, enhancing its surface properties for  $CO_2$  absorption. The rougher and more porous surface morphology observed after  $K^+$  impregnation provides evidence of increased active sites, which could facilitate  $CO_2$  capture. These findings support the potential of  $K^+$ -impregnated CaO as a promising material for  $CO_2$  capture and highlight the importance of surface modifications in enhancing absorption performance. Further studies are recommended to evaluate the absorption capacity and long-term stability of  $K^+$ -impregnated CaO under different operating conditions to assess its practical application in  $CO_2$  capture processes.

### Thermogravimetric (TGA) analysis

The reaction mechanism of  $CO_2$  absorption using  $K^+$ -impregnated CaO sorbent was analyzed through Thermogravimetric analysis (TGA). TGA was employed to monitor the sorption of  $CO_2$  by the potassium impregnated CaO sorbent and to determine the reaction kinetics. The TGA analysis revealed a distinct weight loss of the sorbent as the temperature increased, indicating the release of  $CO_2$ . This weight loss was attributed to the reaction between  $CO_2$  and the  $K^+$ -impregnated CaO sorbent, resulting in the formation of stable carbonates. The TGA thermogram (Fig. 5) exhibited a characteristic three-step weight loss with an initial 0.1% moisture loss, which can be attributed to different reaction mechanisms occurring at different temperature ranges.

The first step of weight loss (20.5%) observed in the TGA curve at 396–494 °C corresponds to the initial decomposition of the carbonates formed during the  $CO_2$  absorption process. This step is typically associated with the release of weakly



**Fig. 5** Thermogravimetric analysis of  $K^+$ -impregnated CaO sorbent after  $CO_2$  absorption with the composition of 4% CaO+5% KCl

bound  $CO_2$  and water molecules from the sorbent. The rate of weight loss in this stage depends on factors such as sorbent composition, temperature, and  $CO_2$  concentration. The second step of weight loss observed in the TGA curve represents the decomposition of the more stable carbonates formed at higher temperatures (494–690 °C). This step is often associated with the release of strongly bound  $CO_2$  and requires higher temperatures to occur and its needed more activation energy than the previous step. The reaction kinetics at this stage can be influenced by factors such as the porosity of the sorbent, surface area, and diffusion of reactants and products.

By analyzing the TGA data, it is possible to extract valuable information about the reaction kinetics of  $CO_2$  absorption using the  $K^+$ -impregnated CaO sorbent. The weight loss profiles obtained from the TGA experiments can be fitted to various kinetic models, such as the Avrami–Erofeev or the shrinking core model, to determine the reaction mechanisms and rate constants. These kinetic models provide insights into the controlling factors of the  $CO_2$  absorption process, including the diffusion of  $CO_2$  through the porous structure of the sorbent and the reaction kinetics at the solid–gas interface. Furthermore, TGA analysis allows for the determination of the maximum  $CO_2$  uptake capacity of the sorbent, which is a crucial parameter for evaluating its efficiency in practical applications. By measuring the weight gain of the sorbent during  $CO_2$  absorption, the equilibrium uptake capacity can be determined and compared with other sorbents or benchmark values.

TGA analysis of the  $CO_2$  absorption using  $K^+$ -impregnated CaO sorbent provides valuable insights into the reaction kinetics and performance of the sorbent. The three-step weight loss observed in the TGA curve indicates the presence of

different reaction mechanisms at different temperature ranges. By applying appropriate kinetic models to the TGA data, it is possible to determine the reaction mechanisms, rate constants, and maximum CO<sub>2</sub> uptake capacity, which are crucial for the design and optimization of CO<sub>2</sub> capture processes.

### Reaction kinetics for the formation of CaCO<sub>3</sub>

Kinetic analysis is important as the process involves a thermal effect on the sample. This study considers the first-order reaction, which includes the three-stage decomposition rate of the materials to establish kinetic parameters. The following kinetic equation was examined for heat deterioration, which is a simple differentiation of the first-order reaction. At temperatures above 400 °C, the carbonation rates of Ca(OH)<sub>2</sub> were higher than those of CaO. However, according to Eq. 1, it is believed that the reaction proceeds through the formation of an interface of water molecules at the solid surface and it is controlled by an inherent chemical reaction that occurs only on the surface that is not covered by CaCO<sub>3</sub>.

$$\frac{dx}{dt} = k_1 \left[ [1 - (2 - n)k_2 X]^{1/(2-n)} \right] \quad (1)$$

Here  $k_1$  and  $k_2$  represent proportionality constants, and  $n$  represents the reaction order.

Since the three steps reaction of weight loss occurs in the TGA curve, the activation energy for each regression factor (R.F) of every step is calculated by the following equation.

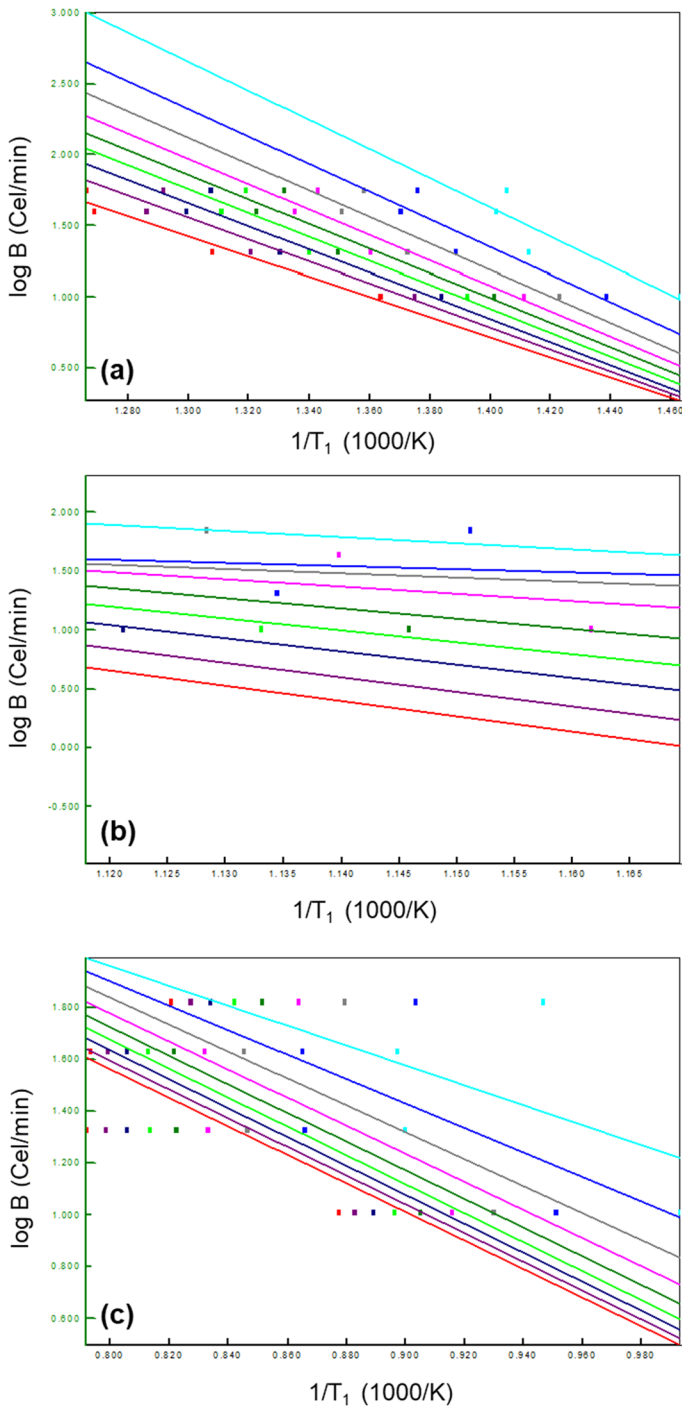
$$\log B = -0.4567 \frac{\Delta E}{R} \cdot \frac{1}{T_1} + \text{Constant} \quad (2)$$

Here  $B$ ,  $\Delta E$ ,  $T_1$ , and  $R$  are heating rate, activation energy, temperature and gas constant. By plotting  $\log B$  versus  $1/T_1$  straight lines were observed in Fig. 6a–c. Activation energy was calculated from the slope of the plotted graph shown in Table 1.

In step 1, the data indicate that the activation energy decreases with increases in R.F which means that the decomposition rate of the reaction is faster. But in the case of step 2, the opposite phenomenon occurs. Activation energy increase with the increase of R.F which indicates the slow rate of weight loss. It may occur due to the high lattice energy of the materials. Moreover, in step 3, up to 70% R.F. the deterioration rate is slow after that the rate of decomposition is increased at maximum R.F. due to a sudden decrease of activation energy.

### Cost analysis

The cost analysis for this study provides an estimate of the expenses involved in the synthesis of Na<sup>+</sup> and K<sup>+</sup>-impregnated CaO sorbent derived from waste eggshell. The analysis should consider raw materials such as eggshells, sodium chloride and potassium chloride, as well as the energy costs for the calcination of sorbent material.



**Fig. 6** Plots of  $\log B$  versus  $1/T_1$  plot of **a** step 1 **b** step 2 and **c** step 3 decomposition reaction of TG curve

**Table 1** Activation energy changes with the change of regression factor of step 1, step 2 and step 3 of TG curve

Regression factor (%)	Step 1		Step 2		Step 3	
	Activation energy (kJ/mol)	TG (%)	Activation energy (kJ/mol)	TG (%)	Activation energy (kJ/mol)	TG (%)
10	187.72	97.84	95.04	78.15	69.99	75.33
20	177.30	95.67	46.89	77.88	85.91	74.99
30	169.60	93.49	67.15	77.61	94.54	74.66
40	163.14	91.32	112.84	77.34	98.78	74.33
50	158.36	89.15	159.56	77.07	100.74	73.98
60	153.60	86.98	184.83	76.80	101.59	73.66
70	148.4	84.80	202.52	76.53	101.64	73.33
80	141.20	82.63	225.37	76.26	101.03	72.99
90	129.19	80.46	237.28	75.99	100.21	72.66

By considering these factors, researchers and stakeholders can gain insights into the economic feasibility and potential challenges associated with the proposed process. The cost analysis with the preparation of sorbent was estimated based on the literature [23]. Table 2 shows the estimated cost analysis for the synthesis of  $\text{Na}^+$  and  $\text{K}^+$ -impregnated CaO sorbent derived from waste eggshell. From the data, it is clear that the net expense of the prepared sorbent in this study was about three times lesser than the commercially purchased one.

## Conclusion

This manuscript explored the synthesis and characterization of  $\text{Na}^+$  and  $\text{K}^+$ -impregnated CaO derived from eggshell as a potential material for  $\text{CO}_2$  absorption. The results demonstrated that the incorporation of  $\text{K}^+$  into CaO derived from eggshell enhanced its  $\text{CO}_2$  absorption capacity and stability. The study utilized various characterization techniques such as XRD, FESEM, TGA, and FTIR to assess

**Table 2** Cost analysis of CaO based sorbent preparation

Materials	Unit price (\$)	Used amount	Net price (\$) (this study)	Net price (\$) (commercial)
Raw eggshell	0/Kg	1 kg	0	167.24 (0.74 kg)
Sodium chloride	55/Kg	0.25 kg	13.33	13.33
Potassium chloride	220/Kg	0.25 kg	55.00	55.00
Cost of calcination energy (heating)*	0.07/kWh	0.74 kg CaO	13.61	0
Total cost			81.94	235.57

\*Price was calculated based on the literature and the Bangladeshi price

the structural and morphological properties of the prepared CaO sorbent. The XRD analysis confirmed the formation of CaO and the presence of Na<sup>+</sup> and K<sup>+</sup> species, while the FESEM images revealed a porous structure, which is beneficial for gas absorption. The CO<sub>2</sub> absorption performance of the K<sup>+</sup> impregnated CaO was evaluated through breakthrough experiments at different sorbent concentrations. The results indicated that the absorption capacity increased with the incorporation of K<sup>+</sup> and reached a maximum at an optimal K<sup>+</sup> loading. The 4% CaO with 5% KCl showed the best absorption capacity with minimum reaction time and absorbed 99.4% CO<sub>2</sub> after 8 min of reaction. Furthermore, the material exhibited good stability and recyclability over multiple absorption–desorption cycles. The enhanced CO<sub>2</sub> absorption performance of the K<sup>+</sup> impregnated CaO derived from eggshell can be attributed to the synergistic effect between CaO and K<sup>+</sup>, as well as the increased surface area and porosity. The K<sup>+</sup> species acted as active sites for CO<sub>2</sub> absorption, while the CaO provided the necessary structural stability. This research contributes to the development of cost-effective and sustainable process for CO<sub>2</sub> capture. The utilization of eggshell waste as a precursor for CaO synthesis adds value to an otherwise discarded resource, while the incorporation of K<sup>+</sup> enhances the material's CO<sub>2</sub> absorption capacity. The findings from this study have implications for addressing climate change and reducing greenhouse gas emissions.

Further research can focus on optimizing the K<sup>+</sup> loading, exploring different impregnation methods, and investigating the long-term stability of the material. Additionally, exploring the potential application of the K<sup>+</sup>-impregnated CaO derived from eggshell in industrial-scale CO<sub>2</sub> capture systems would be valuable.

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**Author contributions** Conceptualization: MH; Methodology: MH, MS; Experimental: MS, TA, JU, MAG; Data Curation: MS, TA, RA, FC; Formal analysis: TA, RA, MS, MAG; Writing main manuscript: TA, MH; Reviewing the manuscript: SA, AAS, MSJ; All authors have read and agreed to the published version of the manuscript.

## Declarations

**Competing Interests** We have no competing interests.

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