EEET ECOLOGICAL ENGINEERING & ENVIRONMENTAL TECHNOLOGY

Ecological Engineering & Environmental Technology, 2025, 26(3), 34–41
https://doi.org/10.12912/27197050/199523
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Received: 2024.12.10
Accepted: 2025.01.20
Published: 2025.02.01

Preparation of oyster shell waste impregnated with bimetal nitrate as a carbon dioxide gas adsorbent to reduce global warming

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ABSTRACT

The increase in greenhouse gas concentrations has intensified the impact of global warming. Oyster shell (OS) as a source of $CaCO_3$ has been considered as one of the methods to reduce CO_2, which is one of the primary contributors to global warming. Among various approaches, the adsorption method has proven effective in reducing CO_2 emissions. This study aims to produce an adsorbent from oyster shells impregnated with metal nitrates that is selective for CO_2 gas. The adsorbent preparation was carried out using the Successive Incipient Wetness Impregnation (SIWI) method, with the material formulation calculated based on stoichiometric ratios. The metal nitrate concentration was 2.5%wt (for both aluminum and magnesium metal oxides). The resulting adsorbent was characterized using SEM-EDS (morphology) to indicate Al and Mg have been impregnated in oyster shells with 0.5% each. CO_2 capture/adsorption was measured using TGA, and it found OS/Al exhibited the highest weight loss (5%). Therefore, aluminum nitrate impregnation (OS/Al 5') is the most effective approach for enhancing the CO_2 adsorption capacity of oyster shells.

Keywords: adsorption, impregnation, calcium carbonat, carbon dioxide.

INTRODUCTION

Greenhouse gas emissions are a significant factor in global warming. Naturally, greenhouse gases are produced from biological activities such as methane (CH_4), nitrogen oxides (NOx), ozone (O_3), and carbon dioxide (CO_2). However, human activities such as the use of fossil fuels, industrial processes(Murawska and Goryńska-Goldmann, 2023), deforestation (Wolff et al., 2021), and the use of fertilizers (Gołasa et al., 2021) can lead to an increase in these gases in the atmosphere, causing the depletion of the ozone layer, which contributes to global warming. In this context, CO_2 is one of the gases more frequently produced by human activities (Liu et al., 2022).

CO_2 is a gas that tends to be inert, odorless, and colorless. This gas naturally exists in the Earth's atmosphere and is essential for plants to carry out photosynthesis. However, excess CO_2 produced by human activities, such as in energy, industry, transportation, and agriculture, can lead to a rise in atmospheric temperatures. The concentration of CO_2 in the atmosphere has increased from 315.98 ppmv in 1959 to 414 ppmv in 2020, reaching the highest level recorded in the last 650,000 years. Data released by the Mauna Loa Observatory shows that the average amount of CO_2 has been increasing since 1958 up to May 2023, reaching 424 ppm (Lindsey, 2023) with an average temperature increase of 0.11 °F (0.06 °C) per decade since 1850, or approximately 2 F in total. The rate of warming since 1982 has been more than three times faster: 0.36 F (0.20 °C) per decade (Lindsey and Dahlman, 2024). Various efforts have been made to reduce CO_2 emissions,

such as managing transportation use, increasing the use of renewable energy, managing industrial waste, forest conservation, green agricultural practices, and using technologies to capture CO_2/Carbon Capture (CC). CC can be achieved through adsorption methods. Previous researchers have used eggshells impregnated with metal nitrate to adsorb CO_2 from industrial processes. The research showed that CO_2 gas adsorption capacity using metal nitrate-impregnated eggshells increased by 30.18% compared to non-impregnated eggshells (Imani et al., 2023). However, the preparation of adsorbents requires eggshells in powder form. A relatively high quantity of eggshells is required to obtain a large mass of them, which is relatively difficult to acquire.

Oysters are abundantly available in Banda Aceh, Indonesia. The extensive production of oysters generates an abundance of OS as waste. OS has characteristics similar to eggshells. Therefore, OS represents a promising alternative material for CO_2 adsorption due to its high calcium carbonate ($CaCO_3$) content, typically ranging from 80% to 90% (Bellei et al., 2023). This calcium source is one of the best materials for adsorbents due to its high porosity, good adsorption capacity, and fast carbonation/calcination kinetics (Oschatz and Antonietti, 2018). Consequently, this study offers the advantage of addressing air pollution using solid waste. Thus, the objectives of this research are not only to reduce solid waste and enhance the value of oyster shell waste into an economically valuable adsorbent but also to explore its potential as an alternative material for capturing air pollutants, particularly CO_2, a greenhouse gas contributing to global warming.

To date, no reports have been made on the utilization of oyster shell waste impregnated with magnesium and aluminium nitrates as adsorbents for CO_2 adsorption. Hence, this study aims to investigate the adsorption performance of oyster shell-based adsorbents impregnated with metal nitrates to effectively capture CO_2 gas.

MATERIAL

Several materials were used in this research, including oyster shell waste (*Crassostrea gigas*), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), and other chemicals.

METHODS

Adsorbent preparation

This research obtained OS from Alue Naga Village, Syiah Kuala District, Banda Aceh (H9X3+Q6 Alue Naga, Kota Banda Aceh, Aceh). The OS waste was cleaned and crushed using an oyster shell crusher and then sieved using a 40-mesh sieve. The OS powder particles were impregnated with a metal nitrate solution using the Successive Incipient Wetness Impregnation (SIWI) method. The solution volume and metal concentration were calculated based on the stoichiometric ratio to achieve the desired metal content in the final adsorbent in terms of weight percentage (the weight percentage is calculated based on the metal oxide form). The synthesis method scheme is presented in Figure 1. After drying the prepared adsorbent at 120 °C in an oven, all samples were stored in a desiccator awaiting characterization (Imani et al., 2023).

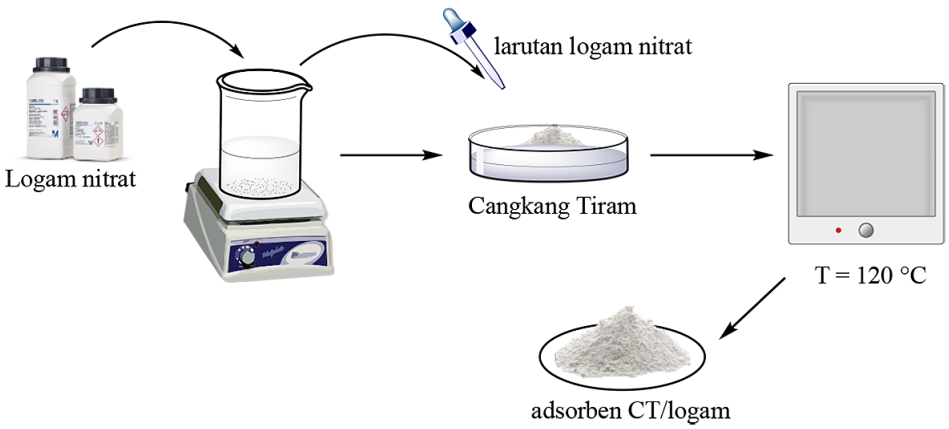

Figure 1. The schematic of the SIWI method used for adsorbent preparation

Characterization of adsorbents

Adsorbents were characterized using several instruments. The morphology of the adsorbent material was also analysed to study the surface of adsorbents using Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) (Phenom Pro X). Additionally, the adsorbent material was tested using thermal gravimetric analysis (TGA) to determine the adsorption of CO_2.

Adsorption study

Several variables, including gas properties, temperature, contact time, surface area, and pressure influence gas adsorption. This study examined the research variables based on the gas flow rate and the mass of the adsorbent used. The setup of equipment used in the adsorption process is illustrated in Figure 2. The determination of CO_2 gas adsorption conditions was conducted at 1 atm pressure, with a gas flow rate of 1–10 L.min^{-1}, an adsorbent mass of 0.5 grams of OS/Al and OS/Mg, and with various contact time 0–20 minutes. The CO_2 uptake capacity using the OS/Metal adsorbent was measured using TGA by analyzing the mass of CO_2 adsorbed per initial mass of the adsorbent (C_n). The adsorption capacity can be calculated using Equation (Imani et al., 2023; Murawska and Goryńska-Goldmann, 2023):

$$C_n = \frac{m(t)-m}{m} \quad (1)$$

where: $m(t)$ is the mass of the adsorbent at time t, and m is the total mass of the adsorbent used to adsorb CO_2 gas.

RESULT AND DISCUSSION

Preparation of adsorbents

Raw OS was obtained from a product created during a previous year's community service program. The OS, identified as *Crassostrea gigas*, was sourced from the mangrove habitat in Gampong Alue Naga, Syiah Kuala District, Banda Aceh City. The OS powder was sieved to pass through a 40-mesh screen. Solutions of magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) and aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) were prepared at 5 wt% by dissolving 5 grams of each nitrate salt in 100 mL of distilled water with heating to speed up dissolution. The OS/Al and OS/Mg synthesis was performed using the SIWI method. A 5 wt% metal nitrate solution was slowly added dropwise to 119 grams of OS, and the mixture was stirred thoroughly to initiate the following reactions:

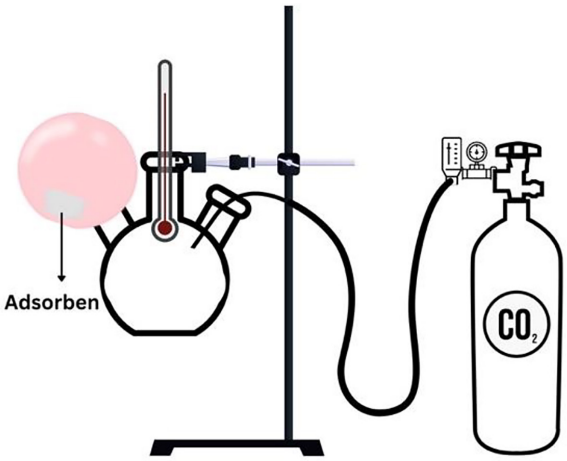

Figure 2. Equipment's setup of the adsorption process

$$CaCO_3\ (s) + Mg(NO_3)_2.6H_2O\ (aq) \rightarrow MgCO_3\ (s) + Ca(NO_3)_2\ (aq) + 6H_2O\ (l) \quad (2)$$

$$CaCO_3\ (s) + Al(NO_3)_2.6H_2O\ (aq) \rightarrow \rightarrow 3Ca(NO_3)_2\ (aq) + 2Al(OH)_3(s) + + 3CO_2\ (g) + 9H_2O(l) \quad (3)$$

The stoichiometric calculations determined the mass of OS needed to yield 100 grams of adsorbent. A double displacement reaction occurred when the metal nitrate solution was added to the OS powder. The calcium carbonate reacted with magnesium nitrate hexahydrate, producing calcium nitrate, magnesium carbonate, and water. The mixtures were then oven-dried at 120 °C for 260 minutes to achieve a constant weight. The resulting adsorbents were white powder and ready for CO_2 gas adsorption (Fig. 3).

Characterization of OS/metal adsorbents

The adsorbents produced in this study, namely aluminum nitrate-impregnated oyster shell (OS/Al) and magnesium nitrate-impregnated oyster shell (OS/Mg), were analyzed using Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS) to study surface morphology and elemental distribution. SEM-EDS provided critical data on how impregnation affected the composition and surface properties of the materials, forming the basis for evaluating the modifications' effects on adsorption performance.

Figure 3. a) adsorbent OS/Al, b) adsorbent OS/Mg

The SEM images at 1000× and 5000× magnifications (Fig. 4) revealed the dominant elements on the adsorbents' surfaces: oxygen (44.9% and 47.6%), calcium (38.0% and 28.5%), and carbon (16.0% and 22.1%) for OS/Al and OS/Mg, respectively, indicating the presence of $CaCO_3$. Additionally, the detection of aluminum (0.5%) and magnesium (0.5%) confirmed successful impregnation. The low concentrations of Al and Mg suggested a thin or evenly distributed layer on the material's surface (Mola et al., 2017). Despite their low levels, Al and Mg could enhance adsorption properties, especially in interacting with heavy metal ions or pollutants like CO_2 gas.

Adsorption study

The characterized adsorbents were subjected for adsorption studies using a simple apparatus as a prototype for CO_2 gas adsorption (Fig. 5a). The adsorption capacity of OS/Al and OS/Mg was measured by varying the contact time between the adsorbent and the adsorbate. One gram of each powdered adsorbent was placed into balloon, and CO_2 gas was passed through at a flow rate of 1 $L \cdot min^{-1}$ for 0–20 minutes. The balloon's mass was measured before and after CO_2 exposure using an analytical balance (Fig. 5b). Subsequently, the adsorbents were analysed using TGA to determine the weight loss, which was assumed to represent the percentage of CO_2 gas adsorbed.

The impregnated OS adsorbents showed a more significant mass difference than unmodified OS, proving that metal nitrate addition improved the adsorbents' ionic adsorption or surface polarity (Ma et al., 2024). This improvement drives the materials more effective in capturing certain pollutants (Soo et al., 2024). Further characterization

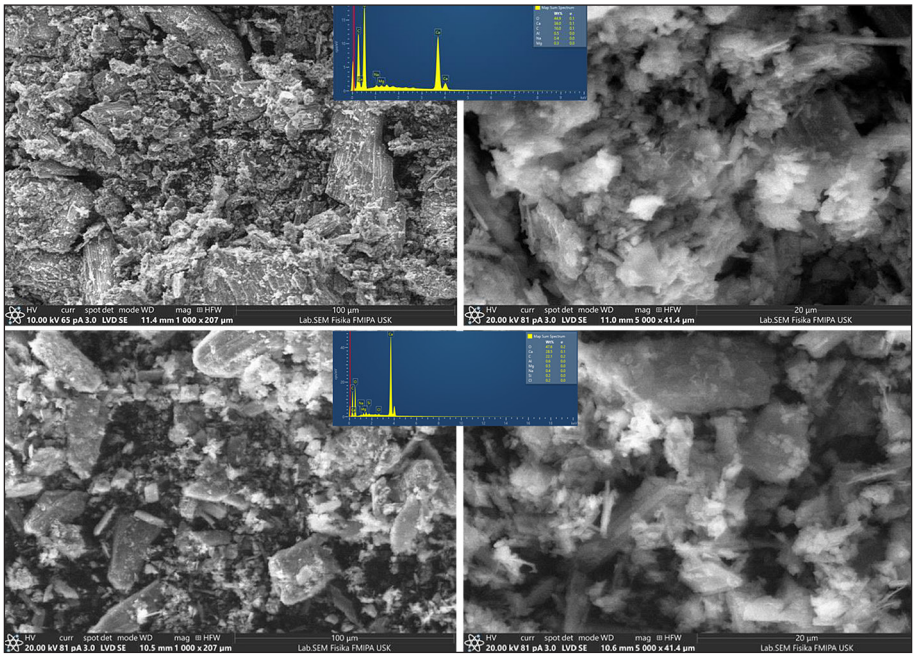

Figure 4. (a) OS/Al 1000× and 5000×, (b) OS/Mg 1000× and 5000×

Figure 5. (a) Adsorbent and encapsulated within a balloon, (b) adsorption process experiment

was conducted using TGA and differential scanning calorimetry (DSC) at temperatures below 600 °C to avoid calcination of the OS (Rahman Md. Rezaur et al., 2017). The TGA results (Fig. 6) revealed different weight loss rates for OS, OS/Mg, and OS/Al in three stages: below 150 °C, below 300 °C, and below 600 °C. The addition of $Mg(NO_3)_2$ and $Al(NO_3)_3$ introduced more complex decomposition patterns due to nitrate decomposition, producing MgO and Al_2O_3,

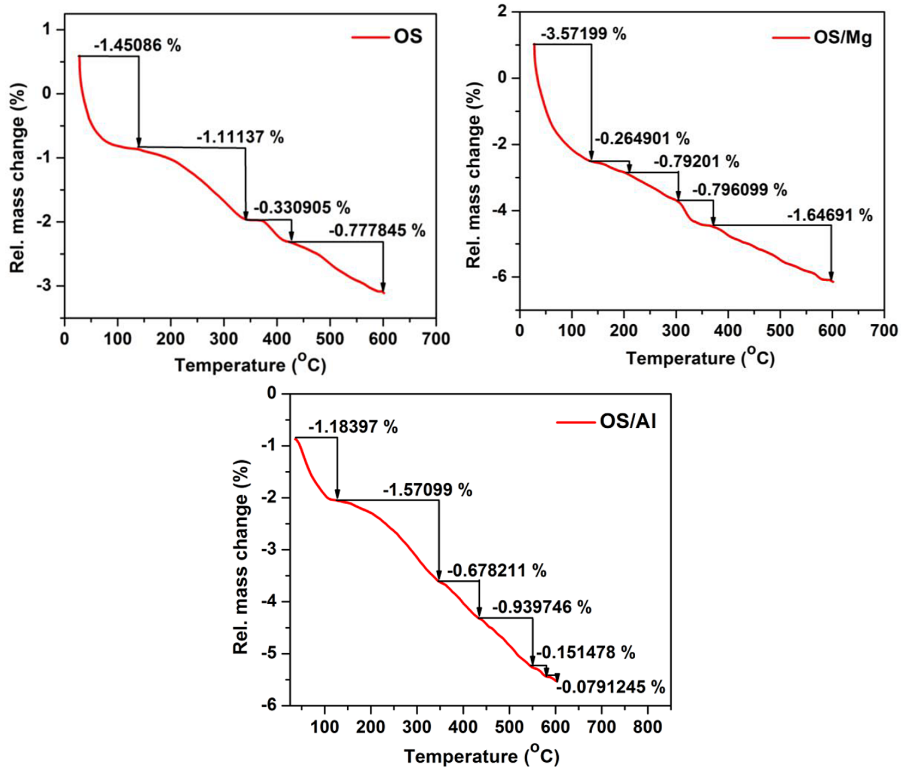

Figure 6. TGA of OS, OS/Mg, and OS/Al

which enhanced material functionality (e.g., increased porosity for gas adsorption applications). The most significant weight loss occurred below 150 °C, indicating water and CO_2 gas release. OS/Mg exhibited the highest weight loss (3.57%) due to Mg's higher hygroscopic properties than Al.

The DSC results (Fig. 7) showed heat flow changes during heating for the three adsorbents. The non-impregnated OS displayed a significant endothermic peak between 200–300 °C, corresponding to organic compound decomposition or bound water loss. Impregnated samples exhibited distinct heat flow patterns: OS/Mg had an additional endothermic peak due to magnesium nitrate decomposition, while OS/Al showed more complex endothermic processes between 400–600 °C, indicating reactions involving aluminum nitrate and calcium carbonate. These differences demonstrate that impregnation affects thermal stability and reaction mechanisms, impacting CO_2 adsorption capacity.

The three TGA graphs illustrate (Fig. 8) the weight change characteristics of oyster shells impregnated with different nitrates (non-impregnated, aluminum nitrate, and magnesium nitrate) under various conditions over time, focusing on the first 15 minutes. The weight change is minimal for the non-impregnated sample (OS/Al 0' or OS/Mg 0'), showing limited CO_2 adsorption and no significant thermal decomposition. This phenomenon serves as a baseline to understand the impact of nitrate impregnation on the oyster shells' adsorption and decomposition properties.

The weight profiles in the aluminum nitrate-impregnated samples reveal distinct behaviors at 5, 10, 15, and 20 minutes. For example, during the initial 15 minutes, OS/Al 5' shows a modest weight gain, indicating active CO_2 adsorption. However, as time progresses, samples like OS/Al 15' and OS/Al 20' exhibit less weight change during the same period, suggesting reduced adsorption activity. This trend may indicate that the sample undergoes gradual saturation with CO_2 or the decomposition of aluminum nitrate begins to counteract adsorption.

Based on Figure 8. the TGA results, the non-impregnated oyster shell sample (OS 0') shows minimal weight change throughout the experiment, confirming that it is ineffective for CO_2 adsorption. The weight remains stable at nearly 0%, indicating negligible adsorption capacity. This sample serves as a baseline comparison for the impregnated samples. The magnesium nitrate-impregnated samples display a more pronounced variation in weight behavior during the first 15 minutes. The OS/Mg 5' sample shows rapid weight loss, likely driven by the thermal decomposition of magnesium nitrate. Meanwhile, OS/Mg 10' exhibits a slight weight gain during this period, reflecting effective CO_2 adsorption before decomposition dominates. Conversely, OS/

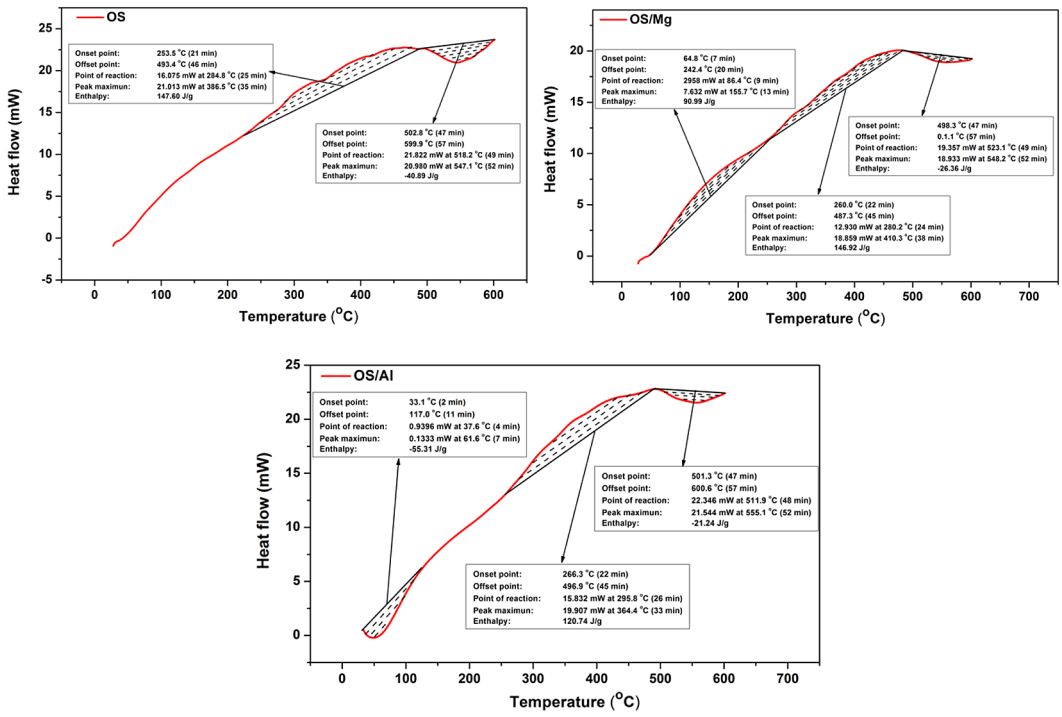

Figure 7. DSC for OS, OS/Mg, and OS/Al

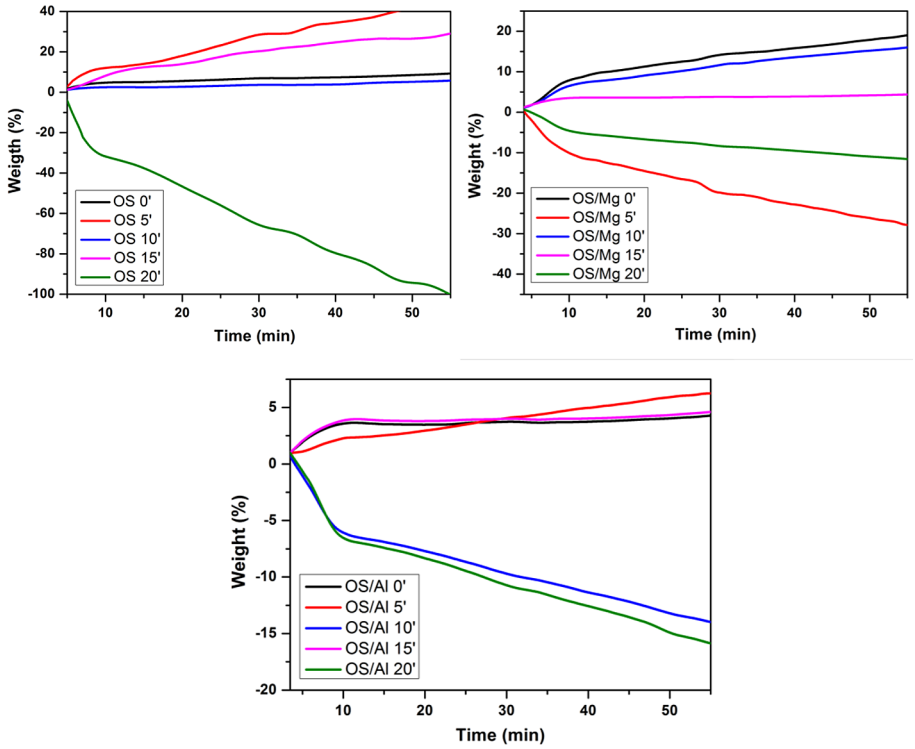

Figure 8. The weight change profile of oyster shells impregnated with different nitrates

Mg 15' and OS/Mg 20' demonstrate progressive weight loss during the first 15 minutes, indicating that the decomposition of magnesium nitrate starts earlier and overshadows adsorption processes.

For the aluminum nitrate-impregnated oyster shells, the highest CO_2 adsorption is observed in sample OS/Al 5', which achieves an optimum weight gain of approximately 5% within the first 15 minutes indicating significant CO_2 capture efficiency compared to other aluminium-impregnated samples, which either show minimal weight changes (e.g., OS/Al 15') or exhibit signs of saturation. The percentage gain reflects the enhanced adsorption ability facilitated by the aluminum nitrate at this stage.

In the case of magnesium nitrate-impregnated oyster shells, sample OS/Mg 10' demonstrates an optimum weight gain of approximately 3% during the first 15 minutes, marking it as the most effective among the magnesium nitrate samples. Other magnesium-impregnated samples, such as OS/Mg 5' and OS/Mg 15', show significant weight losses during this period, dominated by thermal decomposition processes. Among all the samples, OS/Al 5' exhibits the highest CO_2 adsorption efficiency, with a weight gain of 5% within the first 15 minutes, making it the optimal condition for CO_2 capture. This result indicates that aluminum nitrate impregnation is more effective than magnesium nitrate in enhancing the adsorption properties of oyster shells.

CONCLUSIONS

Thermogravimetric analysis (TGA) of oyster shells impregnated with aluminum and magnesium nitrates reveals notable CO_2 adsorption and decomposition profile differences within the first 15 minutes. In contrast, non-impregnated oyster shells exhibit minimal activity, serving as a baseline for comparison. Among the impregnated samples, aluminum nitrate demonstrates superior CO_2 adsorption performance, particularly in OS/Al 5, while magnesium nitrate exhibits a balanced interplay of adsorption and decomposition in OS/Mg 10. These results underscore the importance of experimental timing in evaluating adsorption efficiency and thermal stability for CO_2 capture applications. A comparative analysis of all graphs indicates that OS/Al 5 is the most effective sample for CO_2 capture, achieving a significant weight gain of 5% within the initial 15 minutes, which reflects its more substantial and more consistent adsorption activity. Although OS/Mg 10 exhibits some adsorption potential, the observed weight

change is less pronounced, and decomposition processes rapidly dominate. These findings highlight the critical role of aluminum nitrate impregnation in optimizing the CO_2 adsorption capacity of oyster shells. This study provides a foundational understanding for further advancements in bio-based CO_2 capture materials, paving the way for more efficient and sustainable solutions to address global carbon emissions.

Acknowledgments

This work was supported by Universitas Syiah Kuala LPPM research funding, grant number 324/UN11.2.l/PG.01.03/SPK/PTNBH/2024, dated 3rd May 2024.

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