Comparative study on mechanisms of gases release from Ca-alginate beads

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Abstract. Calcium alginate (Ca-alginate) beads have attracted considerable attention as carriers for the controlled release of volatile compounds due to their biocompatibility and tunable properties. This study aimed to compare the release of ethylene and carbon dioxide gas from Ca-alginate beads. Ca-alginate beads were prepared from a sodium alginate solution containing ethephon and calcium carbonate as the gas-forming agent. The resulting solution was then extruded into a calcium chloride solution. The gas release behavior was studied by monitoring the concentration of released gases over time using gas detectors. Extrusion tip diameter, alginate concentration and gas-releasing agent concentration were systematically varied to assess their effect on the gas release rate. The results indicated distinct release patterns for ethylene and carbon dioxide gas. Ethylene gas exhibited a relatively slower and sustained release, while carbon dioxide gas exhibited a more rapid release. Moreover, the bead size influenced the gas release, with larger beads displaying faster release rates for ethylene and carbon dioxide gas. The concentration of alginate also played a role in modulating the release kinetics, with higher alginate concentration resulting in slower gas release. The findings have implications for designing and optimizing Ca-alginate-based systems for agricultural applications, including plant hormone delivery and modified atmosphere packaging.

1 Introduction

Controlled release systems have become indispensable in a wide range of industries, offering the ability to release specific substances precisely and gradually over time. Within this field, the encapsulation of volatile compounds within polymeric matrices has gained prominence, finding applications in agriculture, pharmaceuticals, environmental science, and more [1-4]. These encapsulation techniques can protect them from environmental...
effects, enhancing their stability, controlling release rates, and ensuring sustained release while promoting ease of handling and extending the shelf life of compounds [5-7].

Ca-alginate beads, derived from the natural polymer alginate and crosslinked with calcium ions, have demonstrated their versatility in controlled release systems. The utilization of calcium alginate offers a wide range of advantageous characteristics include biodegradability, biocompatibility, cost-effectiveness, ease of gelation, and non-toxic nature [8-11]. These make it an excellent choice for encapsulating various gas-releasing substances, particularly volatile compounds. For example, ethylene gas and carbon dioxide gas releasing beads have been used for controlled fruit ripening and drug delivery system respectively.

Ethephon, also known as 2-chloroethyl phosphonic acid, acts as a plant growth regulator and can be effectively encapsulated in Ca-alginate beads. This compound can penetrate plant tissue and decompose to produce ethylene gas when exposed to alkaline and high-temperature conditions [12-13]. Ethylene gas, the active component released by ethephon, is volatile and exists in a gaseous state at room temperature. It has a characteristic sweet odour and is highly flammable. In agriculture, ethylene gas finds applications for various purposes, such as fruit ripening and plant growth regulation [14].

Calcium carbonate exhibits the capability to gradually release carbon dioxide when interacting with acetic acid. The gas produced permeates the alginate structure, forming gas bubbles or generating pores within the beads. This gas entrapment significantly contributes to the buoyancy of the beads, allowing them to float effortlessly on the liquid surface. This application is extensively employed in medical treatments, environmental monitoring, and carbon capture [15-16].

Although several studies have been conducted to encapsulate gas-releasing agent in Ca-alginate beads and characterize beads physical properties, the quantification of gas release from the beads are still lacking. Therefore, this research aims to investigate and compare the release of ethylene gas and carbon dioxide gas from calcium alginate beads. Ethephon and calcium carbonate were encapsulated in calcium alginate beads using a simple extrusion dripping method. The size of the beads was determined using an image analysis system, and the release of gases from the beads was measured using portable gas detectors.

2 Materials and methods

2.1 Materials

All chemicals used for the experiment were analytical grade. The chemicals that were used in the study are Sodium Alginate (KIMICA Cooperation, Japan), Calcium Chloride (Bendosen, Norway), Ethephon 52% S.L. (Local market, Malaysia), Calcium Carbonate (Local market, Malaysia), Sodium Hydroxide (Merck, Germany) and Acetic Acid (Merck, Germany).

2.2 Preparation of solutions

Sodium alginate was dissolved uniformly in distilled water using an agitator motor at 700 rpm (RW 20 digital, IKA, Germany) to produce a sodium alginate solution with a concentration ranging from 1.0% to 2.5% w/v. In this research, ethephon and calcium carbonate were chosen as the model gas-releasing agents. Ethephon (750 ppm) was added to each sodium alginate solution with continuous stirring to ensure a through and uniform mixing. Similarly, 5 g of calcium carbonate was introduced into a separate sodium alginate
solution and stirred continuously. A gelation bath made up of 1.5% w/v was prepared by dissolving calcium chloride powder in distilled water.

2.3 Preparation of calcium alginate beads

Ca-alginate beads were prepared by dripping mixtures of sodium alginate solution (1.0% and 2.0% w/v) and ethephon (750 ppm) through a syringe with different extrusion tip diameters (0.6 mm, 0.8 mm, and 1.2 mm), into a gelation bath made up of 1.5% w/v calcium chloride in an air-conditioned environment (24 °C). The formed beads were allowed to harden in the gelation bath for 30 minutes. Then, the beads were filtered, rinsed with distilled water, and dried at room temperature. These steps were repeated for mixtures of sodium alginate solution (1.5% and 2.5% w/v) and calcium carbonate (10%).

2.4 Determination of bead size

The size of the beads was measured using 2D image analysis. First, the beads were scattered on a piece of transparent plastic petri dish. Then, a white light source was applied at the bottom to create a contrasting background for the gel beads. The images of the beads were captured from a top view using a digital camera (Huawei Nova 5T, Huawei, China). These captured images were then imported into image analysis software (Image J, U. S. National Institutes of Health, USA). For each measurement, a sample of 30 beads was taken, and the diameters of the beads were measured.

2.5 Gas release studies

The release of gases from the beads was studied in desiccators at room temperature. For ethylene gas release studies, 100 mL of beads were placed into a beaker containing pH 11 sodium hydroxide solution and then placed in desiccators for 24 h. The decomposition of ethephon into ethylene gas was measured using a portable gas detector (PG 610, Henan Inte Electrical Equipment Co., China).

For carbon dioxide gas release studies, 300 beads were placed into a universal bottle containing pH 2 acetic acid and then positioned in desiccators. The gas release was measured using a portable gas detector (PG 810, Henan Inte Electrical Equipment Co., China).

2.6 Statistical analysis

Numerical data were presented as the mean ± standard deviation (SD) derived from multiple replicate measurements using Microsoft Excel and Minitab (Version 17; StataCorp LLC, TX, USA).

3 Results and discussion

3.1 Effect of bead sizes on gas release

Table 1 shows the sizes of beads produced from ethephon-encapsulated calcium alginate and calcium carbonate-encapsulated calcium alginate. The results demonstrated that the size of the beads is significantly affected by the extrusion tip diameter regardless of alginate
concentration and encapsulated materials concentration. As the extrusion tip diameter increased from 0.6 mm to 1.2 mm, the size of beads also increased from 2.33 mm to 2.69 mm for ethephon-encapsulated Ca-alginate beads and 2.37 mm to 2.77 mm for calcium carbonate-encapsulated Ca-alginate beads, respectively. These findings are similar to previous studies, which also reported an increase in bead diameter with larger extrusion tip diameters [17].

As depicted in Fig. 1, the results reveal distinct release patterns for ethylene and carbon dioxide gas. Ethylene gas exhibits a relatively slower and sustained release profile, characterized by its gradual and prolonged diffusion from the beads. In contrast, carbon dioxide gas displays a more rapid release behavior, with some samples (D, E, and F) achieving complete release within 4 hours. However, Samples A, B, and C demonstrate an incomplete release of ethylene gas even after 24 hours, indicating that the release of ethylene gas continues over an extended period. Previous studies stated that when ethephon was mixed with phosphate buffer, the release of ethylene gas occurs rapidly within 24 h and shows a significant slowdown on the third day [18].

Furthermore, the rate of gas release was indeed influenced by the size of the beads, as larger beads exhibited faster release rates for both ethylene and carbon dioxide gas. Sample C and Sample F, characterized by the largest bead size, notably demonstrated faster gas release and the highest gas concentration compared to the other samples. In contrast, Sample B and D exhibited slower gas release due to their smaller size.

Table 1. Diameter of beads produced using different material, solution concentration and extrusion tip diameters.

<table>
<thead>
<tr>
<th>Samples No</th>
<th>Encapsulated Material</th>
<th>Alginate Concentration</th>
<th>Encapsulated Material Concentration, ppm</th>
<th>Extrusion Tip Diameter, mm</th>
<th>Bead Diameter, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Etephon</td>
<td>2.0%</td>
<td>750</td>
<td>0.6</td>
<td>2.33±0.22&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>B</td>
<td>Etephon</td>
<td>2.0%</td>
<td>750</td>
<td>0.8</td>
<td>2.25±0.34&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>C</td>
<td>Etephon</td>
<td>2.0%</td>
<td>750</td>
<td>1.2</td>
<td>2.69±0.22&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>D</td>
<td>Calcium Carbonate</td>
<td>1.5%</td>
<td>50,000</td>
<td>0.6</td>
<td>2.37±0.14&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>E</td>
<td>Calcium Carbonate</td>
<td>1.5%</td>
<td>50,000</td>
<td>0.8</td>
<td>2.46±0.16&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>F</td>
<td>Calcium Carbonate</td>
<td>1.5%</td>
<td>50,000</td>
<td>1.2</td>
<td>2.77±0.18&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Data represents the mean ± SD. Means that do not share a letter are significantly different.
3.2 Effect of alginate concentration on gas release

Fig. 2 presents the release of ethylene and carbon dioxide gases from different alginate concentrations. Within the studied time period, the concentration of ethylene and carbon dioxide gases released from lower alginate concentrated beads was higher. The results also demonstrate that the release rates of ethylene and carbon dioxide gases increase with decreasing alginate concentration. This phenomenon can be attributed to the lower cross-link density on the surface of the beads made of low alginate concentration [19]. This observation aligns with prior research findings that during external gelation, the cross-linking of alginate chains with Ca$^{2+}$ ions at the bead surface leads to a denser and less permeable structure. Consequently, the diffusion of gases after the decomposition through the denser bead interior is impeded, resulting in a slower release of gases to the environment [20].
4 Conclusions

In conclusion, the comparative study on ethylene and carbon dioxide gas release from Ca-alginate beads have yielded valuable insights into the release behavior of these gases from controlled release systems. It has been observed that bead size significantly influences gas release rates, with larger beads demonstrating faster release for both ethylene and carbon dioxide gases. Additionally, higher alginate concentrations result in slower gas release due to increased cross-link density, leading to a denser and less permeable bead structure. Ethylene gas exhibits a slower and sustained release profile, while carbon dioxide gas displays a more rapid release. These findings hold practical implications for various applications. The slower and sustained release of ethylene can be advantageous for controlled fruit ripening, ensuring uniform and extended ripening periods. On the other hand, the rapid release of carbon dioxide is valuable in modified atmosphere packaging (MAP) for food preservation, where it efficiently displaces oxygen to extend the shelf life of products.

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