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Article

Fabrication of Functional Gypsum Boards Using Waste Eggshells to Prevent Sick Building Syndrome

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Abstract: Eggshells can adsorb chemicals, but no studies regarding the adsorption of gaseous chemicals using eggshells or eggshell membranes have been reported. The purpose of this study was to apply chemical adsorption using eggshells to the maintenance of human health. Building materials containing eggshells may reduce the concentrations of toxic substances, such as formaldehyde, via the adsorption functions of eggshells. In the bending study, the strength of board-shaped gypsum-containing eggshells was not compromised when the content of eggshells within the gypsum was $\leq$10%. Compared to those of gypsum boards containing seashells, which comprise calcium carbonate, similar to eggshells, gypsum containing eggshells displayed a higher strength. In the adsorption study, board-shaped gypsum containing eggshells placed inside a sealed box rapidly decreased the formaldehyde concentration. A gypsum board with an eggshell content of $\geq$5% could limit the formaldehyde concentration to $\leq$0.08 ppm. Furthermore, the results were compared with those of adsorption studies using plasterboard mixed with other natural materials. Eggshells displayed excellent functionalities as novel formaldehyde adsorbents.

Keywords: eggshell; eggshell membrane; adsorption; formaldehyde; gypsum; calcium carbonate

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1. Introduction

Chicken eggs are commonly consumed by individuals worldwide, regardless of race and religion, but eggshells are not considered edible, and most are discarded, amounting to approximately 8.58 million metric tons of eggshells annually worldwide [1]. Large food processing companies recycle eggshells via a process that involves separating the vastly different chemical constituents of the eggshell, primarily calcium carbonate, and the eggshell membrane, primarily protein. Eggshells are used in chalk production, whereas eggshell membranes are used in cosmetics and similar products. Numerous examples of effective biological applications of eggshells in biosorption materials [2], supporting materials in immobilizing enzymes [3], novel functional foods [4], patch materials for the tympanic membrane [5], and the up-regulated expression of transcripts [6] have been reported. Additionally, chemical applications of eggshells in supercapacitors [7], rechargeable batteries [8], adsorbent materials for gold ions in electroplating waste [9], dyes [10], and the elimination of heavy atoms from dilute waste solutions [11] have been reported. Recently, modifying the stability of dye-sensitized solar cells using ruthenium dyes embedded in eggshell membranes [12] and generating power using a direct methanol fuel cell with the protein components of eggshell membranes as proton conductors [13,14] were reported. However, for continued advancement in the field of eggshell recycling, developing materials wherein eggshells and eggshell membranes exhibit effective functions that have not yet been reported is necessary.

The various requirements of building materials include strength, fire resistance, and sound insulation. Adding a function that improves the environment within a building should result in a highly desirable building material. Sick building syndrome has not been eliminated in the construction industry. This is a condition wherein chemicals vaporized from materials such as adhesives, insecticides, and preservatives, which are required in building construction, adversely affect human health. Although several of the chemicals responsible are known, building materials have not been developed to reduce the use of all of them. The chemical with the most significant negative effect on the human body is formaldehyde, and hydrazine, which chemically captures aldehydes, is added to building materials to reduce the concentration of formaldehyde. Formaldehyde causes sick building syndrome. It is used as a substrate in synthesizing resins and adhesives, but regeneration due to the reverse reactions results in the accumulation of formaldehyde within a building, causing symptoms. The aldehyde group of formaldehyde reacts with an amino group to induce polymerization via acetalization, but the reaction is in equilibrium [15], and formaldehyde may regenerate chemically in air in contact with the wall and be released. No methods of resolving this issue have been developed because constructing buildings without using adhesives is challenging.

Recently, formaldehyde-compliant building materials have been developed and commercialized [16], and organic hydrazides are currently used as additives. These organic compounds react and efficiently combine with formaldehyde [17], but their chemical structures are characterized by the dissociation of hydrazine under natural conditions, although only in small amounts. These are not the most suitable substances for use in preventing sick building syndrome because hydrazine may be harmful when inhaled by humans [18]. However, if formaldehyde can be removed using a safe, low-cost material without hydrazine, this useful material is highly likely to replace hydrazine. Therefore, in our research, to mitigate sick building syndrome, we incorporated eggshells as a novel additive into building materials for use in adsorbing formaldehyde. The development of formaldehyde-scavenger materials is not actively underway. Previously reported studies only focused on tannins [19], sodium sulfite, and sodium metabisulfite [17], and further exploring scavenger materials is necessary. We anticipate that if the levels of adsorptive power of eggshells and eggshell membranes can clearly be applied, building materials containing eggshells and eggshell membranes will be developed.

In this study, the stipulations for developing a material were that its fabrication should be as low-cost as possible and that it should not be harmful to health. Building materials produced to adsorb harmful chemicals via the introduction of eggshells should satisfy these requirements. The adsorption of chemicals is a major function of eggshells and eggshell membranes due to their porous nature [20–22]. Numerous studies have investigated this function via the adsorption of pigment molecules [23–29], but the adsorption of other types of molecules is also possible. However, these reports are limited to solvent systems, and no studies regarding the adsorption of gaseous chemicals by eggshells or eggshell membranes have been reported. Nevertheless, considering the molecules adsorbed from solvents led us to hypothesize that chemicals in the air could also be adsorbed. This may be useful in developing a novel building material designed to remove formaldehyde using a green substance. If the material adsorbs formaldehyde, it may aid in alleviating sick building syndrome.

Generally, when eggs are removed from eggshells for culinary purposes, eggshells are obtained in at least two fragments. In food processing plants, the shells are generally discarded in smaller fragments of between 0.5 and 1.0 cm^2, with the eggshell and eggshell membrane stuck together (Figure 1). In this study, we aimed to develop a method of effectively utilizing samples in this small, fragmentary state. We anticipate the generation of materials that are low-cost and useful in daily life by mixing eggshells with raw building materials.

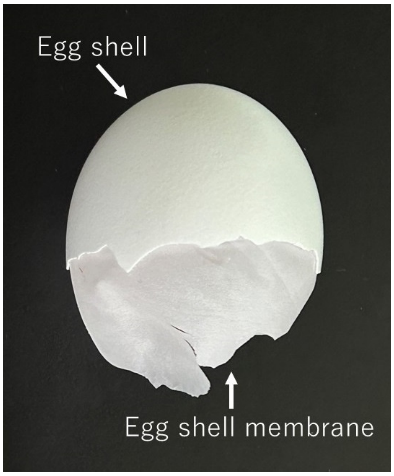

Figure 1. Eggshell and eggshell membrane.

Eggshells comprise porous calcium carbonate crystals [30,31]. Initially, an egg exhibits no shell, and its components are wrapped only in the eggshell membrane. However, when it passes through the oviduct, calcium carbonate—a component of the shell—is deposited onto the surface of the membrane, and a complete egg forms. Eggshell membranes are thin films with thicknesses of approximately 70 μm, comprising fine protein fibers with diameters of 0.1–7 μm [32], and the mesh-like structure of the membrane increases the surface area available for chemical adsorption. Therefore, although the porous nature of the shell and shell membrane is due to different components, they are physically closely joined. The structure of the eggshell is such that the crystals growing from the eggshell membrane adhere closely, and pores occur at the boundary, enabling gases to move back and forth from the interior, resulting in adsorption. Numerous reports have provided evidence of this action in the water, and the adsorption of chemicals in the air can easily be anticipated. Therefore, mixing eggshells with building materials should yield building materials that can adsorb harmful components in the air.

Numerous seashells also contain calcium carbonate [33], the crystal orientation of which is controlled by the protein conchiolin [34], and furthermore, their physical properties differ considerably from those of eggshells. Therefore, the results of comparisons wherein both substances are introduced into building materials should differ, and we should obtain data regarding the affinities of calcium sulfate and calcium carbonate for formaldehyde.

The objective of this study was to develop a high-value-added usable material primarily using eggshells, which are discarded after chicken eggs are eaten or processed. Eggshells are conventionally reused in chalk and fertilizers, but generating revenue from the cost of collection and processing is challenging because the use of chalk is limited and the price of fertilizer is low. However, if eggshells are used as a functional component in a material that is not consumed, the material should provide a use for eggshells with a high added value.

We expect the following two results from this study: (i) Due to the porous nature of eggshells and eggshell membranes and the presence of certain chemical constituents, they should absorb various chemicals from the air via different adsorption mechanisms. (ii) After eggshells are mixed with raw building materials, they should function as eggshell membranes.

2. Materials and Methods

2.1. Preparation of Circular Gypsum Boards

Sterilized eggshells are prepared by storing 500 g of eggshells overnight in a mixture of 2 L of water and 50 mL of Domestos (Unilever, London, UK) before drying the eggshells for 2 d at 110 °C using a drying oven. Water (30.4 mL) is then added to 35.8 g of gypsum to form a slurry, and 1.8 g of eggshells are added. After mixing for 30 s, the slurry is poured into silicone receptacles used in cooking pancakes to produce sample boards with thicknesses of 8.5 mm containing 5% eggshells for evaluation (Figure 2). Subsequently, sample boards of uniform sizes containing 33%, 50%, 66%, and 80% eggshells and blank boards comprising 100% gypsum are also prepared. Finally, the flame of a blowtorch is held at the center of a board for 2 min, and the changes in the board are observed.

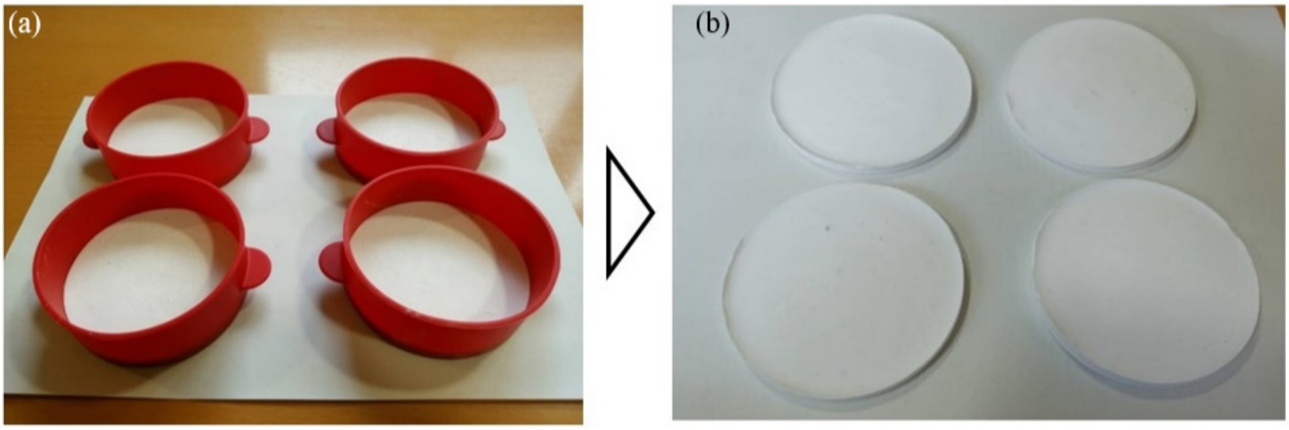

Figure 2. Procedure used in preparing the fire-resistant sample boards: (**a**) gypsum slurry poured into silicone molds; and (**b**) resultant sample boards.

2.2. *Preparation of Rectangular Gypsum Boards*

A mold used for the sample board slurry is assembled by fixing acrylic plates. Water (92.7 mL) is added to 113.7 g of gypsum to form a slurry, and 5.7 g of eggshells are added. After mixing for 30 s with a spoon, the slurry is poured into the mold to prepare a sample board (700 × 200 × 9.5 mm) containing 5% eggshells for use in the heating study (Figure 3). Sample boards containing 0–14% eggshells are prepared by changing the gypsum-to-eggshell ratio. The gypsum boards are then weighed using an electronic balance, and the samples weigh approximately 200 g immediately after fabrication. The samples are then heated in a dryer at 50 °C to remove any moisture adhering to their surfaces. They are weighed daily, and heating is continued until their masses settle at the expected masses. The samples generally reach constant masses after three days, and the treated gypsum boards are placed in sealable polyethylene bags, stored at room temperature, and removed from the bags when evaluated. Other gypsum boards containing various additives are also heated for several days at 50 °C until their masses remain constant.

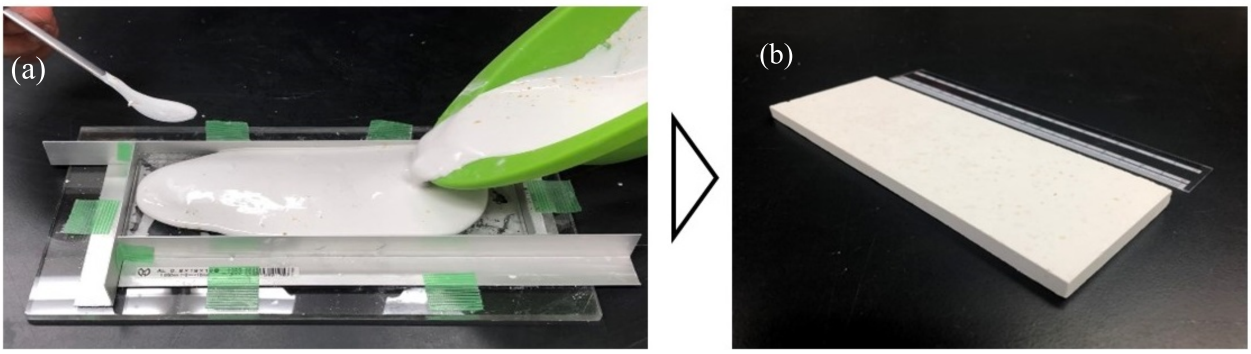

Figure 3. Mold used in preparing sample boards for evaluation: (**a**) before gypsum slurry is poured inside and (**b**) cross-sectional view after the gypsum board is prepared.

2.2.1. Fire Resistance Study

A gas torch is used to heat the center of the sample at a constant level (such that the area of complete combustion is approximately 2 cm in diameter), and the heated area is observed. If no damage, such as cracks or holes, is observed in the sample, it is regarded as fire-resistant. In the fire resistance studies of the circular (Figure 4) and rectangular gypsum boards (Figure 5), the performance objective of the study is to determine if the samples exhibit fire resistance for 10 min, which is the non-combustibility standard for the gypsum boards with thicknesses of 9.5 mm used in this study.

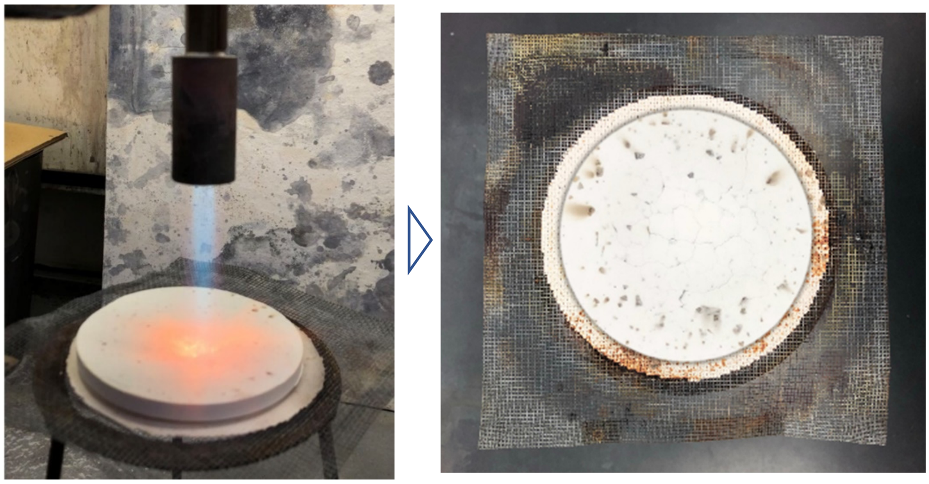

Figure 4. Fire resistance study (2 min) using a circular gypsum board.

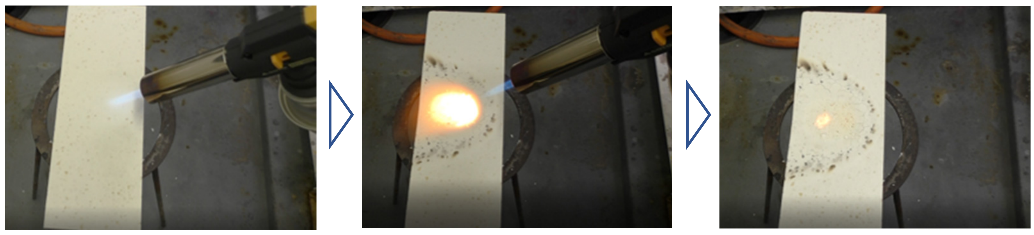

Figure 5. Fire resistance study (10 min) using a rectangular gypsum board.

2.2.2. Three-Point Bending Study

A three-point bending study is used to assess the strength of the gypsum board containing eggshells and eggshell membranes for use as a construction material (Figure 6). The objective is to compare the novel samples with the Japanese construction standards for gypsum boards [35] and verify the superiority of the composite under investigation.

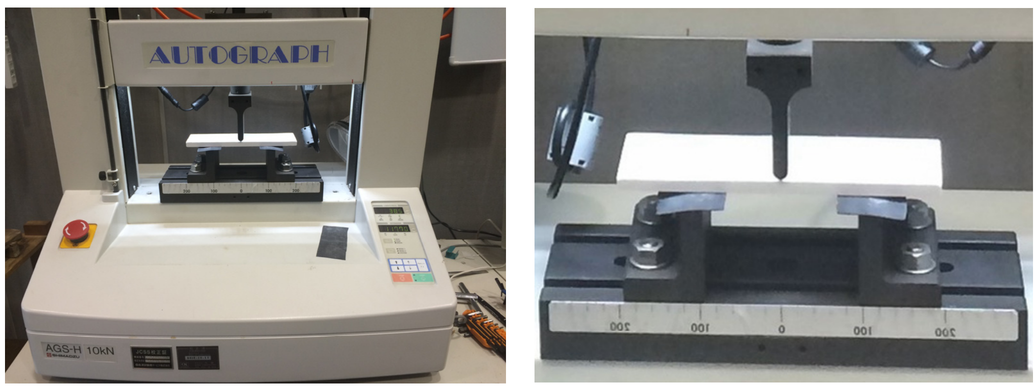

Figure 6. Three-point bending study using the universal tester.

Three-point bending studies were conducted using the fabricated samples and a tabletop precision universal tester (AGS-X, Shimadzu, Kyoto, Japan). The distance from bottom to origin was 10 cm, the pressure was applied from the center to the top at a rate of 1 mm/min, and the pressures were recorded in units of newtons. The means of nine specimens of each type of sample, containing 0%, 2%, 4%, 6%, 8%, 10%, 12%, 14%, 16%, or

18% eggshells, were used as the results. The strength of the sample containing 0% eggshells was used as the control value, and the strengths of the samples containing eggshells were compared with this value. The strengths of gypsum boards mixed with pulverized scallops and crab shells, which are the hard shells of living organisms, were also compared.

2.2.3. Formaldehyde Adsorption Study

A standard formaldehyde solution (1000 mg/L in methanol, Kanto Chemical, Tokyo, Japan) is placed in a glass box (30 × 30 × 30 cm, GEX, Osaka, Japan) using a gas-tight syringe and stored for 24 h. A formaldehyde detector (FP-31, Riken Keiki, Tokyo, Japan) is used to measure the formaldehyde concentration (Figure 7), which is set as the blank value, and then the diffusion of the formaldehyde is confirmed. This detector is certified by the Japanese Ministry of Health, Labour, and Welfare, and the concentration is measured following the guidelines established by the World Health Organization and the Japanese Ministry of Health, Labour, and Welfare. In the first study, four circular gypsum boards containing 5%, 10%, or 50% eggshells are placed within the glass box, and the values measured after 24 h are compared. The control values (measured without placing anything in the measurement tank) are 0.20, 2.0, and 20 ppm. The samples are allowed to stand for 24 h before measurement because the time at which no change in formaldehyde concentration is observable after introducing gypsum samples with eggshells is approximately 24–48 h, based on preliminary studies. The rectangular gypsum boards containing 2%, 4%, 6%, 8%, 10%, 12%, 14%, 16%, and 18% eggshells are then placed within the glass box, and the values recorded inside after 24 h are compared (Figure 8). The control value is set at 0.20 ppm, and the performance of each gypsum board is assessed using a 100% gypsum board as a control. The samples that reduce the formaldehyde concentration in the tanks to <0.08 ppm satisfy the objective of the study.

Figure 7. Formaldehyde adsorption study using circular gypsum boards.

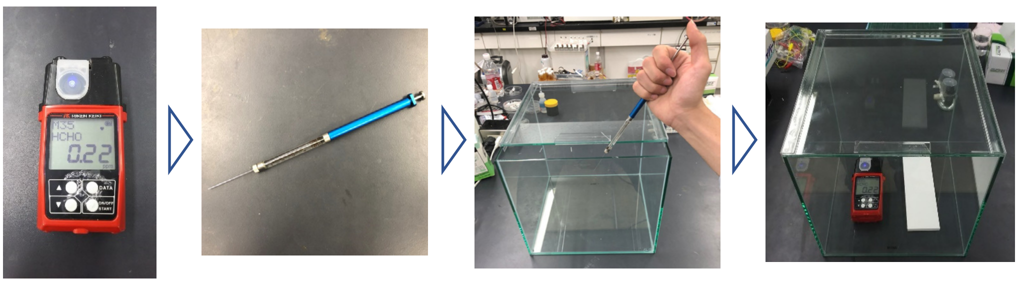

Figure 8. Formaldehyde adsorption study using a rectangular gypsum board.

2.2.4. Smoke Adsorption Study

A polyethylene box (100 × 100 × 200 mm) was assembled, and a plastic case was employed because the measuring container was only used once. A square-shaped gypsum board (control and sample boards containing 100% gypsum and 5% eggshells, respectively) was placed at an angle within the box. An incision was made at the top of the box, and incense with both ends ignited was inserted and allowed to burn to completion. Changes in the state of the smoke within the box were observed using a video camera. Once the oxygen was consumed and a certain amount of smoke originating from the burning incense filled the case, the burning of the incense ceased. This is denoted as "minute zero". Via visual observation and analysis of the video recorded within the container over time, the dissipation of smoke was confirmed visually via the recognition of the text at the bottom of the container and the amount of smoke present. The conditions of the boxes containing the eggshell-composite gypsum board and a control sample of the 100% gypsum board, respectively, and the blank container containing only smoke, were compared. Utilizing this method, if adsorption is confirmed using a gypsum board containing eggshells, this study may identify a novel construction material with an extremely useful function.

3. Results and Discussion

Pure gypsum (control) cracks because of the flame from the blowtorch held against it for 2 min, but no discoloration is observed on its surface. Meanwhile, when sample boards containing 33%, 50%, 66%, and 80% eggshells are heated strongly, blackening due to the organic components within the eggshell membrane and separation of the surface due to the separation of the eggshell membrane are observed. However, no noticeable cracks form and the boards do not break; thus, the natural fire resistance of gypsum is not lost via the addition of the eggshell membrane.

This may be because the main component of eggshells is calcium carbonate, and the only structural change that occurs due to heat is the decomposition of calcium carbonate. Calcium carbonate decomposes into carbon dioxide and calcium oxide at 898 °C, but the calcium oxide formed does not cause changes in shape as it is resistant to flames, with a melting point of 2572 °C. Hence, the structure of the sample board is maintained. Notably, when the same experiment is performed using the sample board containing 5% eggshells (9.5 mm thick), as described in Section 2.2, the board is not damaged, even after 10 min of flame radiation (Figure 9).

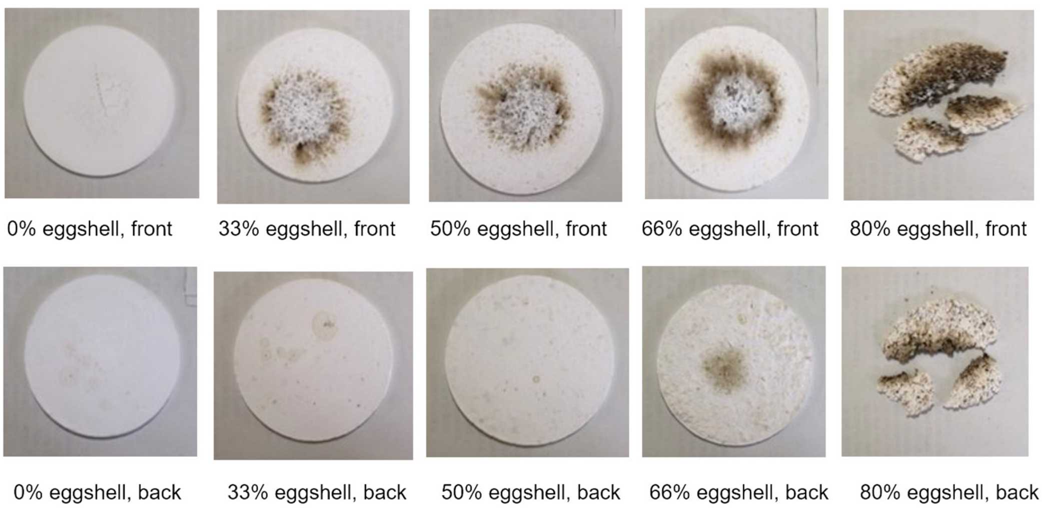

Figure 9. Sample board surfaces after the fire resistance study.

The results of strength determination using the mean of five samples for each eggshell content reveal that strength generally declines with increasing eggshell content. However, the sample boards containing approximately 10% eggshells exhibit bending strengths comparable to those of the 100% gypsum boards used as blanks (Figure 10a).

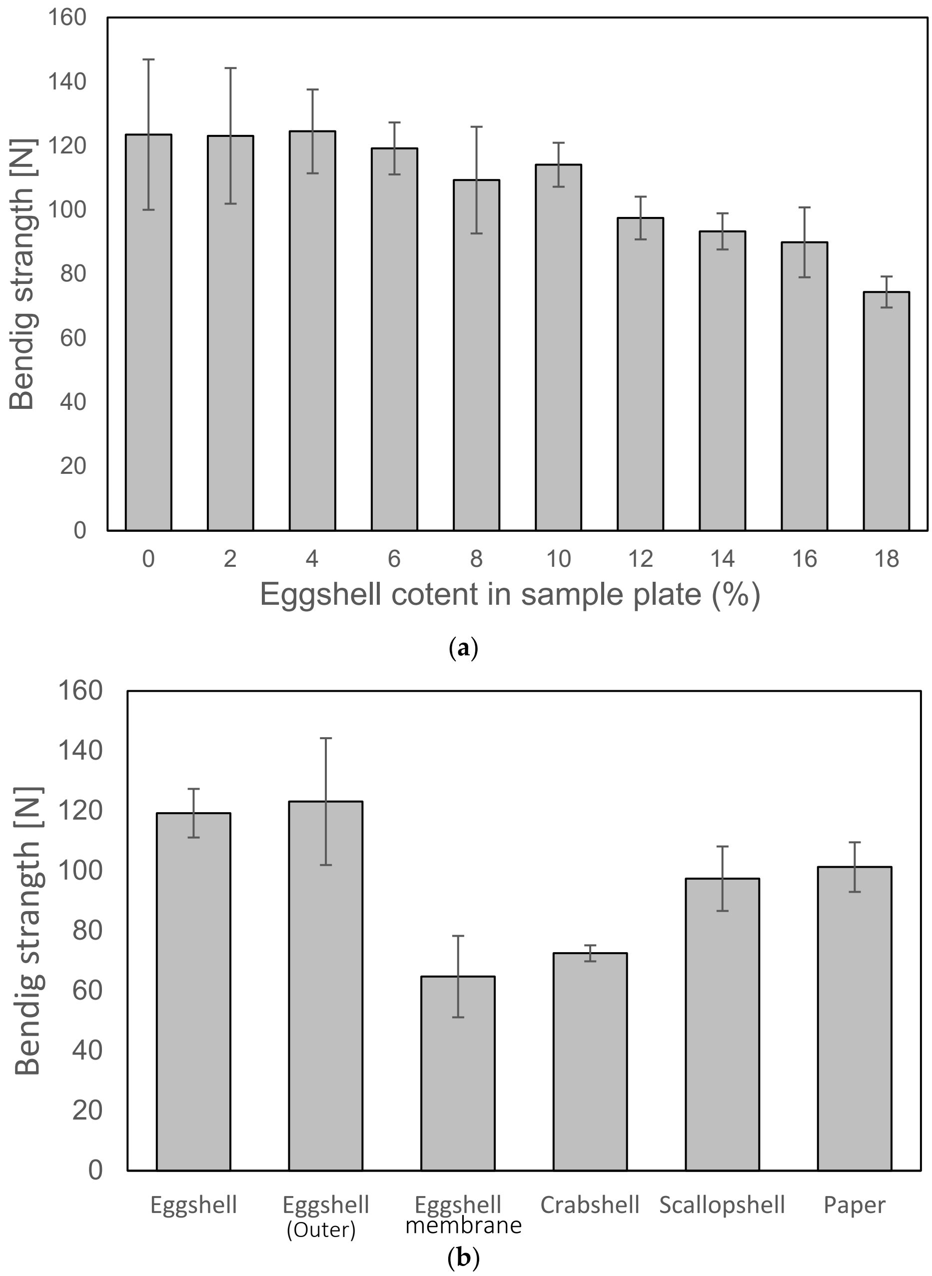

Figure 10. Results of the bending strength study of the (**a**) control gypsum board and gypsum boards with eggshells and (**b**) gypsum boards containing 6% of various additives.

Additives other than eggshells were then considered for comparison, and the results of comparing each additive when mixed at a mass ratio of 6% reveal that the order of decreasing strength is eggshell, paper, and scallop and crab shells. Comparing paper and crab shells, the strengths of the sample boards with added paper are clearly higher, and cellulose, which is a component of paper, is clearly compatible with calcium sulfate, which is a component of gypsum (Figure 10b). Cellulose is flexible, with high strength and stiffness [36,37], and it does not weaken the bending strength. Conversely, the bending strengths of samples with added crab shells are considerably lower than those of the gypsum board containing 0% eggshell used as a control. The different strengths of the boards containing crab shells compared to those of the boards containing paper, despite crab shells containing fibers with high tensile strengths [38], may be because little interaction between the gypsum and chitin fibers is observed. Thus, the fibers are not reflected in the bending strength.

The eggshell membrane used in this study contains a protein-based membrane on the inner side of the shell. While this protein exhibits heat resistance up to approximately 250 °C, it presents a drawback in terms of the fire resistance required for gypsum, as it may undergo combustion. However, addressing this issue by immersing the eggshell in a solution of sodium hypochlorite before the study, which dissolves and removes the protein, is possible. This study demonstrates that the calcium carbonate in the eggshell, excluding the membrane, exhibits sufficient fire resistance.

Comparing eggshells and scallop shells, both of which primarily comprise calcium carbonate, no decrease in strength at an additive rate of 6% eggshells is observed. However, the bending strength of the sample board clearly declines at an additive rate of 6% scallop shells. In scallop shells, calcium carbonate crystals are connected by the protein conchiolin, which forms a regular structure with a high hardness [39]. In this evaluation, the gypsum slurry does not penetrate the calcium carbonate–conchiolin structure, and the solidified sample board acts only as a granular material, which lowers its bending strength In contrast, an eggshell displays a bilayer structure comprising the eggshell and eggshell membrane. The pure calcium carbonate crystals in the eggshell and the protein component of the eggshell membrane combine well with the gypsum slurry, resulting in the sample board maintaining the same strength as that of 100% gypsum. The strength of the gypsum board increases slightly when a small amount of eggshell is added. When examining the gypsum samples with eggshells using scanning electron microscopy, we observe changes in the sizes of the crystals formed by the sulfate component of gypsum. The variations in the sizes of these crystals contribute to the slight enhancements in the strengths of the sample boards. Comparing the crystal lattices using X-ray diffraction, no changes in the diffraction peaks are observed, indicating that the crystal lattice does not change. When the eggshell content is >8%, the brittleness introduced by the eggshells renders the sample board prone to cracking under the applied force. This leads to increased susceptibility to fracturing, influencing the decrease in the bending strength of the sample board. Therefore, at an eggshell content of ≤8%, the strength of the sample board comprising only gypsum is equivalent to or slightly higher than that with eggshells. However, at an eggshell content of >8%, the strength decreases.

The capacity of the sample gypsum boards to adsorb formaldehyde was confirmed via the formaldehyde adsorption study (Table 1). Gypsum boards containing 50% eggshells, in particular, reduce the formaldehyde concentration to fairly low levels. The eggshells, which comprise porous calcium carbonate structures, absorb formaldehyde. The eggshell membrane primarily comprises proteins, and its adsorption mechanism, based on a previous study [40], involves the chemical adsorption of formaldehyde onto the side chains of the amino acids that constitute the proteins. The adsorption capacity likely decreases when all the functional groups on the side chains have reacted with formaldehyde, and this characteristic is thought to be consistent with those of previous additives.

Table 1. Results of the formaldehyde adsorption study using gypsum boards containing eggshells.

Initial Concentration of Formaldehyde (ppm)	**Formaldehyde Concentration 24 h after Initiating the Adsorption Study (ppm)**				
		Eggshell content within the gypsum board (%)			
	blank	0%	5%	10%	50%
0.20	0.20	0.17	0.12	0.04	0.02
2.0	unmeasurable	unmeasurable	0.32	0.24	0.03
20	unmeasurable	unmeasurable	0.35	0.27	0.14

The interior of the measuring chamber containing a formaldehyde concentration of 0.20 ppm and one (square) sample board with an eggshell content of ≤10% was then observed (the strengths determined in the three-point bending study indicate that these boards may be used as building materials). In formaldehyde adsorption studies conducted using sample boards with eggshell contents of 2–10%, the formaldehyde concentration generally decreases as the eggshell content increases. These results suggest that the increase in eggshells in the sample board contributes to the improvement in formaldehyde adsorption performance. The sample boards with eggshell contents of ≥5%, in particular, reduce the formaldehyde concentration to <0.08 ppm, which is the level specified by the Building Standards Act (Figure 11).

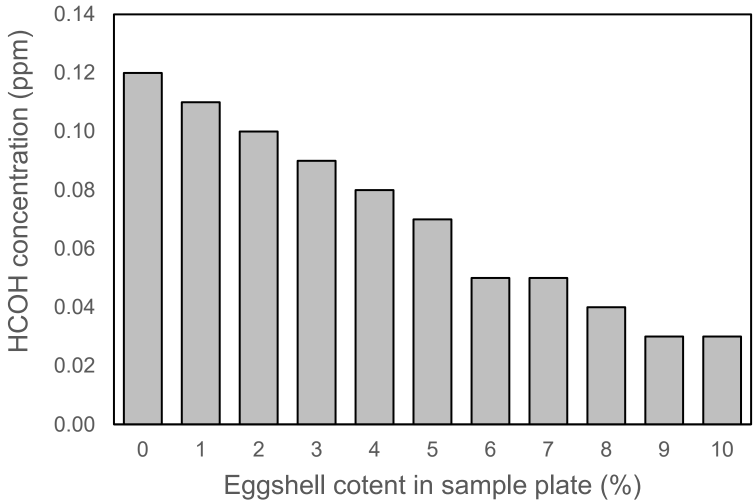

Figure 11. Residual formaldehyde concentration following the formaldehyde adsorption study using gypsum boards containing eggshells.

In the smoke adsorption study, the reduction in smoke using a gypsum board containing eggshells was successfully visualized using the gypsum board inside a clear plastic container filled with smoke (Figure 12). Compared to the empty box, the 100% gypsum board also adsorbs smoke. However, eggshells may play a role in the adsorption of smoke because specks of coloration due to smoke are observed where eggshells are present in the eggshell-containing sample board (Figure 13). The components of smoke released when dried matter derived from plants, such as incense, is burned from small particles and liquids when the combustible gases produced cooling. These products scatter light, rendering them visible as aerosols and PM_{10} [41]. The particles include volatile organic compounds, such as formaldehyde [42,43], which, in the case of incense, have pleasant smells similar to those of oils derived from aromas [44]. However, these organic compounds include substances that cause sick building syndrome. The sample boards containing eggshells reduce the concentrations of these substances, and thus, they exhibit functions that aid in preventing sick building syndrome.

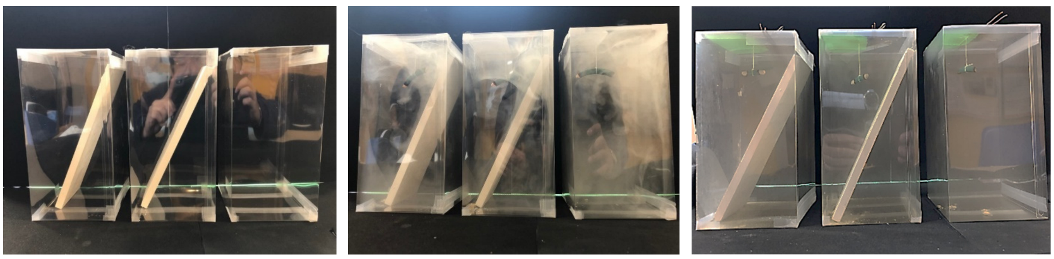

Figure 12. Sample boxes used in evaluating smoke removal: sample boxes (**left**), introduction of smoke (**middle**), smoke removal study after 10 min (**right**).

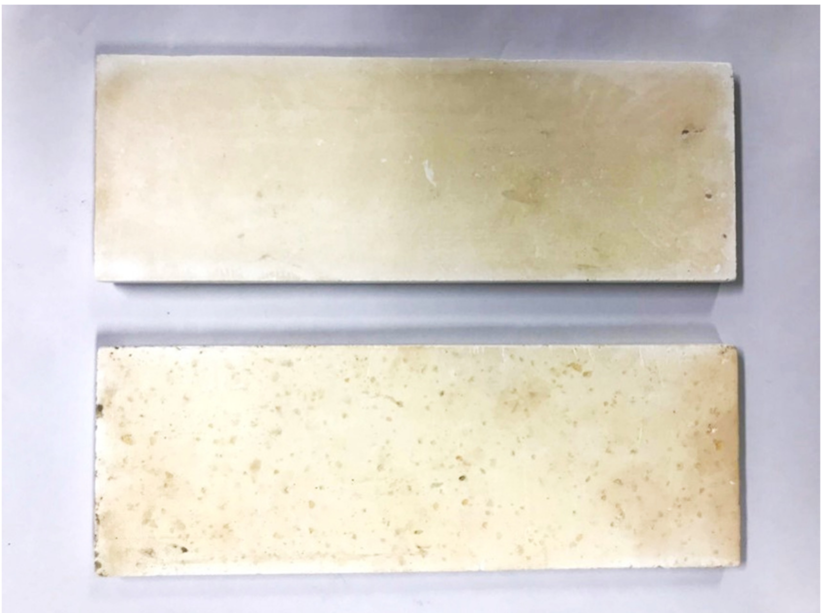

Figure 13. Surface of the sample gypsum board after the smoke removal study ((**top**): 100% gypsum, (**bottom**): gypsum containing 5% eggshells).

Recyclable materials must be assessed for their sustainability via energy analysis using the first and second laws of thermodynamics (as mentioned in the cited literature above). However, the manufacturing process for the material developed in this study requires a relatively low amount of energy. It involves appropriately crushing discarded eggshells, mixing them with dissolved gypsum in water, and then waiting for the mixture to solidify. Notably, the developed product demonstrates its significance by reducing $PM_{2.5}$ without requiring additional power sources, such as the internal electric fan used in an air purifier for $PM_{2.5}$ removal. This renders it a meaningful product in terms of functionality and energy efficiency.

Limited types of materials with formaldehyde adsorption capacities have been reported to date. Evaluations have primarily focused on candidates such as tannins, keratin, components of pine needles, and those introduced into construction materials. Recently, even materials with unspecified components, such as carbon, have been explored. However, in this study, utilizing gypsum as a base material to evaluate the effects of specific additives enabled an easier assessment of the levels of effectiveness of materials with formaldehyde adsorption capacities. Among these, the functionalities of eggshells in not only effectively reducing airborne formaldehyde but also maintaining the strengths of gypsum boards as construction materials were confirmed.

4. Conclusions

In this study, by fabricating a composite material that utilizes the features of waste eggshells, a building material that reduces the concentrations of chemicals, e.g., formaldehyde, which causes sick building syndrome, was developed by incorporating eggshells into gypsum boards. The fabrication method was simple, and the material could be prepared by mixing crushed eggshells discarded by factories with a gypsum slurry. A novel advantage was the capacity of the material to adsorb chemicals without losing the bending strength or fire resistance of conventional gypsum. Furthermore, an incense smoke adsorption study indicated that the material was effective in adsorbing volatile organic compounds other than formaldehyde.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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Conflicts of Interest: The authors declare no conflicts of interest.

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