

A Study on Physicochemical Properties and Formaldehyde Adsorption and Degradation of Purifying Air Quality by Modified Biocalcium

Wen-Cheng Shao and Yu-Wei Dong

Abstract—This study uses egg shell waste recycling in a circular economy to improve indoor air quality and provide a healthy environment as a way to cope with climate change and the greenhouse effect caused by excessive use of the earth's energy. Eggshells are modified and activated into biological calcium at different calcination temperatures and duration. After the calcination of eggshells at 900 °C for 2 hours, the fine porosity crystallization structure is observed and analyzed using the “Scanning Electron Microscope (SEM)” and the “X-ray Powder Diffractometer (XRD)”, the pore space is 0.48 mL/g-0.79 mL/g and the specific surface area is 2.42 m²/g-10.82 m²/g, proving its physical adsorption capacity. Its calcium content is 693 g/kg, Its PH value is 12.7, and the oxidation-reduction potential (ORP) is -196mV, showing its chemical adsorption capacity to neutralize, oxidize or catalyze. Based on experimental results, the modified biocalcium can adsorb and degrade formaldehyde carcinogens. After calculation, each unit can adsorb and degrade formaldehyde with a weight of 3.13 mg/g and decompose it into CO₂ and H₂O. This study can be a reference for further research on adsorption and degradation of other indoor air pollutants and applications and R&D on green building materials.

Index Terms—Sustainable development, circular economy, indoor air quality, biocalcium, absorbent, green building materials.

I. INTRODUCTION

Overexploitation and abuse of petrochemical energy and chemicals since the Industrial Revolution, have seriously affected the environment and the survival and health of all species including humans and leads to climate change and the greenhouse effect. The United Nations Framework Convention on Climate Change (UNFCCC) reaffirmed at the 24th session of the Conference of the Parties (COP24) that climate change and air pollution will have an “accompanied effect”. A study by the U.S. Environmental Protection Agency (EPA) shows that indoor air pollution is 2 to 5 times, sometimes even 100 times higher than that of outdoors. The Environmental Protection Administration, Executive Yuan, (Taiwan) points out that people spend 80%-90% of their time indoors. Given this, indoor air quality has a direct relation with human health and is correlated with the Sick House Syndrome. Therefore, the circular economy has become the strategy and policy for sustainable development [1], and healthy indoor air is an indispensable goal to secure the

survival and longevity of humans.

In addition, the excessive use of interior decoration materials and chemical products is the direct cause of harmful indoor air substances [2]. Interior decoration is the culprit of VOCs and formaldehyde (HCHO) [3]. A study also points out that the indoor formaldehyde concentration hits at over 0.2 ppm even one year after the decoration [4]. With a hot climate that comes with high temperature and humidity, the indoor air in Taiwan has carcinogenic risk due to HCHO that is 2 to 17 times higher than the global standard [5]. According to the integrated estimate, the medical health expenditure of National Health Insurance in Taiwan is expected to increase from RMB 3.73 billion to 4.02 billion [6].

The use of activated carbon is the most common method to control indoor air quality by absorbing HCHO, VOCs and other pollutants at a low cost [7]. However, when the activated carbon is saturated, the adsorption stops and the chemicals will be released at a high temperature, leading to secondary pollution.

From 2008 to 2017, the annual output of eggs in Taiwan increased from 6.47 billion to 7.5 billion and the average annual output of eggs increased by nearly 103 million [8]. Provided that each eggshell weigh 11% of a 60g egg [9], nearly 50,000 metric tons of eggshell wastes are produced. Most eggshell wastes are directly buried and only a small amount of them are dried and ground to add into animal feeds or refined fertilizers. In this way, eggshell wastes can never be reused which also increased treatment costs, creating environmental burden [10]. Currently, scholars at home and abroad have studied the application of calcined eggshell as an adsorbent, which has the physical properties of a multilayer porous structure and the chemical properties of neutralization, oxidation or catalysis. It seems to be feasible to use these properties to degrade indoor air pollution or develop green construction materials.

II. THEORIES AND METHODS

A. Principle of Purification

The purification of indoor air pollution can be divided into two major principles: (1). Physical Adsorption: Based on the principle of Vander Waals force, the molecules of pollutants are bonded on the surface of porous materials by their attractive force with no change in the chemical bonding between them. The adsorption equilibrium can be quickly achieved due to low required active force, low activation energy, and a fast reaction rate. (2). Chemical Adsorption: Pollutants are neutralized, oxidized, or catalyzed through

Manuscript received October 10, 2019; revised May 20, 2020.

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chemical reactions so that their concentration can be decreased to near zero, and the process is irreversible.

In addition, the adsorption capacity of adsorbents depends on the effective acceptance or supply of electrons and active hydrogen. Adsorption is stronger when the chemical structure of the adsorbate has similar electron or relative ion properties with the adsorbent [11].

B. Material

Eggshell, highly bound biocalcium is a porous material that is mainly composed of mineral elements. It has about 6000-8000 holes. Its mineral composition includes 94%-98% calcium carbonate, 0.8% magnesium carbonate, and 0.7% calcium phosphate. It has also slight amounts of sulfur and iron [12], [13]. After being modified by calcination, it can be used as a biological adsorbent for its pore structure. With its ability to be decomposed in the environment without causing secondary pollution, it is considered to have great potential for R&D and utilization [14]-[16].

The main component of eggshell is CaCO₃ which starts to react when being calcined at 600 °C to 700 °C. The calcination completed when the temperature reaches 800 °C to 900 °C. At this point, the main component is converted to CaO (95.91%), while MgO (1.5%), and C (2.5%) are secondary components [17]. It consists of irregular shale flake crystallization structure with very fine pores before calcinations. After calcinations, the structure is changed due to the removal of CO₂. Small crystalline grains are sintered to large grains and large grains are aggregated into interconnected skeleton structure, resulting in pore spaces [18], [19]. Porosity adsorption occurs when there is adsorption by electrostatic force or Vander Waals force between molecules. There are two characteristics of the adsorption: (1). The larger the superficial area is, the higher the saturated adsorption capacity would be. (2). The smaller the pore size is, the higher the adsorption capacity would be [20]. Eggshells with the same calcinations time showed increase in activity when the calcination temperature rises. When the temperature is higher than a certain point, the activity tends to the maximum critical value. The holding time of calcinations also has a correlative influence on the activity of the calcined product. The multi-layer fine porosity crystallization structure formed accordingly also affects the activity of the calcined product. Those with smaller the pore size and larger surface area showed greater activity [21].

C. Method and Test

1) Calcination test and analysis

Calcination is a process of heat treatment with high-temperature furnace. Due to the technical development of industrialization, high-temperature furnace is widely used as necessary industrial process, industrial and mining production, or chemical laboratories of research units.

The high-temperature furnace used in this experiment is JH-2 produced by GAU JIE Company. The temperature difference in the furnace is within (±0.5°C), and the design temperature can change from 700 °C to 1100 °C. It's holding time can be 1 and 2h, respectively. Ten calcined samples can be obtained by matching. An eggshell weighed 30g was selected and put it into crucible, and then after the high-temperature furnace obtains the assigned temperature,

the experimenter starts to count the time and maintain the temperature. When the set holding time is reached, the sample is cooled to room temperature, weighed and recorded, and then put into a sealed bag. After discharging the air in the bag, it will be sealed for subsequent test.

Comparing the products calcined at different time and temperature with the naked eye, it can be observed that the products calcined at 700 °C ~ 800 °C are all grey for 1h or 2h. This is because of the organic matter, protein, and fat contained in the eggshell undergone high-temperature carbonization. When calcined at 900 °C for 1h, there are near 50% of eggshells are changed to white due to the volatilization of carbide. When calcined at 900 °C 2h or above, it can be found that the product has completely turned white and the color does not change with time or temperature. Therefore, it can be inferred that organic matter has been completely decomposed and volatilized into inorganic substances.

Before calcination, the crucible containing 30 g eggshell was put into the high-temperature furnace at 105 °C for 24h drying the eggshells weigh at 27.6 g excluding the crucible. The water content was 0.8% calculated by the formula of mass moisture content. When the weights of calcined eggshells at different time and temperature were measured after deducting the weight of the crucible, the recovery rate was calculated by the formula of mass recovery (1). Then, the curve was drawn according to the recovery rate (Fig. 1). It was observed that the recovery curve tends to be horizontal and the value would fall between 50% to 60% when the sample was calcined at 1000 °C for over 1h, and 900 °C for over 2h. It was inferred that after calcined at this time and temperature, calcium carbonate in eggshells had been completely converted into calcium oxide which called complete the calcination. However, the high-temperature furnace rises from 900 °C to 1000 °C for need 1h, its power consumes is very wasteful. Therefore, calcining at 900 °C for 2h. is the best choice for calcium conversion.

$$u = \frac{m_{wet} - m_{dry}}{m_{wet}} \quad p = \frac{m_{final}}{m_{wet}(1-u)}$$

Formula for mass water content Formula for mass recovery rate (1)

m_{wet}: Mass of eggshell before being dried

m_{dry}: Mass of eggshell after being dried

m_{final}: Mass of eggshell after calcination

u: Mass water content

P: Mass recovery rate

u and *p* are usually indicated by percentage (1)

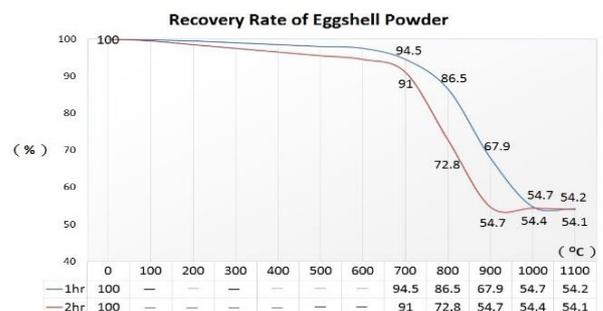


Fig. 1. Curve of recovery rate of Eggshell powder.

2) Scanning Electron Microscope (SEM) test and analysis

SEM uses a high-energy electron focusing beam to scan the surface of the sample and generate images for further observation. Before using SEM, it is necessary to gild on the surface of the sample for conduct electricity after being beaten by an electron beam [22], [23]. The main purpose of SEM is to observe the changes in eggshell microstructures caused by calcination temperature and persistent time to verify physical absorbability.

The SEM used in this experiment is JSM-6510 made by JEOL Company (Hsinchu city, Taiwan). The process includes: (1). Taking out a suitable number of granules and fix them on a circular copper sample plate, (2). Gilding the sample to increase its conductivity, (3). Placing the sample in the electron microscope column for evacuation. (4). Electron beams (15KV, enlarged at 3000 times) were emitted to scan the sample for structural changes.

The microstructure of calcined eggshells was observed by enlarging the electron microscope 3000 times (Fig. 2) which turned to be in shale sheet structure before calcination (Fig. 2-A) and started to change after being calcined at 700 °C for 1h (Fig. 2-B). After being calcined at 700 °C to 800 °C for 2h, the microstructure of the eggshell changed from plain into fine porosity. According to the literature, the temperature in such range is the critical temperature for the conversion of calcium carbonate to calcium oxide (Fig. 2-C, Fig. 2-D and Fig. 4-E). Therefore, chemical bonding of calcium carbonate as the main component of eggshell breaks down at this temperature and decomposes to produce carbon dioxide and calcium oxide, forming microporous structure after the carbon dioxide escapes. After being calcined at 900 °C for 1h, the original planar structure of the sample disappears and becomes porous flocculent (Fig. 2-F). With the increase of calcination time and temperature, calcium carbonate will be increasingly converted into calcium oxide, resulting in flocculent structure increase and pore shrinkage. This is the combination of calcium oxide. When the sample being calcined at 900 °C 2h, almost all calcium carbonate in eggshells is converted into calcium oxide, resulting in a well-arranged and multi-layer fine porosity crystalline structure (Fig. 2-G~Fig. 2-K).

After comparing electron microscopic images, it was observed that the porosity and surface area between microporous structures increased significantly along with the increase of calcination time and temperature. After calcination at 900 °C for 2h, the structure of eggshells tends to change from a large increase in balance growth. Hence, it was more economical to use calcined eggshells as adsorbents already possesses physical properties.

3) X-ray Powder Diffractometer (XRD) test and analysis

After the eggshells were detected and analyzed by XRD before and after calcination at different time and temperature, know when calcium oxide would start to change into calcium carbonate according to the position and height of wave crest. The results show that with XRD, in the calcined eggshells at 900 °C, the crests appear at $2\theta = 32.3^\circ$, 37.4° and 53.9° [24].

The XRD used in this experiment is RINT2000 produced by Rigaku Company (Kyushu city, Japan). XRD is mainly based on the periodicity of atomic arrangement for crystalline substances. The lattice characteristics of different species are

different; thus, the particle, pore space, and specific surface area can be determined by the angle of 2θ reflected by the internal K-layer electrons brought by specific wavelength.

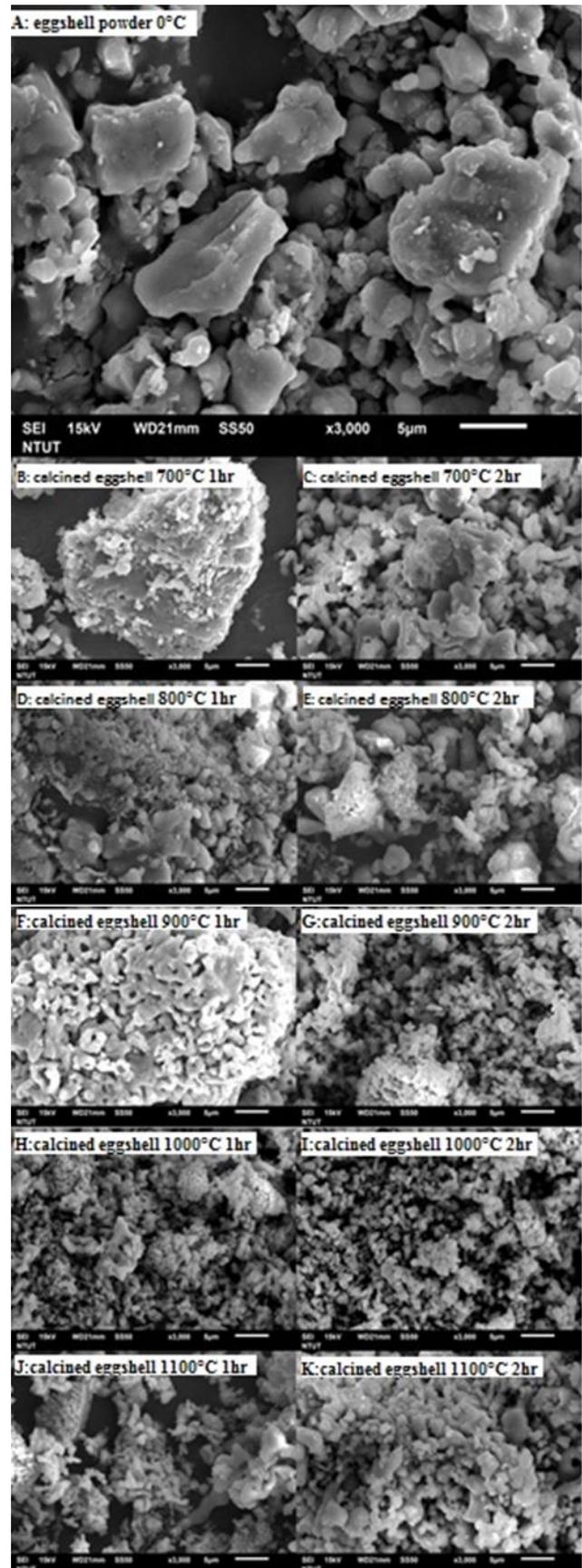


Fig. 2. Enlarged view at 3000 times by SEM.

About 10 samples at different calcination temperature and time and 1 sample without calcination were scanned and

analyzed by XRD to determine chemical composition changes of eggshells by comparing the data of maps and crystallization configuration (Fig. 3). Eggshells without calcination scanned by XRD 2θ showed obvious crest at 23.1° , 29.5° , 36.1° , 39.5° , 43.3° , 47.6° , and 48.6° (Fig. 3-A) and the crest intensity of 29.5° was the largest which revealed to be calcium carbonate by comparing the XRD spectra of eggshells. By comparing the XRD spectra of eggshells at different calcination temperatures and time, the results showed that with the increase of calcination time and temperature, seven original crests appeared. When calcined at 800°C for 1h and 2h, new crests appeared at 32.3° , 37.5° , 54.0° , 64.3° , 67.5° , and 79.8° , respectively (Fig. 3-D and 3-E). Therefore, under 800°C , calcium carbonate in eggshells began to transform into calcium oxide and the molecular structure and crystalline form began to change. When the sample was calcined at 900°C for over 1h (Fig. 3-F), new crests of 32.3° , 37.5° and 54.0° appeared at increased calcination time and temperature. When the sample was calcined at 900°C for 2h or 1000°C for 1h, the waveform of the spectra did not change significantly. It is inferred that original shale lamellar structure in calcium carbonate was completely transformed into multilayer fine porosity crystalline structure in calcium oxide (Fig. 3-G~3) with complete calcination, which pore space was 0.48 mL/g - 0.79 mL/g and the specific surface area was $2.42\text{ m}^2/\text{g}$ - $10.82\text{ m}^2/\text{g}$.

4) Test and analysis of calcium content

Induced by hydroxyl, calcium oxide produces reactive oxygen species. The most common reactive oxygen species are superoxide anion (O_2^-), hydroperoxyl radical ($\text{HOO}\cdot$), and hydrogen peroxide (H_2O_2), all of which have strong oxidizing power. When calcium oxide dissolves in $\text{Ca}(\text{OH})_2$ solution in water, it produces reactive oxygen species at the same time [25]. Therefore, during the calcination of eggshells, the amount of calcium carbonate converted to calcium oxide is the key to the number of reactive oxygen species; the reactive oxygen species produced by calcium oxide have strong oxidizing power, which can attack bacteria and achieve sterilization and bacteriostasis. The higher the proportion of calcium oxide produced, the stronger the sterilizing and bacteriostasis ability it has [26], [27]. Domestic scholars have also proposed that hydroxyl radical (OH^-) and superoxide anion (O_2^-) have high activities, which can destroy and kill the outer membrane of organisms and microbes. Their sterilizing ability is 206% stronger than chlorine and 157% stronger than hydrogen peroxide [28]; the resulting free radical (OH^-) can cause microbial ribonucleic acid (RNA) hydroxylation (OH^- binding to RNA) and affect the ability of protein production [29].

The instruments used in this experiment are as follows: (1). Terminal 320 microwave digestion system made by Milestone Ethos Company. (2). iCAP 7400 inductively coupled plasma optical emission spectrometer (ICP-OES) from Thermo Scientific Company. The process is as follows: (1). Taking out a proper amount of calcined eggshell powder sample and put it into the digestive tube. (2). Add 4 ml nitric acid to the digestive tube first, then 1 ml hydrochloric acid, and finally 5 mL pure water. (3). Put the mixed digestive tube into the microwave digestion system for microwave digestion. (4). After digestion and dilution, analyze the calcium content with the inductively coupled plasma optical emission spectrometer (ICP-OES).

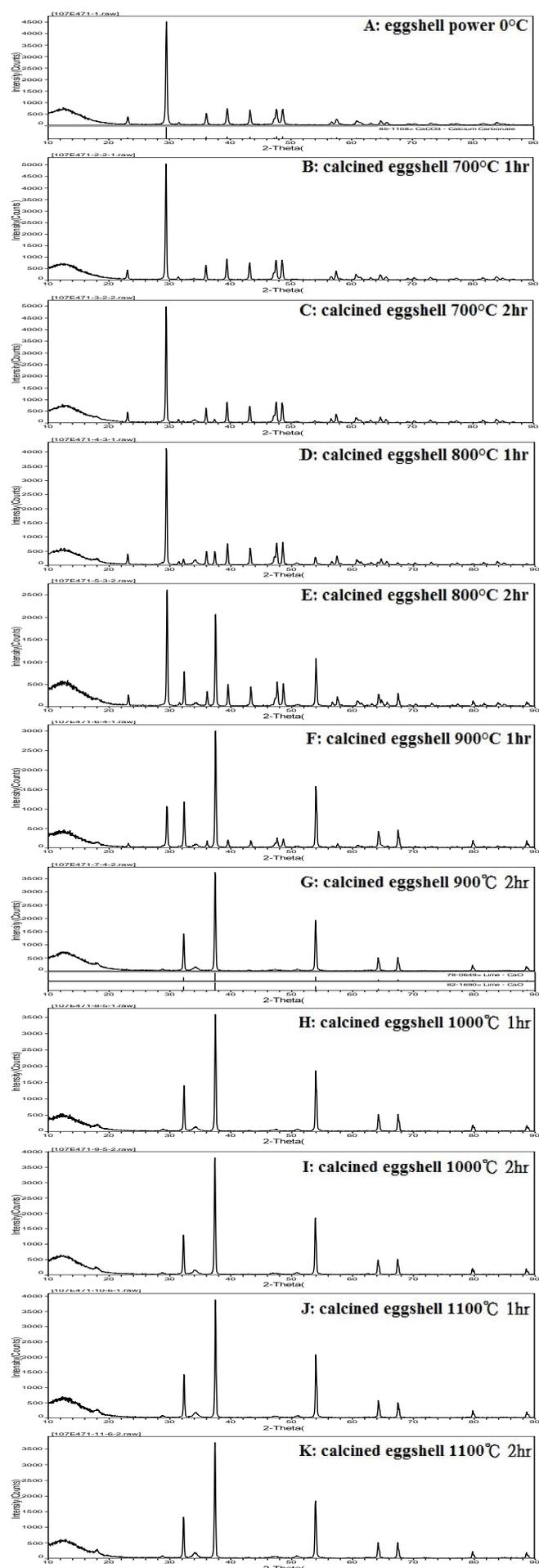


Fig. 3. The XRD map of powder diffractometer scanning.

After eggshells are calcined at high temperature, organic matter and other components will be decomposed and volatilized while the main component of calcium carbonate will be converted to calcium oxide. When the calcination time and temperature increase, the unit weight of calcium oxide will also increase. When the calcination is completed, the calcium carbonate has been completely converted into calcium oxide. Therefore, the calcination time and temperature can be obtained by detecting the change of calcium content. Accordingly, the calcium content in calcined eggshells at different times and temperatures was detected by instruments and then the changing curve was drawn (Fig. 4).

It was found that the changing curve of calcium content tends to be horizontal and the value ranged from 650 to 700 (mg/kg) when calcined at 900 °C for 2h and at 1000 °C for more than 1h. It can be inferred that calcium carbonate has been completely converted to calcium oxide after calcination at this time and temperature. According to the measured values, the maximum calcium content is 693mg/kg when calcined at 900 °C for 2 h.

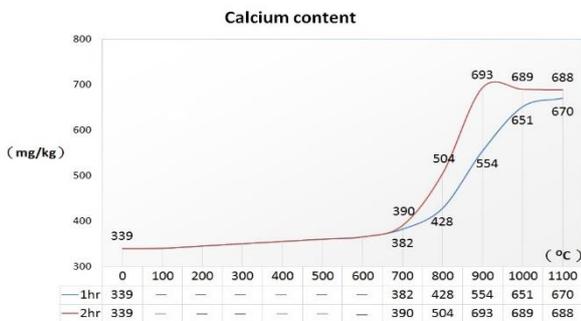


Fig. 4. The changing curve of calcium content.

5) Test and analysis of PH value

Studies on microbes by Japanese scholars have shown that fungus and yeast grew best in a sub-acid environment where PH value is 4.0~6.0; bacteria and eumycete grew best in a neutral or sub-acid environment where PH value is 7.0~8.0. When the PH value of microbes' growth environment exceeds the optimum range, its growth and metabolism are limited, producing the bacteriostatic effect [30]; PH value is one of the main variables affecting the eggshell adsorption process. Because the PH value affects the ionizability and surface activity of the adsorbent while the eggshell contains -OH, -C=O and -PO4 functional groups, the exchangeability of the surface ions is directly affected by the PH value [31].

The PH meter used in this experiment is the PH500 from Clan Company supplemented by the PH30 electrode from the same company. The experimental process is as follows: 1) After calcining the eggshells, dissolve 1 g of its sample in 10 ml pure water. 2) Shake evenly and then put into the centrifuge. Run at 6000 rpm for 15 min. 3) Extract supernatant liquor, measure its PH value and record.

The eggshells were calcined and dissolved in water to form an alkaline solution. When its PH value is higher than 8, it will have bacteriostatic on microbes and ion exchange effect. Accordingly, the PH value in calcined eggshells at different temperatures and times was detected using the mentioned instruments and then the changing curve was drawn (Fig. 5).

It was found that regardless of calcination time, the PH

values measured at any calcination temperature almost overlap on the changing curve. Calcined at 700 °C, the PH value has increased from 5.29 to 12.7, which proves that calcium carbonate has begun to transform into calcium oxide. In addition, the PH values measured at other calcining temperatures made no significant difference. Therefore, when calcined at 700 °C, the content of calcium oxide formed is enough to make the PH value of its aqueous solution reach the critical value of 12.7 or so. Moreover, the PH value will not change with the change in calcining time and temperature. At this time, the PH value is unfavorable for microbes' growth and has the ability of ion adsorption and exchange on the surface.

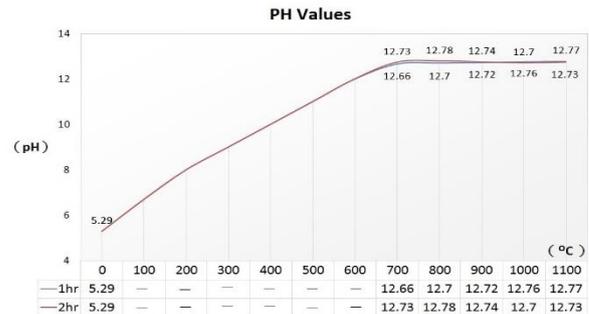


Fig. 5. The changing curve of PH values.

6) Test and analysis of Oxidation Reduction Potential (ORP)

By detecting the oxidation potential in the ambient atmosphere, it was found that the ionic impurity was correlated with the potential value and temperature. The higher the temperature is, the higher the potential value is and the more impurity there is, the higher the potential value is [32]. When ionic materials have high oxidation-reduction potential, the oxide ability will be stronger. When the reactive oxygen species comes into the water in the air, it produces a reduction potential of hydroxyl radical (OH⁻) (2O₂⁻+2H₂O → O₂+H₂O₂+2OH⁻). The higher the reduction potential is, the stronger the adsorption capacity of oxidation potential in the air. And aerobic microbes grow in a positive ORP environment. Their optimum ORP is 200mv~ 820mv [33].

The oxidation reduction potentiometer used in this experiment is the PH500 from Clan Company, supplemented by the CS2010 electrode from the same company. The process is as follows: 1) After calcining the eggshells, 1 g of its sample is dissolved in 10 ml pure water. 2) The mixture is shake evenly and then put into the centrifuge. Run at 6000 rpm for 15 minutes. 3) Extract supernatant liquor, measure its PH value and record.

The ORP coefficient directly affects the adsorption capacity of the solution. The more negative electrons (e-) in water, the lower the negative value of mV reading is; the stronger the reduction capacity of water; and the higher the adsorption capacity of removing reactive oxygen free radicals. Accordingly, the ORP values of the calcined eggshells at different temperatures and times were detected using the mentioned instruments and then the changing curve was drawn (Fig. 6).

It was found that the relative potential before calcination was 172 mV, which decreased with the increase of

calcinating temperature. When the holding time increased, the decreasing range increased. But the decreasing range began to decrease when the calcinating temperature exceeds 800 °C. At 900 °C calcinating temperature, the curves of holding temperature 1h and 2h overlap. After that, even if the calcinating temperature increased, the ORP values measured ranged from - 21 to - 29 and tend to be constant. According to the measured values, the oxidation-reduction potential of eggshells is - 196mV when calcined completely, which is the positive potential condition for the survival of non-aerobic microbes and the target pollutants can be adsorbed and then decomposed by oxidation reduction.

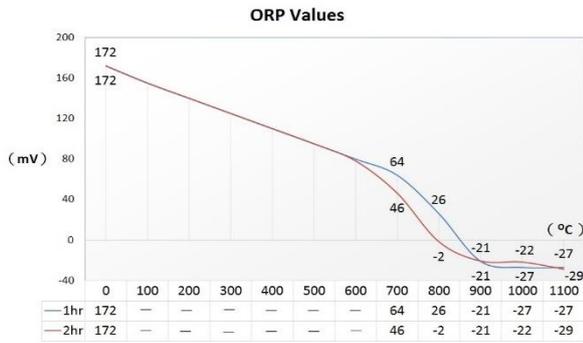


Fig. 6. The changing curve of ORP values.

III. THE ADSORPTION AND DEGRADATION EFFECT OF FORMALDEHYDE

A. Formaldehyde

Formaldehyde, a level 1 carcinogen recognized by WHO, is referred as HCHO. It is a type of toxic gas with colorless, pungent, and high activity, which is always added Methanol to avoid oxidation and polymerization. Apart from external air, indoor formaldehyde mainly comes from the new-built buildings, decoration materials, painting, and furniture. It may also result from smoking and the use of gasoline, gas and other open appliances [34]. When the concentration of formaldehyde reaches to 0.04 ppm, it can be smelled and stimulates mucous membrane. Once eyes, nose, and throat are stimulated, it can lead to cough, tiredness, rash, allergic phenomenon, and even conjunctivitis, rhinitis, laryngitis [34]. Taiwan has a subtropical high temperature and high humidity climate, which will lead to a higher concentration of organic volatiles and formaldehyde in building materials [35].

To mitigate the harm of indoor air pollutant formaldehyde, it is known from previous theories and analyses that eggshell calcination has physical and chemical properties of absorbing indoor air pollutants. Therefore, this study will further verify the adsorption and degradation effect of modified biocalcium on formaldehyde after eggshell calcination though this experiment.

B. Samples and Equipment

Based on the previous experimental results, this experiment selected eggshell calcination at 900 °C for 2h as the experimental material and compared using activated carbon for verification.

Three comparisons will be conducted in this experiment. The first group is a blank filter screen, a honeycomb carrier without additives and non-woven fabric on both sides. The

second group is a control filter screen, a honeycomb carrier with 50 grams of active carbon and non-woven fabric on both sides. The third group is an experiment filter screen, a honeycomb carrier with 50 grams modified biocalcium after calcining at 900 °C for 2h and non-woven fabric on both sides. Three pieces of samples in each group were prepared. During the experiment, three pieces of samples from each group were put into a small test box with a volume of 1m³ and fan circulation. The experiment was carried out after the formaldehyde concentration was evenly distributed.

This test instrument for detecting formaldehyde concentration is the detecting tube and the detector, it is GV-100 product manufactured by Gastece, Japan. The 1m³ miniature experiment box is shown in Fig. 7:

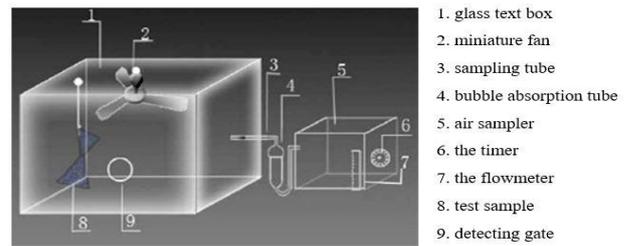


Fig. 7. Schematic diagram of miniature experiment box.

C. Experimental Method

A pre-experiment should be carried out to obtain the data for the experimental design reference. The results are as follows: Three experimental group filters were placed in the experimental chamber with a formaldehyde concentration of 10 ppm. After one hour, the formaldehyde concentration in the experimental chamber was measured to be 0.1 ppm. The adsorption degradation rate is 99%. According to this, the experimental design of this study is set at a temperature of 281 °C and a humidity of 50%-55% under normal pressure and is divided into two experiments.

Experiment 1: Inject the test chamber into the formaldehyde gas to reach the average concentration of the test to be measured at a concentration of 10 ppm. Place three samples and perform seven samplings and test at 5 mins, 10 mins, 20 mins, 40 mins, 60 mins, 120 mins, and 180 mins after the experiment. The concentration was measured according to the three designed groups. The experimental design was based on time, the change of formaldehyde concentration in the test chamber was measured, the degradation rate of formaldehyde adsorption was calculated, and the adsorption degradation rate and time change diagram were plotted (Fig. 8). The analysis results are presented by comparison.

Experiment 2: Inject the test chamber into the formaldehyde gas to reach the average concentration of the test to be measured at a concentration of 40 ppm, and then place three samples. After 1h, sample and test the concentration, and seal the sample in the test chamber to take out the residual formaldehyde gas in the box. And re-inject the formaldehyde gas to an average dispersion concentration of 40ppm, and put the original sample into the experiment, and then sample and measure the concentration after 1h, and then repeat the cycle for 10 times every 1h. The experimental design is to change the formaldehyde concentration and the continuous adsorption mode every 1h, to detect the amount of

formaldehyde concentration change, calculate the formaldehyde adsorption degradation rate, and draw the change graph of adsorption degradation rate and time

(number of times) (Fig. 9). The results were analyzed after comparison.

Experiment I Fixed concentration and Continuous adsorption.

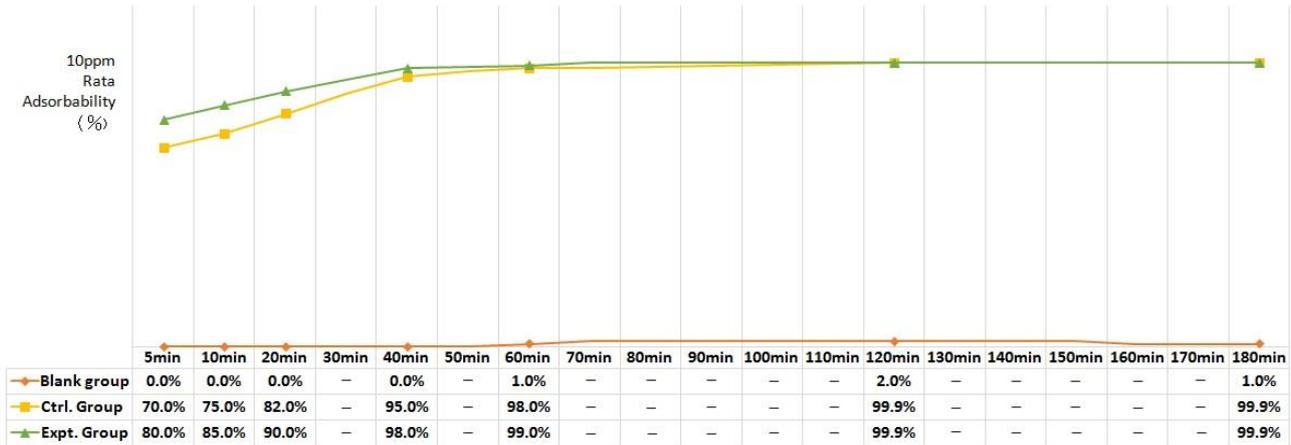


Fig. 8. Curve on fixed concentration and continuous adsorption changes.

Experiment II Repeated concentration and Continuous adsorption.

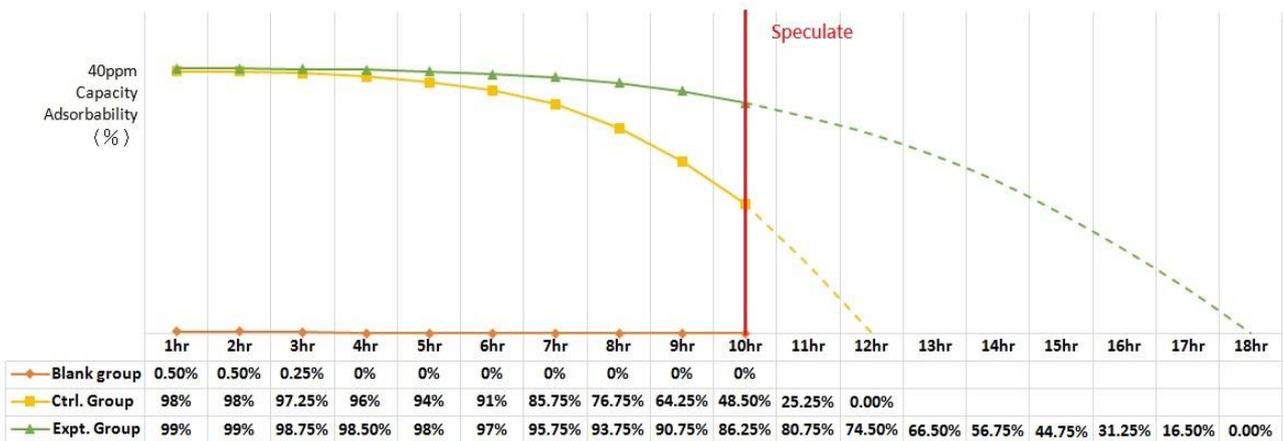


Fig. 9. Curve on repeated concentration and continuous adsorption changes.

D. Results and Discussion

The formaldehyde is injected into the experimental box to a concentration of V0, and the honeycomb sample is placed in the experimental chamber for X h. The gas in the experimental chamber is taken to detect the formaldehyde value of V1 and the removal efficiency calculated by using $(V0-V1) \div V0 \times 100\%$ to obtain formaldehyde and the results of adsorption degradation rate according to different experimental methods are as follows:

Experiment 1: With the method of observation, it the first experiment results was tested after the first 5 mines at the beginning of the experiment. The control group and the experimental group all had extremely high adsorption degradation rates, which were 70% and 80%, respectively, as the calcination time increased. The adsorption degradation rate has a relatively increasing trend but the adsorption degradation rate of the experimental group is faster than that of the control group and the formaldehyde concentration in the experimental chamber is relatively low. After the 10th minute, the adsorption rate between the two groups starts from the original gap of 10%. It fell to 1% at 1 h. after the

experiment, which was 98% in the control group and 99% in the experimental group. The adsorption rate of the two groups was 99.9% at 2h. after the experiment. The formaldehyde has been completely degraded by adsorption.

Experiment 2: It was observed that with the increase in formaldehyde concentration and the continuous adsorption mode, the degradation rate of formaldehyde adsorption decreased in the control group (activated carbon) and the adsorption degradation rate had dropped to 43.5% in the 10th h. If the curve is extended, it is speculated that the control group will reach the saturation of adsorption degradation after the 12th h of the experiment while the experimental group has strong adsorption degradation rate for formaldehyde although it also follows the reset formaldehyde concentration and persistence. The number of adsorption modes decreased but the amplitude was much smaller than that of the control group. At the 10th h, the adsorption degradation rate was still 86.25%. If the curve was extended, the experimental group (modified biological calcium) was speculated. The adsorption degradation will be saturated after the 18th h.

After the values obtained by the control group and the

experimental group are respectively accumulated according to the formula conversion, it can be obtained that the weight of formaldehyde per unit medium can be adsorbed and degraded (2) after repeating the cycle mode for 10h. The activated carbon (control group) is 2.76 mg/g while the modified biocalcium (experimental group) is 3.13 mg/g.

1mg/L=1ppm MW : Molecular weight = 30.026

1mg/m³ = [ppm × MW (g/mole)] ÷ 24.45

1mg/g = 1 mg/m³ × 1m³ ÷ 150g (2)

The experimental data can confirm that the modified biological calcium prepared by calcining the eggshell at 900°C for 2h has the adsorbing effect and degraded formaldehyde while the adsorption efficiency is much larger than that of active carbon. The result can be analyzed from the physicochemical properties of the two adsorbents.

Physical property: Both adsorbents have physical adsorption of porosity and the adsorption efficiency of the porous medium depends on physical properties, such as specific surface area and pore volume. The specific surface area of the modified biological calcium is multiplied by the pore volume. Compared with the product of activated carbon in the literature, the modified biocalcium can be obtained at 4600-5800 times of activated carbon. Compared this result with the experimental results of formaldehyde adsorption degradation, the modified biocalcium is still larger than the activated carbon in the adsorption rate and adsorption amount, but failed to achieve the above effect. The result of the adsorption degradation as the above multiple difference is obtained with the pore of the modified biocalcium at 20-70 nm, far less than the activated carbon 150-20000 nm, which is liable to cause clogging during adsorption.

Chemical property: Since chemical adsorption is a chemical interaction between the adsorbent and the adsorbed substance, chemical bonding is generated. Since the activated carbon is a non-polar substance, the chemical bond is strong, the molecule is stable, and the ion exchange capacity is extremely low so the activated carbon cannot decompose formaldehyde by chemical adsorption. The modified biocalcium has a PH value of 12.7 and an ORP value of -196 mV. It has a relatively high degree of ion exchange capacity and reduction reaction and it should be degraded into CO₂ and H₂O by adsorption as described in the literature. According to the relevant data, the free formaldehyde in the air will produce a condensation reaction to form formic acid. The condensation reaction can be accelerated in an alkaline environment, which can also decompose the formic acid after the condensation reaction into CO₂ and H₂O [36].

IV. CONCLUSIONS

Through the calcined manufacturing, the eggshell has become modified biocalcium, and calcium carbonate has also become calcium oxide. The experimental data and results show that the optimal temperature and time for completing calcination is 900 °C for 2h.

When calcination is completed, the modified biocalcium has dual adsorption properties of physical and chemical properties and can be used as a biological adsorbent. In terms of physical adsorption, the pore structure has been

transformed into multilayer microporous crystals with a pore space of 0.48 mL/g-0.79 mL/g and a specific surface area of 2.42m²/g-10.82m²/g. In terms of chemical adsorption, modified biological calcium produces ions, negative electrons, superoxide ions after contacting water, and have high activity that gives them the ability to neutralize, oxidize, reduce, catalyze, inhibit bacteria and sterilize, and contain calcium content is 693mg/kg, PH value is 12.7, ORP value is -196mV.

As for the adsorption degradation of formaldehyde, it has been experimentally confirmed that the modified biocalcium has a very high "Absorption Degradation Rate". In the experimental chamber of 1m³, the modified biocalcium can absorb and degrade the formaldehyde of 10ppm concentration by 80% in 5 minutes and can reach to 99% after 1h. After 10h adsorption in the mode of resetting formaldehyde concentration of 40 ppm and continuous adsorption, the modified biocalcium adsorption degradation rate is still 86.25% and much higher than that of activated carbon. It can be calculated that each unit of modified biological calcium can be adsorbed and degraded, the formaldehyde weight was 3.13 mg/g which is called "Total Adsorption Degradation", and the formaldehyde was further decompose into CO₂ and H₂O.

According to this study, the modified biocalcium can effectively adsorb and degrade formaldehyde to improve indoor air quality. This result should be widely used in the research of environmental remediation to replace chemical synthetic substances with biological materials. If this material is applied to green building materials, it should enhance the efficacy of building materials and help achieve a sustainable environment.

CONFLICT OF INTEREST

The authors of this research states that there is no conflict of interest and that the manuscript has been read and approved for submission by all named authors. In addition, this research did not receive any specific grant from funding agencies in the public, commercial, or non-for-profit sectors.

AUTHOR CONTRIBUTION

Wen-Cheng Shao, helps at deployment of variables and run statistics, writing discussions and management implication. While Yu-Wei Dong, helps translating the paper into English, organize all tables and figures, also cite all references into the content, as well as finding the literature's connection with this paper's studied variables. Both authors also work out on finding connection between variables with literature, past research, and between theories and practices.

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