Study on the feasibility of improving the indoor air quality from the perspective of circular economy by activation of biological calcium

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Abstract

In order to cope with excessive use of energy since the industrial revolution, environment has been seriously polluted and the large amount of waste has been produced. The circular economy has become the driving force for sustainable development of the earth, with the aim of maximizing resource efficiency and minimizing environmental impacts with the hope of achieving a vision of zero waste and friendly environment. As consumption of eggs increases, most of the discarded shells produced each year are treated as waste, which pollute environment. Researches on the environmental restoration of eggshells as an absorbent have brought a lot of results, but it is only used for absorbing industrial heavy metals, dye and for energy catalysis.

The edible biological calcium of eggshell and its multi-layer microporous structure provide a good absorbing property. Therefore, based on literature, this study will observe the microporous structure through electron microscopy (SEM), and by (XRD) to analyze the crystal structure, pH value and redox potential (ORP), for finding the most economical and absorption-efficient calcination time and temperature.

After eggshells are calcined for two hours at 900 degree Celsius, its detection value has become constant (or nearly), and its structure has also changed from the original shale-flake to a multi-layer microporous structure showing physical absorption capacity for indoor air pollutants, and its chemical absorption conditions are also effective. Preliminary experiments also show degradation results for indoor air pollution. This research can be further used for a study of absorption performance to improve indoor air quality, and as a reference for application and development as a green building material.

Key words: Circular Economy, Environmental Restoration, Biological Calcium, Green Building Materials, Indoor Air Quality

Introduction

Since the industrial revolution, humans rely more on chemicals and petroleum products, causing over and misuse of energy, greenhouse effect, serious environment damage, climate change which threaten survival and health of nature including human beings. 20th contract meeting (COP24), the United Nations Framework Convention on Climate Change (UNFCCC) in 2018, restate the co-adjunct effects of climate change and air pollution, forcing global carbon reduction a must. Based on the research of US Environmental Protection Agency (EPA), indoor air pollution is 2-5 times higher than outdoor pollutions, sometimes can reach 100 times. Therefore, sustainability has become a strategy and policy for environmental protection. Theory of 'circular economy' by Professor Michael Braungart at Department of Chemistry, Leuphana University of Luneburg, in 2002 defines the economy as to be cycled including biological cycle and industrial cycle, and gives insight for environmental problems [1].

Present leftover of eggshells were buried directly without process, some of them being dried and grinded into bits then added to animal feeds or refined fertilizer. Not only wasted its availabilities, but caused extra processing costs, furthermore, overloaded as pollutions to environment [2]. Eggshells have irregular shale-like crystal structure originally with extremely fine stoma. Calcination removes CO_2 and changes its structure. Small crystallized grains are sintered to form larger grains which are aggregated into interconnected bone structures causing pores [3] [4].

There are two methods to purify interior air pollutions, physical absorption and chemical absorption. Physical absorption is based on Vander Waals force, through surface attractions of object's molecule and multi-pores materials. Chemical chain does not change, and faster reaction can be achieved until reaching the balance of adsorption because the force is smaller. By chemical reaction, contaminants can be neutralized, oxidized or catalyzed, to decrease pollutants approach zero and making the reaction irreversible. Up till now, researchers investigating absorbents by study characters in eggshell calcination to produce multi-layer micro porous structural characteristics. It may look promising, if these characteristics could be used to lower indoor pollutions or in green architectural materials.

Materials and Methods

Eggshell is a highly biological calcification combination, containing inorganic porous objects (6000~8000 pores), 94% to 98% of Calcium carbonate, 0.8% of Magnesium carbonate and 0.7% Calcium phosphate, also Sulfur and Iron as minor constituents [5] [6].

After calcination, it can be used as a biological absorber, a natural absorber that can be decomposed in environment without causing second pollutions. Its potentials in development were studied in [7] [8] [9].

With the same calcination time, product's activity increases as temperature rises. When temperature is over a certain degree, its activity reaches maximum limit. Temperature in calcination also affects size of pores [10].

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Calcination is a heating process in a high-temperature furnace. Due to the development of industrial technology, high-temperature furnaces are quite commonly used in industrial processes, and a must-have equipment in industrial and mining production, and in chemical laboratories of scientific research units. The high temperature furnace of this experiment is a JH-2 type manufactured by GAU JIE. Its inside temperature differences are within ±0.5°C, and controlled at 5 levels of temperature from 700°C~1100°C. 10 calcined samples treated for 1 hour and 2 hours are taken for experiments. Microporous through electron microscopy (SEM, JSM-6510 by JEOL) and scanning by powder diffraction instrument (XRD, RINT2000 by Rigaku) to investigate physical adsorption, pH and redox potential value (ORP) were investigated in order to discuss further on the best chemical adsorption. Then the most economical way is found for the best physicochemical adsorption efficiency of modified biological calcium.

Detection and Result

A. Scanning Electron Microscope (SEM) Test and Analysis

There are two characteristics of the physical 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 [11].

3000 times enlarged images by electron microscope to observe microstructure of the calcined eggshells are shown in Fig. 1. Before calcinations, microstructure of the eggshell was a shale-like structure (Fig. 1-A). After calcination at 700°C for 1 hour, the microscopic of the eggshell begins to change in shale flaky structure (Fig. 1-B). At this stage, the main component of the eggshell is $CaCO_3$ molecular bond rupture, which decomposes CO_2 and CaO. After CO_2 dissipates, pores are formed. As calcination time and temperature increased, the microporous structure in its surface pore density increased significantly. When calcination exceeded 900°C for 2 hours, the surface area and numbers of micropores increased obviously and towards a balance (Fig. 1-G). At this stage, a multi-layered microporous crystal structure was formed and reached maximum activity.

B. X-ray diffraction (XRD)Test and Analysis

CaO produces active oxygen under the induction of OH^-, including O_2^-, HOO and H_2O_2, which are capable of degrading and sterilizing microorganism with their oxidative ability. The higher the proportion of calcium oxide is, the stronger the sterilization and inhibition ability becomes [12]. When CaO dissolves into $Ca(OH)_2$ liquid solution, it also produces oxygen [13].

The eggshells showed clear peaks at angles of 23.1°, 29.5°, 36.1°, 39.5°, 43.3°, 47.6° and 48.6° by XRD 2θ scanning (Fig. 2-A). The comparison charts showed that the compositions in eggshell was $CaCO_3$, when calcined at 800 °C for 1 hour, new peaks appeared at 32.3°, 37.5°, 54.0°, 64.3°, 67.5° and 79.8° (Fig. 2-D), at that time $CaCO_3$ in eggshells began to transform into CaO. With the increase of calcination temperature and time, the new peaks of 32.3°, 37.5° and 54.0° were also enhanced. When the calcination was done over 900°C for 2 hours, the wave of the spectrum no longer changes (Fig. 2-G). At this stage, almost every $CaCO_3$ transformed into CaO, and the reaction was nearly completed, the activity of the calcined

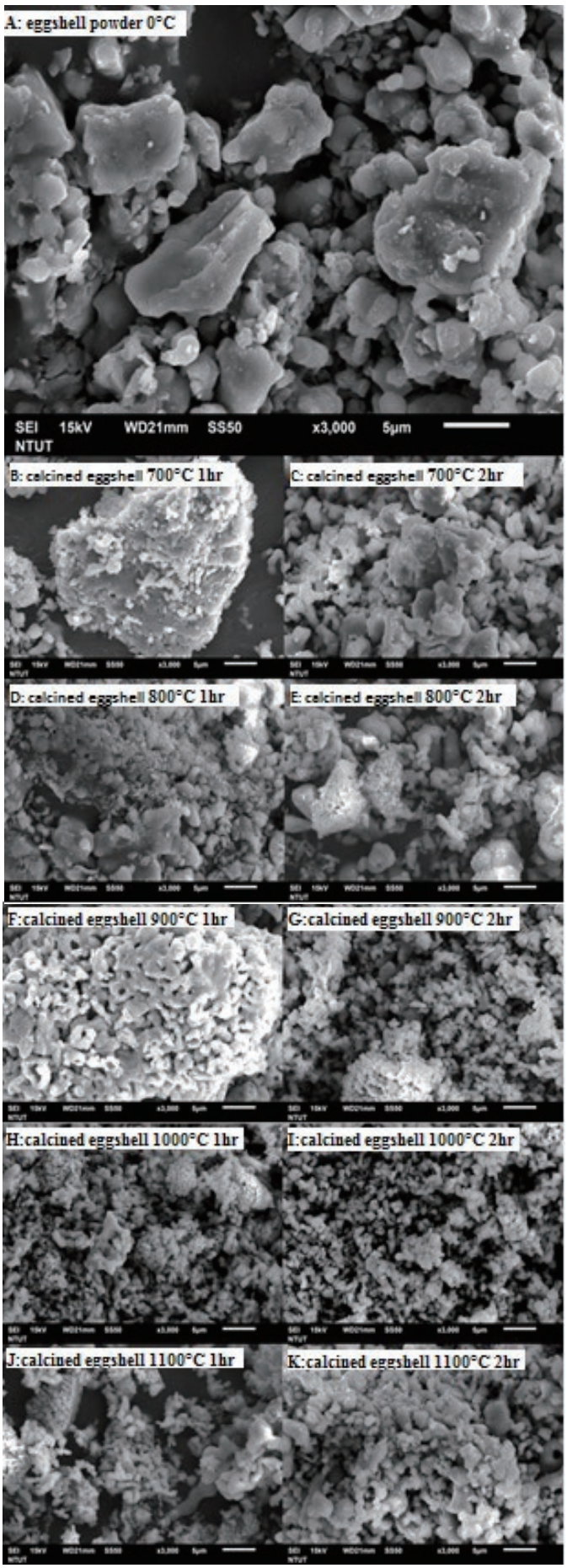

Fig.1. Enlarged view at 3000 times by SEM

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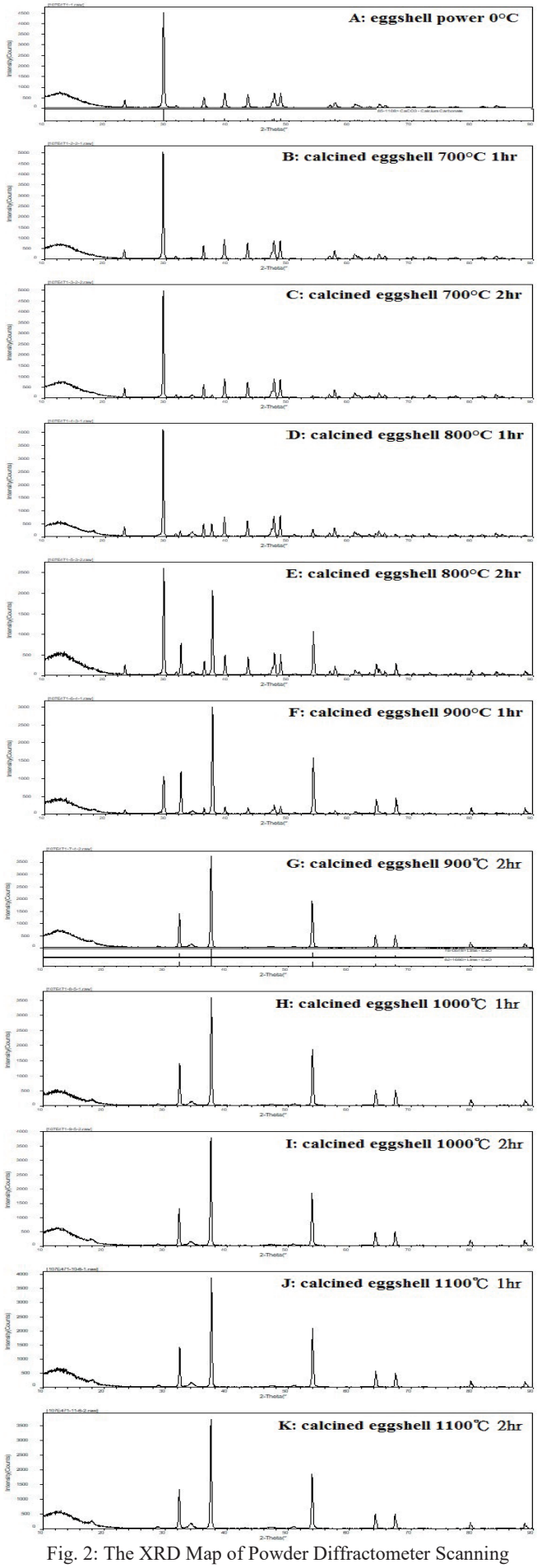


Fig. 2: The XRD Map of Powder Diffractometer Scanning

eggshell reached the maximum limit. Sizes of the pores were measured from 0.48 mL/g to 0.79 mL/g, and ratio surface area was 2.42 m2/g to 10.82 m2/g.

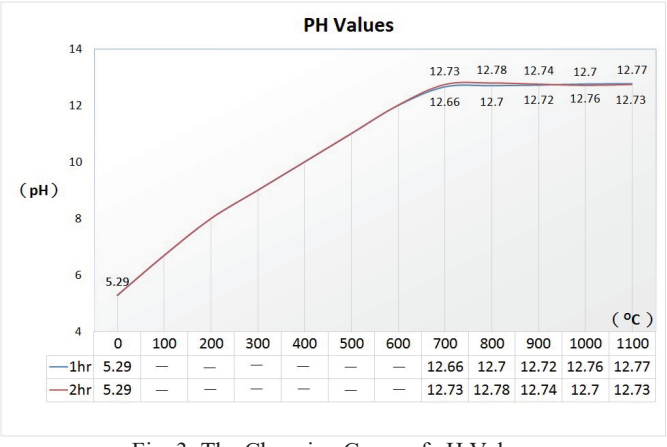
C. Test and Analysis of pH Value

pH value is one of the main variables affecting the chemisorption process of eggshells. 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 [14].

Mold and yeast grow comfortably in slightly acidic range of pH 4.0~6.0 environment, while bacteria and fungi are in the optimal growth environment in neutral to slightly alkaline range of pH 7.0~8.0. When pH level in microbial growth environment exceeds the comfort zone, its growth and metabolism are limited, and reached antibacterial function [15].

The pH meter used in this experiment is the PH500 from Clan Company supplemented by the PH30 electrode from the same company.

Calcining eggshells with different time and temperature, then detected its pH value by an instrument and drew a curve of changes (Fig. 3). It was found that under 1 hour or 2 hours conditions, the pH value measured from any calcination temperatures were almost overlapping one another. At 700°C calcination, pH increased from 5.29 to approx. 12.7, and the pH value measured by increasing calcination temperature didn't have much differences, therefore at 700°C calcination, CaO was formed and its content was sufficiently allowing the pH level of its liquid solution to reach a critical limit of about 12.7, and does not change due to changes in calcination time and temperature.



	0	100	200	300	400	500	600	700	800	900	1000	1100
1hr	5.29	—	—	—	—	—	—	12.66	12.7	12.72	12.76	12.77
2hr	5.29	—	—	—	—	—	—	12.73	12.78	12.74	12.7	12.73

Fig. 3: The Changing Curve of pH Values

D. Test and Analysis of Oxidation Reduction Potential Value

When ionic materials have high oxidation-reduction potential, the oxidatively will be stronger. When the reactive oxygen species comes into the water in the air, it produces a reduction potential of hydroxyl radical (OH^-) ($2O_2^- + 2H_2O \rightarrow O_2 + H_2O_2 + 2OH^-$). The higher the reduction potential is, the stronger the adsorption capacity of oxidation potential in the air [16].

The oxidation reduction potentiometer used in this experiment is the PH500 from Clan Company, supplemented by the CS2010 electrode from the same company.

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Calcine eggshells with different temperature and time was measured for ORP curves (Fig. 4). Before calcination, the relative potential value decreased from 172mV when the temperature increased, when holding temperature increased, its decreased degrees dropped. But its amplitude begins to shrink when it exceeds 800°C. When at 900°C calcinations temperature, temperature of 1 hour and 2 hours curves are overlapped. Since then, discarding the increase of any calcination temperature, the measured ORP value stays between -21mV and - 29mV, towards stable. Then we know when eggshell is completely calcined, the redox potential value will be generated around -196mV.

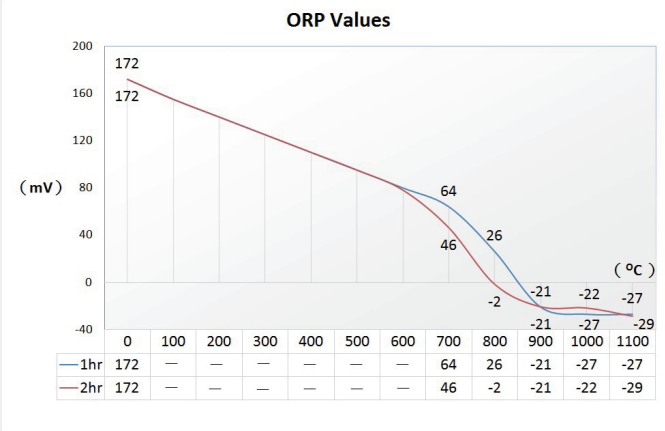

Fig. 4: The Changing Curve of ORP Values

Discussion and Conclusions

Eggshells are edible wastes. If being effectively studied and reused, they can have great potentials. The products of multilayer microporous structure and high calcium content through calcination process make it capable of both physical and chemical adsorption characteristics. In the cross comparison data, eggshell calcined at 900°C for 2 hours forms the best efficiency of adsorbent in economical and optimal adsorption. 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, pH value is 12.7, ORP value is -196mV. This helps purifying the environmental pollutions, improving indoor air quality, and creating a cyclical economic value. If eggshells are used in making green building, it will help to enhance the efficacy of construction materials. Use in biomaterials to replace chemical synthesized substances as adsorbent and its application will improve the strength of sustainable and healthy environment on earth.

Patents

This research of "Biological calcium filter material and method of manufacturing same" was filed in "New Patent of Intellectual Property Office of the Ministry of Economic Affairs of the Taiwan R.O.C." New Patent NO. M584709; And Invention Patent application NO. 10820609.

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