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Research paper

Recovery of Calcium Carbonate from Pre-Treated Duck Eggshell Waste (PDEW) Using Dissolved Air Flotation Technique (DAFT)

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Abstract

Duck eggshell containing rich calcium carbonate was disposed to land fill under economical values application. Effective utilization of Pre-Treated Duck Eggshell Waste (PDEW) may replace calcium carbonate mined from non-renewable sources and chemicals precipitation. The present work evaluates the potential of calcium carbonate recovery from PDEW using Dissolved Air Flotation Technique (DAFT). Operation parameter effects and optimization of PDEW membrane segregation were also investigated. The collected duck eggshell was cleaned in tap water, dried in hot air oven and ground to small pieces. Separation vessel was used for organic membrane partition by various air pressure, eggshell to water ratio and residence time. Characterization of PDEW before and after treatment was carried out using Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The DAFT has successfully recovered 92.5% duck eggshell calcium carbonate, and 60% of eggshell organic membrane removed. Removal rate of duck eggshell membrane was found at optimal condition of 1.62 bar air pressure, eggshell to water ratio of 1:5.68 and 1.41 h of residence time. The DAFT and PDEW spread marvelous results of calcium carbonate recuperation, and it can be ruminated on future technique and carbonate derivation.

Keywords: Air pressure, characterization, eggshell-water, organic membranes, residence time.

1. Introduction

Duck and chicken eggs are consumed worldwide as a source of all essential amino acids, vitamins and minerals. China, is a world leader (46.3%) of the production, the total world duck and chicken eggs were almost 53 million tons in 2012. In Malaysia, the resulted eggshell was 642600 tons (1.22% of the world production). The main composition of eggshell consists of more than 97%wt calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate and the remaining materials (4%) were organic matter of protein membrane. The duck and chicken eggshells weigh are approximately 11% of the total mass of egg [1, 2]. Thus, a significant number of duck and chicken eggshells waste are produced from food processing and manufacturing industries per year globally. Most of eggshells waste are disposed to landfill without further processing. However, the waste management is not a desirable practice because the shells and the attached membrane support microbiological action and attract vermin. Possible applications of duck and chicken eggshells range from low investment processes are such as agricultural fertilizer component, soil conditioner and animal feed additive to high investment for transforming as low-cost biodiesel production catalyst and coating pigments for ink-jet printing paper [3, 4]. Although large investments are required for the last implementation but they can create more valuable products. Next, the duck eggshell can serve as a starting material for preparing calcium phosphate bio-ceramics, humidity adsorbent, nanohydroxiapaptite [5, 6].

The egg production on an industrial level leads to a substantial amount of pollution. The majority of calcium carbonate for industrial purposes comes from marble mining , quarrying and non-renewable natural resources. Superfind grind process via vibarated mill, cellular biomineralization, calcium carbide residue, aragonite polymorph nanoparticles with surface functionalization and causticization have been examined for calcium carbonate synthesis [7, 8, 9, 10, 11]. Precipitation of calcium carbonate using calcium hydroxide and carbon dioxide results more residue, long time and expensive. Moreover, current methods to dissolve the eggshell membrane protein using acid treatment require higher cost and produce chemical wastes which are harmful to the environment. Also, the utilization of dissolved air flotation technique to recover high purity duck eggshells calcium carbonate is an attractive investigation. Duck eggshell waste is abundantly available as free materials. It contains valuable components which can be utilized into commercial products and adds economic value to waste material. The rich calcium carbonate duck eggshell may reduce the impact on the natural reserves of marble. Therefore, the ecological issues and economic concern for waste disposal have generated a great deal of interest to extract value-added by products from duck eggshell waste. Invention of an eggshell and membrane separator has allowed for recovering of the precious products. Various particulate solids could be separated by flotation process, like dissolved air flotation [12, 13, 14]. DAFT is a simple method, non-chemicals technique with low costs. The recovered calcium carbonate using DAFT was optimized based on different operating conditions (air pressure, eggshell to water ratio and residence time). Design-Expert 8 was used for justification of the influenced parameters.

2. Materials and Methods

2.1 Materials

A dissolved air flotation apparatus was specially equipped with storage tanks from polyvinyl chloride (PVC), air compressor and beaker glass with water. All of the used DAFT components were purchased from the local construction materials store. The duck eggshell waste was collected from Steamed Rice My Mama restaurant in Gambang, Kuantan, Pahang, Malaysia.

2.2 Pretreatment of Duck Eggshell

The duck eggshell was washed thoroughly in tap water for removal of unwanted materials adhere on their surfaces. The washed duck eggshells were then dried in hot air oven at 105 ℃ for 24 hours. The dried duck eggshell was ground to small pieces for protein membrane separation. The ground duck eggshell was sieved up to homogenized particles size.

2.3 Characterization of Pre-Treated Duck Eggshell

Pre-treated duck eggshell was characterized using Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The recovered duck eggshell calcium carbonate was analyzed in a thermogravimetric analyzer (TGA) to determine the remnant organic membrane content. The portion of remnant protein membrane is an important index of the duck eggshell calcium carbonate powders in order to make it useful for commercial applications. The residual membrane content was determined by the weight loss after a heating period at a range of proposed temperature. Mass evolved between 240 °C to 470 °C indicated the content of organic membrane. Next, the scanning electron microscopy (SEM) analysis was performed to observe the impacts of pre-treatment and dissolved air flotation on the textural structures of duck eggshells. The crystal structures of natural eggshells are generally irregular and have macro-pores. Composition alteration of duck eggshell may cause their structures replacement. Then, portion of organic membrane in the recovered duck eggshell calcium carbonate was determined in the FTIR spectrum. The appearance of the characteristic peaks at 3370 cm^{-1} and 1638 cm^{-1} is assigned for -NH and -NH-C=O respectively [15].

2.4 Calcium Carbonate Recovery Using DAFT

The duck eggshells membrane which was removed during pretreatment was contacted by a stream of DAFT. Air was supplied by a compressor and injected from the bottom of the separation vessel which dispersed tiny bubbles. The dissolved air flotation was run by a batch separation process as shown in Fig.1. Various sieved duck eggshell to water ratio between 1:5 and 1:9 were poured in the DAFT tank. The mixture was placed in the separation vessel. Air pressure in the range of 0.5 bar - 2.5 bar was injected into the eggshell-water mixture by the air compressor for a residence time interval of 0.5 to 2.5 h. Tiny micro-bubbles rose from the bottom of the separation vessel and caused the lighter duck eggshells membrane to float up while settled out the heavier calcium carbonate at the bottom of the vessel. The calcium carbonate particles were collected and dried overnight in hot air oven at 105 ℃. The recovered calcium carbonate was then weighed and characterized relating with operation parameters. The optimal parameters were then justified with Design-Expert 8.

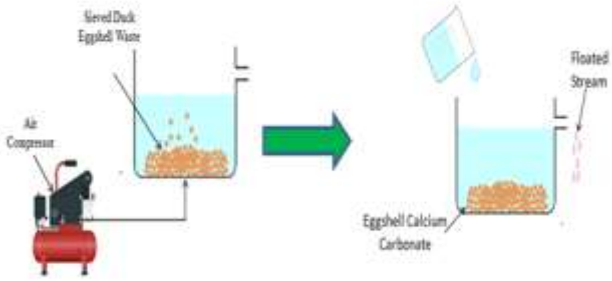

Fig. 1: Sketch of DAFT for duck-egg shell calcium carbonate recovery

2.5 Duck Eggshell Membrane Removal

The removal rate of duck eggshells membrane was calculated by the following equation:

$$\text{Removal rate (\%)} = \frac{M_i - M_f}{M_i} \times 100\,\% \quad (1)$$

, where M_i = Initial mass before the experiment (g), M_f = Final mass after the experiment (g).

2.6 Duck Eggshell Separation Efficiency

The separation efficiency of duck eggshell containing calcium carbonate was determined as follows:

$$\text{Separation efficiency (\%)} = \frac{W_i - W_f}{W_i} \times 100\,\% \quad (2)$$

Percentage loss of calcium carbonate particles (%) = removal rate (experimental results) - removal rate (TGA analysis) (3)

Recovery rate of calcium carbonate particles (%) = 100 % - percentage loss (4)

, where W_i = Weight loss of raw duck eggshell (wt%), W_f = Weight loss of recovered duck eggshell calcium carbonate (wt%).

3. Results and Discussion

3.1 Effect of Air Pressure

The air pressure effect on removal rate of duck eggshell membrane is displayed in Fig. 2. Increasing the air pressure improved the removal rate of duck membrane up to 10.7767 respectively with air pressure at 2.5 bar. DAFT takes advantage of air pressure effect on the solubility of air in the liquid phase [16]. At high pressure, more air is soluble in liquids than at lower pressure. The extra air dissolved in the solution at high pressure must come out when pressure is reduced. There is a decrease of the bubble size and a rised number of bubbles when the discharge or transfer pressure increases, generated micro-bubbles. The micro-bubbles can attach to the surface of duck eggshells membrane and cause more effectively floated membrane.

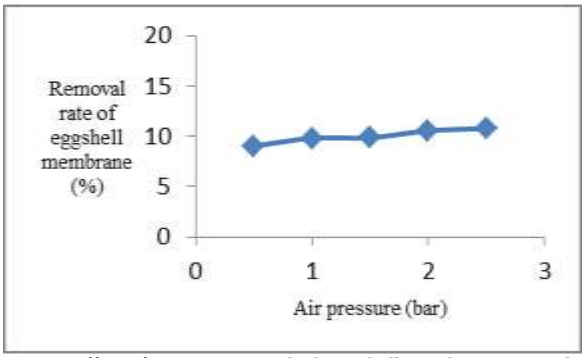

Fig. 2: Effect of air pressure on duck eggshell membrane removal.

3.2 Effect of Eggshell-Water Ratio

The duck eggshell to water ratio affects the recovery of calcium carbonate powders. The curve tendency is exhibited in Fig. 3. Increasing the eggshell to water ratio improved the removal rate of duck eggshells membrane up to 10.1340 respectively with eggshell to water ratio of 1:6. Optimum eggshell to water ratio increased the frequency of collisions between eggshell and the degree of turbulence in water which helped the organic membrane detach from the calcium carbonate more easily as well as boost the buoyancy of the light organic membrane thereby improving the removal rate. Excess water in the DAF separation unit caused the overflow of water as in the case of 1:9 eggshell to water ratio.

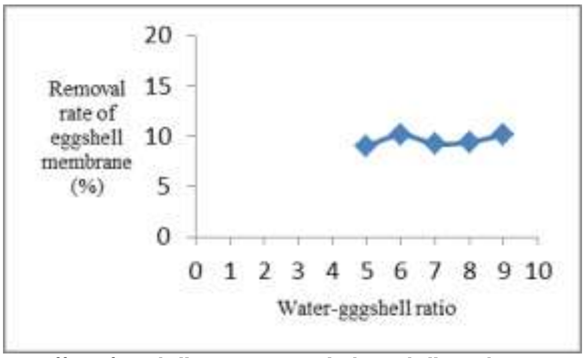

Fig. 3: Effect of eggshell-water ratio on duck eggshell membrane removal.

3.3 Effect of Residence Time

The residence time plays an important role on the eggshell membrane removal as presented in Fig. 4. Therefore, experiments were conduc-ted at a fixed air pressure and eggshell to water ratio.

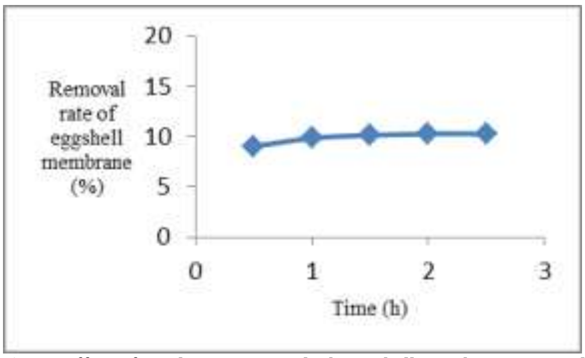

Fig. 4: Effect of residence time on duck eggshell membrane removal

Increasing the residence time improves the removal rate of duck eggshell membrane up to 10.2753 respectively with residence time at 2.0 h. Long residence time led to longer contact time between the duck eggshell and bubbles, thus it has better collision and adhesion probabilities with gas bubbles. Since the mass of raw duck eggshell added to DAF separation unit was fixed, the removal rate tended to maintain almost at 10.28 % for duck eggshell respectively. Therefore, the ideal separation time was reflected to be 2.0 h.

3.4 Morphology Identification

The morphology identification of duck-egg shell was examined by Scanning Electron Microscopy (SEM) as illustrated in Fig. 5. The outside surface of duck eggshells before DAF was a meshwork composed of interwoven and coalescing micron fibers. The shape of the fibers was gradually destroyed and it became smooth after DAF, demonstrating that the cleavage of the disulfide bonds was accompanied by destruction of the fibers.

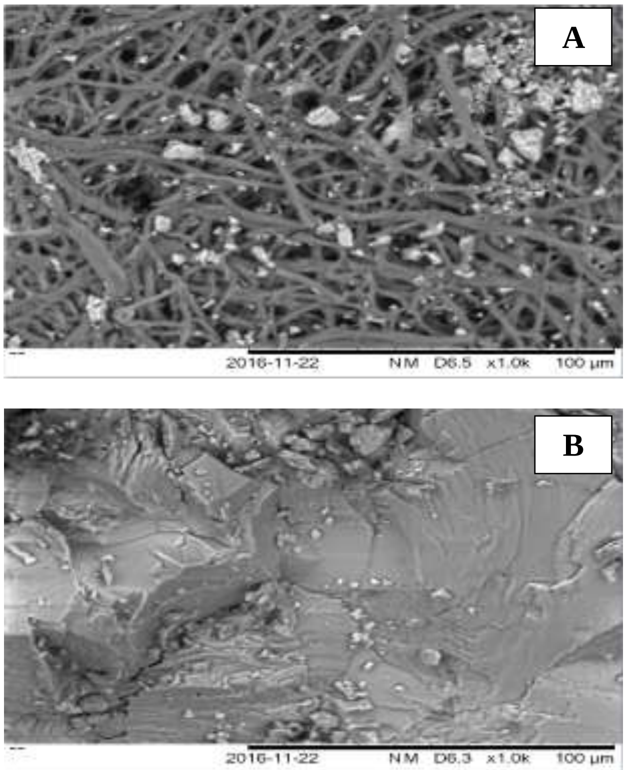

Fig. 5: SEM images of duck eggshell at magnification of 1000x (A) Before DAF and (B) After DAF

The inside surface of raw duck eggshell, instead, was rough and did not contain any fibers, it became smooth as well after DAF, suggesting that the inside surface is also affected. Morphology analysis of cockle shell calcium carbonate bioceramic using SEM and electrocrystallization via phosphorylated chitin have been also demonstrated, it revealed that the surface of the calcium carbonate particles was smooth with micron sized cube-like and calcite crystals [17, 18].

3.5 Thermogravimteric Analysis

The thermogravimetric analysis (TGA) of the raw duck eggshells showed 5.5 wt% and 3.5 wt% weight loss between 240 °C and 470 °C as illustrated in Fig. 6 respectively, which indicated that the raw duck eggshell contains protein membrane.

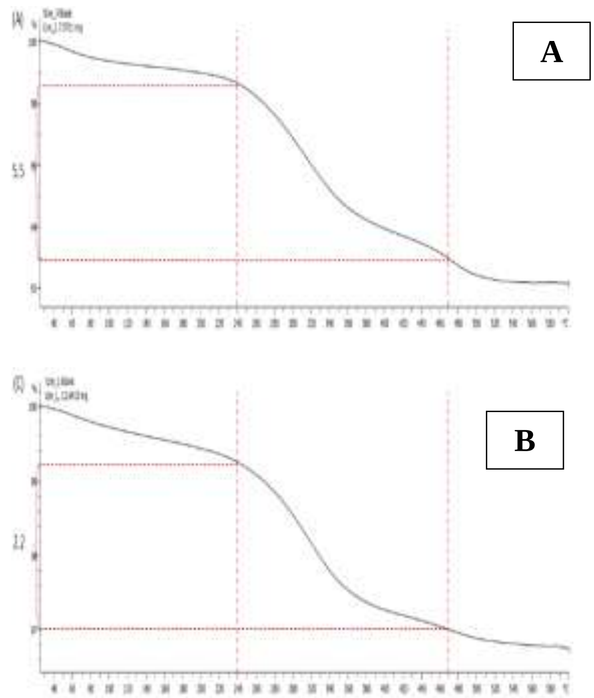

Fig. 6: TGA analysis of (A) Raw duck eggshell and (B) Recovered duck eggshell calcium carbonate

After DAF, the weight loss for TGA analysis of the recovered duck eggshell calcium carbonate was 2.2 wt%. The recovered duck calcium carbonate still contains a little portion of eggshell membrane. The remnant eggshell membrane ranged from 2.2 wt% to 3.8 wt% for the recovered duck eggshell calcium carbonate. Compared with the experimental results, it was found that the removal rate was lower than theoritical calculation. The difference was mainly due to loss of calcium carbonate particles during the sample transfer process from DAF separation unit to the oven.

3.6 Fourier Transform Infrared

The fourier transform infrared (FTIR) analysis of the recovered duck eggshell calcium carbonate as shown in Fig. 7. For most significant peak intensity was observed at 1396 cm^{-1} which was strongly associated with the presence of calcium carbonate in the recovered duck eggshell matrix as reported by former findings [19]. The peak at 1638 cm^{-1} indicated the presence of organic eggshell membrane. The moderately observable peak at 712 cm^{-1} confirmed the in-plane deformation mode of calcium carbonate. It was also reported that the most prominent peak in FTIR spectrum of eggshell particles matched with carbonate minerals [20]. The representative FTIR spectrum of duck calcium carbonate was confirmed by the appeared peak of the calcium carbonate.

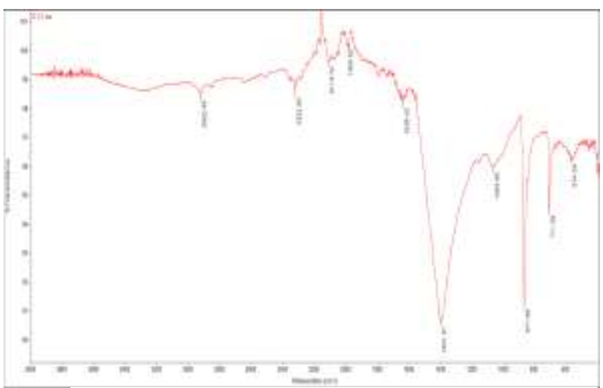

Fig. 7: FTIR spectrum of recovered duck eggshell calcium carbonate

3.7 Optimum Operation Condition Analysis

The optimum condition for removal rate of duck membrane was determined using Design-Expert 8. The implied F-value model was significant and R-Squared was greater than 0.8 for duck eggshells. From the analysis, it reveals air pressure of 1.62 bar, eggshell to water ratio of 1:5.68 and residence time of 1.41 h were given optimum condition for 11.246 % removal rate of duck eggshell membrane. Fig. 8 shows the configuration of 3D surface plots for duck eggshell membrane.

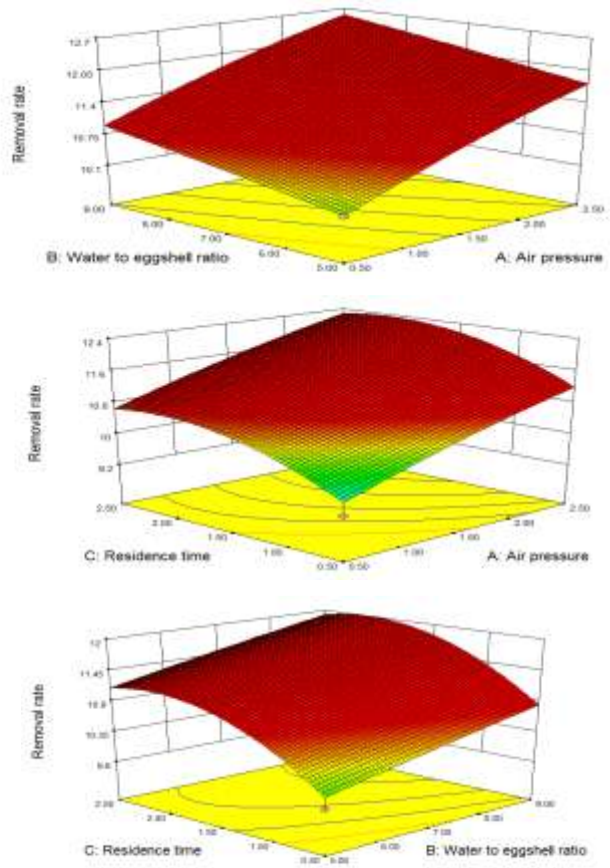

Fig. 8: 3D surface plots of duck eggshell membrane optimization

4. Conclusion

The DAFT has separated 92.5 % of duck eggshells calcium carbonate respectively and 60 % of duck eggshell membrane removed. Duck-egg shell characterization has been approved by the presence of calcium carbonate. The carbonate deduction was also influenced by the operated DAFT parameters for optimal condition of duck eggshell membrane. Hence, the PDEW and DAFT have the proficiency to obey as environmental friendly material and low cost technology. For carbonate recovery improvement, various operation parameters, methods and carbonates sources can be developed **.**

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