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Ultrasound Assisted Extraction of Nano Calcium from Waste Eggshell: A Preliminary Study on Crystal Violet Dye Removal

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Extraction of bio-based calcium carbonate ($CaCO_3$) nanoparticles from eggshell waste materials assisted by horn-type ultrasonic generator was studied. Chicken eggshells (CS) and duck eggshells (DS) were cleaned and ground using pestle and mortar, and further treated with acetone and dichloromethane (DCM) to remove impurities. The treated eggshells were then ultrasonic irradiated for 5 to 20 min, before sending to Dynamic Light Scattering (DLS) for particle size distribution measurement. Results shown that, nano calcium with approximately 300 nm was being recovered successfully. The recovered nano calcium is later subjected to Crystal Violet (CV) dye removal testing and has recorded a high removal efficiency of up to 87.90 % and 83.06 % for DS and CS, respectively. The high removal efficiency is basically due to the large surface area on calcium nanoparticles created by ultrasonic cavitation, as confirmed by Scanning Electron Microscopy (SEM) analysis.

1. Introduction

Nanoscale materials have brought up in a trend to researchers in the recent year. Due to the large surface area provided by nanoscale materials, they are widely used as catalyst, structural material, electronic component, sensor and etc. Chicken eggshell is known as one of the major industrial wastes produced globally. As seen in United State, approximate 465,000 t of eggshell waste was produced from nearly 92 billion eggs in 2011 (Hassan et al., 2013). Calcium nanoparticles could be extracted from chicken eggshells waste for further use. It has been discovered that chicken eggshell has high composition of Calcium contents (94.0 wt%) with the remaining composition carried by other components i.e. magnesium carbonate (1 wt%), calcium phosphate (1 wt%), and other organic materials such as collagen, sulphated polysaccharides and other proteins (4 wt%).
Sonochemistry is a study of the application of ultrasonic radiation which initiated chemical reaction in the solution due to acoustic cavitation activity (Stępniak et al., 2013). The physical phenomenon involving acoustic cavitation (Gedanken, 2004) is basically referring to the creation, growth, and collapse of bubbles that exist in the liquid. The diffusion of solute vapour into volume of bubble leads to the growth of bubble, and collapsed among each other when the bubble size reaches its maximum value. The implosive collapse of bubbles produces a hotspot via the adiabatic compression within the gas phase of collapsing bubble (Bastami and Entezari, 2012). These hot spots with high local temperature (5,000 K – 25,000 K) are useful to break down chemical bonds between molecules in the solution, especially for organic compound. (Neppolian et al., 2008) Either bath-type ultrasonic generator or the horn-type ultrasonic generator, they are equally manageable to produces cavitation bubbles in liquid solution. Neppolian et al. (2008) suggested with the increase of ultrasonic irradiation time, fragmentation of particles will be enhanced, and so the high-velocity inter-particle collision, reduces the formation of large particles. It is also

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reported that a syringe needle could generate microbubbles with a diameter of 4 to 15 μm under an ultrasonic field, nevertheless, coupled with the disadvantage of relatively low gas flow rate generated (usually a few microliters per minute). Thus, horn type sonicator is still generally accepted as the most efficient cylindrical tool to generate massive high energy bubbles.

Dye removal from wastes has become a global industrial issue, especially by the textile manufacturing industry (Khalfaoui et al., 2014) and pulp and paper industry (Pelosi et al., 2013). Dyes are generally categorized into cationic, anionic and non-ionic (Yagub et al., 2014). Cationic dyes, including crystal violet and methylene blue, are highly used in wool dyeing and paint production (Rahman et al., 2012),. The effluent containing high concentration of cationic dyes is highly coloured and poisonous; therefore proper treatment is required before disposal.

It has been reported that the use of eggshells as biosorbent has been increasing in the recent years. A previous study (Tsai et al., 2008) suggested two main physical processes in dye removal, i.e. adsorption and membrane separation. Eggshells were being studied on its high adsorption capacity of heavy metal i.e. Chromium (III) ions from aqueous solution, however, the adsorption capacity for cationic dye is rather discouraging, such as Methylene blue and crystal violet, of less than 1.0mg/g. This paper is aiming for (i) Extraction of nano calcium from eggshell waste using ultrasonication; (ii) Characterization of nano-calcium such as surface morphology and particle size; (iii) Determination of dye removal efficiency by utilizing eggshell waste materials. Due to the large functional area provided by nano calcium, it is believed that the dye absorption efficiency will increase dramatically.

2. Materials and methods

2.1 Materials

Chicken Eggshells (CS) and Duck Eggshells (DS) were separated from chicken eggs (White colour, Nutriplus Omega-3) and duck eggs (brown colour) purchased from local market, respectively. The separated eggshells were soaked with warm water (50 °C, 2 h) to remove adhering eggshell membrane, dust and dirt. The eggshells were recovered and dried in a conventional oven (60 °C) until it was fully dried.

2.2 Pre-treatment of eggshell powder

Oven dried eggshells were crushed into powder using pestle and mortar. Thereafter, the eggshell powder was mixed with 200 mL of acetone solvent under 1 h of continuous stirring before double filtration took place. Eggshell powder trapped on the sieve tray was separated with sample remained on the filter paper. Both samples were further dried under room temperature for 24 h. A half of the dried sample were soaked in dichloromethane (DCM) with continuous stirring for 15 min, and subjected to ultrasonication for 10 min. Samples were again dried in oven (90 °C) for 15 min.

2.3 Ultrasonication

15 ml of distilled water were added into vials containing 0.25 g of pretreated CS and DS, respectively. Horn-type ultrasonic generator was employed to provide ultrasonic cavitation, and ice bath was prepared to prevent overheating. Horn tip was adjusted with an immersion depth of 1.5 cm below suspension surface. Upon completion of ultrasonic treatment, 1mL of samples were collected after settling time of 0 min, 1 h, and 24 h, to establish particles size distribution profile. Experiments were repeated with varied ultrasonication time (U-time) and percent amplitude (Amp %).

2.4 Zetasizer analysis

Samples particles size distribution profile was established using Zetasizer Nano-ZS to determine samples Z-Average (Z-Avg) with Polydispersity Index (PdI). Three measurements were taken down for every samples to obtain higher consistency. Z-Avg is generally regarded as a mean value of hydrodynamic diameter of sample particle measured, and PdI is to determine the width of particle size distribution, as suggested in Eq(1).

$$PdI = \left(\frac{\sigma}{d}\right)^2 \quad (1)$$

Where σ is the standard deviation and d is the average particle size or mean diameter of particle in nm.

2.5 Scanning Electron Microscope (SEM) imaging

Surface morphology was confirmed using Hitachi S-3400 N Scanning Electron Microscope with dispersive spectrometer. Sample was pressed onto a double sided carbon tape and sputtered with gold coating. The applied accelerating voltage was 15.0 kV.

2.6 Crystals Violet (CV) dye adsorption

Ultrasonicated CS and DS samples with desired particle size distribution were dried again in the oven at 90 °C for 24 h.15 mL of 10 ppm working crystals violet (CV) solution was added into vials containing dried eggshells powder. Vials were sealed tightly to prevent leakage, and suspension was stirred continuously at 700 rpm for 2 h to ensure complete mixing. After that, supernatant was separated from absorbent through filtration, and analysed using UV-Vis Spectrophotometer (U-2900/U-2910 double Beam) by monitoring the change in absorbance (abs) value at its maximum wavelength (λ_{max}) = 580.5 nm. Samples were scanned within the range of 300 nm – 700 nm for the absorbance spectrum profile, and the percentage of dye removal efficiency was calculated using Eq(2):

$$Removal\ (\%) = \frac{A_{CV} - A_S}{A_{CV}} \times 100\ \% \quad (2)$$

Where A_{cv} denotes the absorbance value for initial working CV dye solution and A_s is the absorbance value for supernatant collected after absorption study.

3. Results and discussion

3.1 Optimum operating condition of ultrasonication

Optimum operating condition was determined by referring to the experiments that produce the nano calcium with the lowest Z-Average (Z-Avg) and relatively low Polydispersity Index (PdI) value. It was observed from Figure 1(a) that Z-Avg obtained from CS (U-time: 10 min, Amp %: 25) has decreased linearly with respect to setting time, while on the other hand, DS produced smaller but inconsistent size particle distribution as compared to the similar process with CS as raw material. Figure 2(a) SEM analysis shows a relatively smoother surface morphology for nano calcium extracted from chicken eggshells, while structural duck eggshell morphology with the presence of crescent-shaped mammillary layers, as a result of ultrasonic cavitation. Table 1 shows the data of Z-Avg and PdI values obtained for CS (U-time: 10 min, Amp %: 25) with [DCM and without [X-DCM] DCM treatment. Data is presented for DS in Table 2 under the similar experimentation setting. Comparing the data in both Tables 1 and 2, samples without DCM treatment [X-DCM] have shown lower Z-Avg and PdI values in both CS and DS samples. Besides that, both CS and DS samples are showing reduced Z-Avg and PdI values when the settling time increases.

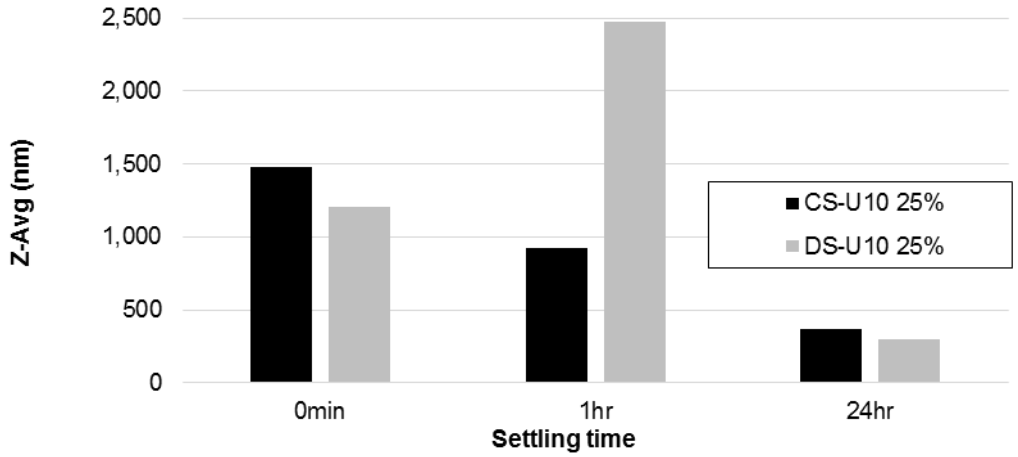

Figure 1(a): CS and DS at optimum operating condition

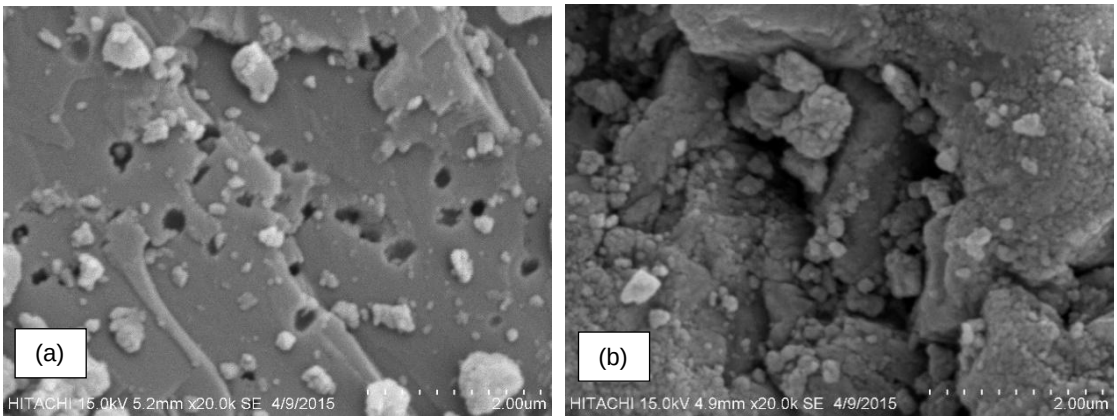

Figure 2: SEM image of nano calcium produced from (A) chicken eggshells and (b) duck eggshells.

3.2 Effect of DCM treatment

CS and DS were further washed with Dichloromethane (DCM) to study the influence of this inorganic solvent on particle size reduction. Generally, DCM-treated CS produced smaller nano-sized calcium after ultrasonication. Figure 2(a) showed particle size distribution of CS (U-time: 10 min, Amp %: 25) treated with DCM, as compared to particle size distribution of CS without DCM in Figure 2(b). It is believed that DCM treatment did further reduce the impurities on eggshells surface to provide a better ground for ultrasonic cavitation in calcium fragmentation. Similar results were obtained for DS (U-time: 10 min, Amp %: 25), as which can be observed from Figure 2(c) and Figure 2(d).

Table 1: Z-Avg and PdI for CS-U10 25 % with and without DCM treatment

Settling time		0 min		1 h		24 h		Average	
		Z-Avg	PdI	Z-Avg	PdI	Z-Avg	PdI	Z-Avg	PdI
25 % [DCM]	0 min	1,240	0.499	1,547	0.131	271.8	0.107	1,204	0.580
	1 h	1,181	0.537	1,477	0.212	269.8	0.133	1,405.3	0.1767
	24 h	1,191	0.704	1,192	0.187	275.3	0.133	272.3	0.1243
25 % [X-DCM]	0 min	1,587	0.731	916.9	0.429	364.2	0.223	1,480.7	0.704
	1 h	1,533	0.542	930.4	0.432	368.5	0.220	927.1	0.437
	24 h	1,322	0.839	934.1	0.449	364.6	0.198	365.77	0.2137

Table 2: Z-Avg and PdI for DS-U10 25 % with and without DCM treatment

Settling time		0 min		1 h		24 h		Average	
		Z-Avg	PdI	Z-Avg	PdI	Z-Avg	PdI	Z-Avg	PdI
25 % [DCM]	0 min	1,596	0.504	533.6	0.28	271.2	0.137	1,455.3	0.482
	1 h	1,426	0.420	536.1	0.224	274.9	0.119	535.83	0.2473
	24 h	1,344	0.523	537.8	0.238	274.9	0.126	273.67	0.1273
25 % [X-DCM]	0 min	1,202	0.606	610.6	0.174	300.6	0.214	1,205.3	0.496
	1 h	1,288	0.439	650.3	0.207	297.4	0.159	2,473.2	0.204
	24 h	1,126	0.444	662.6	0.230	299.8	0.17	299.27	0.181

3.3 CV adsorption study

CV dye of 10 ppm (10 mg/L) was prepared. Abs value received at 580.5 nm was set as the reference value to calculate percentage of removal for CV dye. The initial Abs value for the dye solution was determined to be 0.124 in this study. Absorption spectrum for both CS and DS samples were constructed and compared in among samples produced with ultrasonic time from 10 to 25 min at 25 % amplitude. In comparison with absorption spectrum received for CS, DS gives a better overall CV dye removal (Table 3). It was observed that the effect of u-time does contribute to improve CS nano calcium CV dye removal efficiency, however, u-time was found to be insignificant for DS, probably due to failure in providing larger functional area for DS.

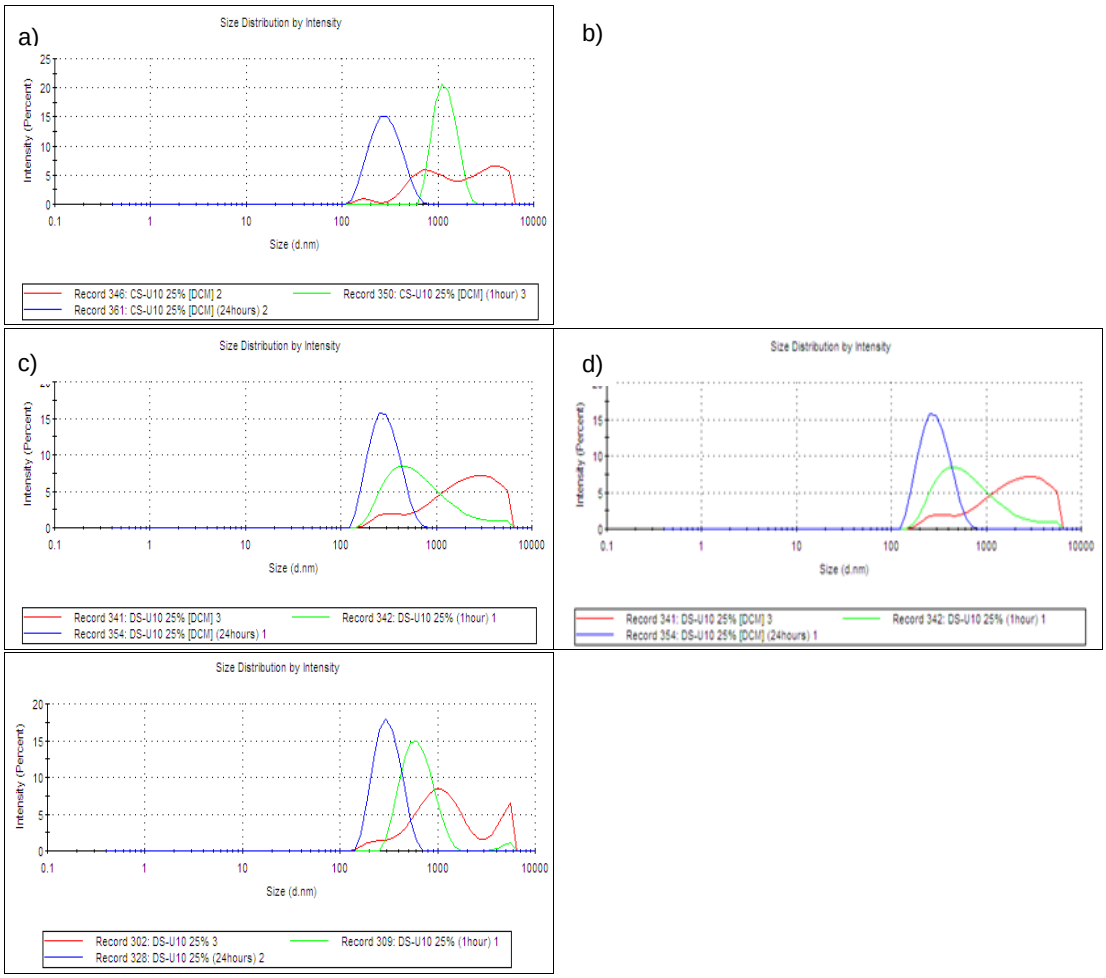

Figure 2: Particle size distribution measured using Malvern Zetasizer (a) CS-U10 25% [DCM], (b) CS-U10 25 % [X-DCM], (c) DS-U10 25% [DCM], and (d) DS-U10 25% [X-DCM]

Table 3: Percentage removal of crystal violet dye calculated based on absorbance value

Sample	Abs Value	Removal (%)
Chicken Eggshell		
CS-U10 25 %	0.021	83.06 %
CS-U15 25 %	0.026	79.03 %
CS-U20 25 %	0.024	80.65 %
CS (X-U)	0.032	74.60 %
Duck Eggshell		
DS-U10 25 %	0.015	87.90 %
DS-U15 25 %	0.018	85.48 %
DS-U20 25 %	0.026	79.03 %
DS (X-U)	0.015	87.90 %

4. Conclusion

In this study, bio-$CaCO_3$ nanoparticles were successfully extracted from chicken and duck eggshells via ultrasonic irradiation using the horn-type ultrasonic generator. The extracted nanosize calcium particle was received with controlled particle size distribution and surface morphology. The optimum operating condition was determined where nano-$CaCO_3$ produced from DS and CS samples with mean Z-Avg of 299.27 nm and 365.77 nm. As compared to the previous study, absorption study showed very encouraging

result in removing CV dye from aqueous solution (10 ppm) at which the highest efficiency was recorded after 2 h of stirring, by sample DS-U10 25 % with 87.90 % of CV dye removal.

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