Nano/submicrometer milled red rice particles-stabilized Pickering emulsions and their antioxidative properties

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Introduction

Current approach to modify particles from natural materials for stabilization of Pickering emulsion is normally based on the following procedure: single component such as protein, starch, cellulose, is isolated from natural materials; then modification methods are used to modify single component as colloid particles, such as starch nanoparticles, cellulose nanocrystals, etc. It is not only a complex procedure requiring extensive time and energy consumption, but the modification methods used are mainly chemical processes, which involve using hazardous chemicals, organic solvent, etc. Moreover, the bioactive compounds with health beneficial effects existed in the natural materials are completely lost or wasted during the process. Developing of methodology to directly modify natural materials as Pickering emulsifiers while maintain the original bioactive compounds would be of great important to promote the application of Pickering emulsion in food industry.

Red rice is a natural material with many natural antioxidants. In this study, whole grain red rice was modified directly using media milling process as colloid particles for the development of Pickering emulsions (**Figure 1**).

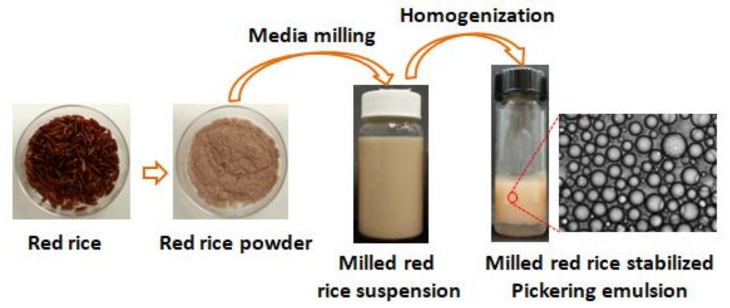

Figure 1. schematic graph of milled red rice particle stabilized Pickering emulsion formation.

Methods and Materials

Wet-milling process: Red rice powder suspended in deionized water were ground with a MiniSeries ball mill. To investigate the influence of milling time, the sample was withdrawn every 1 h within a total grinding time of 4 h.

Antioxidant compounds and activity :Total phenolic content (TPC) and total flavonoids content in different milled red rice and their ferric reducing antioxidant property (FRAP) and DPPH activity were characterized.

Emulsion preparation: Milled red starch suspension with different time was mixed with oil phase through high speed homogenizer.

Effect of milled red rice on lipid oxidation: The lipid oxidation of Pickering emulsion stabilized by native rice starch and bulk oil was investigated by measuring the peroxide value (PV) and the thiobarbituric acid-reactive substances (TBARS) content in different samples during different storage periods.

Results

With the increasing of milling time, the size of red rice particles decreased steadily. After 4 h of processing, the particle size of milled red rice was reduced to around 692 nm (**Figure 2**).

The morphology of different milled red rice were analyzed by optical microscope (**Figure 3**) and SEM (**Figure 4**) . Milled red rice showed irregular granule shape. These pictures confirmed the presence of nano/submicrometer particles in the milled red rice samples.

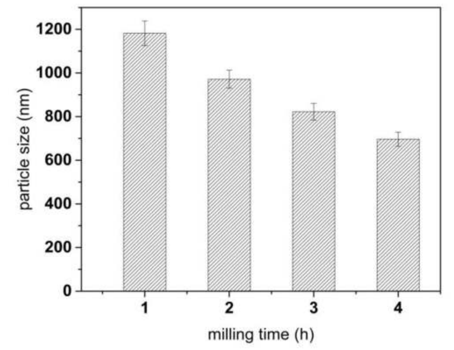

Figure 2. Particle sizes of milled red rice particles with different milling time

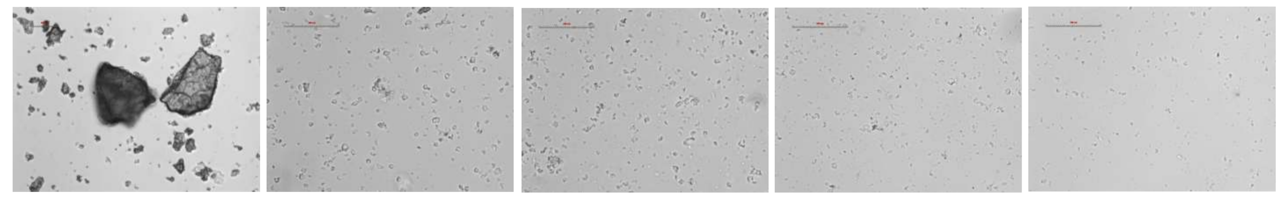

Figure 3. Polarized microscopic images of red rice flour and milled red rice with different milling times (Left-right: 0, 1, 2, 3, 4 h). The solid bars in microscopic images correspond to the length of 100 µm

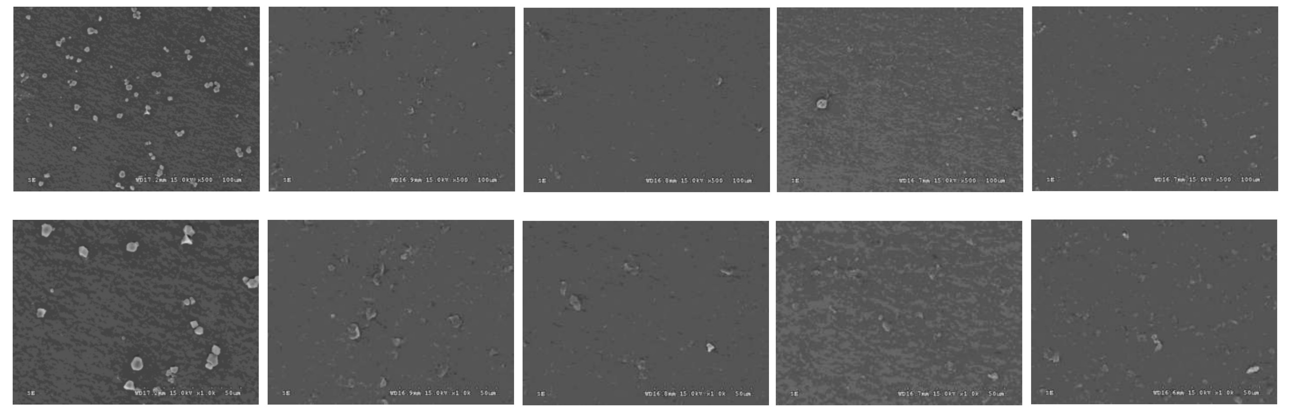

Figure 4. Scanning electron micrographic images of red rice flour and milled red rice (Left-right: 0, 1, 2, 3, 4 h).

The anthocyanin content of milled red rice increased during milling process, while there was a slight decrease in the total phenolic and flavonoid content. The anti-oxidation activity of milled red rice was slightly reduced compared to native red rice (**Figure 5**).

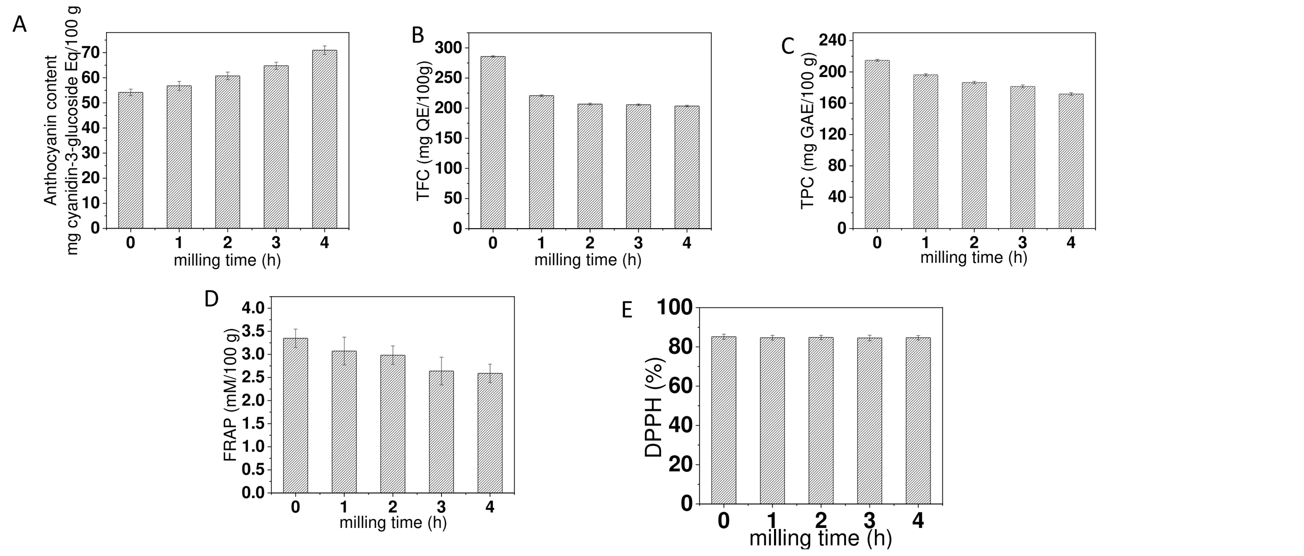

Figure 5. (A) Apparent total anthocyanin content (mg cyanidin-3-glucoside Eq/100 g), (B) Apparent total flavonoid content (mg QE/100 g), (C) Apparent total phenolic content (mg GAE/100 g), (D) FRAP (mM/100 g) and (E) DPPH radical scavenging activity (%) of red rice and milled red rice with different milling time.

The creaming effect and droplet size in the resulting emulsion decreased gradually with the prolonged milling time. The average droplet size of the emulsions dropped sharply from 95 ± 11 µm to 59 ± 9 µm when red rice was milled for 1 h, then further reduced and reached a plateau at 30 ± 5 µm when the processing time was prolonged to 4 h (**Figure 6**).

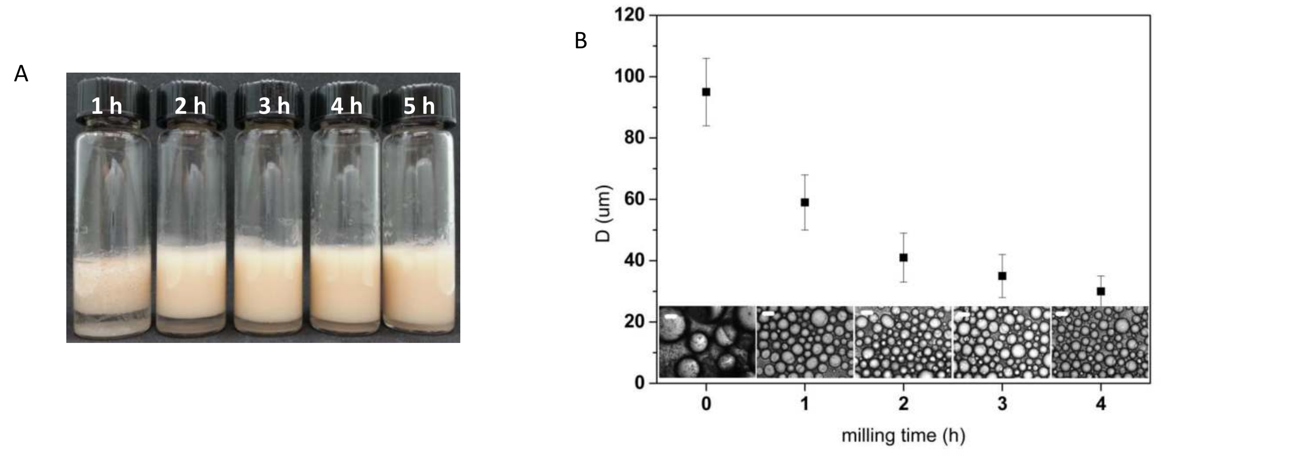

Figure 6. (A) Bulk appearance (after storage for 7 days), (B) Microscopic images and droplet size of Pickering emulsions stabilized by 3.5 wt% red rice and milled red rice particles with different milling time (1-4 h). The solid bars in microscopic images correspond to the length of 100 µm.

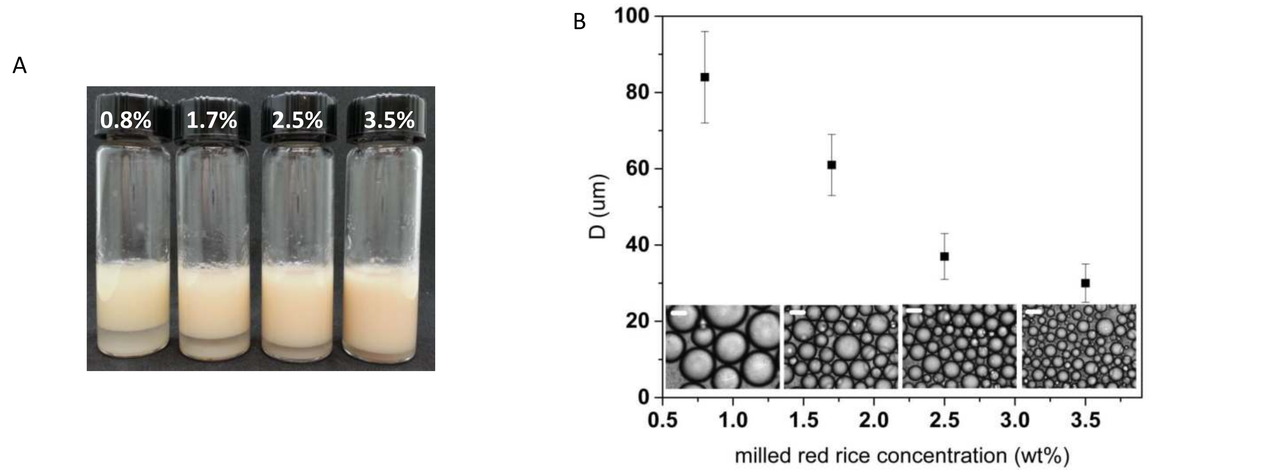

Figure 7. (A) Bulk appearance (after storage for 7 days), (B) Microscopic images and droplet size of Pickering emulsions stabilized by milled red rice particles with different concentrations (0.8-3.5 wt%). The solid bars in microscopic images correspond to the length of 100 µm.

For milled red rice particles with concentration of 3.5 to 0.8 wt%, low concentration of 0.8 wt% milled red rice was able to form stable emulsion during the 7 days' storage. The increase of red rice concentration from 0.8% to 3.5% led to a steady reduction of droplet size from 84 ± 12 µm to 30 ± 5 µm (**Figure 7**).

PV value in milled red rice stabilized emulsion was significantly lower than that of rice starch stabilized emulsion and pure oil after 12-day storage ($P < 0.05$). The TBARS value of rice starch stabilized emulsion was significantly lower than that of bulk oil when storage for 12 days ($P < 0.05$). In emulsion stabilized by milled red rice, the lipid oxidation process was much slower than in other two samples (**Figure 8**).

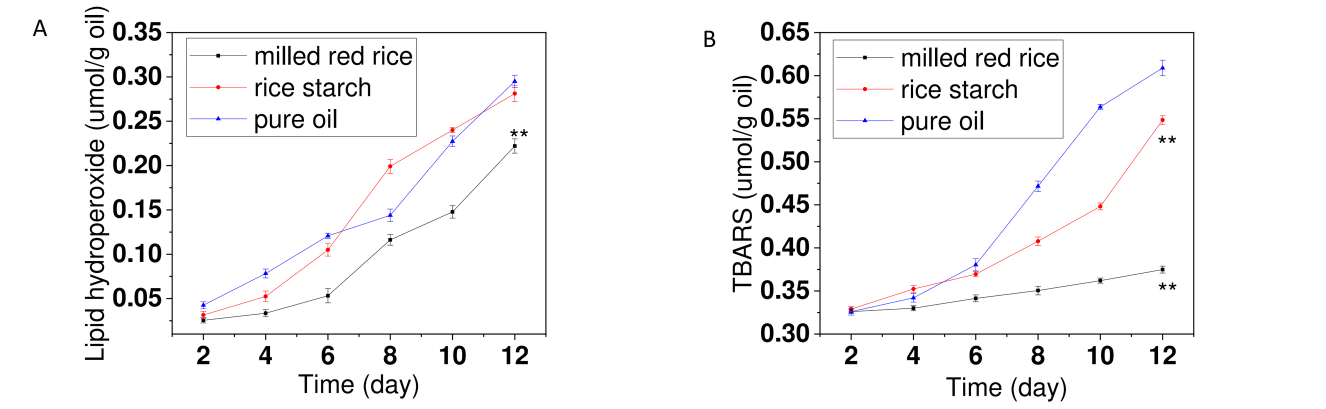

Figure 8. Evolution of (A) lipid hydroperoxides and (B) TBARS in milled red rice stabilized Pickering emulsion, native rice granule stabilized Pickering emulsion, and bulk oil under room temperature storage for up to 12 days. ** indicates that the difference is significant (p < 0.01).

Conclusions

This research studied the effect of media mill process on a type of whole grain red rice. Nano or submicrometer milled red rice particles could be obtained using media milling process, which were able to form stable Pickering emulsions. The media milling process exhibited minor impact on the content of phytochemicals and antioxidant activities of the resulting milled red rice. Media-milled red rice particles stabilized Pickering emulsions presented higher stability against lipid oxidation compared to Pickering emulsion stabilized by white rice starch and bulk oil owing to the presence of intrinsic antioxidants. This study provides an effective approach to modify raw food materials as solid colloid particle stabilizers and the formation of Pickering emulsions with relatively low lipid oxidation rate.

References

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