

Microencapsulation of Anthocyanin-Rich Extract from Indonesian Black Rice using Maltodextrin, Arabic Gum and Skimmed Milk Powder as Wall Material by Spray Drying

Nurhidajah*, Diode Yonata and Bobby Pranata

Department of Food Technology, Faculty of Science and Agricultural Technology, University Muhammadiyah Semarang, Semarang 50273, Indonesia

(*Corresponding author's e-mail: nurhidajah@unimus.ac.id)

Received: 18 January 2024, Revised: 5 May 2024, Accepted: 20 May 2024, Published: 30 June 2024

Abstract

Indonesia is one of country where black rice is abundantly cultivated. Black rice anthocyanin compounds have been confirmed to have various health benefits, and their use as a functional food is increasing after anthocyanin compounds are produced into microcapsules. This study aimed to determine the best coating material in black rice anthocyanin microcapsule production using spray drying with a mono-factor design. The coating materials used consisted of maltodextrin (MD), Arabic gum (AG) and skim milk powder (SMP). The results showed that microcapsules based on MDA and AG were not perfectly spherical, the outside was wrinkled with a smooth surface, while the microcapsules based on SMP were perfectly spherical with a slightly rough surface. All microcapsules had functional components such as anthocyanins (49.46 - 98.02 mg/100 g), total phenolic (63.51 - 95.83 mg GAE/100 g) and antioxidant activity (25.36 - 43.88 % RSA), which were quite good. The low water content (3.17 - 3.27 %) and a_w (0.28 - 0.31) caused the microcapsules to be slightly hygroscopic (18.75 - 21.01 %), with high solubility (87.86 - 96.42 %). The average size of microcapsules was 22.009 - 48.710 nm, where the best flow properties were obtained from SMP-based microcapsules. Microcapsules have a low pH (2.52 - 2.87), with the characteristic color of black rice still preserved (red-violet) due to good stability during drying. In conclusion, SMP is highly recommended as a coating material for black rice anthocyanin microcapsules using the spray drying method.

Keywords: Anthocyanin-rich extract, Black rice, Characterization, Microcapsules, Spray dryer, Wall material

Introduction

Black rice is one of the pigmented rice cultivars that thrive in many countries in Asia. Indonesia (6.2 %) is the third-largest after China (62.0 %) and Sri Lanka (8.6 %) in terms of black rice cultivation [1]. Anthocyanins are the main pigments responsible for the black color of rice [2]. Cyanidin-3-glucoside (88 - 92.5 %) and peonidin-3-glucoside (± 7.5 %) are the largest anthocyanin compounds in black rice [3-5]. Cyanidin-3-rutinoside, cyanidin 3,5-glucoside, malvidin-3-glucoside and peonidin-3-glucoside compounds were also identified in some black rice cultivars in minor concentrations [6-8]. Cyanidin-3-glucoside has been confirmed to have strong antioxidant activity [9].

Black rice may be utilized as a functional food because of its anthocyanins, which have been shown to have several health advantages, including the ability to inhibit the development of cancer cells, lower diabetes and obesity, and have an anti-inflammatory impact [1]. However, anthocyanins are unstable and can be easily broken down by various processing and storage conditions, including light, oxygen, pH and temperature [10]. This can be enhanced by the encapsulation method, which creates microcapsules with greater durability and properties by shielding the anthocyanins as the core material with a coating material [11].

Spray drying is the most effective and applicable encapsulation technique to maintain the stability of anthocyanins from thermal degradation. This is based on the short duration of heat contact received in the drying chamber [12]. Besides having high efficiency, the spray drying technique is also possible to be applied on an industrial scale sustainably [13,14]. Several important factors must be considered in spray dryings, such as inlet and outlet temperatures, as well as the kind and concentration of the coating material [15-17]. Various types of natural biopolymers have been used as coating materials for anthocyanin extracts

from jussara, jaboticaba and blueberries [18]. Maltodextrin (19.56 %), gum (15.22 %) and milk protein (13.04 %) were the most used coating materials in the encapsulation of anthocyanin extracts [12].

MD is a hydrolyzed starch with many advantages, including good film-forming ability, low viscosity and high solubility in water, which has been applied to pomegranate anthocyanin extract [16]. AG has emulsifying and film-forming properties, generally used to conquer hygroscopicity problems and protect sensitive components from oxidation by the encapsulation process [19], this is because AG can increase the thermal stability of anthocyanins after encapsulation by spray drying [20]. SMP provides excellent encapsulation results with its non-sticky, applicable, and has been reported to be very effective in the encapsulation process of black soybean Cyanidin-3-glucoside compounds [21].

Black rice anthocyanins are strong antioxidants and very the potential as functional food ingredients and supplements that have health benefits. Although there are research efforts related to the encapsulation process of black rice anthocyanin extract, information regarding the influence of the various types of coating materials used is still limited [11,22-24]. Thus, there is a gap in information about which coating is most effective in encapsulating anthocyanin extracts by understanding the physicochemical and structural characteristics of black rice microcapsules - important information for their development, especially in the health-based food industry. Each type of coating material will produce the physicochemical properties and structure of the resulting microcapsules. This study aims to compare different coating materials (MD, AG and SMP) using the spray drying method by specifically comparing the physicochemical and structural properties of Indonesian black rice anthocyanin extract microcapsules. This investigation bridges critical knowledge gaps and paves the way for its strategic development.

Materials and methods

Materials

The research material was black rice of the Jeliteng variety collected from organic rice farmers in Karanganyar, Central Java Province, Indonesia, food-grade citric acid from PT Gunacipta Multirasa Indonesia and aquadest.

Extraction of black rice anthocyanin compounds

The anthocyanin compounds were determined according to the method described by Nurhidajah *et al.* [25]. Black rice is ground into flour. The 100 g of black rice flour was added with ethanol (56 % v/v) which was acidified with citrate (4.5 % w/v) in a ratio of 1:10 (w/v). The extraction process was carried out in a thermostatic water bath with a controlled temperature (50 °C) for 120 min with constant stirring (500 rpm). The next process is a separation of liquid and residue using filter paper with a size of 400 mesh. Ethanol in the extract was evaporated using a rotary evaporator at 55 °C. The anthocyanin extract of black rice was stored in a dark glass bottle at 4 °C until used.

Microencapsulation of anthocyanin extract

Anthocyanin was extracted based on the method described by Nurhidajah *et al.* [25]. Solution emulsions of different coating materials (MD, AG and SMP) were prepared at a concentration of 20 % (w/v) with deionized water at room temperature. Anthocyanin extract was mixed with each coating material in a ratio of 1:1 (v/v). Each mixture was homogenized separately for 15 min at 3,000 rpm. The drying process uses a laboratory-scale spray dryer with an inlet air temperature of 120 ± 1 °C, an outlet air temperature of 80 ± 5 °C, and a feed flow rate of 6.0 mL/min at a pressure of 1.5 bar. Acquire microcapsules were collected and stored at -20 °C until analyzed.

Anthocyanin content

A differential pH method was used in determining the anthocyanin content of microcapsules [26]. One g of microcapsules was dissolved with 1 mL of ethanol in a test tube, then mixed separately with 2 buffer solutions (1 mL of potassium chloride buffer pH 1.0; 1 mL sodium acetate buffer pH 4.5), and incubated at room temperature (± 25 °C) for 15 min. The absorbance was measured by spectrophotometer at 520 and 700 nm. Absorbance value concerned by subtracting the difference in absorbance at a wavelength of 520 and 700 nm at pH 1.0 with the difference in absorbance at pH 4.5. Anthocyanin content was obtained by multiplying the absorbance value by the molecular weight of cyanidin-3-glucoside (448.8 g/mol) and the amount of dilution, then divided by the coefficient of molar absorptivity of cyanidin-3-glucoside (26,900 L/mol·cm) and the width of the cuvette (1 cm).

Total phenolics

The Folin-Ciocalteu method [27], with slight modifications, was used in the analysis of total phenolic content. In a dark tube, 0.5 g of microcapsules were prepared, and 5 mL of the 10 % (v/v) Folin-Ciocalteu reagent was added. The solution was homogenized for 5 min and added 4 mL of 7.5 % Na₂CO₃ (w/v). The mixture was incubated for 60 min at room temperature (25 ± 1 °C). Ethanol is used as a blank solution. The gallic acid in ethanol with a concentration of 100 - 500 ppm is used as a standard solution. Then, the absorbance was measured using a UV-Vis spectrophotometer with a wavelength of 765 nm.

Antioxidant activities

Radical scavenging activity (RSA) of microcapsules was measured using the method of Pedro *et al.* [27] with modifications. After mixing 0.2 g of microcapsules with 1.5 mL of 0.2 mM DPPH ethanol, 3.5 mL of ethanol was added. The tubes were tightly closed, homogenized and incubated at room temperature (25 ± 1 °C) for 60 min. The absorbance was measured at a wavelength of 517 nm. The ability of the extract to scavenge DPPH was obtained by subtracting the absorbance of the blank with the sample. The result was then compared with the absorbance of the blank and expressed in % RSA.

Color analysis

Color characteristics of black rice anthocyanin microcapsules were measured using a calibrated Minolta CR-310 Chromameter (Konica Minolta Business Solution Asia Pte Ltd). The hue angle, H° [$\tan^{-1}(b^*/a^*)$] and chroma, C° [$(a^{*2} + b^{*2})^{1/2}$] were also determined. H° is used to identify colors (red, yellow, green and blue), whereas C° distinguishes between bright and dull colors [28].

Yield, moisture content and water activity (a_w)

The yield was calculated from the percentage of the microcapsule's weight (g) with the total solids of the sample (g). The water content of microcapsules was determined using a moisture analyzer (Shimadzu MOC63u, Japan), while the a_w of microcapsules was determined using a water activity analyzer (Rotronic Hygropalm-HP23-Aw-A, Switzerland) at 25 °C.

Hygroscopicity and solubility

The hygroscopicity of microcapsules was determined according to the method described by Kanha *et al.* [29] with modifications. Microcapsules (2 g) were placed in a saturated NaCl (75.5 % RH) at 30 °C for 1 week in a container. The hygroscopicity was subsequently calculated using the equation:

$$\text{Hygroscopicity (g/100 g)} = \frac{\text{adsorbed moisture (g)}}{\text{sample weight (g)}} \times 100$$

The solubility of microcapsules was determined using a modified version of the method reported by Caparino *et al.* [28]. One g of each sample was mixed in 100 mL of distilled water, magnetically stirred for 30 min, and after that, centrifuged at 3,000 g for 5 min at room temperature. The supernatant was completely dried in an aluminum dish in an oven at 105 °C for 12 h. The solubility of the microcapsules was calculated using the equation:

$$\text{Solubility (g/100 g)} = \frac{\text{Weight of the powder in the supernatant (g)}}{\text{Weight of the powder in the solution (g)}} \times 100$$

Flow properties

Bulk density (Bd) was determined by pouring the amount of microcapsules into a 100 mL measuring cup up to the 25 mL mark and then weighing. The weight and volume of the microcapsules were then used to calculate the bulk density expressed as mass/volume (g/cm³). The same procedure was also used to obtain the value of tapped density (Td), with the addition of a measuring cup filled with microcapsules that were mechanically tapped until they reached a constant volume. Td is calculated using the same formula as bulk density [30,31]. The compressibility index (CI) and Hausner ratio (HR) were used to measure the flowability of microcapsules. Both were calculated based on Bd and Td data using the equation described by Lebrun *et al.* [32].

pH value

The pH value of microcapsules was measured with the instrument Hanna HI 2211 bench pH meters (Hanna Instruments Ltd.), calibration solution using standard buffer.

Scanning electron microscopy and particle size

Scanning electron microscopy (SEM) analysis of examined samples was performed using JSM-6510LA analyzer (Jeol Ltd.). The prepared sample was then coated with gold with an ion coating and observed with an acceleration voltage of 12 kV. The particle size of microcapsules was measured with the LLPA-C10 instrument (Labron Equipment Ltd.), using the laser beam scattering principle, with a measurement range of 0.01 - 2,000 nm.

Statistical analysis

All experiments were carried out in 5 repetitions. Results are presented in terms of mean standard deviation. The effect of treatment factors was analyzed using 1-way ANOVA, and Duncan's post hoc test was used to detect differences between treatments. The significance level used is $p < 0.05$. Statistical analysis was carried out with SPSS 22.0 software.

Results and discussion

Anthocyanin, total phenolics and antioxidant activity of microcapsules

Anthocyanins from black rice extract were encapsulated using MD, AG and SMP, the results are presented in **Figure 1**. Black rice extract encapsulated with SMP produced microcapsules with higher ($p < 0.05$) anthocyanin content (98.02 mg/100 g) compared to MD (52.36 mg/100 g) and AG (49.46 mg/100 g). Anthocyanin compounds are investigated to be more stable when complexed with proteins because they involve hydrophobic interactions [33]. Hydrophobic interactions occur due to the presence of casein component in the protein. SMP generally contains α -casein components and has been reported to interact with Cyanidin-3-glucoside compounds from black soybean extract through reversible hydrogen bonding [21]. In addition, hydrogen bonding and hydrophobic complexes of protein casein with maldivin-3-glucoside compounds from grape extracts have also been reported [34]. The thermal stability of anthocyanin compounds increases significantly when interacting with casein [35], in which the protective effect of anthocyanins during drying becomes more optimal. MD is known to have advantages, namely good film formation ability, low viscosity and high solubility in water, which has been applied to the encapsulation of anthocyanin extracts [16]. In this study, the encapsulation results using MD were lower than SMP. This is because the use of MD has been proven to have a negative impact on the total anthocyanin content in rukem fruit extract, as reported in a study [36], which found that certain concentrations of MD caused a decrease in the total anthocyanin content. Compared with SMP and MD, AG provided a less effective protective effect on the stability of anthocyanin pigments. This is due to the structure of AG, which is a highly branched sugar heteropolymer and contains a small amount of protein covalently linked to the carbohydrate chain, which can complicate its use in the encapsulation process. This complexity can pose challenges in achieving consistent encapsulation and stability of anthocyanin pigments [37].

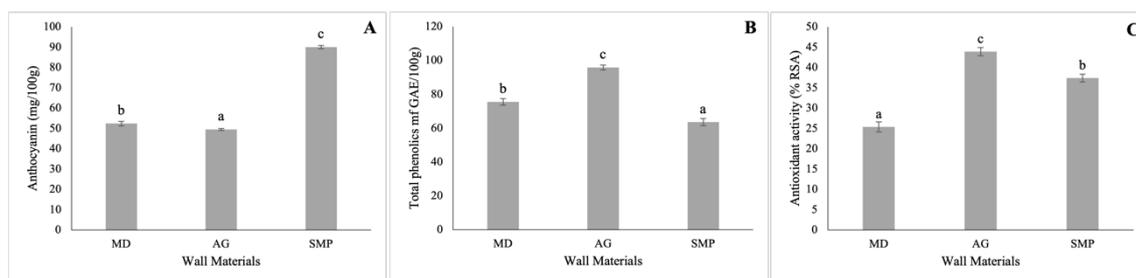


Figure 1 (A) anthocyanin; (B) total phenolics and (C) antioxidant activity of microcapsules.

The total phenolic from black rice extract microcapsules is presented in **Figure 1**. In contrast to anthocyanins, the highest total phenolic was obtained after black rice extract was encapsulated with AG (95.83 mg GAE/100 g), then MD (75.49 mg GAE/100 g) and SMP (63.51 mg GAE/100 g) with a significant level of difference between treatments $p < 0.05$. The effectiveness of AG in the encapsulation of phenolic compounds in black rice extract has been reported by previous studies [21]. Protocatechuic acid was confirmed as the main phenolic acid found in black rice [5]. Ferulic, vanillic, coumaric and sinapic acids were also identified, but in lesser amounts than protocatechuic acids [22]. The better trapping of phenolic compounds in the AG structure is associated with the stability and emulsifying effect of AG in the microencapsulation of several phenolic compounds. In addition, the AG also has good dissolution properties of coating materials at different pH was found to be optimal when used for total phenolic analysis

[38,39]. MD has been found to have some potential disadvantages when used in the encapsulation of phenolic compounds. One of the main disadvantages is the formation of dry skins during the spray-drying process, which can lead to extensive cracking and brittleness of the microcapsules. This can affect the stability of the wall constituents and the ability of the microcapsules to withstand mechanical stresses [40]. Additionally, the use of MD alone may result in lower antioxidant activity compared to other encapsulating agents, such as AG [38]. The SMP results showed the lowest phenolic content compared to other coatings. Phenolic compounds can interact with milk proteins, leading to low recovery of phenolics and a decrease in antioxidant properties [41].

The total antioxidant activity of microcapsules based on MD, AG and SMP was 25.36, 43.88 and 37.73 % RSA, respectively (**Figure 1**). These data indicate that AG is the most recommended coating material for producing black rice extract microcapsules based on the antioxidant activity. In MD-based microcapsules, antioxidant activity can be ascribed to anthocyanins and phenolics of black rice extract. According to Gil *et al.* [42], MD as a coating material does not have the potential to contribute antioxidants to the resulting microcapsules. Unlike MD, AG and SMP coating materials have the potential to contribute antioxidants to microcapsules. This condition was reported by Wang *et al.* [43], whereby the components of sugar in AG and protein in SMP at high temperatures sustain Maillard reactions (MR) and produce melanoidin polymers that have antioxidant activity. This statement is further emphasized by Žilić *et al.* [44], that melanoidin and phenolic compounds contributed greatly to increasing the antioxidant activity of microcapsules of anthocyanin extract. Other studies have also reported that the addition of milk increases and stabilizes the antioxidant capacity of tea. This enhancement is attributed to the binding of milk proteins to tea polyphenols, which increases their bioavailability and scavenging capacity. [45].

Yield, moisture content and a_w of microcapsules

Yield of all microcapsules ranged from 36.82 to 52.89 % (**Table 1**). The yield of microencapsulated MD-based (42.08 %) was better than that of AG-based (36.82 %); this result is obedient with the yield of spray-dried grape skin anthocyanin extract [46]. The highest yield was achieved for SMP-based microcapsules (52.89 %). WPI is a promising coating material for anthocyanin encapsulation, this has previously been proven by Belščak-Cvitanović *et al.* [47], who compared milk protein-based microcapsules with other coating materials. The moisture content of microcapsules varied between 3.17 to 3.27 %, while the a_w value was in the range of 0.28 to 0.31 (**Table 1**). Black rice extract coated with SMP as a carrier showed a lower moisture content value than MD and AG. Čujić-Nikolić *et al.* [17] also reported similar results on chokeberry encapsulation. The high moisture and a_w content of AG-based microcapsules is possible due to the complex nature of hetero-polysaccharide AG and its branched structure containing shorter chains [48]. Thus, resulting in the easier absorption of water from the environment after the drying process [49]. Moisture content below 5 % ensures long-term product stability [50]. Products with a_w below 0.40 can be considered ideal conditions that do not support microbial growth [51] and overcome the problem of coagulation during storage [52].

Table 1 Physicochemical properties of black rice anthocyanin microcapsules.

Parameters	Wall Materials		
	MD	AG	SMP
pH	2.52 ± 0.04 ^a	2.63 ± 0.16 ^b	2.87 ± 0.02 ^c
Yield (%)	42.08 ± 1.22 ^b	36.82 ± 1.41 ^a	52.89 ± 1.83 ^c
Moisture content (%)	3.20 ± 0.02 ^b	3.27 ± 0.02 ^c	3.17 ± 0.03 ^a
a_w	0.31 ± 0.02 ^a	0.31 ± 0.01 ^a	0.28 ± 0.02 ^a

Note: The data are representations of the mean values ± standard deviation. Different superscripts in the same column showed statistically significant differences ($p < 0.05$).

Hygroscopicity and solubility of microcapsules

Low hygroscopicity may be better for the storage of microcapsule products such as anthocyanins, hygroscopicity can be defined as the ability of powdered products to absorb water molecules. The lowest hygroscopicity was observed in AG-based anthocyanin microcapsules, followed by microcapsules produced with MD and SMP. According to Mahdavi *et al.* [53], the difference in water absorption can be attributed to the molecular weight of particles produced with each agent, the high molecular weight coating material being less hygroscopic. Hygroscopicity is also inversely proportional to water content,

microcapsules with low moisture content tend to have a higher ambient moisture absorption capacity [54]. The morphology of a granule can affect its hygroscopicity by influencing its surface area and porosity. SMP has a good shape and a larger surface area (**Figure 3**). A granule with a larger surface area and greater porosity will generally have a higher hygroscopicity, as they have more sites available for water molecules to adsorb. So, it can absorb more moisture from the environment [55].

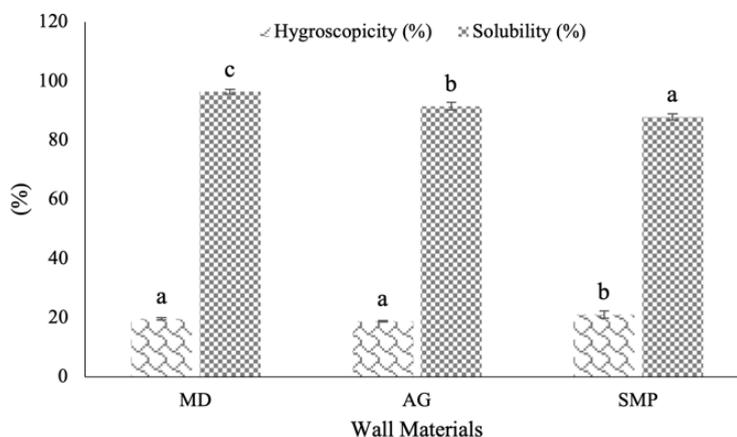


Figure 2 Hygroscopicity and solubility of microcapsules.

Solubility greatly determines the dissolution ability of a particle and is an important parameter that affects the functional characteristics of powders in food systems. The solubility of black rice anthocyanin microcapsules ranged from 87.86 to 96.42 % (MD > AG > SMP), this result was like that of grape skin extract microencapsulated with MD, AG and SMP reported by Kalušević *et al.* [46]. The high solubility in MD-based microcapsules was associated with the presence of a high hydroxyl group (-OH) in the molecule [56]. In addition, MD also produces a more amorphous and hollow particle structure, so it is more soluble in water. Particle size is also a factor in the high solubility of MD-based microcapsules; microcapsules with larger particle sizes are known to be more porous for the particle matrix to be more easily penetrated by liquids [57]. The solubility of a granule is influenced by its morphology. The morphology of a granule, which includes its size, shape and internal structure, affects its ability to dissolve in water. Granules with good shapes with a strongly bonded structure like microcapsules SMP based **Figure 2**. display relatively greater resistance and thus have lower solubility [58].

Table 2 Flow properties of black rice anthocyanin microcapsules.

Parameters	Wall Materials		
	MD	AG	SMP
Bulk density (g/cm ³)	0.35 ± 0.03 ^c	0.33 ± 0.01 ^b	0.29 ± 0.01 ^a
Tapped density (g/cm ³)	0.43 ± 0.03 ^b	0.44 ± 0.01 ^b	0.34 ± 0.02 ^a
Compressibility index (%)	18.27 ± 1.20 ^b	26.57 ± 1.53 ^c	15.34 ± 1.97 ^a
Hausner ratio	1.22 ± 0.02 ^b	1.36 ± 0.03 ^c	1.18 ± 0.03 ^a
Flowability	Fair	Poor	Good

Note: The data are representations of the mean values ± standard deviation. Different superscripts in the same column showed statistically significant differences ($p < 0.05$).

Flow properties of microcapsules

The density of microcapsules ranged from 0.29 to 0.33 g/cm³ for Bd and 0.34 to 0.44 for Td (**Table 2**). The range of Bd and Td values are within the distinctive density values of dry spray powder [59]. MD-based microcapsules showed the highest bulk and tapped density values, while the lowest density was observed in SMP, like those reported by Kalušević *et al.* [46]. Nkurunziza *et al.* [60] previously reported particle density with protein-based coating materials. This is possible because protein-based coating materials have spongy properties of microparticles, as in the case of sodium caseinate reported by Goyal *et al.* [61]. Bulk and tapped density values generally correlated with the CI and HR values of microcapsules. Consistent results were seen in this study where SMP-based microcapsules had the lowest CI (15.34) and HR (1.18), so they had good flow properties [32]. Flow properties of the powder products are also

determined by the structure and size distribution of the particles. When the particle structure is more porous, it tends to have a wider size distribution, so more cavities are formed. Density will increase because small particles fill the voids between particles [31].

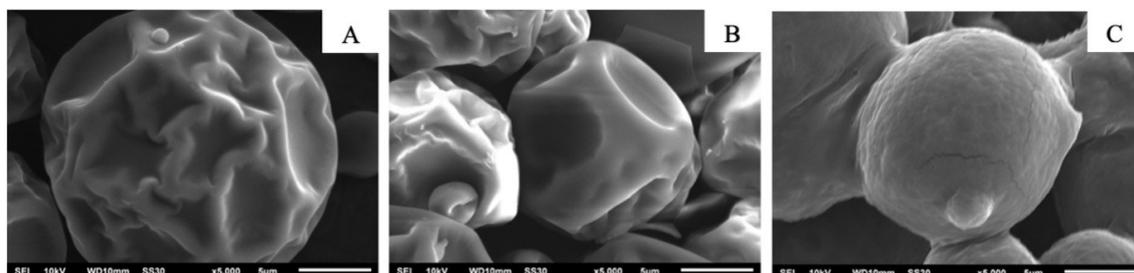


Figure 3 SEM micrographs of black rice anthocyanin microcapsules by (A) MD, (B) AG and (C) SMP.

Morphology of microcapsules

Production of anthocyanin microcapsules using different coating materials resulted in various shapes and sizes of microcapsules. SEM micrographs showed that the particle shape was not perfectly spherical, the outer surface was wrinkled, and the surface was smooth for the MD (**Figure 3(A)**) and GA (**Figure 3(B)**) microcapsules. In contrast, the SMP-based microcapsules (**Figure 3(C)**) were perfectly spherical with a slightly smooth surface. MD has been observed to contribute to the formation of wrinkles on the surface of microcapsules. This occurs due to mechanical stresses caused by moisture movement on the droplet surface during the drying process. The study on the fabrication of spray-dried microcapsules containing noni juice found that the microcapsules had irregular surfaces with wrinkles, and the occurrence of wrinkles was not significantly different among the samples [62]. Similar results were also reported by Ribeiro *et al.* [63] in his research on spray-dried carotenoid-rich microcapsules. Besides that, the wrinkles on the surface of microcapsules made with AG can be attributed to the drying process. Lower temperatures allow more time for the particles to deform, wrinkle and collapse [64,65]. The wrinkles are caused by the formation of a surface film very quickly during the drying process, resulting in the inside achieving a longer drying time. This causes an enlargement of the space in the microcapsules, which leads to the formation of dents [60,66]. In SMP-based microcapsules, the particles appear perfectly spherical with a slightly smooth surface, this result is different from that reported by Kalušević *et al.* [46] where the particles produced with SMP have a non-spherical shape with a very rough surface. The shape is caused by a temperature that is not ideal [67]. Production of casein microparticles and extract solutions with low pH is possible when high air temperature and low feed rate [68,69].

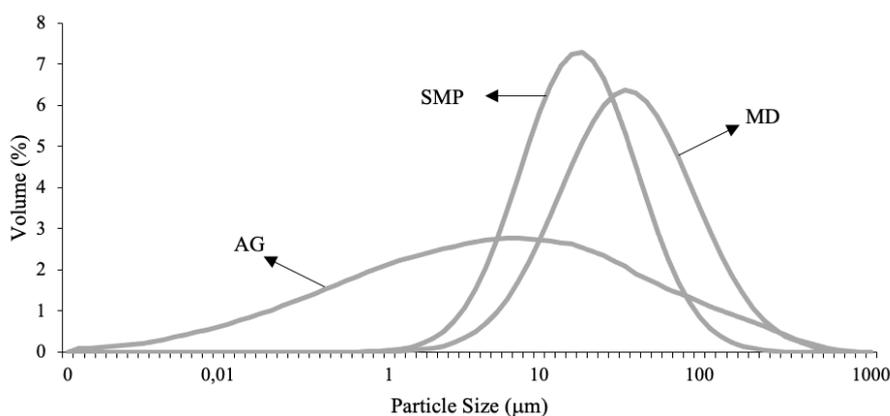


Figure 4 Particle size distribution images of black rice anthocyanin microcapsules.

Particle size distribution of microcapsules

Microcapsules acquired had an average particle size (d_{43}) in the range of 22.009 - 48.710 mm (**Table 3**), with a unimodal distribution pattern (**Figure 4**). The microparticle diameter of spray drying generally ranges from 10 to 100 mm [70]. SMP, as a coating for black rice anthocyanin extract, produced particles with a much smaller size than the MD and AG coatings, as indicated by the d_{90} value of 45.205 mm (**Table**

3). Particles with smaller sizes generally have a little difference in Bd and Td values, this is because the smaller average diameter of particles lowers the interstitial air content between particles, resulting in less free space [31]. The desired particle size depends on its utilization. Particles with a larger size allow the better release of bioactive components due to their large porosity. However, the smaller particle size provides better techno-functional properties [17].

Table 3 Particle size distribution parameters of black rice anthocyanin microcapsules.

Wall materials	d (4.3) μm	d (3.2) μm	d (0.1) μm	d (0.5) μm	d (0.9) μm
MD	48.710	19.553	9.082	30.873	104.916
AG	43.503	0.511	0.256	4.792	89.126
SMP	22.009	10.974	5.343	15.544	45.205

Color characteristic of microcapsules

The color attribute is one of the most important characteristics of a food product and its sensory appeal is first assessed by consumers. Therefore, it is necessary to observe the color attribute testing on anthocyanin microcapsules after the production process. The results of the measurement of chromatic parameters are presented in **Table 4**. Among all microcapsules produced by spray drying, microcapsules with SMP coating material had the lowest brightness values (L^*) and the highest values for attributes a^* and C^* , indicating that these anthocyanin microcapsules were the darkest with the highest proportion of red color. Protein-based coating materials have been widely reported to have anthocyanin stability effects through their molecular interactions. β -lactoglobulin, in protein-based coating materials, has a strong binding affinity for Cyanidin-3-glucoside through hydrophobic interaction for the color degradation of the extract during drying can be minimized [71].

Table 4 Color parameters of black rice anthocyanin microcapsules.

Wall materials	L^*	a^*	b^*	C^*	H°
MD	58.28 ± 0.79^b	29.71 ± 0.66^b	4.43 ± 0.31^b	29.39 ± 0.62^b	9.39 ± 0.81^b
AG	61.61 ± 0.79^c	24.16 ± 0.65^a	2.88 ± 0.32^a	23.68 ± 0.63^a	7.00 ± 0.88^a
SMP	39.58 ± 0.74^a	49.34 ± 1.43^c	12.75 ± 0.83^c	50.17 ± 1.18^c	14.74 ± 1.33^c

Note: The data are representations of the mean values \pm standard deviation. Different superscripts in the same column showed statistically significant differences ($p < 0.05$).

Conclusions

MD, AG and SMP coating materials produced black rice microcapsules with different physicochemical compositions and structure between treatments. In general, black rice microcapsules originating from various coatings contain bioactive anthocyanin and phenolic components as well as antioxidant activities that differ greatly between treatments. This difference is also found in the structural structure of microcapsules, namely structural morphology and particle size. Microcapsules with SMP coating material produced the highest anthocyanin levels and yields. Apart from that, these black rice microcapsules have low moisture content, a_w and hygroscopicity. On the other hand, it has high solubility, which is a very suitable characteristic to be used as a functional beverage product.

Acknowledgements

The authors would like to thank all parties who have been involved and contributed to this research, especially for funding by Ministry of Education, Culture, Research and Technology, the Republic of Indonesia for financial support through the program of PTUPT research scheme on behalf of Dr. Nurhidajah, M. Si.

References

- [1] BJ Prasad, PS Sharavanan and R Sivaraj. Health benefit of black rice - a review. *Grain Oil Sci. Tech.* 2019; **2**, 109-13.
- [2] K Nakagawa and H Maeda. Investigating pigment radicals in black rice using HPLC and multi -EPR. *J. Oleo Sci.* 2017; **66**, 543-7.
- [3] ESM Abdel-Aal, JC Young and I Rabalski. Anthocyanin composition in black, blue, pink, purple, and red cereal grains. *J. Agr. Food Chem.* 2006; **54**, 4696-704.
- [4] N Kanha, S Surawang, P Pitchakarn, JM Regenstein and T Laokuldilok. Copigmentation of cyanidin 3-O-glucoside with phenolics: Thermodynamic data and thermal stability. *Food Biosci.* 2019; **30**, 100419.
- [5] R Sompong, S Siebenhandl-Ehn, G Linsberger-Martin and E Berghofer. Physicochemical and antioxidative properties of red and black rice varieties from Thailand, China and Sri Lanka. *Food Chem.* 2011; **124**, 132-40.
- [6] XQ Chen, N Nagao, T Itani and K Irifune. Anti-oxidative analysis, and identification and quantification of anthocyanin pigments in different coloured rice. *Food Chem.* 2012; **135**, 2783-8.
- [7] Z Hou, P Qin, Y Zhang, S Cui and G Ren. Identification of anthocyanins isolated from black rice (*Oryza sativa* L.) and their degradation kinetics. *Food Res. Int.* 2013; **50**, 691-7.
- [8] D Samyor, AB Das and SC Deka. Pigmented rice a potential source of bioactive compounds: A review. *Int. J. Food Sci. Tech.* 2017; **52**, 1073-81.
- [9] LR Fukumoto and G Mazza. Assessing antioxidant and prooxidant activities of phenolic compounds. *J. Agr. Food Chem.* 2000; **48**, 3597-604.
- [10] O Norkaew, P Boontakham, K Dumri, ANL Noenplab, P Sookwong and S Mahatheeranont. Effect of post-harvest treatment on bioactive phytochemicals of Thai black rice. *Food Chem.* 2017; **217**, 98-105.
- [11] O Norkaew, P Thitisut, S Mahatheeranont, B Pawin, P Sookwong, S Yodpitak and A Lungkaphin. Effect of wall materials on some physicochemical properties and release characteristics of encapsulated black rice anthocyanin microcapsules. *Food Chem.* 2019; **294**, 493-502.
- [12] N Sharif, S Khoshnoudi-Nia and SM Jafari. Nano/microencapsulation of anthocyanins; a systematic review and meta-analysis. *Food Res. Int.* 2020; **132**, 109077.
- [13] H Rajabi, M Ghorbani, SM Jafari, AS Mahoonak and G Rajabzadeh. Retention of saffron bioactive components by spray drying encapsulation using maltodextrin, gum Arabic and gelatin as wall materials. *Food Hydrocolloids* 2015; **51**, 327-37.
- [14] MC Otálora, JG Carriazo, L Iturriaga, MA Nazareno and C Osorio. Microencapsulation of betalains obtained from cactus fruit (*Opuntia ficus-indica*) by spray drying using cactus cladode mucilage and maltodextrin as encapsulating agents. *Food Chem.* 2015; **187**, 174-81.
- [15] YV García-Tejeda, Y Salinas-Moreno, AR Hernández-Martínez and F Martínez-Bustos. Encapsulation of purple maize anthocyanins in phosphorylated starch by spray drying. *Cereal Chem.* 2016; **93**, 130-7.
- [16] SM Jafari, MG Ghalehnoei and D Dehnad. Influence of spray drying on water solubility index, apparent density, and anthocyanin content of pomegranate juice powder. *Powder Tech.* 2017; **311**, 59-65.
- [17] N Čujić-Nikolić, N Stanisavljević, K Šavikin, A Kalušević, V Nedović, J Samardžić and T Janković. Chokeberry polyphenols preservation using spray drying: Effect of encapsulation using maltodextrin and skimmed milk on their recovery following *in vitro* digestion. *J. Microencapsulation* 2019; **36**, 693-703.
- [18] JCG Rocha, FAR de Barros, ÍT Perrone, KWC Viana, GM Tavares, R Stephani and PC Stringheta. Microencapsulation by atomization of the mixture of phenolic extracts. *Powder Tech.* 2019; **343**, 317-25.
- [19] Y Suhag, GA Nayik and V Nanda. Effect of gum arabic concentration and inlet temperature during spray drying on physical and antioxidant properties of honey powder. *J. Food Meas. Char.* 2016; **10**, 350-6.
- [20] Y Gauan and Q Zhong. The improved thermal stability of anthocyanins at pH 5.0 by gum arabic. *LWT Food Sci. Tech.* 2015; **64**, 706-12.
- [21] A Kalušević, S Lević, B ČaliJa, M Pantić, M Belović, V Pavlović, B Bugarski, J Milić, S Žilić and V Nedović. Microencapsulation of anthocyanin-rich black soybean coat extract by spray drying using maltodextrin, gum arabic and skimmed milk powder. *J. Microencapsulation* 2017; **34**, 475-87.

- [22] VA Papillo, M Locatelli, F Travaglia, M Bordiga, C Garino, M Arlorio and JD Coisson. Spray-dried polyphenolic extract from Italian black rice (*Oryza sativa* L., var. Artemide) as new ingredient for bakery products. *Food Chem.* 2018; **269**, 603-9.
- [23] S Raharjo, FA Purwandari, P Hastuti and K Olsen. Stabilization of black rice (*Oryza sativa*, l. *Indica*) anthocyanins using plant extracts for copigmentation and maltodextrin for encapsulation. *J. Food Sci.* 2019; **84**, 1712-20.
- [24] N Kanha, JN Regenstein and T Laokuldilok. Optimization of process parameters for foam mat drying of black rice bran anthocyanin and comparison with spray- and freeze-dried powders. *Drying Tech.* 2022; **40**, 581-94.
- [25] Nurhidajah, A Rosidi, D Yonata and B Pranata. Optimizing extraction of functional compounds from Indonesian black rice using response surface methodology. *Food Res.* 2022; **6**, 83-91.
- [26] S Yamuangmorn, B Dell and C Prom-u-thai. Effects of cooking on anthocyanin concentration and bioactive antioxidant capacity in glutinous and non- glutinous purple rice. *Rice Sci.* 2018; **25**, 270-8.
- [27] AC Pedro, D Granato and ND Rosso. Extraction of anthocyanins and polyphenols from black rice (*Oryza sativa* L.) by modeling and assessing their reversibility and stability. *Food Chem.* 2016; **191**, 12-20.
- [28] OA Caparino, J Tang, CI Nindo, SS Sablani, JR Powers and JK Fellman. Effect of drying methods on the physical properties and microstructures of mango (*Philippine 'Carabao' var.*) powder. *J. Food Eng.* 2012; **111**, 135-48.
- [29] N Kanha, JM Regenstein, S Surawang, P Pitchakarn and T Laokuldilok. Properties and kinetics of the *in vitro* release of anthocyanin-rich microcapsules produced through spray and freeze-drying complex coacervated double emulsions. *Food Chem.* 2021; **340**, 127950.
- [30] N Nurhidajah, B Pranata, M Yusuf, YK Sya'di and D Yonata. Microencapsulation of umami flavor enhancer from Indonesian waters brown seaweed. *Curr. Res. Nutr. Food Sci.* 2022; **10**, 349-59.
- [31] M Yusuf, D Yonata, B Pranata and Nurhidajah. Utilization of swimming crab by-product as a seafood flavor microcapsule obtained by spray drying. *AACL Bioflux* 2022; **15**, 716-24.
- [32] P Lebrun, F Krier, J Mantanus, H Grohgan, M Yang, E Rozet, B Boulanger, B Evrard, J Rantanen and P Hubert. Design space approach in the optimization of the spray-drying process. *Eur. J. Pharm. Biopharm.* 2012; **80**, 226-34.
- [33] W He, H Mu, Z Liu, M Lu, F Hang, J Chen, M Zheng, F Qin and Z He. Effect of preheat treatment of milk protein on their interactions with cyanidin-3-O-glucoside. *Food Res. Int.* 2018; **107**, 394-405.
- [34] Z He, HH Zhu, M Xu, M Zeng, F Qin and J Chen. Complexation of bovine β -lactoglobulin with malvidin-3-O-glucoside and its effect on the stability of grape skin anthocyanin extracts. *Food Res. Int.* 2016; **209**, 234-40.
- [35] L Chen, N Chen, Q He, Q Sun and WC Zeng. Effects of casein on the stability, antioxidant activity, and bioavailability of lotus anthocyanins. *J. Food Biochem.* 2022; **46**, e14288.
- [36] LN Lestario, M Melanie and M Rahardjo. Effect of maltodextrin concentration on anthocyanin content and antioxidant activity of rukem fruits extract powder. *Jurnal Teknologi dan Industri Pangan* 2023; **34**, 142-51.
- [37] A Laga. The effect of encapsulant type on physical and chemical characteristics of anthocyanin extract powder from red dragon fruit *Hylocereus polyrhizus*. *IOP Conf. Ser. Earth Environ. Sci.* 2021; **807**, 022058.
- [38] A Tolun, Z Altintas and N Artik. Microencapsulation of grape polyphenols using maltodextrin and gum arabic as two alternative coating materials: Development and characterization. *J. Biotechnol.* 2016; **239**, 23-33.
- [39] N Čujić-Nikolić, N Stanisavljević, K Šavikin, A Kalušević, V Nedović, D Bigović and T Janković. Application of gum Arabic in the production of spray-dried chokeberry polyphenols, microparticles characterisation and *in vitro* digestion method. *Lekovite Sirovine* 2018; **38**, 9-16.
- [40] W Medfai, I Oueslati, E Dumas, Z Harzalli, C Viton, R Mhamdi and A Gharsallaoui. Physicochemical and biological characterization of encapsulated olive leaf extracts for food preservation. *Antibiotics* 2023; **12**, 987.
- [41] DD Milinčić, NS Stanisavljević, AZ Kostić, UM Gašić, SP Stanojević, ZL Tešić and MB Pešić. Bioaccessibility of phenolic compounds and antioxidant properties of goat-milk powder fortified with grape-pomace-seed extract after *in vitro* gastrointestinal digestion. *Antioxidants* 2022; **11**, 2164.
- [42] M Gil, A Restrepo, L Millán, L Alzate and B Rojano. Microencapsulation of banana passion fruit (*Passiflora tripartita* Var. *Mollissima*): A new alternative as a natural additive as antioxidant. *Food Nutr. Sci.* 2014; **5**, 44208.

- [43] HY Wang, H Qian and WR Yao. Melanoidins produced by the Maillard reaction: Structure and biological activity. *Food Chem.* 2011; **128**, 573-84.
- [44] S Žilić, T Kocadağlı, J Vančetović and V Gökmen. Effects of baking conditions and dough formulations on phenolic compound stability, antioxidant capacity and color of cookies made from anthocyanin-rich corn flour. *LWT Food Sci. Tech.* 2016; **66**, 597-603.
- [45] V Sharma, HV Kumar and LJM Rao. Influence of milk and sugar on antioxidant potential of black tea. *Food Res. Int.* 2008; **41**, 124-9.
- [46] AM Kalušević, SM Lević, BR Čalija, JR Milić, VB Pavlović, BM Bugarski and VA Nedović. Effects of different carrier materials on physicochemical properties of microencapsulated grape skin extract. *J. Food Sci. Tech.* 2017; **54**, 3411-20.
- [47] A Belščak-Cvitanović, S Lević, A Kalušević, I Špoljarić, V Đorđević, D Komes, G Mršić and V Nedović. Efficiency assessment of natural biopolymers as encapsulants of green tea (*Camellia sinensis* L.) bioactive compounds by spray drying. *Food Bioproc. Tech.* 2015; **8**, 2444-60.
- [48] B Bazarria and P Kumar. Effect of dextrose equivalency of maltodextrin together with Arabic gum on properties of encapsulated beetroot juice. *J. Food Meas. Char.* 2017; **11**, 156-63.
- [49] TTA Tran and HVH Nguyen. Effects of spray-drying temperatures and carriers on physical and antioxidant properties of lemongrass leaf extract powder. *Beverage* 2018; **4**, 84.
- [50] A Manickavasagan, K Thangavel, SRS Dev, DSA Delfiya, E Nambi, V Orsat and GSV Raghavan. Physicochemical characteristics of date powder produced in a pilot-scale spray dryer. *Drying Tech.* 2015; **33**, 1114-23.
- [51] B Ray and A Bhunia. *Fundamental food microbiology*. 5th ed. CRC Press, Boca Raton, Florida, United States, 2013.
- [52] SC Chew, CP Tan and KL Nyam. Microencapsulation of refined kenaf (*Hibiscus cannabinus* L.) seed oil by spray drying using β -cyclodextrin/gum arabic/sodium caseinate. *J. Food Eng.* 2018; **237**, 78-85.
- [53] SA Mahdavi, SM Jafari, E Assadpoor and D Dehnad. Microencapsulation optimization of natural anthocyanins with maltodextrin, gum arabic and gelatin. *Int. J. Biol. Macromol.* 2016; **85**, 379-85.
- [54] RV Tonon, C Brabet and MD Hubinger. Influence of process conditions on the physicochemical properties of açai (*Euterpe oleraceae* Mart.) powder produced by spray drying. *J. Food Eng.* 2008; **88**, 411-8.
- [55] ZG Liao, J Wang, XL Liang, N Zhang, SJ Zhong, LS Ming, GW Zhao and Y Luo. The relationship of flowability, hygroscopicity and compressibility properties between microcrystalline cellulose, Sarcandrae extract powder, and the mixture of the two materials. *Adv. Mater. Res.* 2013; **781-784**, 1115-21.
- [56] EL Avila, MC Rodriguez and HJC Velasquez. Influence of maltodextrin and spray drying process conditions on sugarcane juice powder quality. *Revista Facultad Nacional de Agronomía Medellín* 2015; **68**, 7509-20.
- [57] SC Lourenço M Moldão-Martins and VD Alves. Microencapsulation of pineapple peel extract by spray drying using maltodextrin, inulin, and arabic gum as wall matrices. *Foods* 2020; **9**, 718.
- [58] OO Olayinka, KO Adebawale and IB Olu-Owolabi. Physicochemical properties, morphological and X-ray pattern of chemically modified white sorghum starch. (Bicolor-Moench). *J. Food Sci. Tech.* 2013; **50**, 70-7.
- [59] HCF Carneiro, RV Tonon, CRF Grosso and MD Hubinger. Encapsulation efficiency and oxidative stability of flaxseed oil microencapsulated by spray drying using different combinations of wall materials. *J. Food Eng.* 2013; **115**, 443-51.
- [60] D Nkurunziza, SP Silvagnanam, JS Park, YJ Cho and BS Chun. Effect of wall materials on the spray drying encapsulation of brown seaweed bioactive compounds obtained by subcritical water extraction. *Alga Res.* 2021; **58**, 102381.
- [61] A Goyal, V Sharma, MK Sihag, SK Komar, S Arora, L Sabikhi and AK Singh. Development and physico-chemical characterization of microencapsulated flaxseed oil powder: A functional ingredient for omega-3 fortification. *Powder Tech.* 2015; **286**, 527-37.
- [62] C Zhang, SLA Khoo, P Swedlund, Y Ogawa, Y Shan and SY Quek. Fabrication of spray-dried microcapsules containing noni juice using blends of maltodextrin and gum acacia: Physicochemical properties of powders and bioaccessibility of bioactives during *in vitro* digestion. *Foods* 2020; **9**, 1316.
- [63] MLFF Ribeiro, YH Roos, APB Ribeiro and VR Nicoletti. Effects of maltodextrin content in double-layer emulsion for production and storage of spray-dried carotenoid-rich microcapsules. *Food Bioprod. Process.* 2020; **124**, 208-21.

- [64] LC Corrêa-Filho, MM Lourenço, M Moldão-Martins and VD Alves. Microencapsulation of β -carotene by spray drying: Effect of wall material concentration and drying inlet temperature. *Int. J. Food Sci.* 2019; **2019**, 8914852.
- [65] AM Ribeiro, M Shahgol, BN Estevinho and F Rocha. Microencapsulation of vitamin A by spray-drying, using binary and ternary blends of gum arabic, starch and maltodextrin. *Food Hydrocolloids* 2020; **108**, 106029.
- [66] Y Kagami, S Sugimura, N Fujishima, K Matsuda, T Kometani and Y Matsumura. Oxidative stability, structure, and physical characteristics of microcapsules formed by spray drying of fish oil with protein and dextrin wall materials. *J. Food Sci.* 2003; **68**, 2248-55.
- [67] T Laokuldilok and N Kanha. Effects of processing conditions on powder properties of black glutinous rice (*Oryza sativa* L.) bran anthocyanins produced by spray drying and freeze drying. *LWT Food Sci. Tech.* 2015; **64**, 405-11.
- [68] E Bylaitė, PR Venskutonis and R Maždpierienė. Properties of caraway (*Carum carvi* L.) essential oil encapsulated into milk protein-based matrices. *Eur. Food Res. Tech.* 2001; **212**, 661-70.
- [69] OA Bayram, M Bayram and AR Tekin. Whey powder as a carrier in spray drying of sumac concentrate. *J. Food Process Eng.* 2008; **31**, 105-19.
- [70] Z Fang and B Bhandari. Encapsulation of polyphenols: A review. *Trends Food Sci. Tech.* 2010; **21**, 510-23.
- [71] J Cheng, JH Liu, G Prasanna and P Jing. Spectrofluorimetric and molecular docking studies on the interaction of cyanidin-3-O-glucoside with whey protein, β -lactoglobulin. *Int. J. Biol. Macromol.* 2017; **105**, 965-72.