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Color-tunable particles through affinity interactions between water-insoluble protein and soluble dyes

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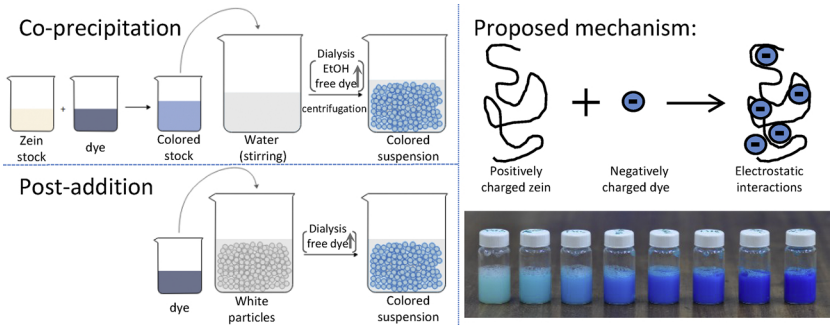
GRAPHICAL ABSTRACT



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ABSTRACT

This research is focused on the delivery of color using zein particles as a carrier and contributes to understanding the interactions between colorants and zein. Co-precipitation of purified zein protein with anionic dyes such as sulfonate group containing azo-dyes (patent blue sodium salt, azorubine, and fast green FCF) are used to prepare red, green, and blue colored nanoparticles. These dyes had electrostatic interactions with zein and they remained bound in the zein particles even after dialysis. This was not the case for purpurin, for with hydrogen bonding was expected as interaction. Upon increasing dye concentration, the particle sizes increased as a result of a change in the kinetics of precipitation, which was affected by the association between zein and the dye. However, the encapsulation efficiency continued to be very high and no plateau was reached for the used concentrations. The post-addition of dye on undyed zein particles was used to confirm that there is indeed a high affinity between the dye and the protein. The amount of free dye was determined and the affinity was again found to be high (dye adsorption < 95%). The amount of dye incorporated into the particles and the resulting color were similar using both techniques. These results show that there is a high affinity between the zein protein and the dye, and may be exploited to produce bio-based and optically-functionalized nanoparticles using zein as a carrier.

1. Introduction

Nowadays, there is more and more a consumer demand for natural food products [1,2]. This consumer pull has led to an enormous growth in research towards hydrocolloids, encapsulation and composite particle formation in which natural or functional ingredients are used for

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the application of food systems [3,4]. Promising types of carriers for such hydrocolloid systems are proteins from both animal and plant origins. Examples include whey, casein, gliadin, and zein [5].

Zein is a hydrophobic protein extracted from corn and is classified as a prolamin. It is generally recognized as safe (GRAS) and is biocompatible, biodegradable, non-toxic, and edible [6,7]. Moreover, it is soluble in food safe solvents, such as water-ethanol mixtures. All of these properties make this protein a good candidate for many applications. Over the years, zein has been extensively researched for its use in forming coatings [8,9], fibers [10,11] and micro- and nanoparticles [12,13]. Encapsulation with zein as a carrier has been investigated for many applications, such as drug delivery, delivery of essential oils, micro-nutrients, and color [14–17]. The capability of zein, or any biopolymer for that matter, to form particles and to entrap colorants is directly influenced by different conditions such as medium polarity, steric and electronic parameters, pH and charge of the solute [18–20]. On the other hand, colloidal particles can also be used to tune the coloring or optical properties of particle suspensions [17] or even as a white colorant on their own without adding additional colorant [21].

This research will be focused on the delivery of color using zein particles as a carrier and contributes to understanding the interactions between colorants and zein. Food products are complex multi-component systems in which molecular interactions are present between macromolecules, small molecules and ions. These molecules have different interactivities including electrostatic interaction, hydrogen bonding, hydrophobic interaction, coordination force, π-π stacking and more. These interactions usually have dual effects on quality and functionality of foods. They can cause undesired properties such as reduced solubility and stability, but also can enhance the quality and functionality of foods [22]. These interactions are important for the addition of colorants in food products, where colorants are used to make these products more attractive to consumers. Color has been shown to be of primary importance in the initial judgment of food, ultimately influencing the acceptance or rejection of this food product [23,24].

Four water-soluble dyes were selected for this project, one of which is non-ionic: purpurin, which results in a red color. Three dyes are anionic, since they are the sodium salts of the conjugate bases of strong acids: patent blue sodium salt (E131), azorubine (E122), and fast green (E143), which result in a blue, red, and green color, respectively. Molecular structures of these dyes are shown in Fig. 1. Patent blue, azorubine and fast green are all used as synthetic food colorants. Purpurin is a naturally occurring colorant not used for food coloring, but for cotton dyeing. To encapsulate colorants or create composite particles, it is important that the carrier and the functional ingredient have some affinity to each other. This affinity can be, for example, electrostatic interactions, a solubility difference of the pre-mix compared to the final medium, or hydrogen bonding [25]. Here, we demonstrate

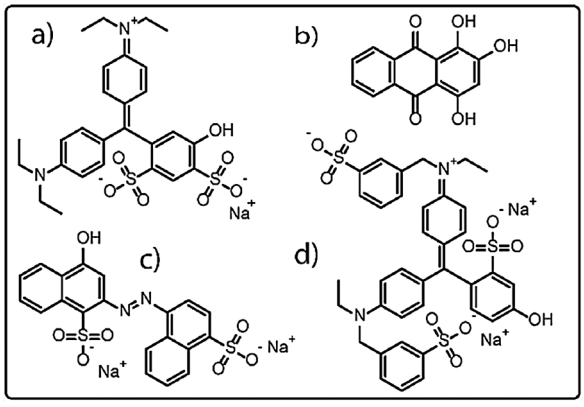

Fig. 1. Structures of used dye molecules, a) patent blue sodium salt, b) purpurin, c) azorubine and d) fast green FCF.

that electrostatic interactions are sufficient for water-soluble dyes to be encapsulated with zein. The same principle may therefore be employed to encapsulate other components, such as anionic natural colorants.

For all of these dyes it is investigated if it is possible to co-precipitate them with zein and stay inside of the particles after dialysis. After that, more specific research will be done for one selected sample. For patent blue V sodium salt, different particle sizes were synthesized and compared to white reference particles without dye. Also the effect of dye concentration on the final particle size was investigated. Then a comparison is made between two different ways to obtain colored particles: via co-precipitation of the zein together with the dye or using post synthesis addition of the dye, in which the dye was added to a white particle suspension. Colorimetric analysis was performed on the resulting particles of both these techniques to map the observed differences between the two techniques.

2. Methods and Materials

Food grade zein was purchased at Flo Chemical Corporation, type F4000C FG (lot nr. F40006021C2). Ethanol (absolute, technisolv) was purchased at VWR. Hydrochloric acid (HCl), purpurin, fast green FCF, and patent blue V sodium salt were purchased at Sigma-Aldrich. Water was purified using a Millipore Direct-Q purification system.

2.1. Particle synthesis by co-precipitation of zein and water-soluble colorant

Prior to all particle synthesis, most of the removable colored impurities were extracted from the zein powder to eliminate effects of these impurities on the particle synthesis and further characterization, by washing this in ethanol, as described in previous work [21].

The purified stock solution was diluted with 85 wt% aqueous ethanol to prepare a range of different wt% zein solutions. The resulting solutions will be referred to as zein solutions. Water soluble dye (patent blue sodium salt, azorubine, fast green, or purpurin, see Fig. 1) was dissolved in the zein solutions in different ratio's dye to zein D:Z) prior to particle synthesis. To synthesize particles, 10 mL of colored zein solution was quickly added to a beaker with water (120 mL), while stirring at 280 rpm with a magnetic stirring bar. Directly after synthesis the encapsulation efficiency was determined (see section 2.2.4.) A three-day dialysis of the resulting suspension against water adjusted to a pH of 4 with HCl was performed to remove the remaining ethanol and free colorant. During dialysis the suspensions was kept in the dark to prevent possible color changes. The pH of the dialysis liquid was measured using pH paper, Whatman indicator 3.8–5.5 range. During this dialysis, the medium was replaced 3 times. Dialysis tubing membranes were purchased at Sigma-Aldrich, and had a molecular weight cut-off of 14,000 Da. The resulting colloidal suspension was then centrifuged for 30 min at 222 rcf to remove possible large aggregates. Finally, the samples were stored in the fridge at 7 °C prior to DLS, zeta-potential and colorimetric experiments. During experiments we did not observe any color change of changes in peak positions during UV-measurements. Also all experiments were performed within two weeks of the particle synthesis, during which time we observed no color changes.

To investigate the effects of increasing concentration of dye, the initial zein concentration in the zein solution was kept the same, while increasing the concentration of dye. D:Z weight ratios varied from 0.0025 to 0.02. No higher dye concentrations were prepared because of difficulties in dissolving higher concentrations of dye.

2.2. Particle synthesis by post-addition of water-soluble colorant

For post-addition of the dye, first particles were synthesized from the purified zein as described in section 2.2.1 but without any dye, also dialysis was performed to remove the ethanol. Then, aqueous solutions of different concentrations of dye were added to the zein particle

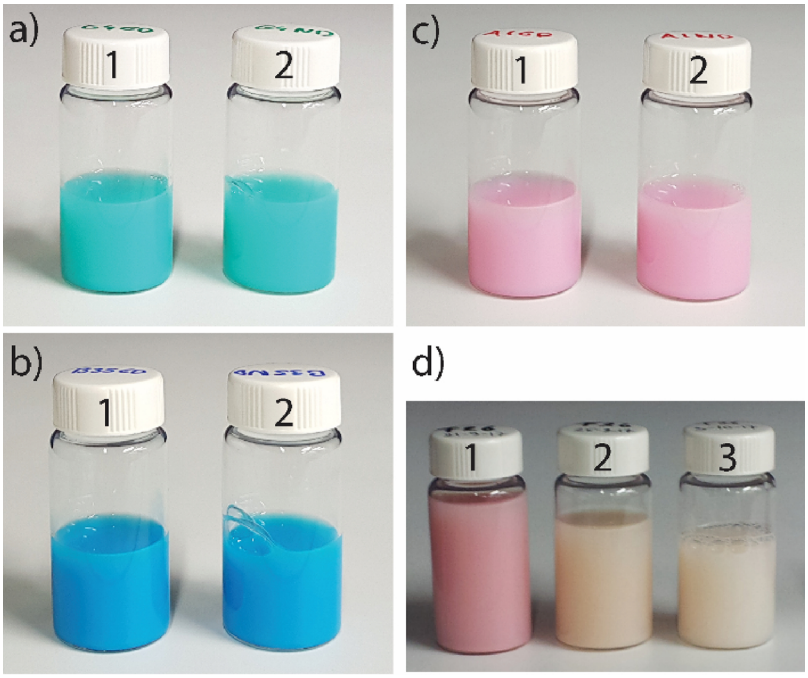

Fig. 2. Zein particle suspensions with different dyes: (a) fast green FCF, (b) patent blue sodium salt, (c) azorubine, and (d) purpurin, before (1) and after (2) dialysis, and (3) after extended dialysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

suspensions while stirring. After addition of the dye, the samples were stirred for 30 min. Then the amount of adsorbed dye was determined spectrophotometrically (section 2.2.5). Finally, the samples were dialyzed against water adjusted to a pH of 4 with HCl to remove any non-adsorbed colorant. Then particle size, zeta-potential, and colorimetric experiments were performed. Samples were stored in the fridge at 7 °C.

2.3. Size and zeta-potential measurement

Particle sizes and charges were measured by dynamic light scattering (DLS) and electrophoresis, using a Zetasizer Nano ZS series, Malvern Instruments. In DLS a CONTIN analysis was used to obtain the size distributions. Prior to the DLS and zeta potential measurements, the samples were synthesized as described in Section 2.2.1 and dialyzed to remove ethanol and remaining free colorant. Then samples were diluted to a suitable, low concentration to prevent multiple scattering, with water adjusted to pH 4 with HCl, which was checked using a Mettler Toledo FiveEasy pH meter, to prevent changes in pH from affecting the measurements.

2.4. Encapsulation efficiency (EE) and adsorption

After co-precipitation or post-addition synthesis, a sample of the suspension was filtered using a Vivaspin tube (Sartorius, equipped with a 100,000 MWCO membrane) using an applied pressure of 4 bar, to separate the particles from the medium. The encapsulation efficiency or adsorption was determined as follows:

$$EE = \frac{c_t - c_m}{c_t} 100\%$$

Here, *EE* is the encapsulation efficiency or adsorption, c_t is the concentration of dye added to the synthesis and c_m is the concentration of free dye in the medium. From this calculation also the total concentration of dye inside of the particles, c_p, can be calculated from $c_p = c_t - c_m$. UV–vis spectroscopy (HP 8953 A spectrophotometer) was used to determine the concentration of free dye in the medium at a wavelength of 638 nm for patent blue, 522 nm for azorubine, 624 nm for fast green, and 256 nm for purpurin. Concentrations were calculated by comparison with an appropriate calibration curve using the same medium as the particle suspensions. All samples were measured within two weeks after synthesis.

2.5. Colorimetry

The color of the zein suspensions was determined by using the Digi-Eye (VeriVide). 5 mL of sample suspension was pipetted into a 3.5 cm diameter petri-dish and placed in the Digi-Eye apparatus. The Digi-Eye is equipped with a D65 daylight lamp which was used as lighting for taking a photograph of colored samples. The Digi-Eye software was used to determine the CIE XYZ tristimulus values and the L*a*b* values. From this the CIE XYZ tristimulus values were calculated to x and y coordinates for representation in the CIE diagram via $x = X/(X + Y + Z)$ and $y = Y/(X + Y + Z)$.

3. Results

3.1. Effects of type of dye on encapsulation

Since zein is extracted from a natural product, colored impurities such as β-carotene, zeaxanthin and lutein are in some quantity still present in the obtained zein powder [26,27]. When performing research on encapsulating color with zein it is important to eliminate color effects from these yellow impurities. Therefore, efforts were made to purify this yellow zein to obtain so called white zein [28], as described in the experimental section.

In this research, the encapsulation into zein nanoparticles of four dyes was investigated: patent blue V sodium salt, purpurin, azorubine, and fast green FCF, see Fig. 1a–d, respectively. D:Z ratios used were 0.0025 for fast green FCF, patent blue V sodium salt, and azorubine, for purpurin a D:Z ratio of 0.0026 was used. Here, patent blue, azorubine, and fast green were used as examples to investigate whether electrostatic interactions play a role in the encapsulation in zein particles and purpurin was used as an example to investigate whether hydrogen bonding plays a role.

Directly after synthesis the suspensions with all used dyes were strongly colored (Fig. 2a, b, c and d vial 1). After dialysis to remove free

dye all suspensions retained their strong coloration, except the sample that was co-precipitated with purpurin (Fig. 2a–d vial 2). After an extended dialysis time of 8 more days, this sample (Fig. 2d vial 3) became less colored. Apparently, the affinity between zein and purpurin is lower than that between zein and the anionic dyes. However, the dialysis clamp used in the purpurin dialysis did get colored, which indicates that purpurin has a higher affinity with the material of the dialysis clamp then with the zein protein. These results suggest that a charge is more important for particle formation with zein than hydrogen bonding [29], which was the affinity between purpurin and zein. This difference can be explained by the fact that the zein particles have a positive charge at a pH of 4. This means that anionic dye molecules will have electrostatic affinity with the zein protein, while purpurin does not. Since the isoelectric point of zein is in the range of 5.8–6.5 [30], samples were always prepared at a pH below this value. When the pH shifts from 4 to above the isoelectric point (6.2), the zein precipitates and the dye is released. This occurs for both co-precipitated and post-addition samples.

This phenomenon, in which anions and therefore electrostatic interactions play a role in formation of complex structures of zein while adding a stabilizer or functional ingredient, has previously been discussed in literature [6,31–33]. More specifically, zein nanoparticles have been recently proposed as a disperse solid-phase extraction adsorbent for determining trace amounts of azorubine in foodstuffs [34], although the particle preparation was somewhat different. It was even possible to use this solid phase extraction technique to extract nitrite ions from environmental samples using zein [35], which again shows that anions in solution can be successfully made into composite particles with zein. For the remaining part of the paper we will focus on patent blue sodium salt, as the behavior of this particular dye is expected to be similar to azorubine and fast green as water soluble dyes.

3.2. Influence anionic dye on zein particles synthesized by co-precipitation

To determine the influence of the addition of dye on the particle size, reference particles without dye were synthesized and compared to colored particles synthesized via co-precipitation, using the same ratio of dye to zein for all particles (0.0025). These samples were compared using DLS, see Fig. 3. Similar to reference samples, without dye, particle sizes can be tuned by using different starting concentrations of zein in the zein solution [21]. Compared to the reference samples, colored particles seem to be similar in size. In Fig. 3 it is visible that, when viewing the particle sizes of the first and the second set of blue particle, the synthesis is not fully reproducible. Particle sizes of the colored samples differ from the reference samples in which there was a trend visible where upon increasing zein stock concentrations particle sizes increased, this was not the case for colored samples. This shows that it is more difficult to control the particle size when co-precipitating with dye compared to particles synthesized without a dye. Especially since the reproducibility of the reference samples was found to be good (see Fig. S1 in the supplementary information). A reason for this observation is that the kinetics of the precipitation is affected by the association between zein and the dye, and therefore the zein/dye solution forms particles in a different way than when no dye was added to the zein solution. It has been reported in literature that after encapsulation, particle sizes can increase or stay a similar size, depending on the used system [36].

For these zein to dye ratios, the encapsulation efficiency was 100% which is due to the relatively low amounts of dye used, and the expected high affinity of zein with the dye. Zeta-potentials were on average 47 ± 7 mV, which is similar to ones found for white zein particles and comparable to values found in literature [37,38].

Next, a series of zein suspensions was prepared by co-precipitation with varying patent blue concentration keeping the zein concentration constant. Results are shown in Table S1. The pH after precipitation was measured to test for differences between the colored and reference sample. The pH of the colored suspension directly after synthesis was on average 4.4 ± 0.1 and was nearly similar for all concentrations of dye added to the synthesis, see Table S1. The pH of the colored samples was slightly higher than the pH of the reference sample (pH = 4.2). The pH and ζ-potential of the reference sample precipitated without dye are comparable with values found in literature [37,38]. A variation in zeta potential from 37 to 50 mV is observed for the colored particles. However, no clear trend is observed (see Fig. 4). It was expected that when incorporating anionic molecules, the zeta potential would decrease when the dye is encapsulated to a high extent Overall, the zeta potential does seem to decrease upon increasing dye concentration. Further inspection reveals that any possible trend is masked by the spread between different preparations.

Interestingly, particle sizes increased upon increasing dye concentration, see Fig. 5. Probably, the kinetics of the precipitation are affected by the association between the zein and the dye, resulting in larger particles upon higher dye concentrations and a less clear trend in the zeta potential. Encapsulation efficiencies are all very similar and very high, even at the highest dye concentrations, see table S1. When higher concentrations of dye are incorporated, the encapsulation efficiency seems to decrease slightly, however, not as much as expected when adding an excess of dye. No plateau is reached, even after addition of relatively high dye concentrations. This indicates that there must

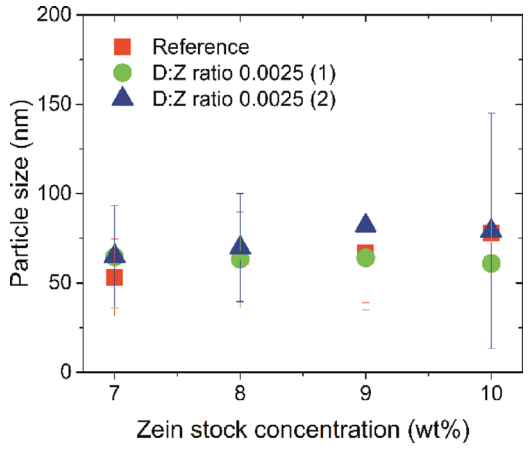

Fig. 3. Particle sizes measured by DLS of colloidal suspensions synthesized with and without (reference) the addition of patent blue of one set of blue particles (1) and a second set (2). The vertical bars show the standard deviation of the size distribution.

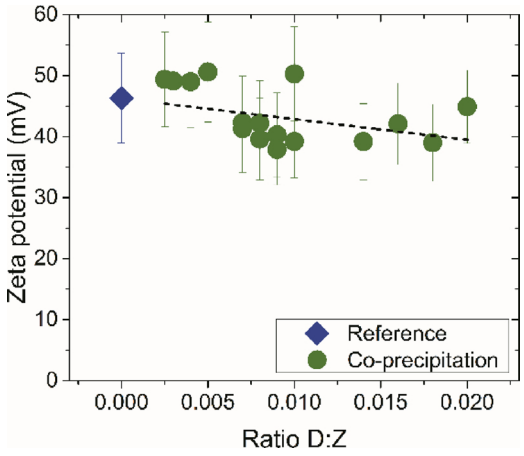

Fig. 4. Zeta-potentials of co-precipitation samples, upon increasing concentrations of patent blue used in the co-precipitation. of an initial zein solution concentration of 10 wt%. The dotted line is present to guide the eyes.

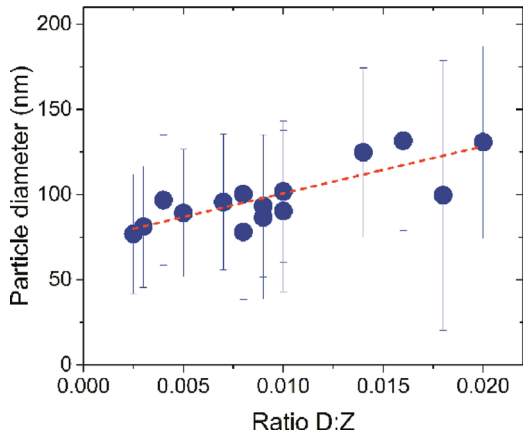

Fig. 5. Particle diameter, measured by DLS, upon increasing patent blue concentration in the particles while keeping the initial zein solution concentration at 10 wt%. The vertical bars show the standard deviation of the size distribution. The dotted line is present to guide the eyes.

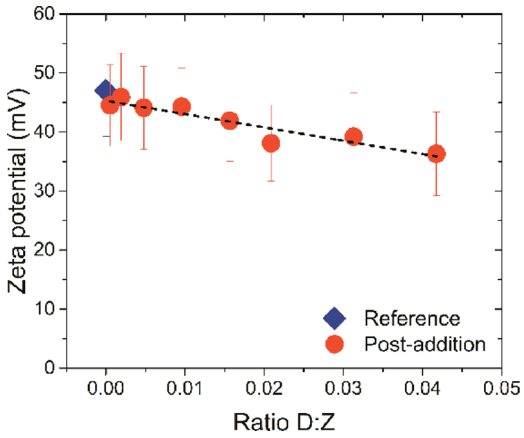

Fig. 7. Zeta-potentials of post-addition samples, upon increasing concentrations of patent blue added to white particles of an initial zein solution concentration of 10 wt%. The dotted line is present to guide the eyes.

be a very high affinity between dye and zein protein, which is also indicated by the increase of particle sizes upon increasing dye concentration, see Fig. 5 and Table S1. An increase of particle size upon higher loading has been described for a different system, in which anionic surfactant sodium dodecyl sulfate was added to zein particles [39], for the case here we have an anionic dye which behaves in a similar manner. To show that there is indeed a high affinity between zein and the dye we will show that particles can also be dyed with post-precipitation addition of dye to **white** particles, which will be discussed in the next section.

3.3. Co-precipitation versus post-addition of dye

The nature of interaction was not only determined by using co-precipitation as described earlier in this paper, but also by using post-addition of the dye. Here, white particles were synthesized first, after which different concentrations of dye (ranging from a D:Z ratio of 0.0005 to 0.0417) were added to the suspensions. After dialysis to remove free dye, colored suspensions were again obtained, see Fig. 6.

Particle sizes are constant upon increasing dye concentrations, see table S2. This is different compared to the co-precipitation technique but this is expected since the particles were synthesized prior to adding the dye. Zeta potentials start from a similar value as the reference (which is the original white particle suspension). From this value the zeta potential gradually decreases as more dye is added, see Fig. 7 and Table S2. This can be caused by the adsorption of the dye onto the surface of the particles, thus lowering the zeta potential. The zeta potential seems to be lower for post-addition samples than for the co-precipitated samples with increasing dye concentration. A reason for this might be that in the co-precipitated samples the zein was pre-mixed with the dye and therefore the dye is more homogeneously dispersed in the particle, while in the post-addition samples the surface of the particle is enriched with dye.

When studying the affinity between the dye and the zein particles, it was found that the amount of free dye in the medium was very low and therefore the affinity was found to be high, > 95%. It is interesting that, similarly to the co-precipitation experiments, also here no plateau is reached, underlining the high affinity between zein and dye. When looking at D:Z ratios and concentration in the particles of Tables S1 and S2, it is clear that for both co-precipitation and post-addition comparable concentrations of dye end up bound to the particles. The high affinity makes it possible to reach equally high dye concentrations in zein particles by both co-precipitation and post-addition techniques.

Different shades of blue can be easily created by varying the concentration of dye added to the particle suspension. This is similar to samples synthesized via co-precipitation. Color data of the post-addition samples, a reference, and co-precipitated samples are shown in Table 1 and are summarized after calculating their CIE x,y-values in the CIE diagram in Fig. 8. The reference sample is observed as white, and upon increasing dye concentration, the color shifts to dark blue for both co-precipitated and post-addition samples.

The first co-precipitated sample (Co-p 1) yields a color that is placed in the CIE-diagram between sample B and C. This is the expected location in the CIE-diagram for this sample when looking at the D:Z ratios, similar results are shown for other dye concentrations in Table 1 and Fig. 8. For higher concentrations the values are much closer together, however, the same trend continues. Sample Co-p 5 should be

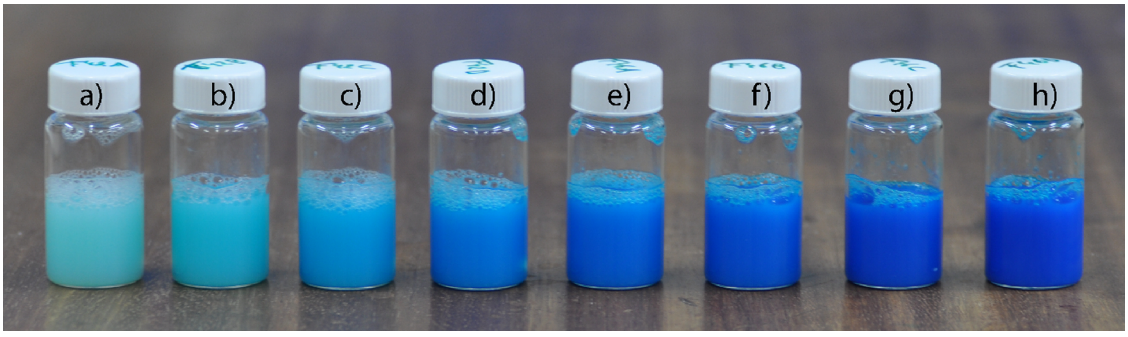

Fig. 6. A range of dye concentrations, D:Z ratios (a) 0.0005, b) 0.0019, c) 0.0048, d) 0.0096, e) 0.0156, f) 0.0209, g) 0.0313, and h) 0.0417) were used in post-addition of dye in the same batch of particles. This resulted in suspensions with different shades of blue (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 1
CIE and L*a*b* color data measured by the DigiEye for a reference sample without dye, post-addition samples A to H, and samples synthesized via co-precipitation (co-p 1–11).

Sample	Zein (wt%)	D:Z	X	Y	Z	L*	a*	b*
reference	10	0	78.63	83.32	83.12	93.15	−0.72	4.52
A	10	0.0005	45.09	59.50	71.47	81.56	−30.25	−6.45
B	10	0.0019	34.58	49.95	68.91	76.04	−39.50	−13.86
C	10	0.0048	20.68	33.81	60.56	64.81	−47.37	−25.95
D	10	0.0096	14.88	25.83	55.41	57.88	−48.71	−33.08
E	10	0.0156	12.89	21.37	51.67	53.35	−41.83	−37.19
F	10	0.0209	11.38	17.78	47.05	49.22	−34.46	−39.49
G	10	0.0313	10.21	14.77	41.99	45.32	−26.42	−40.57
H	10	0.0417	9.63	12.78	37.97	42.43	−18.60	−40.72
Co-p 1	10	0.0025	29.72	44.87	69.74	72.81	−43.14	−20.13
Co-p 2	10	0.0040	19.57	32.84	61.48	64.03	−49.48	−28.14
Co-p 3	10	0.0050	17.84	30.6	60.23	62.16	−50.41	−30.21
Co-p 4	10	0.0070	16.21	27.34	58.29	59.29	−47.02	−33.38
Co-p 5	10	0.0080	15.57	26.33	57.69	58.35	−46.67	−34.44
Co-p 6	10	0.0090	14.9	25.08	56.56	57.15	−45.49	−35.44
Co-p 7	10	0.0100	14.56	24.5	56.62	56.58	−45.09	−36.47
Co-p 8	10	0.0140	12.93	21.47	53.43	53.46	−41.99	−38.77
Co-p 9	10	0.0160	12.09	20.3	51.75	52.17	−42.17	−39.31
Co-p 10	10	0.0180	11.84	18.97	50.01	50.65	−37.4	−40.14
Co-p 11	10	0.0200	11.63	18.52	49.13	50.12	−36.59	−40.14

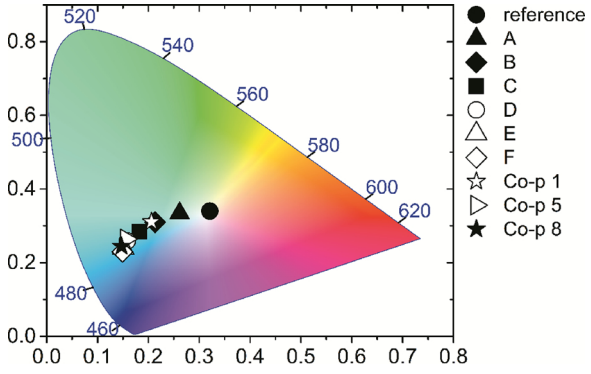

Fig. 8. CIE diagram with CIE color data calculated from Table 1.

between C and D, which is the case. It can even be observed that Co-p 5 is closer to D than to C, which is to be expected when viewing the D:Z ratio in Table 1. According to the D:Z ratio, sample Co-p 8 should be in between sample D and E, which also follows from the CIE diagram. This result shows that the observed color is independent of whether the particle was synthesized using co-precipitation or that the color is added to the particles via post-addition of the dye. Which means that similar colors can be achieved by using both techniques.

4. Conclusions

Summarizing, co-precipitation of purified zein protein with anionic dyes, such as patent blue sodium salt, azorubine and fast green FCF, were able associate with the zein colloids, even after dialysis. This was not the case for the non-ionic dye, purpurin. Observing similar results for the three anionic dyes, the remaining experiments were performed with patent blue sodium salt. It is found that co-precipitation and post-addition techniques yield similar results in terms of concentration and adsorption or encapsulation, zeta potential, and color appearance. Particle sizes increased upon increasing dye concentration for co-precipitated samples, while for post-addition samples the particle size was similar to the original white particles. The results described in this paper show that there is high affinity between anionic dyes and the zein protein. It is expected that for the co-precipitation technique the mechanism is as follows: first, zein is dissolved in aqueous ethanol, then the dye is added which adsorbs on the zein proteins and then particles are formed by precipitation after mixing with the anti-solvent water. Colored particles synthesized via post-addition follow a different route. First particles are synthesized and then dye is added and adsorbs from the outside of the particle, indicating the high affinity between zein and dye. These results show that there is a high affinity between the zein protein and the dye. This may be exploited to produce bio-based and optically-functionalized nanoparticles using zein as a carrier.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.colsurfa.2018.11.021.

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