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## Preparation of composite zein/natural resin nanoparticles

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**Abstract:** The aim of this work was to investigate a possibility of preparing composite zein/natural resin (shellac and rosin) nanoparticles by antisolvent co-precipitation from their aqueous ethanol solutions. Influence of zein/resin mass ratio (1/0, 0.8/0.2, 0.5/0.5, 0.4/0.6 and 0/1) and pH (2–12) on particle size, *d*, and zeta potential,  $\zeta$ , of the prepared particles was studied. The functional properties of zein/rosin composite nanoparticles were evaluated by studying carvacrol encapsulation. It was shown that the antisolvent precipitation can be successfully used to prepare the shellac and rosin nanoparticles, as well as the composite zein/shellac and the zein/rosin nanoparticles. Colloidal properties, *d* and  $\zeta$ , of the obtained nanoparticles are influenced by the zein/resin mass ratio and the pH of nanoparticles' dispersions. The isoelectric point of composite nanoparticles can be modulated by varying the zein/resin mass ratio. It was found that the zein/rosin nanoparticles are suitable for carvacrol encapsulation, where carvacrol release is enhanced by increasing the rosin share in the composite zein/rosin nanoparticles.

**Keywords:** zein; shellac; rosin; biopolymer; encapsulation.

### INTRODUCTION

There has been a great interest in developing novel biopolymer nanoparticles, with tuned properties, which are aimed at different niche applications such as encapsulation, drug delivery, and agro-formulations.<sup>1–3</sup> To this purpose, various procedures are developed, and a multitude of biomaterials are used for preparing biopolymer nanoparticles. In this regard, zein is especially interesting due to its commercial availability, GRAS status, plant origin, and unique physico-chemical properties.

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Zein is a corn protein, comprising 50 % of all corn proteins. Raw zein consists of  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  protein fractions, differing in their structure and molecular weight, with  $\alpha$ -zein being the most abundant. Commercial zein, however, is almost exclusively  $\alpha$ -zein, consisting of two polypeptide chains of 19 kg mol<sup>-1</sup> and 22 kg mol<sup>-1</sup>.<sup>4,5</sup> Zein is a prolamin. It is therefore insoluble in water, and soluble in concentrated aqueous ethanol (60–90 % ethanol). It is also soluble in a range of other primary (*e.g.*, acetic acid, glycerol, and propylene glycol), secondary (*e.g.*, mixtures of water and acetone, isopropanol, or methanol) and ternary (*e.g.*, mixtures of water, lower aliphatic alcohol and acetaldehyde or benzene) solvents.<sup>4,6</sup> Zein is a film forming material, and it is commercially used for preparing edible films to extend shelf life of fresh fruits.<sup>7</sup> On the other hand, zein nanoparticles are readily prepared by antisolvent precipitation, where zein solution, typically in aqueous ethanol, is sheared into a bulk of water to precipitate zein.<sup>8</sup> Zein nanoparticles were evaluated for encapsulation of different bioactive materials,<sup>9,10</sup> as stabilizers for Pickering emulsions,<sup>11</sup> or, *e.g.*, as white pigments for liquid products.<sup>12</sup>

Composite zein nanoparticles, where zein is combined with another biomaterial (*e.g.*, gum Arabic, caseinate, propylene glycol alginate, carboxymethyl chitosan) were also prepared, in order to adjust various properties of nanoparticles (*e.g.*, colloidal stability, wetting properties, encapsulation efficiency *etc.*).<sup>13–16</sup> Composite nanoparticles are usually prepared by shearing aqueous ethanol zein solution into a water solution of a biopolymer. In such composite particles, zein core is typically surrounded by a biopolymer or a polymeric surfactant layer, where, during anti-solvent precipitation, zein firstly precipitates to form nanoparticles, and subsequently a biopolymer attaches to the surface of the particles *via* electrostatic or hydrophobic forces. On the other hand, when fast diffusing, small surfactant molecules are used (*e.g.*, Tween 20), zein–surfactant interaction and complex formation take place prior to zein precipitation, and zein–surfactant complexes aggregate to form composite nanoparticles.<sup>17</sup> This strategy for preparing zein-based composite nanoparticles, works only for water soluble biopolymers or surfactants.

There is, however, also an interest in preparing composite nanoparticles of zein with water insoluble compounds, such as natural resins shellac and rosin (*i.e.*, colophony). Shellac is the purified product of the natural material lac, which is secreted by parasitic insect *Kerria Lacca*. It is a complex mixture of esters and polyesters of polyhydroxy acids. It has GRAS status, and is used in food industry as a coating for citrus fruits or confectionaries.<sup>18</sup> Rosin is derived from the oleoresin of pine trees. It consists mainly of resin acids (90 %) that are diterpene monocarboxylic acids. It is widely used in industry as a component of varnishes, adhesives or drug coatings.<sup>19</sup> Both shellac and rosin are insoluble in water, and well soluble in concentrated aqueous ethanol. To the best of our knowledge, pre-

paration of composite zein/shellac and zein/rosin nanoparticles was thus far not investigated.

The aim of this work was therefore to investigate the possibility of preparing composite zein/shellac and zein/rosin nanoparticles by antisolvent co-precipitation of zein/shellac and zein/rosin, from their aqueous ethanol solutions. The influence of zein/resin mass ratio on colloidal properties (particle size and zeta potential) of composite nanoparticles, as well as on encapsulation of carvacrol, was investigated.

### EXPERIMENTAL

Zein, shellac, and carvacrol (5-isopropyl-2-methylphenol) were obtained from Sigma–Aldrich, USA. Colophony (rosin) was obtained from Fluka Chemie AG, Switzerland. Non-ionic surfactants Tween 20 (polyoxyethylenesorbitan monolaureate) and Tween 80 (polyoxyethylenesorbitan monooleate) were obtained from SERVA Electrophoresis GmbH, Germany. Ethanol (96 %) was purchased from Reahem, Serbia, sodium hydroxide was obtained from Centrohem, Serbia and 36 % hydrochloride acid was obtained from ZorkaPharm, Serbia, and all were of *p.a.* quality. Demineralized water was used in all experiments.

#### *Preparation of stock solutions*

25 g of 2 mass % zein, shellac and rosin solutions in 90 vol. % aqueous ethanol were prepared, in 100 ml flask with the ground joint, by constant stirring on a magnetic stirrer during 1 h. The solutions were left over night in the sealed container at room temperature to ensure full dissolution of zein and resins. The solutions were subsequently filtered through quantitative filter paper to remove any undissolved particles.

2 mass % zein/shellac (0.8/0.2 and 0.5/0.5 mass ratio) and zein/rosin (0.8/0.2 and 0.4/0.6 mass ratio) stock solutions were prepared in the similar manner, where zein and resin (in an appropriate mass ratio) were firstly jointly dissolved in 90 vol. % aqueous ethanol, while the rest of the procedure was the same as for the pure zein, shellac and rosin nanoparticles.

#### *Preparation of nanoparticles*

Dispersions of zein, shellac, rosin, as well as composite zein/shellac and zein/rosin nanoparticles in water were prepared by antisolvent precipitation,<sup>8</sup> where 20 mL of a stock solution was dropwise added to 80 mL of water, in a 200 mL flask with the ground joint, with constant stirring on a magnetic stirrer. The stirring was continued 30 min after all of the stock solution was added to water, in order to ensure complete precipitation of zein. Ethanol was removed from the dispersions by rotary evaporation (Rotavapor R300, Büchi, Switzerland), and thereby aqueous dispersions of zein nanoparticles were obtained.

Thus obtained dispersions were diluted to 0.1 % concentration of nanoparticles, and pH of the dispersions was then adjusted (pH 2–11) by 0.1 M HCl or 0.1 M NaOH. The dispersions were left over night at room temperature, when pH was checked and, if necessary, adjusted, prior to further use.

#### *Particles size and zeta potential measurements*

Zeta potential ( $\zeta$ ) and average intensity diameter ( $d$ ) of zein nanoparticles were measured by dynamic light scattering (DLS), using ZetaSizer Nano ZS (Malvern Instruments Ltd, UK), at 25 °C. Folded capillary cell (DTS 1060) was used for zeta potential measurements, and disposable polystyrene cuvette (DTS 0012) for particle size measurements. Zeta potential and

particle size were measured at least three times for each sample, and average values were reported.

#### *Solubilization of carvacrol*

Maximum additive concentration (MAC) of carvacrol in 1 % Tween 20 and 1 % Tween 80 solutions was determined spectrophotometrically (Halo DB-20S UV-Vis Double Beam, Dynamica, Switzerland) in order to evaluate suitability of using Tween solutions as a sink medium during testing the release of encapsulated carvacrol. Carvacrol was added in 15 µL aliquots to 100 mL of 1 % Tween 20 and 1 % Tween 80 solutions in an extraction funnel, to obtain mixtures with varying carvacrol concentrations (from 0.015 to 0.18 vol. % v/v). The mixtures were vigorously shaken, and absorbance at 275 nm was measured. The mixtures became turbid and the absorbance sharply increased when MAC was reached, indicating the saturation of Tween micelles with solubilized carvacrol and emulsification of unsolubilized carvacrol. The emulsion droplets scatter light and cause an apparent increase in absorbance.

#### *Encapsulation of carvacrol*

Carvacrol was added (5 mass %, based on zein/rosin mass) to 2 mass % zein/rosin solution in 90 vol. % aqueous ethanol, with zein/rosin mass ratio 1/0, 0.8/0.2 and 0.6/0.4. Thus prepared mixture was dropwise added to a bulk of water to prepare the zein/rosin nanoparticles encapsulating carvacrol, in the same fashion as preparing the pure zein/resin nanoparticles. Thus prepared suspensions of nanocapsules were ultrafiltered (L/S Economy Drive, Masterflex, USA, peristaltic pump; Vivaflow 200 crossflow cassette with 10000 HY membrane, Sartorius, Germany; at trans membrane pressure of 3 bar) in order to remove ethanol and non-encapsulated carvacrol. 100 mL of nanocapsule suspensions were ultrafiltered, until 60 mL of permeate was collected. The concentrate was then diluted with water to obtain 100 mL of purified nanocapsule suspension. The ultrafiltration step was then repeated for three more times to further purify the suspension.

3 mL of the purified nanocapsule suspension were diluted with 3 mL of 2 % Tween 20 solution. The mixture was then left on a magnetic stirrer during 24 h to allow the release of carvacrol into the sink medium. The nanocapsules were then precipitated by adding 0.01 M NaOH or 0.01 M HCl. The precipitate was separated from supernatant by 0.45 µm filtration (cellulose nitrate membrane filter, Sartorius, Germany), and carvacrol content in the supernatant was determined spectrophotometrically (Halo DB-20S UV-Vis Double Beam, Dynamica, Switzerland) by measuring absorbance at 275 nm.

## RESULTS AND DISCUSSION

Zein, shellac and rosin share a common property of being soluble in concentrated aqueous ethanol, but insoluble in water. Therefore, antisolvent precipitation of these biomaterials takes place when their aqueous ethanol solutions are added to a bulk of water, and consequently nanoparticles of zein, shellac and rosin may be prepared.<sup>8</sup>

#### *Colloidal properties of zein, shellac and rosin nanoparticles*

Dispersions of zein (Z), shellac (S) and rosin (R) nanoparticles were prepared by the antisolvent precipitation. The influence of pH on zeta potential of the nanoparticles is shown in Fig. 1. It can be seen that zein nanoparticles are positively charged at pH lower than 6, while at higher pH they acquire negative

charge. The point of zero charge is around six, in agreement with the literature data, where commonly reported isoelectric point for zein nanoparticles is 6.2.<sup>20</sup> Zein powder dissolves at highly alkaline  $\text{pH} > 11$  and forms transparent solutions, as it was visually observed. Stable dispersions of shellac and rosin nanoparticles were prepared at  $\text{pH} 4\text{--}9$  and  $\text{pH} 3\text{--}8$ , respectively. Throughout these  $\text{pH}$ s, both shellac and rosin nanoparticles have negative charge, Fig. 1. The negative charge comes from ionized carboxylic groups of esters and polyesters of polyhydroxy acids in shellac (mainly aleuritic, butolic, shellolic and jalaric acid), and from resin acids in rosin (mainly isomeric abietic acids).<sup>19,21</sup> Shellac and rosin nanoparticles precipitate at  $\text{pH} 3$  and  $2$ , respectively, as zeta potential approaches zero. Isoelectric point of zein, shellac and rosin nanoparticles, as obtained by zeta potential measurements and visual observations are given in Fig. 2. Shellac and rosin nanoparticles dissolve at  $\text{pH}$ s higher than  $9$  and  $8$ , respectively.

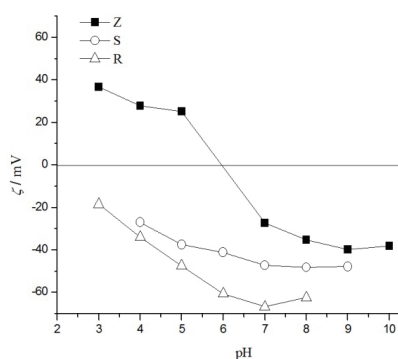


Fig. 1. Influence of  $\text{pH}$  on zeta potential of zein (Z), shellac (S) and rosin (R) nanoparticles.

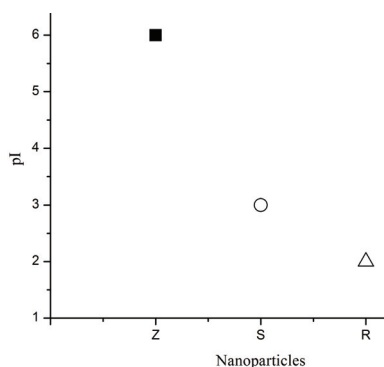


Fig. 2. Isoelectric point of zein (Z), shellac (S) and rosin (R) nanoparticles.

The influence of  $\text{pH}$  on particle size of zein (Z), shellac (S) and rosin (R) particles prepared by the antisolvent precipitation is shown in Fig. 3. It can be seen that  $\text{pH}$  has no influence on size of shellac nanoparticles, where the particles with  $d = 100$  nm were obtained at all  $\text{pH}$ s tested. On the other hand,  $\text{pH}$  influences the size of both zein and rosin particles. Zein nanoparticles with the small-

est particle size of  $d \approx 100$  nm were obtained at the lowest and the highest pHs tested, pH 3 and 4 and pH 9 and 10, respectively. Particle size increases as pH approaches *pI* of zein, due to a decrease in particle charge, which favours particle agglomeration. In the like manner, the largest rosin nanoparticles with  $d = 370$  nm were prepared at pH 3, which is close to *pI* of rosin. At pH 4, 5 and 6, rosin nanoparticles with  $d = 330$  nm are obtained, and in this pH range the particle size does not change. At still higher pHs, pH 7 and 8, the particle size decreases to  $d = 300$  nm and  $d = 220$  nm, respectively. The decrease in particle size at pH 7 and 8 is attributed to the increased rosin dissolution at the increased pH values.<sup>22</sup> There are three competing mechanisms during antisolvent precipitation which influence size of the obtained particles.<sup>8</sup> These are: 1) breakup of aqueous ethanol solution droplets by shear forces on impacting bulk of water; 2) coalescence of the droplets in analogy to emulsions; 3) solidification of dissolved material during solvent attrition. Dynamics of these three processes is influenced by different parameters such as ethanol concentration in aqueous ethanol solution, concentration of a material dissolved in aqueous ethanol, applied shear forces, *etc.*

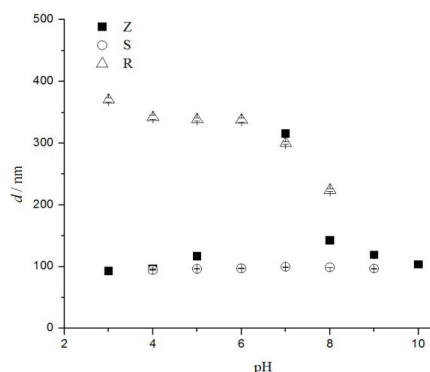


Fig. 3. Influence of pH on particle size of zein (Z), shellac (S) and rosin (R) nanoparticles.

#### *Colloidal properties of composite zein/shellac and zein/rosin nanoparticles*

The suspensions of composite zein/resin particles, prepared by the antisolvent precipitation of dissolved biopolymer mixtures in water, were diluted and suspensions' pH was adjusted.

The images of zein/shellac dispersions at various pHs (3–11) and at different zein/shellac mass ratio (1/0, 0.8/0.2, 0.5/0.5 and 0/1) are shown in Fig. 4. The dispersed particles scatter light and make dispersions turbid. 1/0 Z/S samples at pH 11 and all other Z/S samples at pH 10 and 11 appear transparent, indicating the dissolution of Z/S particles, where both, zein and shellac are known to dissolve at aqueous alkaline.<sup>18,23</sup> The precipitation of Z/S particles was observed at pH 6 for 1/0 Z/S, at pH 5 and 6 for 0.8/0.2, at pH 5 for 0.5/0.5 Z/S, and at pH 3 for 0/1 Z/S particles. The precipitation took place due to the low particle charge and thereby to the decreased electrostatic repulsion between the particles in the

vicinity of isoelectric point of the particles, which makes the particles colloiddally unstable. The influence of pH on zeta potential of Z/S particles of different zein/shellac mass ratio is shown in Fig 5a. It can be seen that the point of zero charge shifts to lower pH values, as mass ratio of shellac in composite Z/S particles increases, in agreement with the visual observations. We were unable to prepare the Z/S particles at Z/S ratio >0.5/0.5 due to the excessive coagulation during the antisolvent precipitation. The influence of pH on particle size of Z/S particles of different Z/S mass ratio is shown in Fig. 5b. It can be seen that the prepared Z/S dispersions contained nano-sized particles, where particles size increases as pH approaches pI of the corresponding Z/S particles. The influence of pH on particle size becomes more prominent as the zein portion in Z/S particles increases.



Fig. 4. Dispersions of composite zein/shellac (Z/S) nanoparticles of different Z/S mass ratio (1/0, 0.8/0.2, 0.5/0.5 and 0/1), and of different pH (3–11).

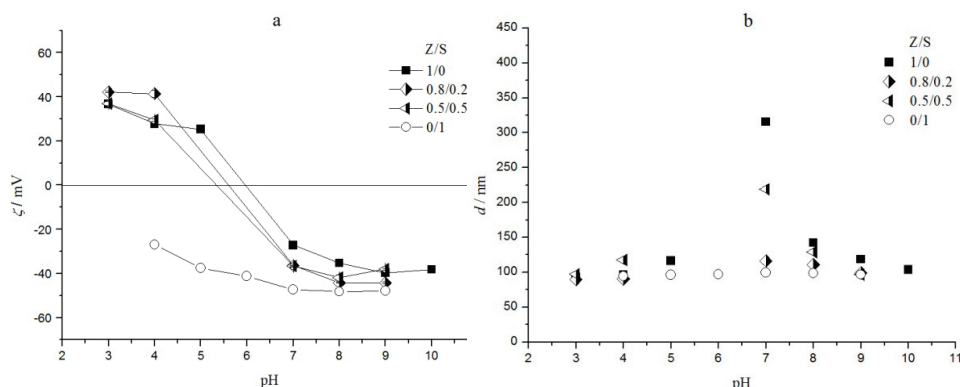


Fig. 5. Influence of pH on zeta potential (a) and particles size (b) of composite zein/shellac (Z/S) nanoparticles of different Z/S mass ratio (1/0, 0.8/0.2, 0.5/0.5 and 0/1).

The dispersions of composite zein/rosin particles at different Z/R mass ratio and at different pH are shown in Fig. 6. Similarly to Z/S dispersions, Z/R dispersions appear turbid, unless particles are precipitated or dissolved. It can be seen that by increasing the rosin share, Z/R particles dissolve at lower pH, where 1/0, 0.8/0.2 and 0.4/0.6 Z/R particles dissolve, by visual judgment, at pH 11, 10 and 8, respectively. In the like manner, the point of zero charge of Z/R particles decreases on an increase in rosin share, as evidenced by the zeta potential measurements, supported by the visual observations, Figs. 6 and 7a. The prepared Z/R dispersions contained nano-sized particles, where composite Z/R nanoparticles proved to be much smaller than pure rosin nanoparticles, Fig. 7b.

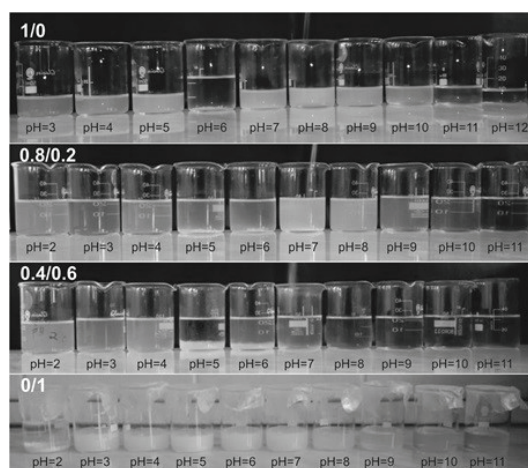


Fig. 6. Dispersions of composite zein/rosin (Z/R) nanoparticles of different Z/R mass ratio (1/0, 0.8/0.2, 0.4/0.6 and 0/1), and of different pH (2–12).

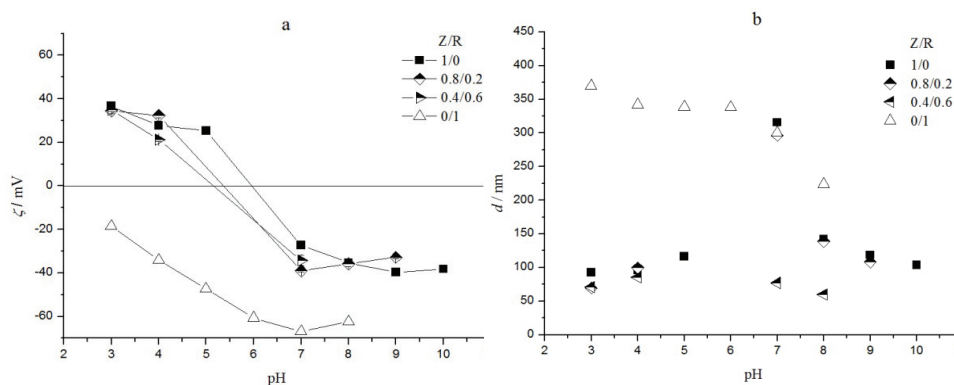


Fig. 7. Influence of pH on zeta potential (a) and particles size (b) of composite zein/rosin (Z/R) nanoparticles of different Z/R mass ratio (1/0, 0.8/0.2, 0.4/0.6 and 0/1).

As seen in Figs. 4, 5b, 6 and 7b, the composite Z/R nanoparticles dissolve at lower pH compared to Z/S nanoparticles, closer to neutral pH, which is desirable for spontaneous release of active compounds in natural mediums.



Within stable dispersions, at pH 3–4 and 8–9, both Z/S (Fig. 5b) and Z/R (Fig. 7b) nanoparticles are about the same size, or smaller than other previously reported nanoparticles based on zein.<sup>7,24,25</sup> Carvacrol was also encapsulated in pure zein nanoparticles, with diameter of 293.6 nm at pH 4,<sup>9</sup> which is about twice larger than nanoparticles prepared in this paper. Smaller particles are prepared from less concentrated stock solutions. Same authors also report the average diameter decrease at pH 10.<sup>9</sup>

#### *Encapsulation of carvacrol in composite zein/rosin nanoparticles*

Encapsulation of carvacrol in composite zein/rosin nanoparticles, prepared at different Z/R mass ratios, is further investigated. Carvacrol is a hydrophobic compound, insoluble in water. In order to study the release of encapsulated carvacrol in water, an appropriate method had to be identified. Hydrophobic compounds are known to be soluble in the presence of surfactants above CMC, which are often used to improve the solubility of hydrophobic compounds in water.<sup>26</sup> Therefore, the solubilization of carvacrol in 1 % Tween 20 and 1 % Tween 80 water solutions are studied spectrophotometrically, in order to investigate if the Tween solutions are suitable to be used as the test medium for the carvacrol release from composite zein/rosin nanoparticles.

Influence of carvacrol concentration on absorbance of 1 % micellar solutions of Tween 20 and Tween 80 is shown in Fig. 8. It can be seen that at low carvacrol concentrations, the solutions remain optically transparent, where the absorbance of both Tween 20 and Tween 80 solutions remains close to zero, indicating that all of the added carvacrol is solubilized in Tween micelles. On further carvacrol addition, the absorbance of Tween solutions sharply increases when a maximum additive concentration (*MAC*) is reached. It was found that *MAC* for 1 % Tween 20 and 1 % Tween 80 is 0.86 and 1.16 g L<sup>-1</sup>, respectively. The sharp increase in the absorbance is due to the emulsification of unsolubilized carvacrol. Namely, at carvacrol concentrations higher than *MAC*, all Tween micelles are saturated with carvacrol, and any further addition of carvacrol leads to carvacrol emulsification and droplet formation. The emulsified droplets scatter light and the mixtures become optically turbid, which consequently leads to an increase in measured absorbance.<sup>26</sup> The obtained *MAC* values shows that both 1 % Tween 20 and 1 % Tween 80 solutions successfully solubilized carvacrol, and that both solutions can be used as the test medium for the release of encapsulated carvacrol. 1 % Tween 20 was chosen for carvacrol release experiments, because of better correlation coefficient (*R*<sup>2</sup>) between absorbance value and concentration of carvacrol solubilized, compared to *R*<sup>2</sup> when 1 % Tween 80 is used (data not shown).

Carvacrol was encapsulated in composite Z/R nanoparticles with different Z/R mass ratio (1/0, 0.8/0.2, 0.6/0.4 and 0/1). The influence of rosin share in composite zein/rosin nanoparticles on carvacrol released after 24 h in 1 % Tween

20 solution is shown in Fig. 9. It can be seen that the composition of Z/R nanoparticles influence the release, where on the increasing rosin share more carvacrol is released.

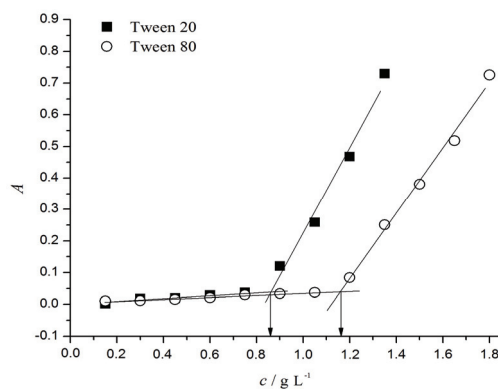


Fig. 8. Influence of carvacrol concentration on absorbance of 1 % Tween 20 and 1 % Tween 80 solutions in water. The arrows indicate the maximum additive concentration (MAC).

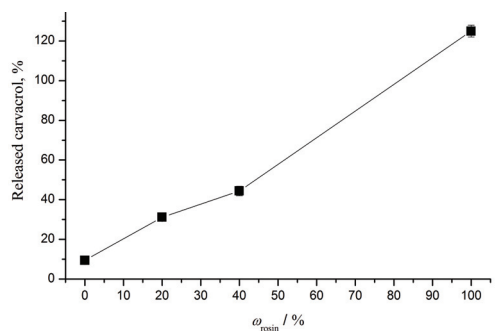


Fig. 9. Influence of rosin share in composite zein/rosin nanoparticles on the released carvacrol.

## CONCLUSION

The antisolvent precipitation was successfully used to prepare shellac and rosin nanoparticles, as well as the composite zein/shellac (Z/S) and the zein/rosin (Z/R) nanoparticles with different zein/resin mass ratio (1/0, 0.8/0.2, 0.5/0.5 and 0/1 for Z/S, and 1/0, 0.8/0.2, 0.4/0.6 and 0/1 for Z/R nanoparticles). Particle size, zeta potential and isoelectric point of the obtained nanoparticles was influenced by the zein/resin mass ratio, as well as by the dispersion's pH. It was found that the zein/rosin nanoparticles are suitable for carvacrol encapsulation, where an increase in the rosin share in composite zein/rosin nanoparticles contributes to the carvacrol release.

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## ИЗВОД

## ПРИПРЕМА КОМПОЗИТНИХ НАНОЧЕСТИЦА ЗЕИН/ПРИРОДНА СМОЛА

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Циљ рада био је испитивање могућности припреме композитних наночестица зеина и природних смола (шелака и калафонијума), растворених у етанолу, применом копреципитације у нерастварачу. Проучаван је утицај масеног удела зеин/смола (1/0, 0,8/0,2, 0,5/0,5, 0,4/0,6 и 0/1) и рН вредности (2–12) на величину и зета потенцијал припремљених наночестица. Могућност инкапсулације карвакрола у наночестицама зеин/калафонијум испитивана је у циљу карактерисања њихових функционалних особина. Показано је да је применом преципитације у нерастварачу могуће припремити наночестице шелака и калафонијума, као и композитне наночестице зеин/шелак и зеин/калафонијум. Такође, резултати су показали да масени однос зеин/смола и рН вредност суспензије наночестица, утичу на колоидне особине, односно на пречник и зета потенцијал наночестица. На изоелектричну тачку наночестица може се утицати променом односа зеин/смола. Показано је да су наночестице зеин/калафонијум погодне за инкапсулацију карвакрола, те да се отпуштање карвакрола из честица повећава са повећањем удела калафонијума у саставу наночестица.

(Примљено 1. априла, ревидирано 1 јула, прихваћено 5. јула 2019)

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