Plant-based nanoparticles prepared from protein containing tribenuron-methyl: fabrication, characterization, and application

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Abstract
Background: Tribenuron-methyl is a registered herbicide for broad-leaf weed control in wheat, however, low solubility in water and reacting with hard water’s ions could substantially decrease its efficacy. The present work aimed to enhance the dispersing and bioactivity of this herbicide by developing nanoparticles using zein as a promising nanodelivery system and to assess the effects of nanoparticles on the efficacy of tribenuron-methyl in the suppression of Convolvulus arvensis as a problematic weed in wheat fields.

Results: Based on SEM analyses nanoparticles sizes were 80–120 nm. DLS results showed an average size of 170 nm for tribenuron-methyl zein-based nanoparticles (TMZNP-5). The entrapment efficiency (EE%) of tribenuron-methyl inside the zein nanoparticles was ca. 81% ± 3. Five-week after application of tribenuron-methyl nanoparticles on C. arvensis, it was able to reduce the dry weight (53%), acetolactate synthase (ALS) enzyme activity (82%), and plant height (77%) of C. arvensis as compared with untreated plants. Additionally, tribenuron-methyl used in nanoparticles at the half rate of the recommended dose had the same efficacy as commercial tribenuron-methyl.

Conclusion: Based on these results, zein nanoparticles can be potentially utilized as nanocarriers for enhancing the solubility of tribenuron-methyl to further enhance its bioavailability and performance on sensitive weeds.

Highlights
- Tribenuron-methyl-loaded zein nanoparticles synthesized.
- TM-loaded zein nanoparticles characterized by DLS, FTIR, SEM.
- The TM’s drug encapsulation efficiency (EE%) within the nanoparticles was ca. 81% ± 3.
- F127/VPA and lignin/VPA microemulsions were tested for their cytotoxic activity.
- Use of nanoparticles containing tribenuron-methyl (TMZNP-5) herbicides had a significant effect on weed control.
- After 5 weeks, TMZNP-5 was able to completely suppress the C. arvensis.

Keywords: Herbicide, Convolvulus arvensis, Weed, Wheat, Zein nanoparticle

Background
Nowadays, weed competition results in a 10–100% reduction in crop yields [1]. Conventional control methods have long been used, including mechanical control...
(such as tillage, hand pulling), biological control, and chemical applications in agricultural environments [2]. Each of the conventional methods of weed control has its strengths and weaknesses, which makes the use of some methods more popular with farmers and others less so. Chemical weed control is still the main method of weed control after more than seven decades [3]. Herbicides play a role in the productivity and safety of food production by cost-effectiveness, and reduction of labor costs, as well as saving on land preparation [4].

Sulfonylurea is one of the largest families of selected herbicides, which includes a large number of different herbicides for weed control [5–8]. Herbicides in this chemical family inhibit the biosynthesis of the three essential amino acids valine, leucine, and isoleucine by inhibiting the enzyme acetolactate synthase (ALS) [9]. Tribenuron-methyl [(methyl2-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) methylcarbamoyl sulfamoyl benzoate)] is one of the most commonly used selective herbicides in the sulfonylurea chemical family. It has been registered for control broad-leaf weeds in cereals mainly wheat, barley and, triticale [10]. Low solubility in water and reacting with hard water’s ions could substantially decrease its effectiveness. There are several solutions to such problems, one of which is using nanotechnology and reducing particle size.

In nanoscale, which is basically water-soluble, the rate of uniform dissolution and dispersion increases [11]. Recently, nanotechnology was discovered owing to its potential at revolutionizing the agricultural industry. Efficacy has been improved by pesticides and herbicides with nano-encapsulation [12] with the even dispersion and adherence of actives to the leaf surface. Several nanostructured materials in the production of agricultural chemicals (herbicide, pesticides, and chemical fertilizers) due to their features including low toxicity, high biodegradability, high recyclability, low cost, quick and easy preparation, good absorption water, and its reversible properties have been used as carriers of active ingredients in herbicides and pesticides [13, 14]. Owing to their very high surface-to-volume ratio, they create an integrated coating on the leaves and also improve the emission properties in the soil, which has increased the interest of those interested in using nanomaterials in agriculture [15–17]. One of the types of nanomaterials is biopolymers such as natural proteins nanoparticles that are extensively utilized in the pharmaceutical and food industry these days [18, 19]. Recently, biopolymer-based nanoparticles have been extensively utilized in the drug delivery system. Within drug delivery systems the dissolution rate of drugs is incremented by increasing the surface area of the drug and the corresponding carrier. Plant proteins-based carriers present several advantages over animal lipid, proteins, or synthetic polymer as a result of their availability, biodegradability, and high drug-binding capacity [20–22].

Zein is a plant protein (extracts from Zea mays) with a molecular weight of about 40 kDa that due to properties such as biodegradability, biocompatibility, nontoxicity, and economic reasons has drawn increase to use for different purposes including oral delivery of peptides and proteins, DNA transfection, vaccine delivery, and scaffold for tissue engineering [23–27]. It can be simply transformed into various structures and shapes such as microsphere, films, micelles, nanoparticles, fibers, and gels [28, 29], so zein could be an alternative for encapsulation carriers to deliver nutrition and drugs. According to earlier studies, biopolymer-based nanoparticles (e.g., zein) possessed more hydrophilic groups as well as a smaller size and displayed good bioactivity and solubility [25–30]. On the one hand, the use of polymeric nanoparticles have been introduced as ideal nanocarrier systems for delivery of hydrophobic agents to protect against degradation, and the controlled cargo release at the optimal rate with an improvement of its bioavailability [31, 32]. In this case, polymeric nanoparticles are formed based on the procedure governing on formation of phospholipids in water. Phospholipids are amphiphilic molecules with water-soluble groups and oil-soluble tails [24–27]. With this in mind, this work was initiated to prepare zein nanoparticles as well as zein nanoparticles loaded with tribenuron-methyl and then to investigate the possible effects of these nanoparticles on tribenuron-methyl efficacy on Convolvulus arvensis, as a problematic weed in wheat fields.

Material and method

Material

DuPont Far East Inc., New Delhi, India, supplied a technical scrupe of tribenuron-methyl (methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)) (95% purity). It was used as received. Tween 80 and acetone were purchased from Merck Co, and also purified a-zein was bought from Acras Orgamics (Morris Plains, NJ) and dissolved in ethanol (70% (v/v); 200 Proof, Decon Laboratories, King of Prussia, PA). It was utilized as the dispersing phase. Merck Chemical Co provided Na-pyruvate, (NH₄)₂SO₄, ZnSO₄, MnSO₄, naphthol-1, and HCl. Also 2, 2-diphenyl-1-picrylhydrazyl (DPPH) was prepared from Sigma-Aldrich. Doubly distilled, deionized Millipore water was utilized. Also, dialysis bags were bought from SERVAPOR.
Fabrication of tribenuron-methyl-loaded zein nanoparticles
Zein (0.66 g) was dissolved in 25 mL aqueous acetone solutions (70% v/v) and stirred with a magnetic stirrer for 24 h at room temperature till obtaining a homogeneous solution and tribenuron-methyl (TM) was added then to the zein solution (first solution) [33]. Then, 0.75 g of Tween 80 was dissolved in 25 mL PBS (0.1 M pH = 4) stirred with a magnetic stirrer for 30 min at room temperature (second solution). This was followed by adding the zein solution dropwise into the second solution while moderately stirring [34] and finally acetone was removed under vacuum rotary evaporation. Three different TM amounts (0.016 g, 0.033 g, and 0.066 g) were used in the formulation to obtain three zein nanoparticles with different TM content which were coded TMZNP-2.4, TMZNP-5 and TMZNP-10, respectively, in which the number refers to the weight percent of TM to zein content (Scheme 1).

The freshly prepared TM-loaded nanoparticles in solutions were exposed to characterizations such as encapsulation efficiency and particle size measurements. The specimens were freeze-dried for release profile and other measurements and stored at −18 °C for further assay. Besides TM-loaded zein nanoparticles, TM-free zein nanoparticles were prepared as a control.

Characterization
Physico-chemical characterization of TM-loaded zein nanoparticles
Dynamic light scattering (DLS) was conducted utilizing a commercial laser light scattering instrument (DelsaMax PRO, Beckman Coulter Instruments) with a 90° scattering angle at 25 °C. Also, the SEM images of nanoparticles were acquired using an AIS-2100 scanning electron microscope, Seron Technology, operating at 15 kV. The nanoparticles dispersions were adjusted on a clean glass slide and dried. Then, they were vacuum coated with gold before imaging.

Thermal stability of zein and TM-loaded nanoparticles were measured by thermogravimetric analysis (TGA/SDTA 851, Switzerland) under N₂ flow of 20 mL min⁻¹ with a heating rate of 10 °C min⁻¹ in a range of ambient temperature to 600 °C.

To prepare pellets of TMZNPs, ca. 2 mg of zein, and tribenuron-methyl samples separately, 200 mg of spectroscopic grade KBr were combined. A Nicolet 520P spectrometer was used with a resolution of 4 cm⁻¹ and 64 scans per sample to record IR spectra (4000–400 cm⁻¹). Some bands shielded by the extensive OH bending mode of bound water were elucidated using an FTIR spectrometer (BIO-RAD 175C) armed with an evacuation line. In this regard, the pellets were created with no KBr. To press zein (about 4 mg), TM-nanoparticles and tribenuron-methyl specimens in a standard tool, a pressure of 98 kN cm⁻² was used to create pellets in diameter of 13 mm [35].

Entrapment efficacy (EE%) and release of TM experiments
Utilizing a UV–visible spectrophotometer (Agilent Technologies, Cary 60, USA), the quantity of TM entrapped within the developed nanoparticles was determined spectrophotometrically [36, 37]. Before determining TM content, a calibration curve was obtained for ethanolic TM solutions at various concentrations. The TM-loaded zein nanoparticles were then dissolved in 2 mL of ethanol and centrifuged at 15,000 rpm for 20 min (model 5415D, Eppendorf, Germany). By UV–Vis absorbance at 230 nm, the TM content of the resultant supernatant solution was achieved. Ultimately, the encapsulation efficiency was determined (EE%) (Eq. 1):

\[ \text{EE(\%)} = \frac{\text{Amount of TM in the supernatant}}{\text{Total amount of TM used for formulation}} \times 100. \]

By dialysis method [37, 38] the release profile of TM-loaded zein nanoparticles (TMZNP-5) was evaluated. 1 mg at a concentration of 1 mg mL⁻¹ of the TM-loaded nanoparticles was placed into dialysis bags and then
immersed in 30 mL PBS (0.1 M pH = 7) comprising 30% (v/v) ethanol for ensuring sink circumstances. For measurement, 1 mL of the release medium was withdrawn at specific time intervals and up to 168 h and replaced quickly by a fresh medium (1 mL). The control sample (the release profile of neat TM) was performed under similar circumstances. Via UV–Vis spectroscopy (a 230 nm wavelength), the samples were analyzed. By using the obtained standard calibration curve at PBS 0.1 M pH = 7, the released drug concentration was determined. The results were stated as the cumulative release of 3 replicates.

Planting and applying nanoparticles containing herbicides on plants
The wheat seeds (cv. Pishgam) were soaked first with sodium hypochlorite for 10 min and washed with water. Mature seeds of *C. arvensis* were gathered from a naturally infested winter wheat field in Zanjan County (Iran) in summer 2019 and then kept at room temperature. The soil was taken from 0 to 20 cm depth in the research farm of the University of Zanjan, Iran (Table 1). The soil was sterilized at 121 °C and 1.5 atmospheres for 1 h after air drying. Planting the four seeds of *C. arvensis* in plastic trays (25 × 15 × 25 cm), they were kept for 3–4 weeks at 4 °C for cold treatment for breaking the dormancy and enhancing germination. The trays were then moved to a greenhouse. When germination, seedlings were transplanted in 5 kg pots at the 2–3 leaf stage. They were grown in a greenhouse at 26/18 °C, 15/9 h a day/night photoperiod with 60 ± 10% relative humidity and 750 µmol m⁻² s⁻¹ photosynthetic photon flux density.

To evaluate the efficacy of the new formulation, TM-loaded zein nanoparticles (TMZNP-5) were sprayed on the *C. arvensis* plants reproduce by seed. Dry flowable (DF) commercial formulation of TM (Granstar) as well as untreated plants (not treated with herbicide) was also included for comparison. About 15 mL of a solution containing herbicide was utilized for each pot. Triburon-methyl solutions were employed with a laboratory sprayer armed with a flood-jet nozzle, calibrated for delivering 240 L ha⁻¹ at 210 kPa. Herbicide treatment was made when *C. arvensis* had 2–3 leaves. The experiments were performed by a completely randomized design (CRD) with eight replications.

Data collection on plant traits
Since ALS is the main target enzyme of the sulfonylurea family, the in vivo activities of ALS enzymes in mature leaves were assayed several days after treatment. ALS enzyme assays were performed as previously described [39]. Enzyme activity was determined based on the amount of acetoin formed from acetolactate using a well-established methodology [40]. Plant heights were calculated by the ruler at 14, 21, and 35 days after spraying. The fresh weight was measured by weighing the samples via a digital balance with an accuracy of 0.01 g. The dry weight was measured by placing the plants for 48 h in an oven at 75 °C and then weighting.

Table 1 The soil characteristics of experiment site

| Depth (cm) | pH | EC (dS m⁻¹) | Texture | N (%) | K (mg kg⁻¹) | P (mg kg⁻¹) |
|-----------|----|-------------|---------|-------|-------------|-------------|
| 0–20      | 7  | 0.9         | Loam    | 0.5   | 301.8       | 20.33       |
Figure 3 shows the SEM images of the TMZNPs to study their morphology. These images revealed spherical morphology with an approximately narrow size distribution. A size range of 80–120, 100–180, and 120–230 nm, was estimated for TMZNP-2.4, TMZNP-5 and TMZNP-10, respectively (Fig. 3). The increase in the size of the nanoparticles more likely relates to the increased TM content in the nanoparticles.

Figure 4 shows the FT-IR spectra of the neat zein and TMZNPs. The neat zein showed the characteristics peaks including stretching vibration of –OH of physically adsorbed water at 3100–3600 cm$^{-1}$, stretching vibration of C–H at 2850–2959 cm$^{-1}$, and stretching vibration of N–H of amide groups at 3071 cm$^{-1}$. Moreover, the peaks at 1240, 1307, 1534, and 1654 cm$^{-1}$ were related to the amide III (axial deformation vibrations of C–N stretching), amide II (N–H bending) and amide I (C=O stretching vibration), respectively [47]. However, the FT-IR spectrum of TM is more crowded owing to the existence of various functional groups. The peaks at 2957 and 3104 cm$^{-1}$ are associated with the stretching vibration of C–H and N–H, respectively. The sharp peak at 1564 and 1731 cm$^{-1}$ are correlated with the vibration of C=N and C=O in ester groups. The stretching vibrations at 1348 cm$^{-1}$ are allocated for S=O and ultimately the stretching vibration of C–O of the ester group is found at 1268 cm$^{-1}$ (Fig. 4) [48].

Drug encapsulation and release
The entrapment efficiency (EE%) of TM inside the zein nanoparticles was measured. The entrapment efficiency (EE%) of TM inside the TMZNPs-5 was ca. 81% ± 3. The cumulative release of TM from TMZNPs-5 (in vitro) was measured (Fig. 5). Dialysis bags comprising the TMZNPs-5 were submerged in
PBS at pH 7 and 25 °C for mimicking the physiological circumstances of the plant conditions. For comparison and control, the free TM release was also performed the release of TM from the TMZNP-5 was biphasic, with a burst release phase within the first 5 h after the trend was fixed and a more sustained pattern. Almost 50% of TM was released from the nanoparticles after 40 h, while during first 5 h free TM was completely released (Fig. 5).

**Effect on physiological and morphological traits of weed**

Analysis of variance indicated positive effects of using biopolymer-based nanoparticles and commercial TM on physiological and morphological characteristics of C. arvensis (Table 2). The results of Table 2 show the significant effects ($P \leq 0.01$) of biopolymer-based nanoparticles on the ALS enzyme activity, plant height, fresh and dry weight of C. arvensis (Table 2).
The results of morphological and physiological features of weed are shown in Fig. 6. The highest ALS enzyme activity ($340\pm0.30$ μmol mg$^{-1}$ fw) was measured in the untreated plants while TMZNP-5 application decreased it to $61\pm0.20$ μmol mg$^{-1}$ fw (Fig. 6A). Considering the high ALS activity variability in various treatments, further ALS assays were performed utilizing tissues of the same developmental stage, which were chosen carefully, i.e., young developing tissue. In plants treated with TMZNP-5, the ALS activity was significantly decreased by 82%. While in plants treated with the commercial TM, ALS enzyme activity was obtained approximately 48 μmol mg$^{-1}$ fw. However, commercial TM and TMZNP-5 treatments were included in a common statistical group.

The highest weed height (97.5 cm) was observed from untreated plants (Fig. 6). The application of TMZNP-5 and commercial TM reduced plants height by 77 and
Table 2  Analysis of variance the effects of experimental treatment on the ALS enzyme activity, plant height, fresh and dry weight of *C. arvensis*

| A.O.V       | df | ALS          | Dw1          | Dw2          | Dw3          | Fw1          | Fw2          | Fw3          | Height       |
|-------------|----|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Treatment   | 2  | 217,698.66** | 59,7636**    | 1042,165**   | 519,545**    | 1129,470**   | 4377,935**   | 17,950,335** | 15,790,627** |
| Error       | 21 | 5.8333       | 0.05561      | 0.207221     | 0.310208     | 0.261980     | 0.323980     | 0.36041      | 0.11375     |
| F value     |    | – 37,319.8   | 1075.54      | 5029.25      | 1674.83      | 4311.28      | 13,513.0     | 49,805.1     | 138,819     |
| CV          |    | – 1.61       | 7.04         | 3.68         | 3.48         | 4            | 2.25         | 1.17         | 1.72         |

Dw: dry weight; Fw: fresh weight; ** not significant

* Significant at 5% probability level; and ** significant at 1% probability level

Fig. 6  Mean of comparing the impacts of various treatment (TM: tribenuron-methyl, TMZNP-5: tribenuron-methyl zein-based nanoparticles) on the ALS activity (A), plant height (B), fresh weight, and dry weight of *C. arvensis* at first sampling (C), second sampling (D), and third sampling (E). Columns with different letters are significantly different based on Duncan’s multiple range test (*P* < 0.05)
81%, respectively. Biopolymer-based nanoparticles containing tribenuron-methyl at 15 g a.i. ha$^{-1}$ significantly reduced dry weight of C. arvensis compared to untreated plants by 71, 75, and 53% at 2, 3, and 5 weeks after spraying, respectively (Fig. 6). This treatment also reduced the fresh weight of weed compared with the control by 76% at three samplings (Fig. 6). Although commercial tribenuron-methyl represents the relatively less fresh weight and dry weight than TMZNP-5, no statistically significant differences were found between the performances of these two treatments.

**Discussion**

As mentioned above, DLS results showed an average size of 170 nm for TMZNP-5, and also based on the SEM result, the approximate size of the nanoparticles was in the range of 80–120 nm, which indicates good results for zein nanoparticles and was consistent with the results of former studies [42–47].

The results of FTIR appearance of the main distinctive peaks of zein and TM in the spectrum of all the TMZNPs indicate a higher ability of zein nanoparticles to encapsulate TM molecules.

The encapsulation efficiency (EE%) is one of the key physicochemical factors of nanocarriers. Reducing potential side effects requires ensuring high encapsulation efficiencies which are achieved with the herbicidal effectiveness of the loaded agents at lower concentrations compared to the case of administered free bioactive compounds [47, 48]. The obtained higher EE% may be associated with the interactions between TM and the zein molecules [30]. Moreover, the herbicide release profile and its rate are other characteristics for nanocarriers.

With the application of TM loaded to zein-based nanoparticles, the activity of ALS enzyme decreased by 82%. TM is insoluble in water, due to strong intermolecular bonds [49]. Loading active ingredients to zein-based nanoparticles resulted in increased dissolution and dispersion in the water [30]. It is likely that loading TM to zein nanoparticles increased the solubility and dispersing rate of the active ingredients in the tank, and as a result plants uptake more herbicide. The application of TMZNP-5 reduced plants height by 77%. Also, TMZNP-5 reduced the plant’s dry and fresh weight in comparison with other treatments. The decrease of weed height and dry weight can be caused by the higher solubility of nanoparticles in water and ultimately greater uptake by the weed, which causes the inhibiting of the ALS enzyme and decreasing the activity of the enzyme causing reduced biosynthesis of the amino acids valine and leucine that ultimately prevents protein biosynthesis [39], which in turn prevents cell division in the plant. As a result, it reduces the growth of weed and reduces height, and dry weight. Due to the fact that the concentration of tribenuron-methyl used in TMZNP-5 was approximately 1/2 of the recommended dose of commercial tribenuron-methyl, the results were very favorable for the performance of these nanoparticles. According to the zein-based nanoparticles form represented considerably higher dispersibility and solubility of an ingredient than the crude zein in water suspension [30]. In small-scale herbicides (nano and micro) and colloidal, which are essentially water-soluble, the rate of uniform dissolution and dispersion increases [39]. On the other hand, due to their unique conditions, nanoparticles have the ability to trap various ions and gradually release them into the plant. Therefore, the use of TMZNP-5 improved the solubility of this insoluble herbicide in water and consequently increased its uptake and efficiency. In addition, as the size of the herbicide decreases and the surface-to-volume ratio increases, more solubility, and more uptake can be the main reasons for the significant reduction in plant height, fresh and dry weight in the weed. These findings can be clarified by inhibiting TM insolubilization owing to nanoparticles, leading to the reduced molecular mobility of the TM and therefore the enhanced dispersibility or solubility of the entrapped TM. Particularly, the TM solubility was enhanced by zein hydrophilicity [50]. It is indicated that TM dispersibility and solubility are incremented by TMZNP-5. Moreover, zein nanoparticles have a key role in enhancing the solubility of TM.

**Conclusion**

TM is one of the most commonly used selective herbicides for control of broad-leaf weeds in cereals mainly wheat, barley and, triticale. However, poor water solubility limits its applications. Zein could provide alternative encapsulation carriers to deliver nutritional and functional components. In the present work, zein-based nanoparticles containing the TM were prepared. DLS results showed an average size of 170 nm for TMZNP-5. According to the SEM result, the approximate size of the nanoparticles is within the range of 80–120 nm. The TM’s drug encapsulation efficiency within the nanoparticles was ca. 81% ± 3. Based on in vitro cumulative drug-release profile, the developed nanoparticles enable a more controlled and sustained release of the loaded drug. The use of nanoparticles containing tribenuron-methyl (TMZNJP-5) had a significant effect on weed growth and TMZNP-5 was able to completely suppress the C. arvensis. Overall, encapsulation of tribenuron-methyl caused more solubility in water, slower release, more absorption, and eventually increased TM bioactivity. These findings indicate that zein nanoparticles can be potentially utilized as nanocarriers for enhancing the solubility of TM,
which can further enhance its performance and bioavailability on weeds.

Abbreviations
TM: Tribenuron-methyl; TMZNP: Tribenuron-methyl-based zein nanoparticle.

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Authors’ contributions
ARY designed and supervised the experiment. MS performed the greenhouse and laboratory workload and wrote the first manuscript draft. NN analyzed the data. AR gave scientific advice and practical laboratory helps. GK, MB, all authors revised and edited the manuscript. All authors read and approved the final manuscript.

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Declarations

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All authors listed have contributed significantly to the research and agree to be in the author list.

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