Research Article

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Synthesis, characterization, and evaluation of nanoparticles of clodinofop propargyl and fenoxaprop-*P*-ethyl on weed control, growth, and yield of wheat (*Triticum aestivum* L.)

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Abstract: Nanoherbicides are articulated by exploiting the prospective of nanotechnology for effectively delivering chemical and biological herbicides using nanomaterial-based herbicide combinations. The nanoparticles were characterized using X-ray diffraction and FT-IR. On the targeted weeds, the nanoherbicides were sprayed at the third to fourth leaf stage. Six different doses were applied. The mortality and visual injury caused by both chitosan-based nanoherbicides reached 100% at the recommended dose of standard herbicide. The 5-fold lower dose exhibited weed density and maximum wheat yield and related parameters. For the same traits, the nanoherbicide at 10-fold lower dose of commercial herbicides showed a comparable influence as the suggested dose. The size of both herbicides was found to be 35–65 nm. It was observed that the clodinofop-propargyl nanoherbicide has an intense peak appearing at a 2θ value of 29.83°, corresponding to the (176) plane of the anatase phase and NPs of fenoxaprop-*P*-ethyl showed an intense peak around the 2θ value of 30.55° corresponding to the (74) plane of the anatase phase. The FT-IR spectra of fenoxaprop-*P*-ethyl clearly showed that the major functional groups were located in the FT-IR region between 610 and 1,840 cm^{-1} and the major functional ones of clodinofop propargyl were located in the FT-IR region between 640 and 1,740 cm^{-1}. Nanoherbicides could restore the efficacy of conventional herbicides by improving stability and reducing toxicity.

Keywords: clodinofop-propargyl and fenoxaprop-*P*-ethyl nanoherbicides, weed control, wheat and yield parameters

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1 Introduction

Wheat is an important food crop that is used extensively in daily life, and its sustainable production is essential for human welfare [1]. However, wheat cultivation is affected by poor input management, water shortage, and yield loss due to weeds, pests, and diseases [2–4]. Weeds are a significant cause of yield loss in wheat. The most problematic grassy weeds in wheat (*Triticum aestivum* L.) are wild oat (*Avena fatua* L.) and canary grass (*Phalaris minor* Ritz.), which reduce yield by about 30% [4,5]. In addition to lowering output, these weeds also interfere with harvesting processes, cause deterioration of produce quality, and mix their seeds with grains [6]. Chemical weed control is considered the most effective and least time-consuming method. However, the emergence of herbicide resistance in weeds [7] and environmental and health disquiet due to the overuse and misuse of synthesized herbicides [8] led researchers to emphasize alternative strategies for weed control. Nanoherbicides for wheat are herbicide formulations developed using nanoparticles to improve their efficacy and reduce their environmental impact. The use of nanoherbicides for weed control has shown promising and potential benefits. The smaller particle size of nanoparticles allows them to better penetrate plant tissue, increasing the overall effectiveness of the herbicide. This means that lower doses of herbicide can be used, resulting in less environmental impact and lower costs. In addition, nanoherbicides can be designed to be more selective, attacking only the weeds and leaving the crop unharmed. This is achieved by attaching a targeted molecule to the nanoparticle that recognizes and binds to specific weeds. Moreover, the use of nanoherbicides can lead to reduced environmental impact. The smaller particle size of the nanoparticles reduces the amount of herbicide needed, which in turn reduces the amount of herbicide residue in the soil and water. Furthermore, the controlled nature of the nanoherbicides improves the efficacy and longevity of the herbicide. This means that the herbicide can be released over a longer period, providing continuous weed control. The use of nanoherbicides can potentially reduce the development of herbicide-resistant weeds. The smaller particle size of the nanoparticles allows for better herbicide uptake by the plant, which may reduce the likelihood of weed resistance.

The chitosan matrix containing agrochemicals can act as a defensive reservoir for functional constituents, protect the active components from the surrounding environment, and monitor their spread, allowing them to perform as applicable gene delivery schemes for plant modification. Clodinofop-propargyl and fenoxaprop-*P*-ethyl are two widely used herbicides that belong to the aryloxyphenoxypropionate chemical class. These herbicides are commonly used in the control of grassy weeds in wheat. Nanoparticle-based formulations of these herbicides have been developed to improve their efficacy and reduce their environmental impact. For example, the use of clodinofop-propargyl nanoparticles resulted in better weed control and higher yields compared to the conventional herbicide formulation. Also, the use of fenoxaprop-*P*-ethyl nanoparticles resulted in a lower dosage requirement for effective weed control and, hence, lower herbicide residues in the soil compared to the conventional formulations.

The present study aims to investigate the synthesis, characterization, and evaluation of nanoparticles of clodinofop-propargyl and fenoxaprop-*P*-ethyl on weed control, growth, and yield of wheat (*Triticum aestivum* L.).

2 Materials and methods

2.1 Chemicals

The following chemicals were utilized during experimentation: chitosan (MW: 27 kDa, degree of deacetylation: 75–85%), tripoly phosphate (TPP), clodinofop-propargyl (recommended dose 55 g a.i ha^{-1}), and fenoxaprop-*P*-ethyl (93.75 g a.i ha^{-1}).

2.2 Synthesis of chitosan-based clodinofop-propargyl and fenoxaprop-*P*-ethyl

The nanoparticles were prepared by the ionic gelification technique [9]. A solution of 0.1% chitosan (MW: 27 kDa, degree of deacetylation: 75–85%) in 0.2% acetic acid was maintained under magnetic agitation for 12 h at pH 4.7. A separate aqueous solution of 0.1% TPP was prepared and refrigerated at 4°C. Both solutions were filtered through a membrane (0.45 m, Millipore) to remove any aggregated or insoluble material. After the preparation of these solutions, 5 mL of the TPP solution was added to 20 mL of the chitosan solution under magnetic stirring. Thereafter, the mixture was stirred for another 10 min. The resulting chitosan/TPP nanoparticles were stored in amber flasks at ambient temperature (25°C). Commercial herbicide (12 mg) was incorporated into the chitosan solution prior to the preparation of the nanoparticles, and the final concentration of the herbicide in the solution containing the NP was 0.48 $mg\cdot mL^{-1}$. Then, the liquid was evaporated by using a rotatory evaporator till the paste was formed and the paste was oven dried for 24 h at 60°C. Solid material was ground to powdered form. The ground material was passed through 200 µm sieve for confirmation nanoparticle. Then, the nanoparticles were stored for further experimentations and characterization.

2.3 Characterization of chitosan-based nanoparticles of clodinofop-propargyl and fenoxaprop-*P*-ethyl

The size distribution of the chitosan-based nanoherbicides of clodinofop-propargyl and fenoxaprop-*P*-ethyl was examined by passing the resulting particles through 200 μm sieve. To determine the types, the prepared NP powder was characterized by X-ray diffraction (XRD) (PAN analytical X-pert powder, with Cu-Kα as X-ray source). Scanning of NPs was performed at 2θ with a scanning speed of $1°\cdot min^{-1}$ and a step size of 0.02° [10]. Binding properties were investigated using FT-IR. FT-IR spectroscopy was performed to study the functional groups on the NPs with spectrometer FT-IR (Thermo-Nicolet 6700) using the KBr disk technique [11].

2.4 Site description

Field studies were conducted in two consecutive growing seasons (2020–2021 and 2021–2022) at the Agronomic Research Area, College of Agriculture, University of Sargodha. The texture class of the field soil was sandy clay loam with a slightly alkaline reaction (pH 7.7) and an organic matter of 0.71%. The contents of total nitrogen, available phosphorus, and available potassium were 0.44%, 5.12 ppm, and 127 ppm, respectively. Bulk density and cation exchange capacity were $1.33\ g\cdot cm^{-3}$ and $3.9\ cmolc\cdot kg^{-1}$, respectively. The climate in Sargodha is semi-arid, with an average winter (November to March) rainfall of 10–15 mm and a relative humidity of 60%.

2.5 Experimental details

Wheat (cv. FSD-2008) was sown in the third week of November with a manual single-row drill at a row spacing of 22.50 cm and a seed rate of $125\ kg\cdot ha^{-1}$. The recommended fertilizer dose of $105–85–65\ kg\cdot ha^{-1}$ (N:P:K) was applied in the form of urea (46% N), diammonium phosphate (46% P_2O_5 and 18% N), and potash sulfate (50% K_2O). All of the potassium and phosphate fertilizers and half of the nitrogen were applied as a basal dose at the time of seeding. The remaining half of the nitrogen ($53\ kg\cdot ha^{-1}$) was topdressed in two equal splits at the tillering and sprouting stages of wheat. All other practices, except the one studied, were kept the same for all treatments. In this study, only the weeds *P. minor* and *A. fatua* were retained, and all other grassy and broadleaf weeds were manually removed. The two weeds were sprayed with different doses of clodinofop-propargyl and fenoxaprop-*P*-ethyl nanoherbicides. Those doses were optimized during a previous pot study. The recommended herbicide doses for control of the studied weeds were considered 100% doses, and the other doses were calculated on that basis. The nanoherbicides were sprayed at the three to four leaf stage of the target weeds with a Knapsack handheld sprayer using an apartment fan nozzle at a pressure of 30 psi. The sprayer was calibrated, and the amount of water was calculated for 1 m^2.

2.6 Herbicidal activity of chitosan-based nanoparticles of clodinofop-propargyl and fenoxaprop-*P*-ethyl

Experiments were arranged in RCBD using a factorial arrangement with three replicates. The nanoherbicides were sprayed at the three to four leaf stage of the target weeds at seven different doses (D_0 = weedy check, D_1 = normal herbicide at the recommended dose, D_2 = nanoherbicide at the recommended dose of normal herbicide, D_3 = 05-fold lower dose of nanoherbicide, D_4 = 10-fold lower dose of nanoherbicide, and D_5 = 15-fold lower dose of nanoherbicide). The data regarding weed density (m^{-2}), number of grains per spike, number of spike-bearing tillers (m^2), 1,000-grain weight (g), and grain yield ($kg\cdot ha^{-1}$) were calculated using the standard procedure.

2.7 Statistical analysis

The data were examined using Statistical Analysis Software (version 8.1 Statistix, Tallahassee, FL, USA), and the highest significant difference (HSD) was used to compare the mean values of the treatments at a 5% probability level.

3 Results

3.1 Characterization of clodinofop-propargyl and fenoxaprop-*P*-ethyl nanoherbicides

3.1.1 Nanoparticle size

The size of nanoparticles of both herbicides under investigation was determined using a 200 μm sieve and ranged from 35 to 65 nm for clodinofop-propargyl and fenoxaprop-*P*-ethyl, respectively.

3.1.2 FT-IR analysis

Physical and chemical compatibility of the herbicide-loaded chitosan-based nanoparticles of clodinofop-propargyl and

Table 1: FT-IR analysis of clodinofop-propargyl and fenoxaprop-*P*-ethyl

Sample	Frequency (wave number) (cm^{-1})
Clodinofop-propargyl	640–3,470
	640–714
	810–1,015
	1,040–1,370
	1,420–1,740
	1,740–3,470
Fenoxaprop-*P*-ethyl	610–3,240
	610–712
	780–1,012
	1,030–1,360
	1,840–3,240

fenoxaprop-*P*-ethyl was investigated using FT-IR. The major functional groups were in the FT-IR region between 640 and 1,740 cm^{-1}. Free and esterified carboxyl groups were indicated by carbonyl bands in the 640–714 and 810–1,015 cm^{-1} regions, respectively. The absorption band at 1,040–1,370 cm^{-1} was due to the presence of ether, while the band between 1,420 and 1,740 cm^{-1} was due to the cyclic C–C bonds. The broadband from 1,700 to 3,400 cm^{-1} was due to the polymeric O–H stretching band, while the band at 1,600 cm^{-1} reflected the O–H stretching band of the carboxyl group (Table 1). Moreover, the FT-IR spectra of fenoxaprop-*P*-ethyl clearly showed that the major functional groups were in the FT-IR region between 610 and 1,840 cm^{-1}. Free and esterified carboxyl groups were indicated by carbonyl bands in the 610–712 and 78,018–1,012 cm^{-1} regions, respectively. The absorption band at 1,030–1,360 cm^{-1} was due to the presence of ether, while the band between 1,840 and 3,240 cm^{-1} was due to the cyclic C–C bonds in the fenoxaprop-*P*-ethyl (Table 1).

3.1.3 XRD analyses

The crystallinity and crystallite size of the clodinofop-propargyl and fenoxaprop-*P*-ethyl nanoherbicides were tested. It was noticed that the clodinofop-propargyl nanoherbicide has an intense peak appearing at a 2θ value of 29.83°, which corresponds to the (176) plane of the anatase phase (Figure 1a). Additionally, various smaller peaks were detected at 2θ values of 23.59°, 41.47°, 43.71°, and 51.80°, which correspond to the (150), (70), (57), and (54) planes of the anatase phase. The fenoxaprop-*P*-ethyl NPs showed an intense peak around the 2θ value of 30.55° corresponding to the (74) plane of the anatase phase, and several other peaks were also observed at 2θ values of 24,65°, 28.71, 38.33°, 53.53°, 47.19°, and 46.16° corresponding to the (64)-, (68)-, (78)-, (45)-, (42)-, and (33)-planes of the anatase phase, respectively (Figure 1b).

3.2 Effect of clodinofop-propargyl and fenoxaprop-*P*-ethyl nanoherbicides on weeds

3.2.1 Density of *P. minor*

The density of weed species is an important yield-reducing factor for the crop. The data on the effect of the different nanoherbicide doses are presented in Table 2. Clodinofop-

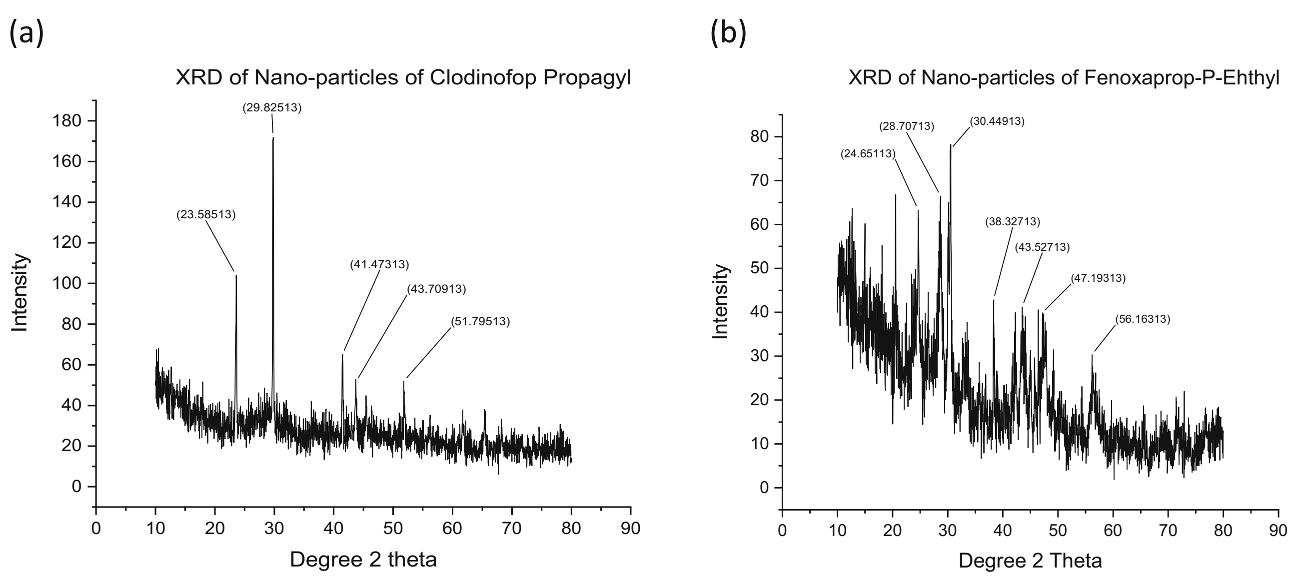

Figure 1: XRD analyses of NPs of clodinofop-propargyl (a) and fenoxaprop-*P*-ethyl (b).

Table 2: Effect of nanoparticles of narrow-leaved herbicides on the density of *P. minor* (m^{-2})

Doses of herbicides	Density of *P. minor* (m^{-2})					
	2020–2021			2021–2022		
	Clodinofop-propargyl	Fenoxaprop-*P*-ethyl	Mean	Clodinofop-propargyl	Fenoxaprop-*P*-ethyl	Mean
D_0	18.33 a	17.00 a	17.66 A	19.33 a	17.33 b	18.33 A
D_1	3.66 c	2.66 cde	3.16 C	4.00de	3.00 def	3.33 C
D_2	0.00 f	0.00 f	**0.00D**	0.00 g	0.00 g	**0.00D**
D_3	1.33 def	1.00 ef	1.16 D	1.667 efg	1.33 fg	1.50 D
D_4	3.33 cd	2.33 cde	2.83 C	3.667 def	2.66 def	3.17 C
D_5	8.33b	4.33 c	6.33 B	9.00c	4.667 d	6.83 B
Mean	5.83 A	4.55 B		6.38 A	4.83 B	
HSD at 5%	**Doses** = **1.26**, **herbicides** = **0.48**, **doses** × **herbicides** = **2.09**			**Doses** = **1.57**, **herbicides** = **0.60**, **doses** × **herbicides** = **2.60**		

The lettering of Means always in Capital letters and interaction in small letters. D_0 = weedy check, D_1 = normal herbicides at the recommended dose, D_2 = nanoparticles of herbicides at the recommended dose of normal herbicide, D_3 = 05-fold lower dose of nanoparticles of herbicides, D_4 = 10-fold lower dose of nanoparticles of herbicides, D_5 = 15-fold lower dose of nanoparticles of herbicides.

propargyl caused lower mortality of *P. minor* compared to fenoxaprop-*P*-ethyl. There were no significant differences between the mean values of each herbicide in the 2 years, with the maximum reported in clodinofop-propargyl (5.83 and 6.38 m^{-2}) and the minimum reported in fenoxaprop-*P*-ethyl (4.55 and 4.83 m^{-2}). The main effect of the different doses was found to be statistically significant for the density of *P. minor* in both studied years. The maximum density of *P. minor* (18.33 and 19.33 m^{-2}) was recorded in plots treated with no dose of clodinofop-propargyl nanoparticles (control) in both experimental years (D_0). However, the interaction between the different herbicide doses and the nanoherbicides showed that the nanoparticles of both herbicides at the recommended dose of the commercial herbicides caused 100% mortality of *P. minor* (D_2). The fivefold lower dose of nanoherbicides (D_3) showed the minimum density (1.16 and 1.50 m^{-2}) as a mean for both herbicides during the 2 years.

3.2.2 Density of *A. fatua*

The data regarding the effect of different doses of nanoparticles herbicides on the density of *A. fatua* (Table 3) showed that different doses of nanoherbicides significantly affected the density of *A. fatua* in both studied years. The application of nanoherbicides at the suggested dose of the normal ones (D_2) caused 100% mortality to *A. fatua.* The maximum density of *A. fatua* (20.16 and 22.16 m^{-2}) was detected in plots treated with the recommended dose of normal herbicides (D_0) in both experimental years. Among the herbicide treatments, the maximum density of *A. fatua* was recorded in

Table 3: Effect of nanoparticles of narrow-leaved herbicides on the density of *A. fatua* (m^{-2})

Doses of herbicides	Density of *A. fatua* (m^{-2})					
	2020–2021			2021–2022		
	Clodinofop-propargyl	Fenoxaprop-*P*-ethyl	Mean	Clodinofop-propargyl	Fenoxaprop-*P*-ethyl	Mean
D_0	22.67 a	17.67 b	**20.16 A**	19.67^{NS}	24.66	**22.16 A**
D_1	5.00 def	3.33 efg	**4.16 C**	4.33	3.67	**4.00 CD**
D_2	0.00 h	0.00 h	**0.00 E**	0.00	0.00	**0.00 E**
D_3	2.00 gh	1.33 gh	**1.66 D**	2.00	2.33	**2.17 D**
D_4	5.67 de	3.00 fg	**4.33 C**	5.00	3.33	**4.16 C**
D_5	10.00 c	6.33 d	**8.16 B**	11.00	5.66	**8.83 B**
Mean	**7.55 A**	**5.27 B**		**7.00^{NS}**	**6.61**	
HSD at 5%	**Doses** = **1.47**, **herbicides** = **0.56**, **doses** × **herbicides** = **2.43**			**Doses** = **1.96**, **herbicides** = **NS**, **doses** × **herbicides** = NS		

The lettering of Means always in Capital letters and interaction in small letters. D_0 = weedy check, D_1 = normal herbicides at the recommended dose, D_2 = nanoparticles of herbicides at the recommended dose of normal herbicide, D_3 = 05-fold lower dose of nanoparticles of herbicides, D_4 = 10-fold lower dose of nanoparticles of herbicides, D_5 = 15-fold lower dose of nanoparticles of herbicides.

plots treated with nanoherbicides at 15-fold lower doses of clodinofop-propargyl (10.00 and 11.00) and fenoxaprop-*P*-ethyl (6.33 and 5.66). The 5-fold lower dose of nanoherbicides (D_3) showed the minimum density (1.66 and 2.17 m^{-2}) as a mean for both herbicides during the 2 years, respectively.

3.3 Effect of clodinofop-propargyl and fenoxaprop-*P*-ethyl on growth and yield of wheat

3.3.1 Number of spikes bearing tillers (m^{-2})

The number of spikes bearing tillers is an important yield-determining component of the wheat crop. Data on the effect of nanoparticles of narrowleaf herbicides on the number of spike-bearing shoots were found to be significant, as illustrated in Table 4. The main effect of different herbicide doses showed that the maximum number of tillers (379.33 and 376.50 m^{-2}) with nanoparticles of narrowleaf herbicides was recorded at the recommended dose of commercial herbicides and the minimum number was reported under control (284.33 and 286.50 m^{-2}) during both studied years. Among herbicide treatments, clodinofop-propargyl resulted in a minimum number of spikes bearing tillers (346.00 and 340.61 m^{-2}), and the maximum (346.00 and 345.50 m^{-2}) was reported with fenoxaprop-*P*-ethyl. The interactive effect of different doses × herbicides showed that the nanoparticles of fenoxaprop-*P*-ethyl at the recommended dose of normal herbicides resulted in a maximum number of spikes bearing tillers (382.00 and 378.33 m^{-2}) with the nanoparticles of clodinofop-propargyl at the recommended dose of normal herbicide and minimum (282.33 and 283.67 m^{-2}) under control by clodinofop-propargyl that was statistically comparable to that of fenoxaprop-*P*-ethyl under control during both years.

3.3.2 Number of grains per spike

The number of grains per spike is a main yield-determining component in wheat. The results regarding the effect of nanoparticles of narrowleaf herbicides on the number of grains per spike were found to be significant, as shown in Table 5. The main effect of different doses of nanoparticles of herbicides showed that the maximum number of grains per spike (54.00 and 52.33) was recorded in both study years (2020–2021 and 2021–2022) with nanoherbicides at the recommended dose of commercial herbicides and the minimum was under control (35.00 and 33.50). The main effect of herbicides showed that nanoparticles of clodinofop-propargyl resulted in a minimum number of grains per spike (47.06 and 45.44 cm) and maximum (48.94 and 47.22) for fenoxaprop-*P*-ethyl. The two-way interaction of different doses × herbicides proved to be significant for the number of grains per spike. The nanoparticles of fenoxaprop-*P*-ethyl at the recommended dose of the normal herbicides resulted in a maximum number of grains per spike (54.33 and 52.67) and a minimum (53.67 and 52.00) under the control of clodinofop-propargyl in 2020–2021 and 2021–2022, respectively. This higher number of grains per spike could be due to successful weed control using nanoherbicides at the recommended dose of normal herbicides. The treatments reduced weed density at low weed infestation,

Table 4: Effect of nanoparticles of narrow-leaved herbicides on the number of spikes bearing tillers (m^{-2}) of wheat

Doses of herbicides	Number of spikes bearing tillers (m^{-2})					
	2020–2021			2021–2022		
	Clodinofop-propargyl	Fenoxaprop-*P*-ethyl	Mean	Clodinofop-propargyl	Fenoxaprop-*P*-ethyl	Mean
D_0	282.33 h	286.33 h	**284.33 E**	283.67 g	289.33 g	**286.50 E**
D_1	351.33 e	353.00 e	**352.17 C**	346.67 de	349.00 d	**347.83 C**
D_2	376.67 ab	382.00 a	**379.33 A**	374.67 ab	378.33 a	**376.50 A**
D_3	365.00 cd	367.00 cd	**366.00 B**	364.67 c	365.33 bc	**365.00 B**
D_4	354.67 de	355.33 de	**355.00 C**	350.00 d	352.00 d	**351.00 C**
D_5	319.00 g	333.67 f	**326.33 D**	324.00 f	339.00 e	**331.50 D**
Mean	341.78 B	346.00 A		340.61 B	345.50 A	
HSD at 5%	**Doses = 5. 86, herbicides = 2.25, doses × herbicides = 9.67**			**Doses = 7.72, herbicides = 2.20, doses × herbicides = 2.59**		

The lettering of Means always in Capital letters and interaction in small letters. D_0 = weedy check, D_1 = normal herbicides at the recommended dose, D_2 = nanoparticles of herbicides that the recommended dose of normal herbicide, D_3 = 05-fold lower dose of nanoparticles of herbicides, D_4 = 10-fold lower dose of nanoparticles of herbicides, D_5 = 15-fold lower dose of nanoparticles of herbicides.

Table 5: Effect of nanoparticles of narrow-leaved herbicides on the number of grains per spike of wheat

Doses of herbicides	Number of grains per spike					
	2020–2021			2021–2022		
	Clodinofop-propargyl	Fenoxaprop-*P*-ethyl	Mean	Clodinofop-propargyl	Fenoxaprop-*P*-ethyl	Mean
D_0	34.00 f	36.00 f	35.00 E	32.67 e	34.33 e	33.50 E
D_1	49.33 cd	51.33 abc	50.33 C	48.00 bc	49.33 ab	48.67 C
D_2	53.67 ab	54.33 a	54.00 A	52.00 ab	52.67 a	52.33 A
D_3	52.67 abc	53.00 abc	52.83 AB	50.67 ab	51.67 ab	51.17 AB
D_4	50.33 bcd	52.33 abc	51.33 BC	49.00 abc	50.33 ab	49.67 BC
D_5	42.00 e	47.000 d	44.50 D	40.33 d	45.00 c	42.67 D
Mean	47.06 B	48.94 A		45.44 B	47.22 A	
HSD at 5%	**Doses = 2.39, herbicides = 0.92, doses × herbicides = 3.96**			**Doses = 2.43, herbicides = 0.93, doses × herbicides = 4.01**		

The lettering of Means always in Capital letters and interaction in small letters. D_0 = weedy check, D_1 = normal herbicides at the recommended dose, D_2 = nanoparticles of herbicides at the recommended dose of normal herbicides, D_3 = 0.5-fold lower dose of nanoparticles of herbicides, D_4 = 10-fold lower dose of nanoparticles of herbicides, D_5 = 15-fold lower dose of nanoparticles of herbicides.

resulting in less weed competition for water, light, and nitrogen, which helped the wheat crop to have a higher number of grains per spike. Mekonnen [12] found that the number of grains per spike was higher under complete weed control (weed-free plots) than under the weedy check.

3.3.3 1,000-grain weight (g)

Since 1,000-grain weight is a main yield component, higher 1,000-grain weight results in higher wheat yield. The effect of nanoparticles of narrowleaf herbicides on 1,000-grain weight was significant, as shown in Table 6. The main effect of different doses of nanoherbicides showed that the maximum 1,000-grain weight of wheat plants (43.31 and 41.31 g) was recorded in both years with nanoherbicides at the recommended dose of commercial herbicides and the minimum under control (30.17 and 29.75 g). The main effect of herbicides showed that nanoparticles of clodinofop-propargyl resulted in minimum 1000-grain weight (38.43 and 37.38 cm) and maximum (39.41 and 37.96 g) with fenoxaprop-*P*-ethyl. The interaction between the different doses and the herbicides proved to be significant for the 1,000-grain weight of wheat. The nanoparticles of fenoxaprop-*P*-ethyl at the suggested dose of standard herbicides resulted in maximum 1,000-grain weight (43.37 and 41.37 g) and minimum (29.00 and 28.67 g) under control of clodinofop-propargyl in 2020–2021 and 2021–2022, respectively.

Table 6: Effect of nanoparticles of narrow-leaved herbicides on 1,000-grain weight (g) of wheat

Doses of nanoparticle of herbicides	1,000-grain weight (g)					
	2020–2021			2021–2022		
	Clodinofop-propargyl	Fenoxaprop-*P*-ethyl	Mean	Clodinofop-propargyl	Fenoxaprop-*P*-ethyl	Mean
D_0	29.00 d	31.33 d	30.17 E	28.67 d	30.84 d	29.75 D
D_1	40.33 b	40.50 b	40.42 C	38.50 bc	39.20 abc	38.85 B
D_2	43.24 a	43.37 a	43.31 A	41.25 a	41.37 a	41.31 A
D_3	42.00 ab	42.17 ab	42.083 AB	40.07 ab	40.20 ab	40.13 AB
D_4	40.37 b	41.63 ab	41.002 BC	39.00 abc	39.50 ab	39.250 B
D_5	35.63 c	37.467 c	36.55 D	36.67 c	36.81 c	36.74 C
Mean	38.43 B	39.41 A		37.38 NS	37.96	
HSD at 5%	**Doses = 1.42, herbicides = 0.54, doses × herbicides = 2.35**			**Doses = 1.54, herbicides = 0.59, doses × herbicides = 2.54**		

The lettering of Means always in Capital letters and interaction in small letters. D_0 = weedy check, D_1 = normal herbicides at the recommended dose, D_2 = nanoparticles of herbicides at the recommended dose of normal herbicide, D_3 = 0.5-fold lower dose of nanoparticles of herbicides, D_4 = 10-fold lower dose of nanoparticles of herbicides, D_5 = 15-fold lower dose of nanoparticles of herbicides.

3.3.4 Grain yield (kg·ha^{-1})

A wheat crop's grain production is a crucial factor; a higher grain yield means a higher economic return for farmers. As shown in Table 7, the impact of nanoherbicides on grain yield was discovered to be substantial. With nanoherbicides at the recommended dose of commercial herbicides, the maximum grain yield of wheat plants was recorded during both study years (2020–2021 and 2021–2022) at 6,332.6 and 6,197.2 kg·ha^{-1}, and the minimum under control was 3,812.8 and 3,677.00 kg·ha^{-1}. The main effect of herbicides demonstrated that clodinofop-propargyl nanoparticles caused a minimum grain yield (5,313.2 and 5,277.7 kg·ha^{-1}). The major effect of herbicides revealed that fenoxaprop-*P*-ethyl and clodinofop-propargyl produced the highest and lowest grain yields, respectively (5,469.5 and 5,340.4 kg·ha^{-1}), when used as nanoherbicides. For the grain yield, the two-way interaction of different dosages of herbicides was found to be significant. The maximum grain yield (6,106.0 and 6,002.7 kg·ha^{-1}) and a minimum (3,740.4 and 3,645.5 kg·ha^{-1}) under control by clodinofop-propargyl throughout 2020–2021 and 2021–2022 were achieved using fenoxaprop-*P*-ethyl nanoparticles at the approved dose of conventional herbicides.

4 Discussion

Sethy et al. [13] and Khan et al. [14] showed that NPs were found in the size range of 35–65 nm. The major functional groups were in the FT-IR region between 640 and 1,740 cm^{-1}. Free and esterified carboxyl groups were indicated by carbonyl bands in the 640–714 and 810–1,015 cm^{-1} regions, respectively. The band at 1,040–1,370 cm^{-1} was due to the presence of ether, while the band between 1,420 and 1,740 cm^{-1} was due to the cyclic C–C bonds. The broadband from 1,700 to 3,400 cm^{-1} was due to the polymeric O–H stretching band, while the band at 1,600 cm^{-1} reflected the O–H stretching band of the carboxyl group. Moreover, the FT-IR spectra of fenoxaprop-*P*-ethyl clearly showed that the major functional groups were in the FT-IR region between 610 and 1,840 cm^{-1}. Free and esterified carboxyl groups were indicated by carbonyl bands in the 610–712 and 78,018–1,012 cm^{-1} regions, respectively. The absorption band at 1,030–1,360 cm^{-1} was due to the presence of ether, while the band between 1,840 and 3,240 cm^{-1} was due to the cyclic C–C bonds in the fenoxaprop-*P*-ethyl. Reflected the O–H stretching band of the carboxyl group [15]. This distinct signature shows the NP formation as reported by Irshad et al. [11]. It was observed that the clodinofop-propargyl nanoherbicide has an intense peak appearing at a 2θ value of 29.83°, corresponding to the (176) plane of the anatase phase. In addition to this peak, several smaller peaks were also observed at 2θ values of 23.59°, 41.47°, 43.71°, and 51.80° corresponding to the (150), (70), (57), and (54) planes of the anatase phase. The NPs of fenoxaprop-*P*-ethyl showed an intense peak around the 2θ value of 30.55° corresponding to the (74) plane of the anatase phase, and several other peaks were also observed at 2θ values of 24,65°, 28.71, 38.33°, 53.53°, 47.19°, and 46.16° corresponding to the (64)-, (68)-, (78)-, (45)-, (42)-, and (33)-planes of the anatase phase, respectively, as reported in the literature [13,16,17]. The application of nanoherbicides resulted in a reduction in the number of

Table 7: Effect of nanoparticles of narrow-leaved herbicides on grain yield (kg·ha^{-1}) of wheat

Doses of nanoparticle of herbicides	Grain yield (kg·ha^{-1})					
	2020–2021			2021–2022		
	Clodinofop-propargyl	Fenoxaprop-*p*-ethyl	Mean	Clodinofop-propargyl	Fenoxaprop-*p*-ethyl	Mean
D_0	3,740.4 f	3,885.1 f	3,812.8 E	3,645.5 d	3,708.5 d	3,677.0 D
D_1	5,551.1 d	5,690.0 bcd	5,620.5 C	5,524.5 b	5,548.6 b	5,536.5 B
D_2	6,295.8 a	6,369.3 a	6,332.6 A	6,171.8 a	6,222.6 a	6,197.2 A
D_3	6,009.9 abc	6,106.0 ab	6,058.0 B	5,979.9 ab	6,002.7 ab	5,991.3 A
D_4	5,603.5 cd	5,703.3 bcd	5,653.4 C	5,569.5 b	5,622.6 b	5,596.0 B
D_5	4,678.2 e	5,063.9 e	4,871.0 D	4,774.9 c	4,937.2 c	4,856.0 C
Mean	5,313.2 B	5,469.6 A		5,277.7 A	5,340.4 A	
HSD at 5%	**Doses = 266.30, herbicides = 102.41, doses × herbicides = 439.61**			**Doses = 295.20, herbicides = 113.52, doses × herbicides = 487.21**		

The lettering of Means always in Capital letters and interaction in small letters. D_0 = weedy check, D_1 = normal herbicides at the recommended dose, D_2 = nanoparticles of herbicides at the recommended dose of normal herbicide, D_3 = 05-fold lower dose of nanoparticles of herbicides, D_4 = 10-fold lower dose of nanoparticles of herbicides, D_5 = 15-fold lower dose of nanoparticles of herbicide.

weeds per unit area of both weeds under investigation. This could be because the nanoherbicides penetrate the weeds more due to the better charge-to-mass ratio, resulting in no weeds growing on a plot treated with nanoherbicide particles at the recommended dose of normal herbicides. Preisler et al. [18] reported that the application of nano-atrazine results in maximum mortality and a smaller number of weeds per unit area than commercial atrazine. Khan et al. [4] reported that the application of chitosan-based clodinofop-propargyl and fenoxaprop-*P*-ethyl nanoherbicides, even at 10-fold lower doses as compared to commercial herbicides resulted in a smaller number of *P. minor* weeds. In this study, both nanoherbicides at the suggested dose of standard herbicides cause toxic effects to *P. minor* and *A. fatua* weeds of wheat crop resulting in 100% weed control and no weed crop competition for applied resources and maximum growth, physiological and yield attributes of wheat crop. This lower number of spikes bearing tillers in weedy check compared to plots treated with NPs of herbicides under investigation at the recommended dose of commercial herbicides may be due to the greater weed density of initiating inaccessibility to a larger area, diminished nutrients, and moisture for the crop. The results are supported by Rizwan et al. [19], which demonstrated that applying herbicides significantly elevated the number of spike-bearing tillers (m^2). The increment in number of grains per spike, 1,000-grain weight, and grain yield with the NPs of herbicides over control might be due to reduced competition between weeds and the crop for the accessible supplies and enhancing resources (water and nutrient) use efficiency in wheat [20–22]. The conclusion of this study is supported by Colbach et al. [23], who confirmed that post-emergence herbicide application influenced plant height and resulted in a trade-off between potential plant production driving parameters and minimizing yield losses caused by weeds. Shah et al. [24] depicted that the application of 50% clodinofop + 50% bromoxynil at the tillering stage enhanced both more growth and physiological traits as well as grain yield attributes and reduced weed biomass.

5 Conclusion

When coupled with herbicides, NPs can serve as efficient transporters and produce nanoformulations. The growth of plants resistant to herbicides, which is the main issue facing the herbicide industry, is helped by these nanoformulations. The simplicity of making chitosan-loaded herbicide complexes leads to their improved release characteristics, which can significantly change how herbicides are applied. Overall, the findings indicated that clodinofop-propargyl and fenoxaprop-*P*-ethyl are capable of 100% control of the weeds under investigation at the recommended dose of normal herbicide. The maximum weed control efficacy, wheat yield, and related parameters were observed with both chitosan-based nanoherbicides under investigation at the suggested dose of standard herbicide. The nanoparticles at a 10-fold lower dose of commercial herbicides and suggested dose produced comparable effects on weeds under study and yield-related parameters of wheat.

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