Detoxification of Cypermethrin and Diafenthiuron in Tomato Fruits When Combined With "Argitos-Argo" and Their Effect on Crop Quality in Unheated Greenhouse Conditions

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Abstract

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This study investigated the impact of colloidal silver (Argitos-Argo) on the detoxification rate of cypermethrin and diafenthiuron residues in tomato fruits cultivated under unheated greenhouse conditions. Dissipation kinetics were modeled using first-order equations, revealing biological half-life of 2,3 days for cypermethrin and 2 days for diafenthiuron. When combined with Argitos-Argo, the two pesticides half-life were reduced to 1.76 days and 1.59 days, respectively, indicating enhanced residue disappearance. Furthermore, the combined use of these insecticides with Argitos-Argo did not significantly alter the dry matter or titratable acidity of the tomato fruits but increased the vitamin C level. Additionally, the combined use of cypermethrin and Argitos-Argo increased the mono-sugar level and improved the sugar-acidity ratio, suggesting potential nutritional benefits.

Keywords: Colloidal silver, insecticides, detoxification, tomato, crop quality.

Introduction

The greenhouse industry is the fastest-growing sector of agriculture in Armenia, with tomatoes and cucumbers as the primary crops cultivated for 8–9 months each year. Greenhouse farming ensures a consistent year-round supply of fresh vegetables for the local market and, more importantly, facilitates exports to the Eurasian Customs Union and Europe. However, strict regulations mandate that crops be free of pesticide residues or contain only trace amounts within permissible limits.

Greenhouse vegetables are grown under two different conditions: heated environments from November to April and unheated conditions from April to August. In the latter case, where conditions resemble open-field farming, pesticide detoxification occurs more slowly. Despite these environmental differences, pre-harvest interval (PHI) regulations remain uniform throughout the entire greenhouse cultivation period.

Given these challenges, accelerating pesticide detoxification is crucial to ensure that harvested crops either contain no residues or remain within acceptable safety limits. Currently, the most common approach involves pre-treatment with growth regulators. However, recent studies highlighted the potential of silver nanoparticles in degrading pesticide residues, presenting promising opportunities for environmental remediation and sustainable agriculture (Akhter *et al.,* 2024; Arulsoosairaj *et al.,* 2024; Hassan *et al.,* 2023; Naing *et al.,* 2021).

To address this issue, this study aimed to explore the combined application of pesticides with colloidal silver, specifically the Argitos-Agro preparation, as a potential solution.

Materials and Methods

Argitos-Agro is a high-tech plant growth stimulator with fungicidal properties, formulated with colloidal silver nanoparticles (AgNPs). It is produced by the Nano-Sphere scientific production enterprise in Russia and packaged at the Arsil innovation center in Armenia. The silver ion (Ag^+) concentration in the formulation is 0.01%. Cypermethrin is a synthetic pyrethroid insecticide effective against a wide range of pests, particularly Lepidoptera, acting as a fast-acting neurotoxin in insects. Diafenthiuron is a broad-spectrum insecticide with systemic, contact, and stomach action. It disrupts mitochondrial function in target pests, including phytophagous mites, and has demonstrated high efficacy against major agricultural pests such as mites, aphids, thrips, and whiteflies.

Tomato plants (*Maxik B* hybrid) were cultivated under greenhouse conditions in Armenia, with an average temperature of 20–26°C and relative humidity of 65%. The experimental plot was divided into four sections (70 m² each, with 175 plants per section), separated by 1 m² buffer zones to prevent cross-contamination. For spraying, manufactured products containing cypermethrin EC (25% active ingredient) (Atrin, Ukraine) and diafenthiuron EC (25% active ingredient) (Pegasus, Desenda, China) were used, with application rates of 300 g/ha and 375 g/ha, respectively. A 1% Argitos-Agro solution was used as a diluent for pesticide application, while only water was used as the control treatment. Spraying was conducted once at the mass ripening stage using an accumulator sprayer (Usadba, RF, ESL-8 L). Test samples (≥2 kg) were taken 1, 3, 5 and 7 days after spraying from the middle of the experimental plot. Diafenthiuron and cypermethrin residues were analyzed

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following protocols' of (Amelin *et al.,* 2012; Panhwar *et al.,* 2014).

Briefly, residual amounts of cypermethrin were extracted from the fruits (20 g) using 50% aqueous acetone and then redissolved in hexane. For diafenthiuron, the extraction was performed using chloroform. The sample extracts were concentrated, purified with activated carbon, and applied to Czech plates of the brand "Silufol-UV 254".

The mobile phase for cypermethrin was hexane-acetone (4:1), while for diafenthiuron, it was hexane-chloroform (1:2). Detection of cypermethrin was performed using an ammoniacal silver nitrate solution, followed by decolorization with a 2% citric acid solution. For diafenthiuron, a mixture of bromophenol and silver nitrate solutions were used.

Quantitative determination was conducted by comparing the coloration of the test and standard solution spots at Rf 0.44 for cypermethrin and Rf 0.5 for diafenthiuron. The lower detection limit for both diafenthiuron and cypermethrin was 3 µg. The recovery rate was 84.3% for diafenthiuron and 75% for cypermethrin. Fruit quality parameters in the harvested crop were evaluated using standard biochemical analysis methods (Yermakov *et al.,* 1987). To determine the nature of dissipation kinetics and biological half-life of pesticides, we used the first-order equation by Timme *et al.* (1986) was used.

Statistical analysis employed the windows software package. All analyses were performed in 4 replicates and data were reported as Mean±SD. The significant difference between means for various treatments was determined by using the paired t-test and Anova LSD test.

Results and Discussion

The study revealed the presence of significant pesticide residues in tomato fruits one day after treatment. Internal diafenthiuron residues ranged from 1.12±0.17 to 1.32±0.11 mg/kg, whereas cypermethrin residues ranged between 0.43±0.03 and 0.48±0.08 mg/kg. These elevated levels likely result from the ability of these compounds - particularly diafenthiuron - to penetrate the cuticular layer and translocate into the fruit along with nutrients from the leaves and stems. Once inside, plant defense detoxification mechanisms worked to mitigate toxicity (Zhang *et al.*, 2024).

When combined with Argitos-Agro, pesticide detoxification in tomato fruits occurs more rapidly than in control. Three days after spraying, total residues in the Argitos-Agro-treated variants were 278 % lower for cypermethrin and 19.5% lower for diafenthiuron. This trend continued throughout the seven-day study.

However, detoxification rates differed between the two pesticides: within the five days period, total diafenthiuron residues declined by 80.0-88.1%**,** whereas cypermethrin residues decreased by 72.9-74.5 %**.** These differences may be influenced by various factors, including the pesticides' physicochemical properties, such as vapor pressure, water solubility, hydrolysis rate, penetration ability, translocation, and excretion. The addition of colloidal silver nanoparticles further amplified this effect, strengthening Argitos-Agro's potential to accelerate pesticide detoxification in tomato fruits.

Dissipation kinetics, modeled using first-order equations, revealed biological half-lives of 2.3 days for cypermethrin and 2.0 days for diafenthiuron. When combined with Argitos-Agro, these half-lives decreased to 1.76 days and 1.31 days, respectively (Figure 1).

However, despite the accelerated dissipation rates, pesticide residues remained above the maximum residue levels (MRLs) during the designated pre-harvest intervals - three days for cypermethrin and seven days for diafenthiuron (EUR-Lex, 2005). Cypermethrin concentrations exceeded the MRL of 0.2 mg/kg by 2.7 times (0.54±0.05 mg/kg), whereas diafenthiuron levels reached 0.08 ± 0.03 mg/kg, surpassing the MRL of 0.05 mg/kg.

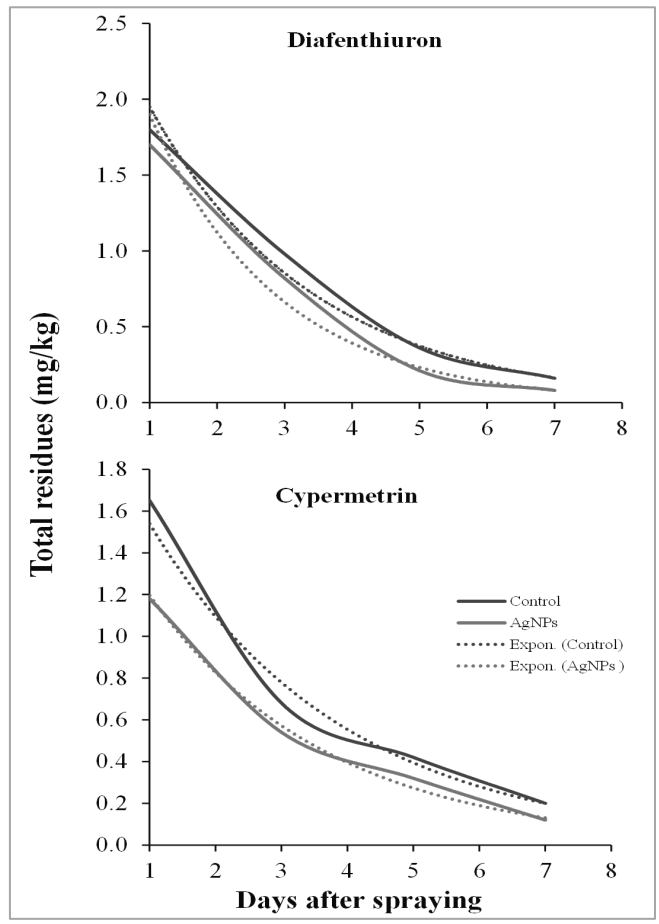


Figure 1. Dissipation kinetics of diafenthiuron and cypermethrin in tomato fruits, applied either singly (Control) or in combination with "Argitos-Agro" (AgNPs).

It was found that the combined use of preparations containing colloidal silver did not significantly affect the dry matter content or titratable acidity in tomato fruits but contributed to an increase in vitamin C levels by 61.2% ($p = 8.07\times10^{-7}$) with cypermethrin and 13.3% ($p = 0.032$) with diafenthiuron, compared to single-application treatments. Additionally, the combined use of cypermethrin and Argitos-Argo increased the monosaccharide content in tomato fruits by approximately 23.1% ($p = 0.022$) and improved the sugar-acidity ratio (Table 1).

Table 1. Effect of diafenthiuron and cypermethrin in combination with "Argitos-Agro" (AgNPs) on key qualitative characteristics of tomato fruits (P<0.05, n=4).

Treatment	Dry matter (%)	Vitamin C (mg/100 g)	Titratable acidity (%) (according to malic acid)	Monosugars (%)	Sugar–acid ratio (SAR)
Diafenthiuron (Control)	7.0±0.39	11.3±0.95	0.24±0.01	2.7±0.08	11.3
Diafenthiuron + AgNPs	7.1±0.23	12.8±0.50	0.23±0.02	2.8±0.07	12.2
Cypermetrin (Control)	7.1±0.44	9.8±0.29	0.23±0.02	2.6±0.14	11.3
Cypermetrin + AgNPs	7.4±0.17	15.8±0.50	0.25±0.01	3.2±0.39	12.8
$LSD_{0.05}$	0.25	0.94	0.02	0.36	

These results align with our previous studies (Atchemyan *et al.,* 2023) and that of others, which reported that certain concentrations of silver nanoparticles exert a significant phytostimulatory effect on cucumber, wheat, and fenugreek plants. This stimulation enhances yield quantity, antioxidant activity, and overall quality (Pociecha *et al.,* 2021; Sadak, 2019).

Residue dynamics and fruit quality parameters (vitamin C and sugars) differed significantly between the two variants ($p < 0.05$). These differences were attributed to the nature of the insecticides, the rapid detoxification effect observed when combined with the colloidal silver preparation Argitos-Agro, and their impact on fruit quality.

It can be concluded from this study that Argitos-Agro enhanced pesticide detoxification in tomatoes, leading to a significant reduction in diafenthiuron and cypermethrin residues. However, despite the improved dissipation rates, residue levels remained above MRLs within the pre-harvest intervals, indicating a need for further refinement. The combined use of preparations with colloidal silver does not significantly affect the dry matter content or titratable acidity in tomato fruits but contributes to an increase in vitamin C levels. Additionally, the combined use of Cypermetrin and Argitos-Argo increases the monosugar levels and improve the sugar-acidity ratio.

These findings suggest the potential of using colloidal silver for safer, higher-quality crop production, warranting further research to refine application strategies and maximize benefits.

الملخص

أتشميان، ليفون، فارسيك ميرزويان* ونيلي بيتروسيان. 2026. إزالة سمّية المبيدين سايبرمثرين وديافينثيورون في ثمار البندورة/الطماطم عند دمجهما مع «أرغيتوس–أرغو» وتأثير ذلك في جودة المحصول تحت ظروف البيوت المحمية غير المُدفّأة. مجلة وقاية النبات العربية، 44(3):423–426. https://doi.org/10.22268/AJPP-001410

هدفت هذه الدراسة إلى تقييم تأثير الفضة الغروية (أرغيتوس–أرغو) في معدل إزالة سمّية متبقيات المبيدين سايبرمثرين وديافينثيورون في ثمار البندورة/الطماطم المزروعة تحت ظروف البيوت المحمية غير المُدفّأة. جرى توصيف حركية تلاشي المتبقيات باستخدام نماذج من الرتبة الأولى، حيث بلغ العمر النصفي الحيوي 2.3 يوم للسايبرمثرين ويومين للديافينثيورون. وعند دمج هذين المبيدين مع أرغيتوس–أرغو، انخفض العمر النصفي للمبيدين إلى 1.76 و 1.59 يوماً، على التوالي، مما يشير إلى تعزيز تلاشي المتبقيات. كما أظهرت النتائج أن الاستخدام المشترك للمبيدين مع أرغيتوس–أرغو لم يُحدث تغيرات معنوية في محتوى المادة الجافة أو الحموضة المعايرة لثمار البندورة/الطماطم، في حين أدى إلى زيادة محتوى فيتامين C. إضافةً إلى ذلك، أدى الاستخدام المشترك للسايبرمثرين مع أرغيتوس–أرغو إلى زيادة مستوى السكريات الأحادية وتحسين نسبة السكر إلى الحموضة، بما يشير إلى فوائد غذائية محتملة.

كلمات مفتاحية: الفضة الغروية، مبيدات حشرية، إزالة السمّية، البندورة/الطماطم، جودة المحصول.

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