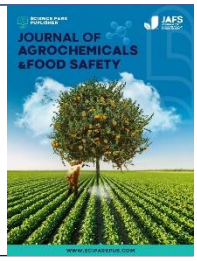
Journal of Agrochemicals and Food Safety, 2025, Vol. 1, Iss. 1, 42-52

DOI: 10.62184/jafs.jafs1000202515

Research Article

SCIENCE PARK PUBLISHER



Journal of Agrochemicals and Food Safety

Residue dissipation and risk assessment of conventional and nanoemulsion imidacloprid in greenhouse-grown cucumber

Moustafa A. Abbassy, Mona A. Abdel-Rasoul, Belal S.M. Soliman, Atef M.K. Nassar*

Department of Plant Protection, Faculty of Agriculture, Damanhour University, Egypt

Received: 27, 01, 2025; Accepted: 27, 11, 2025; Published: 28, 12, 2025

Abstract

Imidacloprid (IMD), a neonicotinoid insecticide classified as moderately hazardous (class II) according to WHO, is widely used in greenhouses for managing diverse plant pests. Therefore, the current study aimed to examine the residual levels of IMD formulations (conventional (SC) and nanoemulsion (NE)) in cucumber fruits, leaves, and soil, and to assess their potential risks to humans. Samples were extracted using QuEChERS extraction and clean-up kits and analyzed by High-Performance Liquid Chromatography (HPLC) coupled with Diode Array Detector. Results indicated that the half-life ($t_{1/2}$) of IMD in cucumber fruits was 2.135 and 1.701 days for SC and NE formulations, respectively. In leaves, the half-lives were 2.976 and 2.2499 days for SC and NE formulations. The SC formulation showed greater persistence in and on cucumber fruits, leaves, and soil than the NE. Post-harvest treatments, including washing and pickling fruits, especially with a 1% Na_2CO_3 solution, reduced the residues significantly. Additionally, the dietary risk assessment of the residue levels of IMD in cucumber fruits posed no risk to humans.

Keywords: Imidacloprid residues; Cucumber; Dissipation; QuEChERS; HPLC-DAD; Nanoemulsions; Risk assessment

1. Introduction

Cucumber, *Cucumis sativus* L. Cucurbitaceae, is an essential and commercially popular cucurbitaceous vegetable crop holding a prestigious position in the vegetable market [1]. In 2020, the world cucumber production was estimated to be 91.258 million tons from an area of 2.261 million hectares (4.04 Kg/m^2) [2]. In recent years, greenhouse, an approach to controlled environments, cultivation has evolved to conserve water and soil resources and produce off-season products [3]. In Egypt, cucumber is produced under open field conditions, considered one of the main greenhouse-cultivated vegetables. The total greenhouse area for cucumber production increased from 5.40 million m^2 in 2004 to 11.92 million m^2 in 2014, and production increased from 60,000 tons in 2004 to 161,000 tons in 2014 [4].

Globally, pests destroy up to 40% of crops, causing about $220 billion in losses annually [2]. Pesticides play a key role in managing insect pests and pathogens and thereby promoting crop production [5, 6]. The extensive use of pesticides, driven by efforts to intensify crop production, has become an inevitable yet controversial practice, raising significant concerns about their adverse impacts on the environment, non-target organisms, and human health [7-9]. A major negative impact of the intensification of pesticide use is the accumulation of residues, which is a major food safety concern for consumers [10].

Therefore, determining pesticide residues in produce, especially cucumber, is important to avoid harmful effects. Also, it would help to confirm that pesticide levels do not exceed the maximum residue limits (MRLs) established by various international organizations. Also, the accumulation of these residues depends upon fate in the environment rather

DOI: 10.62184/jafs.jafs1000202515

than depending on their chemical properties (vapor pressure, solubility, and adsorptive behavior), environmental characteristics (precipitation, temperature, soil, sediment, and water), and agricultural practices (cropping scheme, application process, timing of application, and canopy) [11, 12].

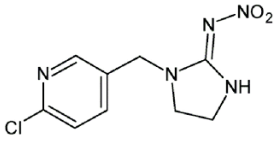
On the other side, nanoemulsions (NEs) of pesticides are characterized by droplet sizes less than 200 nm. They are advantageous over macro- and micro-emulsions [13] with improved stability, reduced gravitational separation, less viscosity, and optical transparency. These features make NEs highly desirable for various industrial applications because they enhance delivery and efficacy [14, 15]. Also, they are effective in facilitating the spray solution formulation, handling, and production at low costs [16]. The development of NEs could be achieved via a plethora of simple and complex methods that are classified into either high-energy (complex, such as using mechanical devices) or low-energy (simple, depending on the basic chemical properties of the material) [17].

Therefore, the present study aimed to a) prepare and characterize the NE formulations of IMD, b) measure the residues of the NE and SC formulations in cucumber fruits, leaves, and soil under greenhouse conditions, and c) study the safety of IMD (SC and NE) residues.

2. Materials and methods

2.1. Materials

The tested insecticide IMD is shown in Scheme 1.



Scheme 1. Imidacloprid structure.

IMD is a neonicotinoid insecticide belonging to the chloronicotinyl nitroguanidine chemical family. Its IUPAC name is *1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine*. It is sold in Egypt under the commercial name ImiDOR® (35% SC; field application rate of 75 mL/100 L), and it was obtained from Chema Trade Company, Nasr City, Cairo, Egypt.

2.2. Nanoemulsions (NEs) preparation and characterization

NE formulation of IMD, characterization, stability, and application under greenhouse conditions were completed as described in our published work [18].

2.3. Sampling and extraction

After 0 (initial: two hours after application), 1, 3, 7, 10, 13, and 16 days after treatment (DAT), samples of treated and untreated cucumber fruits, leaves, and planting soil were collected randomly from each replicate. Immediately after collection, all samples were kept in plastic bags, transferred gently to the laboratory, and stored at –20 °C until being analyzed. Precisely 1 kilogram of each sample was chopped and homogenized at high speed for 5 minutes using a laboratory homogenizer, then extracted following the procedure outlined and modified by Lehotay [19]. 10 g of each homogenized sample was extracted and cleaned up using an optimized QuEChERS method [20] and then analyzed by Agilent 1100 HPLC-DAD.

2.4. Chromatographic analysis of IMD residues

An Agilent system (1100 series) equipped with an analytical Hypersil ODS HPLC column (150 mm×4.6 mm ×5 µm) attached to a photodiode array detector. The flow rate of the mobile phase (acetonitrile/water (65/23 v/v)) was 1 mL/min with an injection volume of 20 µl. The detection wavelength was set at 270 nm. Residues in the unknown or spiked samples were estimated by comparing their peak areas to those of standards, which run under identical conditions [21]. The analysis was conducted at the Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food, Agricultural Research Centre (QCAP), Giza, Egypt.

2.5. Removal of IMD using pickling and washing

Washing and pickling cucumber fruits were studied in removing residues of the studied formulations of IMD in and on (non-washed) treated cucumber fruits after 2 hours of spraying (initial deposit). Samples were divided into two parts; the first part was divided into five subsamples, each of which was soaked in a plastic jar filled with one of the following solutions: tap water, 1% solution of each soap, potassium permanganate ($KMnO_4$), sodium carbonate (Na_2CO_3), and acetic acid (CH_3COOH) for two minutes and then allowed to dry. The second part was pickled in water, salt (10%), and

DOI: 10.62184/jafs.jafs1000202515

vinegar (10%) according to Ryad and Mahmoud [22], then the residues were measured after one week and two weeks of pickling using HPLC-DAD.

2.6. Recovery studies of IMD

To determine recovery percentages, 0.01, 0.1, and 1 mg/kg of each formulation of IMD were added to the cucumber fruits, leaves, and soil of the control group. Samples were extracted and cleaned up as described in the previous steps. Then all results of residues detected in different samples were corrected according to the recovery percentages obtained.

2.7. Limits of detection and quantification

Limits of detection (LOD) and quantification (LOQ) were calculated mathematically using data extracted from the standard curve of IMD (NE and SC). The calibration curve was plotted, the slope (S) was assessed using the regression equation, and then LOD = 3.3×SE/S and LOQ = 10×SE/S were estimated [23].

2.8. Kinetic calculations

The rate of degradation constant (K) and half-life time (t½) of IMD were calculated [24] by plotting the logarithm of residue levels and time intervals. Then a linear trend line was fitted in Microsoft Excel® with an intercept equal to the lowest residue level and the slope was defined. Accordingly, K and $t_{½}$ of IMD in fruits, leaves, and soil samples were calculated as follows: K = 2.303 × slope and $t_{½}$=0.693/K.

2.9. Estimation of dietary exposure dose (EED) and risk quotient (RQ)

Dietary exposure calculation and risk were calculated using equations (1) and (2):

EED = calculated residue limit (mg/kg) × food intake (Kg/capita/day) (1)

RQ (Risk Quotient) = EED/acceptable daily intake (ADI) (mg/kg b.w.) (2)

According to the 2011 report of the Food and Agriculture Organization (FAO), the average estimated daily cucumber intake for an Egyptian adult (weighing 60 kg) is 34.92 g (0.03492 kg/capita/day) [25]. The acceptable daily intake (ADI) for IMD is 0.06 mg/kg body weight per day [26]. An RQ value exceeding one suggests a potential risk to human health, whereas a value below one indicates minimal risk [27].

2.10. Statistical analysis

Results of IMD residues were analyzed using the General Linear Model (GLM) procedure of the Statistical Analysis System as repeated measures over time (SAS, version 9.3). Means were compared using Student-Newman-Keuls least significant difference (LSD) *post-hoc* multiple comparison test ($P \leq 0.05$) [28].

3. Results and discussions

3.1. Suitability of analytical protocol

The employed analytical method efficiently detected IMD residues in cucumber fruits, leaves, and planting soil. This was evident by the results of recovery percentages, coefficients of variability (inter- and intra-assay), and limits of detection and quantification of IMD standard material (Table 1). Fortification of tested samples collected from the control treatment with predefined amounts of 1, 0.1, and 0.01 mg/Kg of IMD showed recovery (%) in fruits, leaves, and soil samples ranging from 101.83 to 103.54, 99.83 to 104.879, and 98.86 to 99.92%, respectively. Also, the relative standard deviation of means ranged from 1.55 to 5.46% and 2.62 to 4.38% for SC and NE formulations of IMD, respectively, which were within the appropriate limits for the analysis of pesticide residues [26]. Also, the results of the intra-day assay and inter-day assay showed that the employed method was precise, where CV% values were less than 10%, which emphasizes the reliability and effectiveness of the analytical method. The detection and quantitation limits of IMD revealed that all residue levels of SC and NE forms in the examined samples (fruits, leaves, and soil) were greater than the LOD and LOQ values. Results conveyed herein were lower than the limit of quantification of IMD reported by Germany [29] using the QuEChERS with HPLC–MS/MS of 0.01 mg/kg in cucumbers. Also, the unknown concentrations of IMD were calculated from a standard curve with a linearity range of 1 to 10 ng/mL (Figure 1).

Journal of Agrochemicals and Food Safety, 2025, Vol. 1, Iss. 1, 42-52
DOI: 10.62184/jafs.jafs1000202515

Research Article

Table 1. Recovery percentages (%) ± relative standard deviation (RSD), and coefficients of variation (CV %) of spiked cucumber samples and detection limit (LOD) and quantification limit (LOQ) of imidacloprid after analysis using HPLC-DAD.

Sample	Level (mg/kg)	Conventional formulation					Nanoemulsion				
		Recovery (%) ±RSD	CV (%)		LOD	LOQ	Recovery (%) ±RSD	CV (%)		LOD	LOQ
			Intra-Assay	Inter-Assay				Intra-Assay	Inter-Assay		
Leaves	1	104.897±3.04	3.87	5.34	0.0023	0.007	104.47±3.46	6.2	6.8	0.00019	0.0008
	0.1	99.83±1.35	1.88	3.56			104.42±2.62	1.71	2.1		
	0.01	102.13±3.195	0.58	1.54			104.89±3.21	0.6	2.3		
Fruits	1	101.83±5.46	7.79	8.24	0.0059	0.0178	105.66±3.79	6.49	9.3	0.0056	0.0169
	0.1	102.74±1.88	1.45	3.54			103.53±4.38	2.21	3.2		
	0.01	103.54±3.71	0.64	2.1			103.98±2.34	0.51	1.3		
Soil	1	99.01±2.53	5.3	6.7	0.003	0.009	100.62±3.39	6.14	8.34	0.0029	0.0076
	0.1	99.92±2.88	1.79	3.4			101.32±2.77	1.75	2.4		
	0.01	98.86±1.55	0.42	2.5			100.61±3.32	0.61	1.4		

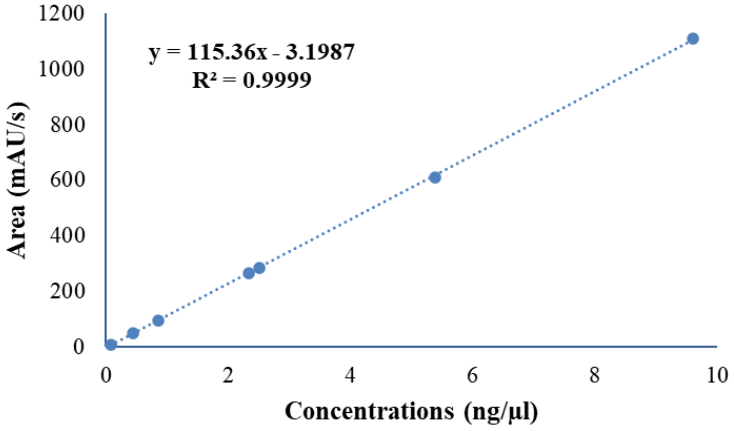


Figure 1. Standard curve of imidacloprid analyzed using HPLC-DAD.

Table 2. Average residues (mg/Kg) of the conventional formulation of imidacloprid detected in cucumber fruits, leaves, and soil using HPLC-DAD.

Days after treatment	Fruits	Dissipation (%)	Leaves	Dissipation (%)	Soil	Dissipation (%)
0 (2 hr.)	2.316	-	5.403	-	0.995	-
1	1.406	39.29	3.413	36.83	0.632	36.48
3	0.660	71.50	2.074	61.61	0.225	77.39
7	0.286	87.65	1.048	80.60	0.071	92.86
10	0.142	93.87	0.662	87.75	0.036	96.38
13	0.047	97.97	0.269	95.02	0.006	99.40
16	0.007	99.7	0.09	98.33	0.002	99.80
Slop	0.141		0.101		0.163	
K	0.325		0.232		0.375	
$t_{½}$	2.135		2.976		1.847	

K = rate of degradation, $t_{½}$= half-life values

DOI: 10.62184/jafs.jafs1000202515

Research Article

3.2. Dissipation behavior and kinetics

Data summarized in Tables 2 and 3 represent the residue amounts of SC and NE formulations of IMD detected in cucumber fruits, leaves, and soil after different time intervals of spray. For the SC formulation of IMD, initial residue (measured two hours post-spray) in cucumber fruits was 2.316 mg/kg. Then, residues decreased with days after treatment (1.406, 0.660, 0.286, 0.142, 0.047, and 0.007 mg/kg after 1, 3, 7, 10, 13, and 16 DAT, respectively) (Table 2). Additionally, the dissipation percentage of IMD SC residues increased (39.29, 71.5, 87.65, 93.87, 97.97, and 99.7%) across the studied time intervals, with a calculated half-life ($t_{½}$) of 2.135 days (Figure 2A and Table 2).

The residues of the SC formulation in non-washed leaves, the initial deposit after spraying was 5.403 mg/kg. Residues decreased to 3.413, 2.074, 1.048, 0.576, 0.269, and 0.09 mg/kg after 1, 3, 7, 10, 13, and 16 days, respectively. The dissipation rates from leaves were 36.83, 61.61, 80.60, 87.75, 95.02, and 98.33% at 1, 3, 7, 10, 13, and 16 DAT, with a calculated $t_{½}$ of 2.976 days (Figure 2A and Table 2). Also, its residue in soil was initially reported to be 0.995 mg/kg and declined to 0.225 mg/kg by the 3rd day, 0.036 mg/kg by the 10th day, and further to 0.002 mg/kg by the 16th day. Dissipation rates in soil were 36.48, 77.39, 92.86, 96.38, 99.4, and 99.8% at the 1, 3, 7, 10, 13, and 16-day intervals, respectively, with a half-life ($t_{½}$) of 1.847 days (Figure 2A and Table 2).

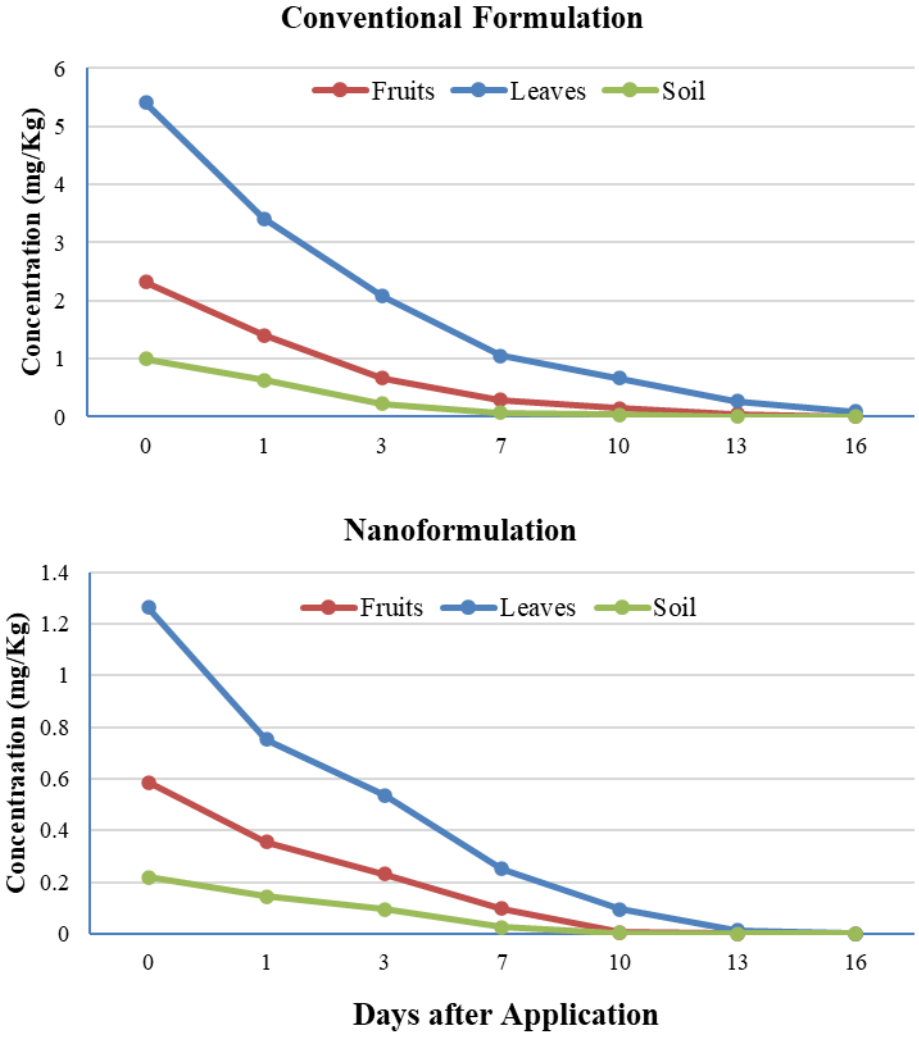


Figure 2. Average decline patterns of imidacloprid (conventional and nanoemulsion formulations) residues in cucumber fruits, leaves, and soil samples after being analyzed using HPLC-DAD.

DOI: 10.62184/jafs.jafs1000202515

Concerning the residues of the NE formulation of IMD, Table 3 clearly shows that the initial deposits in fruits, leaves, and soil samples were 0.585, 1.263, and 0.218 mg/kg, respectively. These residues decreased to 0.354, 0.751, and 0.144 mg/kg after 1 day and to 0.231, 0.536, and 0.095 mg/kg after 3 DAT. After 7 DAT, the residues of the tested NE formulation recorded 0.98, 0.25, and 0.025 mg/kg. On the sixteenth DAT, residues were not detected in all samples studied. The loss or dissipation percentages of IMD NE were 39.49, 60.51, 83.25, 98.97, 100, and 100% (in fruits), 40.54, 57.56, 80.21, 92.48, 98.89, and 100% (in leaves), and 34.94, 56.42, 88.53, 98.62, 100, and 100% in the soil after 1, 3, 7, 10, 13, and 16 DAT, respectively. The t½ values were 1.701, 2.249, and 1.715 DAT in cucumber fruits, leaves, and planting soil, respectively (Figure 2B and Table 3).

Residues of IMD (both SC and NE formulations) in cucumber fruits were below the maximum residue limit (MRL) of 0.5 mg/kg [30] by the 3rd DAT with the recommended application rate [31]. Consequently, the pre-harvest interval (PHI) for SC IMD was determined to be 7 DAT. Overall, SC IMD residues were higher in cucumber leaves compared to fruits and soil, indicating a greater persistence in the foliage. Levels of NE IMD residues were lower than the MRL from 1 DAT in cucumber fruits, and the determined PHI was 1 DAT.

The initial amounts of IMD in leaves were higher than in fruits and soil samples. The diverse levels of initial deposits on fruits and leaves of cucumber are mainly due to many factors, including the ratio of surface to mass area and the nature of the treated surfaces that are smooth or rough and waxy or non-waxy [32]. Other factors, such as systemic characteristics of different pesticides, especially the hydrophilic to lipophilic balance, along with the elevated wax content of fruit surface, significantly control their penetrability into fruit tissues [33]. Also, it was reported that degradation and dissipation of residues of IMD from cucumber fruits might be because of the evaporation from surfaces. Weather conditions (i.e., temperature and sunlight), biological factors, chemical or biochemical decomposition, metabolism, and photolysis occur simultaneously [34-36]. Christensen [37] described that the decline of pesticides from crop surfaces was due to biological, chemical, and/or physical processes, or crop growth. Additionally, the plant growth (particularly fruits) is significantly responsible for decreasing the residue amounts due to growth dilution effects [38].

Currently, the results of the disappearance of IMD residues were higher in fruits than in leaves. This agreed with Shalaby [39], who reported half-life (t½) values in the peel and whole cucumber fruits and leaves of 1.88, 2.02, and 2.47 days for IMD. Shokr [40] estimated the approximate pre-harvest interval for IMD of 2 days on tomato and cucumber. Fossen [41] reported that IMD is translocated rapidly through the plant tissues after application and could be detected in leaves with vascular fluids. Also, as a systemic pesticide, IMD has physical and chemical properties that allow its residues to move inside treated plants throughout the xylem. Leili [42] found that MRLs of IMD were higher than what was reported by Codex Alimentarius after one hour of application and decreased by about 31% one DAT, but still greater than the MRL.

Table 3. Average residues (mg/Kg) of nanoemulsion of imidacloprid detected in cucumber fruits, leaves, and soil using HPLC-DAD.

Days after treatment	Fruits	Dissipation (%)	Leaves	Dissipation (%)	Soil	Dissipation (%)
0 (2 hr.)	0.585		1.263		0.218	
1	0.354	39.49	0.751	40.54	0.144	33.94
3	0.231	60.51	0.536	57.56	0.095	56.42
7	0.098	83.25	0.25	80.21	0.025	88.53
10	0.006	98.97	0.095	92.48	0.003	98.62
13	ND	100	0.014	98.89	ND	100
16	ND	100	ND	100	ND	100
Slop	0.1769		0.134		0.175	
K	0.4075		0.308		0.404	
$T_{1/2}$	1.701		2.250		1.715	

K = rate of degradation, t½= half-life values

DOI: 10.62184/jafs.jafs1000202515

Research Article

3.3. Removal efficiency via washing and pickling

Pickling showed varying effectiveness in reducing IMD residues between the SC and NE formulations (Table 4). The residue reductions were 88.25 and 100% after 1 and 2 weeks of pickling of SC formulation-treated fruits. For the NE formulation, pickling completely removed (100%) residues within just one week.

Results in Table 5 show that various washing solutions differed in their effectiveness in removing IMD residues from SC or NE formulations. For fresh cucumber fruits, the initial residue of IMD two hours post application was 2.316 mg/kg. Washing solutions might be ranked according to their efficacy in the reduction of the SC formulation as follows: sodium carbonate (54.83%), soap solution (38.26%), potassium permanganate (31.56%), acetic acid (30.59%), and tap water (20.17%), with sodium carbonate being the most effective. For the NE formulation, the solutions were ranked in ascending order based on the efficiency of residue removal: sodium carbonate (71.97%), acetic acid (64.27%), potassium permanganate (50.68%), soap solution (47.69%), and tap water (46.41%). Also, sodium carbonate solution was the most effective in reducing IMD residues for NE.

In this respect, the effectiveness of any washing solution varies based on several factors, including the pesticide's physicochemical features, water solubility, mode of action, and pre-harvest intervals. The basic routine for consumers to clean fruits is to use tap water. Meanwhile, the type of washing agents significantly affects the performance of processes in pesticide removal from agricultural commodities. The tap-water washing process was experimented in previous studies to reduce residue levels on commodity surfaces [43, 44]. Different other chemical agents, such as acetic acid, sodium carbonate, and sodium chloride, were evaluated as washing agents of different agricultural commodities [45-48].

Also, similar to our results, Randhawa *et al.* [49] used tap water, different concentrations of acetic and citric acid solutions (1.5, 3, 6, and 9%), and their combinations in removing pesticide residues of pepper and cucumber samples. The great reduction rates were obtained with acetic acid and citric acid treatments of 9% for both cucumber (82.29 and 93.75%) and pepper (68.48 and 72.48%). Similarly, washing rice with Na_2CO_3 (0.1%) was more effective than NaCl (0.9%) or tap water for the removal of residues of acephate and methamidophos [50].

Table 4. Average residue amounts of imidacloprid (conventional and nanoemulsion formulations) detected in and on cucumber fruits after one week and two weeks of pickling.

Formulation	Initial deposits (mg/kg)	Time of Pickling			
		One week		Two weeks	
		Residue (mg/kg)	Removal (%)	Residue (mg/kg)	Removal (%)
Conventional	2.316	0.272±0.054	88.25	0.0	100
Nanoemulsion	0.585	0.0	100	0.0	100

Table 5. Effect of different washing solutions (tap water, soap, $KMnO_4$, Na_2CO_3, and CH_3COOH) on removal of imidacloprid (conventional and nanoemulsion formulation) residues from cucumber fruits.

Washing Solution	Conventional		Nanoemulsion	
	Residue (mg/kg)	Removal (%)	Residue (mg/kg)	Removal (%)
Control	2.316	-	0.585	-
Tap water	1.849	20.17	0.314	46.41
Soap (1%)	1.430	38.26	0.306	47.69
$KMnO_4$ (1%)	1.585	31.56	0.289	50.68
Na_2CO_3 (1%)	1.046	54.83	0.164	71.97
CH_3COOH (1%)	1.608	30.59	0.209	64.27

DOI: 10.62184/jafs.jafs1000202515

Shalaby [51] found that Na_2CO_3 (1%) solution was the most efficient in removing residues of λ-cyhalothrin from treated sweet pepper fruits, while the lowest one was the tap water.

3.4. Risk assessment

The risk assessment studies revealed that the RQ values for both SC and NE formulations of IMD in cucumber fruits were significantly below one, indicating negligible risk to human health when applied at the recommended dosage. This aligns with previous findings of Abbassy [24], who reported no risk from chlorpyrifos-methyl and IMD residues in certain crops, though fipronil posed a potential risk depending on consumption patterns. This study further highlights that NE formulations reduce hazards associated with treated commodities compared to SC formulations, emphasizing their suitability for safer agricultural practices.

Table 6. Residues mean (mg/kg), estimated exposure dose (EED; mg/kg/b.w./day), and risk quotient (RQ) of imidacloprid in cucumber fruits after different time intervals of application.

Days after treatment	Conventional formulation				Nanoemulsion formulation			
	Residue amount	EED	RQ	Health risk	Residue amount	EED	RQ	Health risk
0 (2 h)	2.316	1.4×10^{-3}	2.3×10^{-2}	No	0.585	3.4×10^{-4}	5.7×10^{-3}	No
1	1.406	8.2×10^{-4}	1.4×10^{-2}	No	0.354	2.1×10^{-4}	3.4×10^{-3}	No
3	0.660	3.8×10^{-4}	6.0×10^{-3}	No	0.231	1.3×10^{-4}	2.2×10^{-3}	No
7	0.286	1.7×10^{-4}	2.8×10^{-3}	No	0.098	5.7×10^{-5}	9.5×10^{-4}	No
10	0.142	8.3×10^{-5}	1.4×10^{-3}	No	0.006	3.5×10^{-6}	5.8×10^{-5}	No
13	0.047	2.7×10^{-5}	4.6×10^{-4}	No	ND	-	-	No
16	0.007	4.0×10^{-6}	6.8×10^{-5}	No	ND	-	-	No

4. Conclusions

The study demonstrated that both SC and NE formulations of IMD dissipated rapidly over time in cucumber fruits, leaves, and soil, with residues decreasing to below maximum residue limits (MRLs) within 1 to 3 DAT. However, the NE formulation showed faster residue degradation in all tested samples compared to SC formulations. Moreover, washing and pickling treatments effectively reduced IMD residues, with sodium carbonate emerging as the most effective washing solution. Yes, risk assessment revealed that the residues of IMD in cucumber fruits posed a negligible risk to human health, especially with the NE formulation, highlighting its potential as a safer alternative for pesticide applications.

Acknowledgements

The authors would like to acknowledge the Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food, Agriculture Research Centre (QCAP), Giza, Egypt, for renting the HPLC–DAD equipment.

Conflict of interest statement

The authors declare that they have no conflict of interest.

Funding statement

This manuscript received no external funding.

Disclaimer

Atef M. K. Nassar, as the Editor-in-Chief of this journal, didn't participate in the peer review, editorial handling, or decision-making of this manuscript. Full responsibility for the editorial process was under the supervision of another Editor.

Author information

Corresponding author: Atef M.K. Nassar*

E-mail: atef.nassar@dmu.edu.eg

ORCID iD: 0000-0002-0394-1530

Data availability

Data will be available on request.

References

[1] Patil, M. A., & Bhagat, A. D. (2014). Yield response of cucumber (*Cucumis sativus* L.) to shading percentage of shade

DOI: 10.62184/jafs.jafs1000202515

net. International Journal of Agricultural Engineering, 7, 243–248.

[2] FAO (2021). Climate change fans spread of pests and threatens plants and crops, new FAO study. https://www.fao.org/news/story/en/item/1402920/icode/

[3] Hossien, Y., Hassanpour, B., & Hassanshahi, M. (2013). Economic analysis of marketing margin for greenhouse cucumbers and tomatoes in Kohgiluyeh-va-Boyerahmad province, Iran, Annals of Biological Research, 4 (2),146-153. www.scholarsresearchlibrary.com

[4] Ministry of Agriculture and Land Reclamations, Economic Affairs Sector (2015) being implemented by CARDI in Haiti, Jamaica and, Trinidad & Tobago. Agricultural Statistics.

[5] Prodhan, M. D. H., Papadakis, E. N., & Papadopoulou-Mourkidou, E. (2015). Determination of multiple pesticide residues in eggplant with liquid chromatography - mass spectrometry. Food Analytical Methods, 8, 229-235. https://doi.org/10.1007/s12161-014-9898-3

[6] Adamson, H., Turner, C., Cook, E., Creissen, H. E., … & Clarke, J. (2020). Review of evidence on Integrated Pest Management. DEFRA, Project_ 27269, 196.

https://pure.sruc.ac.uk/files/26612788/14799_300326IPMFinalreportpDF.pdf

[7] Hajslova, J., & Zrostlikova, J. (2003). Matrix effects in ultra-trace analysis of pesticide residues in food and biotic matrices. Journal of Chromatography Analysis, 1000(1-2), 181-197. https://doi.org/10.1016/S0021-9673(03)00539-9

[8] Fenik, J., Tankiewicz, M., & Biziuk, M. (2011). Properties and determination of pesticides in fruits and vegetables. Trends in Analytical Chemistry, 30(6), 814-826. https://doi.org/10.1016/j.trac.2011.02.008

[9] Pathak, V. M., Verma, V. K., Rawat, B. S., Kaur, B., … & Cunill, J. M. (2022). Current status of pesticide effects on environment, human health and it's eco-friendly management as bioremediation: A comprehensive review. Frontiers of Microbiology, 13, 962619. https://doi.org/10.3389/fmicb.2022.962619

[10] FAO,& WHO (2023). Report 2022, Pesticide residues in food, Joint FAO/WHO Meeting on Pesticide Residues. https://www.fao.org/3/cc4115en/cc4115en.pdf

[11] Gavrilescu, M. (2005). Fate of pesticides in the environment and its bioremediation. Engineering in Life Sciences, 5(6), 497-526. https://doi.org/10.1002/elsc.200520098

[12] Singh, N. K., Sanghvi, G., Yadav, M., Padhiyar, H., … & Singh, V. (2023). Fate of pesticides in agricultural runoff treatment systems: Occurrence, impacts and technological progress. Environmental Research, 237, 117100. https://doi.org/10.1016/j.envres.2023.117100

[13] Rao, J., & McClements, D. J. (2011). Formation of flavor oil microemulsions, nanoemulsions and emulsions: influence of composition and preparation method. Journal of Agricultural and Food Chemistry, 59(9), 5026-5035. https://doi.org/10.1021/jf200094m

[14] Wang, L., Li, X., Zhang, G., Dong, J., & Eastoe, J. (2007). Oil-in-water nanoemulsions for pesticide formulations. Journal of Colloid and Interface Science, 314(1), 230-235. https://doi.org/10.1016/j.jcis.2007.04.079

[15] Feng, J., Zhang, Q., Liu, Q., Zhu, Z., … & Jafari, S. M. (2018). Application of nanoemulsions in formulation of pesticides. Nanoemulsions, 379- 413. https://doi.org/10.1016/B978-0-12-811838-2.00012-6

[16] Pavoni, L., Pavela, R., Cespi, M., Bonacucina, G., …& Benelli, G. (2019). Green micro-and nanoemulsions for managing parasites, vectors and pests. Nanomaterials, 9(9), 1285. https://doi.org/10.3390/nano9091285

[17] Koroleva, M. Y., & Yurtov, E. V. (2012). Nanoemulsions: The properties, methods of preparation and promising applications. Russian Chemical Reviews, 81(1), 21. https://doi.org/10.1070/rc2012v081n01abeh004219

[18] Abbassy, M., Abdel-Rasoul, M., Soliman, B., & Nassar, A. (2023). Evaluation of conventional and nanoemulsion formulations of some insecticides against the cotton aphids, Aphis gossypii Glover (Hemiptera: Aphididae). Journal of Agricultural and Environmental Sciences, 22(2), 238-263. https://doi.org/10.21608/jaesj.2023.239529.1114

[19] Lehotay, S. J., Koesukwiwat, U., van der Kamp, H., Mol, H. G. J., & Leepipatpiboon, N. (2011). Qualitative aspects in the analysis of pesticide residues in fruits and vegetables using fast, low- pressure gas chromatography–time of-flight mass spectrometry. Journal of Agriculture and Food Chemistry, 59(14), 7544–7556. https://doi.org/10.1021/jf104606j

[20] Anastassiades, M., Lehotay, S. J., Stajnbaher, D., & Schenck, F. J. (2003). Fast and easy multiresidue method

employing acetonitrile extraction/partitioning and "dispersive solid phase extraction" for the determination of pesticide residues in produce. Journal of AOAC International, 86(2), 412–431. https://doi.org/10.1093/jaoac/86.2.412

[21] Nassar, A. M. K., Abbassy, M. A., & Salem, Y. M. (2015). Mammalian detrimental effects of imidacloprid residues in tomato fruits. Research Journal of Environmental Toxicology, 9(3), 149-159. https://doi.org/10.3923/rjet.2015.149.159

[22] Ryad, L. M., & Mahmoud, A. A. (2016). Study the effect of household processing on some pesticide residues in olive fruits. Middle East Journal of Applied Sciences, 6(3), 588-593.

[23] Ermer, J., & McMiller, J. H. (2005). Method validation in pharmaceutical analysis: A guide to best practice. Willey-VCH, Weinheim, Germany. https://doi.org/10.1002/3527604685

[24] Abbassy, M. A., Salim, Y. M. M., Shawir, M. S., & Nassar, A. M. K. (2017). Disappearance and hazard quotient of chlorpyrifos-methyl, fipronil, and imidacloprid insecticides from dates. Journal of Consumer Protection Food Safety, 12(3), 223-230. https://doi.org/10.1007/s00003-017-1111-3

[25] WHO/GEMS/Food Cluster diets (2012). https://www.who.int/data/gho/samples/food-cluster-diets

[26] Codex Alimentarius Commission (2017). Guidelines on performance criteria for methods of analysis for the determination of pesticide residues in food and feed (CXG 90-2017).

[27] Zhang, Z., Li, H., Wu, M., Yuan, Y., Hu, X., & Zheng, W. (2009). Residue and risk assessment of chlorothalonil, myclobutanil and pyraclostrobin in greenhouse strawberry. Chinese Journal of Pesticide Science, 11(4), 449–455.

[28] SAS (2013). Statistical Analysis System User Guide, Version 9.2. SAS Institute Inc., Cary, NC, USA.

[29] European Food Safety Authority (2021). MRL review under article 12 of Reg. (EC) 396/2005: Work instructions.

[30] Abdourahime, H., Anastassiadou, M., Brancato, A., Brocca, D., …& Villamar-Bouza, L. (2019). Review of the existing maximum residue levels for imidacloprid according to Article 12 of Regulation (EC) No 396/2005. EFSA Journal, 17(1), e05570. https://doi.org/10.2903/j.efsa.2019.5570

[31] Agricultural Pesticides Committee. (2022). Technical recommendations for agricultural pest control. Ministry of Agriculture and Land Reclamation. http://www.apc.gov.eg/Files/Releases/Recomm22.pdf

[32] Abo El-Ghar, M. R., & Ramadan, M. M. (1963). Studies on residue of certain organophosphorus-insecticides on some vegetables. Bulletin de la Societe Entomologique d'Egypte, 46, 359–363. https://www.cabidigitallibrary.org/doi/full/10.5555/19650501577

[33] Cabras, P. A., Angioni, V. L., Garau, F., Pirisi, M., & Brandolini, V. (1998). Gas chromatographic determination of azoxystrobin, fluazinam, kresoxim-methyl, mepanipyrim, and tetraconazole in grapes, must, and wine. Journal of AOAC International, 81(6), 1185-1189. https://doi.org/10.1093/jaoac/81.6.1185

[34] Lichtenstein, E. P. (1972). Environmental factors affecting fate of pesticides. National Academy of Sciences-National Research Council Report, USA.

[35] Awad, T. M., Vinson, S. B., & Brazzel, J. R. (1967). Effect of environmental and biological factors on persistence of malathion applied as ultra-low volume or emulsifiable concentrate to cotton plants. Journal of Agriculture and Food Chemistry, 15(6), 1009-1013. https://doi.org/10.1021/jf60154a032

[36] Zeep, R. G., & Cline, D. M. (1977). Rate of direct photolysis in aquatic environment. Environmental Science and Technology, 11(4), 359-986. https://doi.org/10.1021/es60127a013

[37] Christensen, H. B. (2004). *Fungicides in food: Analytical and food safety aspects* [Doctoral dissertation, Technical University of Denmark]. https://orbit.dtu.dk/en/publications/fungicides-in-food-analytical-and-food-safety-aspects/

[38] Walgenbach, J. F., Leidy, R. B., & Sheets, T. G. (1991). Persistence of insecticides on tomato foliage and implications for control of tomato fruit worm (Lepidoptera: Noctuidae). Journal of Economic Entomology, 84(3), 978-986. https://doi.org/10.1093/jee/84.3.978

[39] Shalaby, A. A., Abd-El Rahman, T. A., & Shalaby, M. A. (2022). Study of imidacloprid, azoxystrobin and difenoconazole residues and their biochemical effects on cucumber. Journal of Plant Protection and Pathology, 13(7), 161-167. https://doi.org/10.21608/JPPP.2022.148665.1085

[40] Shokr, A. A., Nasr, I. N., & Hassan, A. S. M. (2006). Residues of imidacloprid and tetraconazole on and in

cucumber and tomato fruits. Journal of Agricultural and Environmental Sciences, Alexandria University, Egypt, 5(3), 39-51.

[41] Fossen, M. (2006). Environmental fate of imidacloprid. California, Department of Pesticide Regulation, 1-16.

[42] Leili, M., Pirmoghani, A., Samadi, M. T., Shokoohi, R., … & Poormohammadi, A. (2016). Determination of pesticides residues in cucumbers grown in greenhouse and the effect of some procedures on their residues. Iranian Journal of Public Health, 45(11), 1481-1490.

[43] Duman, A., Çiftçi, U., & Tiryaki, O. (2021). Farklı yıkama işlemlerinin üzümlerde tebuconazole kalıntısına etkisi. ÇOMÜ Ziraat Fakültesi Dergisi, 9(2), 259-269. https://doi.org/10.33202/comuagri.878597

[44] Lozowicka, B., Jankowska, M., Hrynko, I., & Kaczynski, P. (2016): Removal of 16 pesticide residues from strawberries by washing with tap and ozone water, ultrasonic cleaning and boiling. Environmental Monitoring and Assessment, 188(1), 51. https://doi.org/10.1007/s10661-015-4850-6

[45] Acoglu, B., & Omeroglu, P. Y. (2021). Effectiveness of different type of washing agents on reduction of pesticide residues in orange (*Citrus sinensis*). LWT, 147, 111690. https://doi.org/10.1016/j.lwt.2021.111690

[46] Kim, S. D., Kim, I. D., Park, M. Z., & Lee, Y. G. (2000). Effect of ozone water on pesticide-residual contents of soybean sprouts during cultivation. Korean Journal of Food Science and Technology, 32(2), 277-283. https://agris.fao.org/search/en/providers/122646/records/6472397d53aa8c896302cfa3

[47] Polat, B., & Tiryaki, O. (2020). Assessing washing methods for reduction of pesticide residues in Capia pepper with LC-MS/MS. Journal of environmental science and health, Part. B, Pesticides, Food Contaminants, and Agricultural Wastes, 55 (1), 1–10. https://doi.org/10.1080/03601234.2019.1660563

[48] Ruengprapavut, S., Sophonnithiprasert, T., & Pongpoungphet, N. (2020). The effectiveness of chemical solutions on the removal of carbaryl residues from cucumber and chili presoaked in carbaryl using the HPLC technique. Food Chemistry, 309, 125659. https://doi.org/10.1016/j.foodchem.2019.125659

[49] Randhawa, M. A., Anjum, M. N., Butt, M. S., Yasin, M., & Imran, M. (2014). Minimization of imidacloprid residues in cucumber and bell pepper through washing with citric acid and acetic acid solutions and their dietary intake assessment. International Journal of Food Properties, 17 (5), 978-986. https://doi.org/10.1080/10942912.2012.678532

[50] Kong, Z., Dong, F., Xu, J., Liu, X., … & Zheng, Y. (2012). Determination of difenoconazole residue in tomato during home canning by UPLC-MS/MS. Food Control, 23(2), 542-546. https://doi.org/10.1016/j.foodcont.2011.08.028

[51] Shalaby, A. A. (2017). Residues of lambda-cyhalothrin insecticides and its biochemical effects on sweet pepper fruits. Journal of Productivity and Development, 22 (1), 65-81. https://doi.org/10.21608/jpd.2017.41707