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Original Article

Reduction and Health Risk Assessment of Imidacloprid Insecticide Residues in Grapes Using Home Washing Methods

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Abstract

Background: Grapes are one of the most important agricultural products in Malayer, and the pest *Psalmocharias alhageos* affects them. Imidacloprid, a systemic neonicotinoid insecticide, is commonly used to control pests. This study aims to assess the effectiveness of non-toxic household methods in reducing imidacloprid residues on grapes.

Methods: The grape samples were collected from five different vineyards and immersed in various solutions (acetic acid, sodium bicarbonate, sodium chloride, detergents, and tap water). The QuEChERS method was used for pesticide residue extraction.

Results: Washing treatments significantly reduced pesticide residues in the grapes. The reduction in imidacloprid residues varied, with sodium bicarbonate showing the highest reduction (50.41%), followed by acetic acid (30.03%), detergent (9.44%), sodium chloride (8.81%), and tap water (3.45%). The processing factors (PFs) after washing with these solutions were all less than 1, indicating that all treatments were effective in reducing imidacloprid residues.

Conclusion: Imidacloprid residues were detected in all grape samples from the five vineyards. However, the imidacloprid concentrations after washing were below the CODEX maximum residue limit (MRL) (0.7 mg/kg). Health risk assessments indicated that consumers are not exposed to significant health risks from imidacloprid residues in grapes, with no serious side effects observed for adults, adolescents, or children.

Keywords: Food security, Maximum residue limit, Household processing, Pesticide residue, Risk assessment

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Introduction

Pesticides are extensively used in conventional agriculture to enhance crop yields. They help control weeds, insects, and fungi but also contribute to environmental pollution, pose health risks to consumers, and reduce the quality of agricultural products.[1,2] Educating farmers about pesticide persistence in soil, residues in crops, the required pre-harvest interval (PHI), and adherence to hygiene principles has become essential.[3] Grapes (*Vitis vinifera* L.) are among the most valuable and nutritious fruits globally, cultivated in over 90 countries.[4] Malayer city is a major hub for grape production in Iran, with an annual output of 240 000 tons.[5] Recognized as a Globally Important Agricultural Heritage System (GIAHS) by the FAO,[6] Malayer's vineyards are vital to Iran's agricultural landscape. However, like other crops, grapes are susceptible to diseases and pests during production and storage, impacting their yield and quality. The average daily per capita grape consumption in Iran is 58 grams (0.05 kg).[7] One of the significant vineyard pests in Malayer is *Psalmocharias alhageos*. In addition to physical and agronomic control methods, the insecticide imidacloprid (Confidor) is commonly used against this pest.[8] While pesticides offer benefits in pest management, their residues in agricultural products pose risks to human health.[9] Improper pesticide use or harvesting crops before the PHI can lead to contamination, causing environmental imbalances, pathogen resistance, and poisoning risks for producers and consumers.[10] Globally, managing pesticide residues in fresh fruits and vegetables is a critical issue due to its impact on public health, environmental safety, and trade.[11,12] Processing agricultural products before consumption can reduce pesticide residues. The reduction percentage varies depending on the methods employed, the physicochemical properties of pesticides, and the nature of the products.[13] Among control methods, chemical approaches are favored for their quick action, ease of application, and efficiency over large areas. However, their long-term disadvantages include residue persistence, resistance in target organisms, adverse effects on non-target species, and risks to human health and the environment.[14] Given the heavy reliance on chemical pesticides to meet food demand, addressing pesticide residue contamination in food has become increasingly important. Studies have explored the effects of various household washing methods on reducing imidacloprid residues in products such as cucumbers, bell peppers,[15] tomatoes,[16] and greenhouse cucumbers.[7] However, little is known about imidacloprid residue reduction in grapes.

As Malayer is a significant grape production hub, addressing pesticide residue contamination is economically and socially critical. While some research has examined the removal behavior of pesticides in grapes, information on the kinetics of imidacloprid elimination post-harvest, during storage, and with washing under various conditions remains limited. This study investigates the effectiveness of household washing methods for reducing imidacloprid residues in grapes. The treatments include simple, non-toxic solutions such as sodium bicarbonate ($NaHCO_3$), sodium chloride (NaCl), acetic acid (CH_3CO_2H), and washing liquid with water. The aim was to identify effective, accessible methods to enhance food safety and consumer health by removing pesticide residues from grapes using readily available household solutions.

Materials and Methods

Chemicals

Acetonitrile solvent (99.99% purity), magnesium sulfate, and sodium chloride (99.5% purity) were obtained from Merck, Germany. Carbon black graphite was sourced from Aldrich-Sigma (Supelco, Germany). An imidacloprid insecticide standard (99.9% purity) was procured from Dr. Ehrenstorfer Inc., Augsburg, Germany.

Grape Sampling

This study began with the identification of grape orchards infested by *P. alhageos* in Malayer city (central part, Jozan valley orchards). Sampling was conducted in late September after the grapes had fully ripened and during the harvest from five vineyards treated with imidacloprid to combat the chain worm pest. The cultivar selected was a seedless raisin white grape. Approximately 6 kg of grapes were harvested from each vineyard. To ensure sample homogeneity, grapes were randomly collected from various trees. After mixing, the samples were placed in polythene bags and quickly transferred in ice-filled containers to the laboratory to prevent rapid decomposition of pesticide residues.

Household Processing

Grape samples from each vineyard were divided into three groups (a, b, and c), and each group was further split into six portions, subjected to various washing treatments with homemade solutions (experiments performed in duplicate). Each portion consisted of 150 g of grapes. The treatments included:

- Group 1: A solution of 2 liters of ordinary water and 20 mL of acetic acid (vinegar).
- Group 2: A solution of 2 liters of ordinary water and 20 g of sodium bicarbonate (baking soda).
- Group 3: A solution of 2 liters of ordinary water and 20 g of sodium chloride (salt).
- Group 4: A solution of 2 liters of ordinary water and 2.5 mL of detergent.
- Group 5: Immersion in 2 liters of ordinary water only.
- Group 6: No washing treatment.

The washing time for all groups was 15 minutes. After washing, the samples were immediately subjected to extraction.

Extraction Procedure

The QuEChERS method was employed to analyze imidacloprid residues in grape samples, as described in previous studies.[17,18] Grapes were chopped and homogenized for 5 min at high speed using a laboratory homogenizer. A 10.0 g portion of homogenized sample was placed in a 50 mL centrifuge tube with 10 mL of acetonitrile. The tube was sealed and shaken vigorously for 1 min to ensure thorough solvent interaction with the sample. Subsequently, 4.00 g of anhydrous $MgSO_4$ and 1.00 g of NaCl were added, and the tube was shaken again for 1 minute. After centrifuging at 1789 × g for 5 minutes at 4 °C, the upper layer was cleaned by dispersive solid-phase extraction with 0.5 g of graphite carbon black (GCB) and 1.50 g of anhydrous $MgSO_4$. The mixture was shaken for 1 minute and centrifuged again for 5 min at 1789 × g. The extract was filtered through a 0.45 µm PTFE filter, concentrated to 1.0 mL under a gentle stream of ultra-pure nitrogen gas, and 20 µL of the solution was injected into the HPLC.

Apparatus

Imidacloprid residues were identified and quantified using a Knauer high-performance liquid chromatography (HPLC) system equipped with a UV-Vis detector and an analytical column (C18, 4.6 mm × 250 mm). Imidacloprid in the samples was identified by comparing the retention time of peaks in the chromatogram with those from the standard solution. Residual concentrations were calculated using the area under the chromatogram peaks and the imidacloprid standard calibration curve.[19]

Method Validation

To validate the method, the calibration curve for imidacloprid was generated. This involved determining the retention time and calculating the slope of the calibration line to estimate imidacloprid concentrations in samples. The recovery percentage was calculated to evaluate the accuracy of the extraction method (equation 1). Imidacloprid standards of varying concentrations (0.05, 0.5, 5, and 10 mg/kg) were prepared in acetonitrile and injected into the HPLC system.[19] The retention time and area under each peak were recorded. A chromatogram of the imidacloprid retention time is shown in Figure S1, and the corresponding calibration curve is presented in Figure S2.

$$\text{Recovery percentage} = \frac{\textit{Amount of pesticide measured in the spiked sample}}{\textit{Amount of pesticide measured in the sample} + \textit{amount of pesticide added to the sample}} \times 100 \quad (1)$$

The recovery value in this study was 89%. The lowest concentration detectable in a matrix, but not accurately measurable, is referred to as the limit of detection (LOD). In contrast, the lowest concentration measurable with acceptable precision is known as the limit of quantification (LOQ). In this study, the LOD and LOQ values were determined to be 0.19 mg/kg and 1.9 mg/kg, respectively. Moreover, a relative standard deviation (RSD) value of 17.02% was obtained.

Health Risk Assessment

A long-term risk assessment for imidacloprid was conducted on the grape samples under various conditions, both before and after washing. The estimated daily intake (EDI) was calculated using equations 2 and 3.[20,21]

$$\text{EDI}\ (\text{mg/kg bw/day}) = \frac{\text{STMR}\ (\text{mg/kg}) \times \text{FI}\ (\text{kg/day})}{\text{BW}\ (\text{kg})} \quad (2)$$

Where, STRM represents the imidacloprid residue in mg/kg, FI denotes the daily per capita consumption of grapes in kg, and BW refers to body weight in kg. It is worth noting that the average daily per capita grape consumption in Iran is 58 g/day, equivalent to 0.05 kg/day. For children, adolescents, and adults, body weights were considered to be 35, 50, and 70 kg, respectively. For the washed grape samples, the EDI was calculated using equation (2):

$$\text{HQ} = \frac{\text{EDI}\ (\text{mg/kg bw/day})}{\text{ADI}\ (\text{mg/kg bw/day})} \quad (3)$$

The acceptable daily intake (ADI) of imidacloprid is 0.06 mg/kg of body weight per day.[18] If the hazard quotient (HQ) is ≥ 1 for a pesticide, potential adverse health effects are likely, whereas HQ < 1 indicates that adverse health effects are unlikely.[22] The impact of various washing treatments on the residual concentration of imidacloprid in grapefruit was assessed by calculating the reduction ratio (CR) using equation (4):

$$CR(\%) = \frac{A - B}{A} X 100 \quad (4)$$

Where, 'A' represents the residual amount of imidacloprid (mg/kg) in the untreated control grape sample (Q), while 'B' represents the residual amount (mg/kg) in grape samples washed with different solutions. The processing coefficient (Pf)[23] was calculated using equation 5:

$$PF = \frac{B}{A} \quad (5)$$

The processing factor (PF) indicates whether the level of residue during food processing steps has decreased or increased. A PF value > 1 represents a reduction in the residual level (i.e., a reduction factor), while a PF value < 1 signifies a concentration effect (i.e., a concentration factor). [24]

Statistical Analysis

In this study, data analysis was performed using IBM SPSS Statistics 23.0 and Excel 2016. To improve the accuracy of risk assessment for exposure to pollutants, such as pesticides, while accounting for uncertainties, the USEPA recommended the Monte Carlo simulation (MCS) method. This method was implemented using Crystal Ball v11.1.2.4.600 software (Oracle, Decisioneering, Denver, CO, USA) with 10 000 repetitions. Given the normality of the data, a one-way analysis of variance (ANOVA) was used to examine differences between test groups. Means were compared using Dunnett's test at a 95% significance level, with a P value < 0.05 considered statistically significant. All values are reported as mean ± standard deviation (SD).

Results and Discussion

The results of the statistical analysis revealed that imidacloprid residues were detected in all untreated samples across all vineyards (Table S1). Furthermore, the Tukey test indicated a statistically significant difference in the residual levels of imidacloprid insecticide among the different vineyards. Table S2 presents the descriptive statistics of imidacloprid residue in untreated grape samples and those treated with various solutions across different vineyards.

Figure 1 compares the effectiveness of different washing methods across various vineyards in reducing the residual concentration of imidacloprid in grapes. Overall, the results indicated that the highest levels of imidacloprid residue were observed in untreated samples, followed by normal water, sodium chloride, washing liquid, acetic acid, and sodium bicarbonate.

The analysis of pesticide residues in untreated grape samples from five different vineyards revealed the presence of imidacloprid insecticide residues in all samples. A statistically significant difference was observed in the amount of imidacloprid residues between the vineyards (P < 0.05). The maximum residue limit (MRL) for imidacloprid on grapes, set by the European Union, is 0.7 mg/kg.[25]

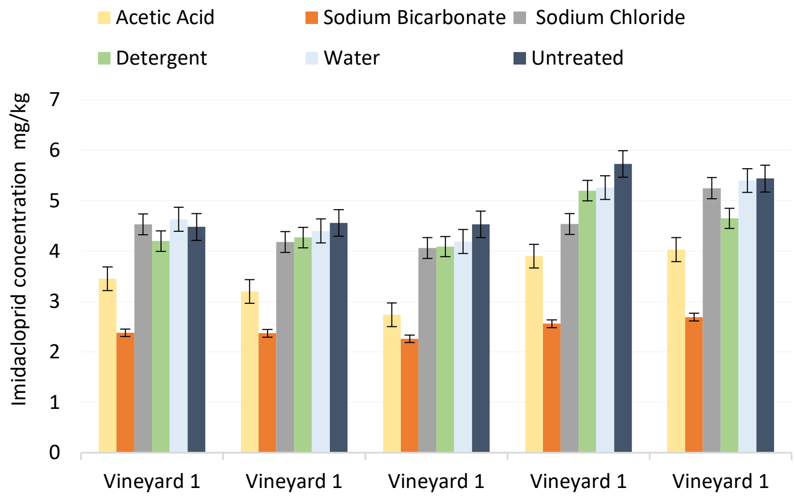

Figure 1. Comparison Among Different Washing Groups in Different Vineyards to Reduce the Residual Concentration of Imidacloprid in the Grapes

Imidacloprid Insecticide Residue After Washing the Grapes with Sodium Bicarbonate Solution

Washing with sodium bicarbonate solution is one of the preferred methods to remove pesticide residues from fruits and vegetables. The present study showed that sodium bicarbonate solution has a removal efficiency of 50.41% for imidacloprid residues in grapes. in a study showed that the stability of hexaconazole in alkaline environmental conditions is lower than in acidic conditions. Thus, alkaline/acidic environmental conditions may be considered as an effective factor for pesticide degradation.[26] In a study conducted by Chen et al the results showed that washing lettuce with sodium bicarbonate solution reduced the diazinon residual by 49%-51%, but washing grape samples with normal water reduced the residual diazinon by 3.54%-37.52%. However, the reduction of diazinon residue in grapes with acetic acid and sodium bicarbonate was further than the lettuce samples washed with acidic (pH = 4.6) and alkaline (pH = 10.7) water, it showed that the alkaline environment (bi-sodium carbonate) is more effective in removing diazinon than acidic medium (acetic acid) and normal water. It seems that these differences are related to different initial concentration of pesticide, pH value of water, washing time and type of method (immersion or washing).[27] Andrade et al reported that washing with 10% sodium bicarbonate solution caused a 62% reduction of dimethoate residue in tomato samples.[16] Zhang et al conducted a study on removing pesticide residues from cabbage by washing it with a mixture of sodium bicarbonate, sodium chloride, and regular water. The results demonstrated that the combination of sodium bicarbonate and sodium chloride was more effective. When dissolved in water, sodium bicarbonate forms carbonic acid, which acts as the primary agent for pesticide removal through an oxidation process.[28]

In the study by Wu et al, the results showed that alkaline solutions were more effective for reducing pesticide residues when the washing time was further than 15 minutes. Also, their results showed that pesticides were removed more easily in alkaline solutions compared to oxidizing solutions, and the removal efficiency of other washing solutions was better than normal water, which was also the case in our study. Also, the review of different studies showed that the percentage of pesticide removal depends on different washing solutions and washing time, as well as the characteristics of pesticides, similar as low octanol-water partition coefficient (Kow), mode of action, and hydrolysis and photolysis stability.[29]

Yang et al reported that washing with sodium bicarbonate is more effective in removing surface pesticide residues on apples. In the presence of sodium bicarbonate, thiabendazole and phosmet can be decomposed, which contributes to the physical removal power of the wash. However, the washing method with sodium bicarbonate solution was not completely effective in removing the residues that penetrated the apple skin. As the pesticides penetrated deep into the fruit, the overall effectiveness of the method to remove all pesticide residues decreased. In practical application, washing apples with sodium bicarbonate solution can further reduce pesticides from the surface. Exfoliation is more effective for removing infiltrated pesticides. However, bioactive compounds are also lost in exfoliation.[30]

In addition, Harinathareddy et al, in a study reported a higher removal value of fuzalone (44.7%) in tomatoes washed with tap water for 10 minutes. The reduction rate of these pesticides in tomatoes (26.6%) washed with 4% acetic acid solution was similar to grape samples (26.96%). However, 0.1% sodium bicarbonate solution caused more removal of this pesticide (32.9%). In general, the difference in reducing the concentration of pesticides after washing with sodium bicarbonate solution can be related to the difference in the initial concentration of pesticides, the concentration of the washing solution and the ratio of vegetables/fruits to water. In general, the difference in reducing the concentration of pesticides after washing with sodium bicarbonate solution can be related to the difference in the initial concentration of pesticides, the concentration of the washing solution and the ratio of vegetables/fruits to water. The amount of reduction during washing depends on the mode of entry i.e. systemic or non-systemic (contact), water solubility and octanol-water partition coefficient (log P) of the pesticide. In another study, the removal rate of non-systemic pesticides such as diazinon, which had high solubility in water and low log P, was higher than other pesticides that were introduced systematically or had low solubility in water. Therefore, it can be said that the removal of pesticides during washing is not always related to its solubility in water and other characteristics of the pesticide also affect its removal. The amount of reduction during washing depends on the mode of entry i.e. systemic or non-systemic (contact), water solubility and octanol-water partition coefficient (log P) of the pesticide. In another study, the removal rate of non-systemic pesticides such as diazinon, which had high solubility in water and low log P, was higher than other pesticides that were introduced systematically or had low solubility in water. Therefore, it can be said that the removal of pesticides during washing is not always related to its solubility in water and other characteristics of the pesticide also affect its removal.[31] Keikotlhaile et al reported that the wax layer on fruits prevents the dissolution of pesticides in normal water, Sodium bicarbonate and acetic acid remove this layer and increase pesticide removal during washing, which was also the case in our study.[32]

Imidacloprid Insecticide Residue After Washing Grapes with Acetic Acid Solution

It was found that acetic acid solution had a removal efficiency of 30.03% for imidacloprid insecticide residues in grapes. While washing with acetic acid solutions is a common method for reducing pesticide residues, there are limited studies on its effectiveness in household applications.[16,33-35] Satpathy et al examined the removal of pesticides from various fruits and vegetables, including tomatoes, using different household solutions (water, NaCl 0.9%, $NaHCO_3$ 0.1%, acetic acid 0.1%, $KMnO_4$ 0.001%, ascorbic acid 0.1%, malic acid 0.1%, and oxalic acid 0.1%). Their results indicated that acidic solutions were more effective than water in reducing pesticide residues.[36] The current study found that sodium bicarbonate solution also had a removal efficiency of 30.03% for imidacloprid residues in grapes, consistent with findings by Abou-Arab, who reported that washing with organic acids significantly reduced pesticide residues in both raw and processed vegetables.[37] In addition, Randhawa et al found that immersion in organic acids reduced imidacloprid content by 80% in cucumber and bell pepper. They noted that some pesticides dissolve in the upper wax layers and penetrate deeper into plant tissues, making acidic solutions more effective than sodium chloride solutions with the same concentration and exposure time.[15] Furthermore, an increase in the concentration of the washing solution leads to a gradual improvement in residue reduction during simultaneous treatments.[38-41] Osman et al reported that 1-2% citric and acetic acid washing solutions were more effective than treatments such as H_2O_2, $KMnO_4$, and normal water in reducing chlorpyrifos residues in horticultural crops.[42] Similar results were observed by Pugliese et al, who found that pesticide residues in nectarines were significantly reduced by washing with solutions of citric acid, ethanol, glycerol, H_2O_2, $KMnO_4$, sodium metabisulfite, sodium lauryl sulfate, sodium hypochlorite, and urea, compared to washing with normal water.[43] Washing with acetic acid solution resulted in up to 91.5%, 86.0%, and 93.7% reduction in tomato contamination with dimethoate, profenofos, and pyrimiphos-methyl, respectively. Furthermore, ascorbic acid (10%) and citric acid (10%) solutions reduced aldrin content by approximately 85-90% in vegetables.[29]

Imidacloprid Insecticide Residue After Washing Grapes with Sodium Chloride Solution

The present study showed that sodium chloride had a removal efficiency of 8.81% for imidacloprid residues in grapes. Washing with sodium chloride solution is another method used to reduce pesticide residues in fruits and vegetables. Pesticides are more soluble in saline environments, and immersing grape samples in the solution allows them to interact more easily with the salt solution.[9,35] Similar to the findings of this study, Rasolonjatovo et al noted that pesticides may exhibit different solubility in water depending on the salt concentration.[44] Furthermore, Alister et al reported that sodium chloride solution plays an important role in removing pesticides from fruits and vegetables due to its strong electrolyte properties, which facilitate the precipitation of organic compounds through the desalination phenomenon.[45] On the other hand, Heshmati et al found that the reduction of various pesticides, such as diazinon, malathion, permethrin, propargite, and fenpropathrin, does not significantly depend on the concentration of sodium chloride used to wash edible mushrooms. They also reported that the reduction rate is more closely associated with an increase in washing time.[9]

Imidacloprid Insecticide Residue After Washing the Grapes Using Detergent Solution

The reduction rate of imidacloprid during the washing process with detergent liquid in this study was about 9.44%. Washing fruits and vegetables with a detergent solution before consumption can remove some of the pesticide residue. This theory is supported by the research of Holland et al,[46] Dejonckheere et al,[47] Cabras et al,[48] Soliman,[49] and Uysal-Pala & Bilisli[50] on the effectiveness of the washing process in removing pesticide residues. Washing operations are more effective at removing surface residues of pesticides, while they have little effect on systemic residues in the tissues. For example, methamidophos was highly systemic and the only pesticide whose residues could not be removed from field tomatoes by washing. There is evidence for various crops and pesticides that the proportion of pesticide residues in fruits and vegetables decreases over time with washing.[15,41,51,52] This has been interpreted as being due to the affinity of the residues for cuticular waxes or deeper layers of plant tissue. For instance, the fraction of fenitrothion or methidathion residues on cauliflower that can be removed by washing or blanching is inversely related to the number of days after spray application.[33] Hot washing and blanching are more effective than cold washing and may be even more effective with liquid detergent in reducing pesticide residues.[51] Awasthi and Lalitha reported that washing with a detergent solution reduced pyrethroid residues in cauliflower by 50%–60%.[52] Liang et al found that organophosphorus pesticides (trichlorfon, dimethoate, dichlorvos, fenitrothion, and chlorpyrifos) in cucumbers decreased from 31.1% to 98.8% after washing with a detergent solution for 20 min.[33] Several researchers have also reported the effect of simple household washing with normal water to reduce pesticide residues on produce.

Imidacloprid Insecticide Residue After Washing the Grapes Using Normal Water

The present study showed that ordinary water had a removal efficiency of 3.45% for imidacloprid residues in grapes. Kruve et al reported that washing oranges with normal cold water reduced thiabendazole and imazalil residues by 14% and 38%, respectively.[53] In a study conducted by Balinova et al, a simple wash using plain water removed 51% of residual procymidone in peach fruit.[54] Deshmukh and Lal reported that normal water washing of carbaryl-treated eggplants greatly reduced carbaryl residues.[55] Romeh et al showed that the removal of penconazole in tomatoes harvested 1, 3, 7, and 14 days after spraying and washing with normal water was 15%, 11.76%, 7.69%, and 6.25%, respectively.[56] Although they did not specify the washing time, the removal of imidacloprid in our study during washing with plain water was lower than other treatments, which is consistent with the findings of Heshmati et al and Leili et al[9,57] This difference may be attributed to variations in the washing methods and the timing of the treatment (a few days after spraying). Over time, the pesticide tends to concentrate more in the outer layers and skin of the fruit, and as the pesticide penetrates deeper into the fruit tissue, the effect of washing with plain water diminishes.[57]

Health Risk Assessment

The effect of different washing treatments on the imidacloprid PFs in grapes was also examined. The results showed that the average PF values for washing with sodium bicarbonate, acetic acid, detergent, sodium chloride, and normal water were 0.70, 0.49, 0.90, 0.91, and 0.96, respectively. Given that the PF value in all samples was less than 1, it can be concluded that all treatments were effective in reducing the residual imidacloprid insecticide in grapes. Figure 2 presents a radar diagram of the processing coefficient obtained to reduce imidacloprid residue in grapes with various household washing solutions across different vineyards. The most effective treatments for reducing imidacloprid insecticide residue in grapes were sodium bicarbonate, acetic acid, detergent solution, and normal water, in that order.

EDI and HQ values were calculated for three groups: children (35 kg), teenagers (50 kg), and adults (70 kg). The findings of this study indicated that the highest EDI was associated with grape samples washed for 15 min with sodium bicarbonate solution, followed by acetic acid, liquid detergent, sodium chloride, and normal water. The lowest EDI was observed in untreated grape samples. The calculation of EDI values showed lower intake in children and higher intake in adults (Table 1, Figure 3). The HQ values for imidacloprid, based on the consumption of fresh untreated grapes and those washed with various solutions, were all less than 1 in the three groups (children, teenagers, and adults). This suggests that there is no significant risk of imidacloprid residues for consumers through grape consumption (Table 2). The results also showed that the risk factor was higher for children and lower for adults (Figure 4). Furthermore, as long as imidacloprid residues remained below the MRL, the dietary intake risk was considered acceptable for consumers.

The consumption risk assessment (HQ) for

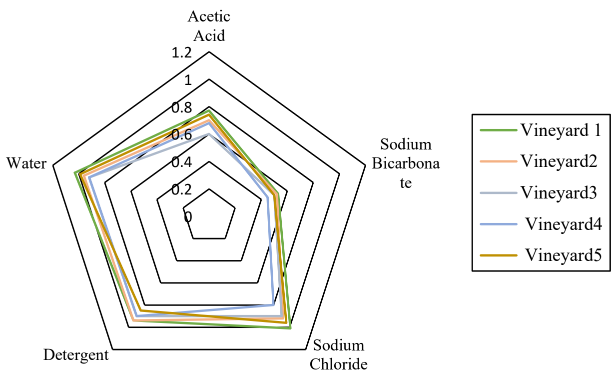

Figure 2. Radar Diagram of Processing Factors Obtained to Reduce Imidacloprid Residue in Grapes with Different Household Washing Solutions in Different Vineyards

Table 1. Estimated Daily Intake (EDI) (mg/kg bw/day) of Imidacloprid Residual in the Grape Samples Without Treatment and After Washing with Different Solutions in Different Age Groups

EDI	Children	Teens	Adult
Acetic acid	0.0049	0.0035	0.0025
Sodium bicarbonate	0.0035	0.0024	0.0017
Sodium chloride	0.0064	0.0045	0.0032
Detergent	0.0064	0.0045	0.0032
Water	0.0068	0.0047	0.0034
Untreated	0.0071	0.0049	0.0035

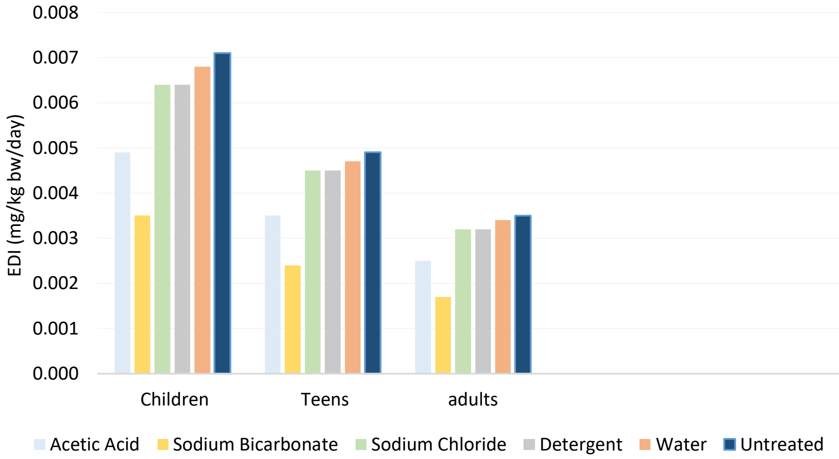

Figure 3. Estimated Daily Intake of Imidacloprid Insecticide Residue Through Consumption of Grapes Without Treatment and After Washing with Washing Solutions i Different Age Groups

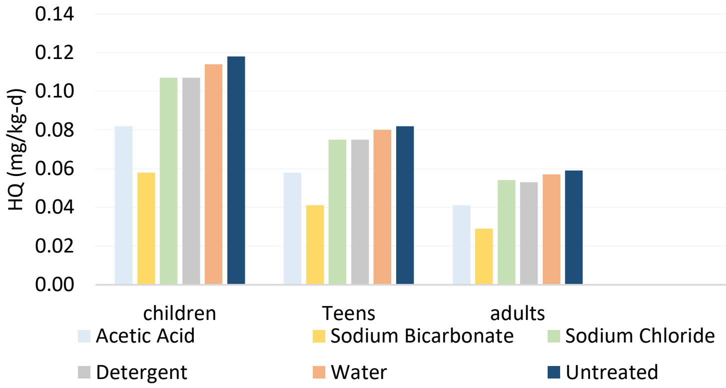

Figure 4. Risk Factor (HQ) of Imidacloprid Pesticide Residual Through Consumption of Grapes Without Treatment and After Washing with Different Solutions in Different Age Groups

Table 2. Hazard Quotient (HQ) (mg/kg) of Imidacloprid Residual in Grape Samples Without Treatment and After Washing With Different Solutions in Different Age Groups

HQ	Children	Teens	Adult
Acetic acid	0.082	0.058	0.041
Sodium bicarbonate	0.058	0.041	0.029
Sodium chloride	0.107	0.075	0.054
Detergent	0.107	0.075	0.053
Water	0.114	0.080	0.057
Untreated	0.118	0.082	0.059

imidacloprid residues in grape samples, calculated using the MCS method (Crystal Ball software) for three groups-adults, adolescents, and children-is presented in Table 3. The results showed that the 90th percentile HQ values for children and adolescents, both in untreated grapes and after washing with various solutions, exceeded 1. In contrast, for adults, HQ values were below 1 only when grapes were washed with sodium bicarbonate solution (8.71E-1), acetic acid solution (8.97E-1), and detergent solution (9.35E-1).

The results of the risk assessment, calculated using the MCS, indicated that the 90th percentile for children and teenagers, both in untreated grape samples and after washing with various solutions, suggests potential non-carcinogenic and carcinogenic health risks. In contrast, for adults, the HQ values were below 1 only when grapes were washed with sodium bicarbonate solution (8.71E-1), acetic acid solution (8.97E-1), and detergent solution (9.35E-1), indicating no significant risk to consumers. Based on these findings, the use of imidacloprid insecticide in grape cultivation in Iran is not entirely without risk. Therefore, it is essential to develop guidelines and establish a monitoring program to mitigate these risks.

Conclusion

The study demonstrates that various washing solutions can effectively remove imidacloprid residues from grapes due to their chemical properties, such as acidity, alkalinity, electrolytes, ions, and surfactants. These properties disrupt the binding of pesticides to the grape cuticle, facilitating their removal during washing. The results showed that washing with sodium bicarbonate and acetic acid solutions was more effective than using tap water alone. Among the tested solutions, sodium bicarbonate combined with normal water significantly reduced imidacloprid residues.

Table 3. Hazard Quotient (HQ) (mg/kg) of Adults, Teenagers, and Children for Imidacloprid Insecticide Residue by Monte Carlo Simulation Method by Crystal Ball Software

HQ	Treatments	Percentile 0.5%	Percentile 50%	Percentile 75%	Percentile 90%
Children	Acetic acid	9.13E-1	1.27E+0	1.48E+0	1.77E+0
	Sodium bicarbonate	8.89E-1	1.23E+0	1.42E+0	1.71E+0
	Sodium chloride	9.73E-1	1.35E+0	1.54E+0	1.88E+0
	Detergent	1.02E+0	1.43E+0	1.61E+0	1.89E+0
	Water	1.56E+0	2.17E+0	2.50E+0	3.03E+0
	Untreated	1.92E+0	2.63E+0	3.02E+0	3.73E+0
Teens	Acetic acid	6.50E-1	8.93E-1	1.10E+0	1.23E+0
	Sodium bicarbonate	6.13E-1	8.62E-1	9.90E-1	1.20E+0
	Sodium chloride	6.59E-1	9.32E-1	1.07E+0	1.32E+0
	Detergent	7.22E-1	9.91E-1	1.15E+0	1.39E+0
	Water	1.11E+0	1.51E+0	1.72E+0	2.09E+0
	Untreated	1.32E+0	1.87E+0	2.13E+0	2.52E+0
Adults	Acetic acid	4.60E-1	6.44E-1	7.27E-1	8.97E-1
	Sodium bicarbonate	4.54E-1	6.28E-1	7.20E-1	8.71E-1
	Sodium chloride	4.77E-1	6.70E-1	7.72E-1	9.35E-1
	Detergent	5.09E-1	7.14E-1	8.10E-1	1.01E+0
	Water	7.68E-1	1.08E+0	1.24E+0	1.51E+0
	Untreated	9.46E-1	1.29E+0	1.47E+0	1.79E+0

For future research, the following suggestions are proposed:

- Investigate other pesticides in Malayer grapes.
- Explore the combined use of multiple treatments to reduce imidacloprid residues.
- Compare the effectiveness of washing solutions at different concentrations and durations.
- Evaluate the use of ozonated and chlorinated water for reducing pesticide residues.
- Optimize washing methods to balance pesticide removal and nutritional value, considering food quality and health.

A limitation of this study was the small sample size, as the washing and preparation steps were time-consuming and conducted at home, restricting the number of samples used.

Authors' Contribution

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Competing Interests

The authors declared that there is no conflict of interest.

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Supplementary Files

Supplementary file 1 contains Tables S1-S2 and Figures S1- S2.

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