Effect of Talc Particle Size in Detergents for Fruits and Vegetables on the Ability to Remove Pesticide Residues

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ABSTRACT: Detergents containing abrasive talc particles for washing fruits and vegetables were designed and investigated. Detergent prototypes were developed with the following composition: 40% talc particles, 1.5% surfactants, 5% ethyl alcohol, 1% sodium citrate, 1% sodium carbonate, 1.5% glycerin, and 0.5% preservative. Xanthan gum (0.5% concentration) was used as a viscosity modifier to stabilize the dispersion of talc particles. Three types of detergent prototypes were prepared, differing in the size of the talc particles. The following fractions were used: 50−125, 250−500, and 710−1000 μm. The particle size effect on the effectiveness of the removal of surface pesticide residues was investigated. A specially developed methodology was used. Three types of pesticides (boscalid, acetamiprid, and pyraclostrobin) were applied to a cherry tomato, tangerine, and cucumber, and then a model washing process was performed using the developed detergents. The changes in the pesticide content on the surface of fruit and vegetables were assessed by liquid chromatography−tandem mass spectrometry. Detergents with talc particles of sizes 50−125 and 250−500 μm were more efficient in the removal of pesticide residues from the surface of fruit and vegetables compared to detergents with 710−1000 μm talc particles.

1. INTRODUCTION

Recently, there has been a significant increase in consumer interest in products that improve widely understood consumer safety. Such products are developed through the introduction of new raw materials, manufacturing technologies, new forms of products, packaging, methods of use, and techniques to monitor undesirable substances.1−11 Consumers pay particular attention to food products, especially the location and method of their production, as well as their suitability for consumption and the packaging used.12 Ideologies related to sustainable development, especially taking care of human health and lowering the consumption of natural resources, are becoming particularly important.13

A significant and often perceived problem is the use of various types of plant protection products in agriculture, which consequently pass into food with crops and are consumed. There is a theoretically positive aspect to pesticide use in agriculture—they account for an increase in farm productivity and enable the transportation of produce from remote locations.14−16 However, pesticide residues may remain on agricultural produce, causing foodborne illnesses and posing a serious risk to the health and life of humans.17,18

The idea promoted for several years by the health and nutrition service is the proper preparation of agricultural products (fruits and vegetables) immediately before consumption. It is recommended to thoroughly wash the products to remove all substances (pesticides, protective waxes, and environmental pollutants). Washing fruits and vegetables is also the most effective way to reduce the risks of foodborne diseases [also recommended by the Food and Drug Administration (FDA)]. However, despite clear recommendations, in the current market, there is a large gap in terms of suitable detergents for this purpose. Consumers often use tap water or, worse, household chemicals designed and dedicated for other purposes. The result may be a very low efficiency of such a washing process19 and likely the introduction of additional undesirable substances on the fruits’ and vegetables’ surface, leading to diarrhea or vomiting.20

Furthermore, it is well known that common domestic processes, such as peeling, cooking, and blanching, are known to be effective in antimicrobial properties and pesticide removal.21,22 However, these procedures reduce the content

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of favorable flavonoids, carotenoids, phytochemicals, and micronutrients in fruits and vegetables.

After harvesting, the obvious step before consuming fruits and vegetables is to wash them, which is the most common and direct form of food processing. Washing is used to remove dirt and possible pesticide residues from the surface of fruits and vegetables. Fresh fruits and vegetables are often washed with tap water and then consumed directly. However, due to the hydrophobic nature of many pesticides, washing has a limited effect on their removal. Therefore, scientists around the world are actively looking for chemicals to effectively remove pesticide residues from the surface of fruits and vegetables.

The objectives of this work were based on recognizing the expectations of fruit and vegetable consumers regarding the demand for cleaning agents. Rao et al. have studied the pesticide residues removal from brinjals by immersion in 0.1% sodium bicarbonate for 10 min. The results revealed that the residues of pesticides were removed by 20−60%. Tomer et al. investigated the elimination of blended pesticides from Chinese cabbage treated for 10 min with different cleaning solutions. The study showed the removal of 11.5 and 32.5% of the 10 pesticides. Yu-Shan et al. investigated the elimination of blended pesticides from Chinese cabbage washed with garlic juice and soda-salt solution, respectively. Wu et al. described the effects of removing 10 different pesticide residues in spinach, cucumber, and kumquat using sodium bicarbonate, micron calcium solution, active oxygen, ozone water, alkaline electrolyzed water, and tap water. The effectiveness of tap water washing in removing 10 pesticide residues from cucumber was lower than 35%. Washing for 20 min with a 2% active oxygen solution resulted in a loss of 40−63% of the 10 pesticides. Washing with a micron calcium solution for 20 min caused a greater loss of pesticides in cucumbers, and the removal efficiency was in the range of 35−86%. Increasing the duration of the washing procedure resulted in a positive effect on the efficiency of removing pesticide residues from fruits and vegetables. The effect of removing pesticide residues after a 15 min washing treatment was vastly different from 5 min, and there was no significant difference in pesticide residue after washing for 20 min.

The objective of this study was to develop a very high-quality cleaning agent in a novel form as a “scrub” for effective washing of fruits and vegetables at home. Talc, a clayey mineral composed of hydrated magnesium silicate, was selected as an abrasive. It is a raw material of mineral origin and can be used in products intended for contact with skin and food. Talc is a nontoxic, colorless, relatively soft material which shows high resistance to microbiological contamination and does not pose a threat to the environment after the washing process is completed. Talc can be a magnesium cation donor, and talc particles have a hydrophobic surface—these factors may reduce the irritating effect of anionic surfactants, which are the basis of the developed detergents.

The studies on the removal of pesticides from food products indicated a tendency to search for preparations based mainly on surfactants, various types of salts, and substances having an acidifying or alkalinizing effect in the washing process. In this work a multiaction detergent was developed. The designed products were based on the combination of the detergent performance of surfactants, amphiphilic solvents, alkalinizing agents, sequestering agents, and abrasive substances. It was assumed that the developed detergent will contain particles of solids, acting as a kind of scrub (peeling) during the cleaning process of fruits and vegetables. Particular attention was paid to the selection of the size of the abrasive particles. The effect of particle size of talc, a key component of the detergent, on the ability to remove pesticide residues from fruit and vegetable surfaces was determined.

2. MATERIALS AND METHODS

2.1. Materials. 2.1.1. Plant Materials. Fruits and vegetables (cherry tomatoes, tangerines, and cucumbers; five pieces for fruits/vegetables for one test) were obtained commercially from the local market (Biedronka, Opole, Poland). Plant materials were selected based on uniform size and ripeness and were stored at 4 °C in a refrigerator before use for selected pesticide application.

2.1.2. Chemicals and Reagents. Raw materials used in the commercial household products were applied to develop detergents for fruits and vegetables: Laureth-7 (Rokanol L7, PCC Rokita SA, Poland), sodium/disodium cocoyl glutamate (Perlastan SC 25 NKW; Schill & Seilacher, Germany), sodium carbonate, sodium citrate (POCH, Poland), ethyl alcohol (Polmos, Poland), talc particles (Elementis, USA), benzyl alcohol, ethylhexyl glycerin, tocopherol (Euxyl K900, Schulke & Mayr GmbH, Germany), xanthan gum (Keltrol 1000, CP Kelco, USA), glycerin (Brenntag, Germany), and talc fractions: 50−125, 250−500, and 710−1000 μm (Elementis Minerals BV, USA), and distilled water.

Pesticides (boscalid, fungicide 2-chloro-N-[2-(4-chlorophenyl)phenyl]pyridine-3-carboxamide, 99.5%, analytical grade; acetamiprid, insecticide N-[(1,4-dichlorophenyl)phenyl]-N′-cyano-N-methylethanimidamide, 99.9%, analytical grade; and pyraclostrobin, fungicide methyl N-[2-[(6-chloropyridin-3-yl)methyl]-N′-cyano-N-methylthianimidamide, 99.9%, analytical grade; and pyraclostrobin, fungicide methyl N-[(6-chloropyridin-3-yl)methyl]-[2-(4-chlorophenyl)]pyrazol-3-yl]oxymethyl]phenyl]-N′-methoxy carbamate, 99.9%, analytical grade) were purchased from Sigma-Aldrich (Saint Louis, MO, USA). Individual stock standard solutions with a concentration of 1000 mg/L were prepared by dissolving 10 mg of each pesticide individually in acetonitrile in a 10 mL volumetric flask and stored below −18 °C. Working standard mixtures with concentrations of 0.001, 0.005, 0.02, 0.05, and 0.2 mg/L were prepared for use as calibration standards and were stored in a refrigerator (4 °C). Water was delivered by a Direct-Q3 UV remote system, Merck Millipore (Darmstadt, Germany). Acetonitrile and formic acid of LC−MS grade were purchased from Merck (Darmstadt, Germany). Dry ice was purchased from Cryopoland (Bielsko-Biała, Poland).

Supel QuE citrate (EN) tube (4 g MgSO₄, 1 g NaCl, 0.5 g Na citrate dibasic sesquihydrate, 1 g Na citrate tribasic dehydrate) and Supel QuE PSA (EN) tube (150 mg Supelclean PSA, 900 mg MgSO₄) were purchased from Merck (Darmstadt, Germany).

2.2. Methods. 2.2.1. Scanning Electron Microscopy. Pictures of the tested materials (talc particles) were taken using a scanning electron microscope at 200X or 50X magnification using a high vacuum. A FEI Quanta 250 FEG microscope (FEI Inc., Eindhoven, The Netherlands) was used.

2.2.2. Particle Size Distribution. Particle size analysis was performed using Alpine/Hosokawa sieving equipment. Talc lumps were crushed to a size of 3−1 cm. The crushed material...
was sieved into fractions: 50–125, 250–500, and 710–1000 μm using Alpine/Hosokawa sieving equipment.

2.2.3. Stability Test. Detergent stability was measured by the mechanical loading test. After 24 h of detergent preparation, the samples were subjected to centrifugal force using an MPW 260R centrifuge. Each sample was centrifuged at 200 rpm for 3 min at room temperature.

2.2.4. Viscosity Measurements. The viscosity was measured using a Brookfield rheometer DV2TRV with a small sample adapter and cylindrical spindle SC4 (Brookfield, USA) at 20 °C in triplicate. An aliquot of 8 mL of the sample was used in each test. Different shear stresses and shear rates were applied to the sample, and the resulting rheogram was prepared to determine the rheological behavior.

2.2.5. Experimental Methodology. Three pesticides: boscalid, acetamiprid, and pyraclostrobin were selected for application on the surface of fruits and vegetables. Pesticide stock solutions with a concentration of 1000 mg/L were prepared by dissolving 10.0 ± 0.5 mg of individual compounds in 10 mL of acetonitrile. The stock solutions were mixed and then diluted with ultrapure water, yielding a boscalid, acetamiprid, and pyraclostrobin mixed solution with a concentration of individual pesticides of 50 mg/L.

The plant materials, cherry tomatoes, tangerines, and cucumbers (five pieces per fruit/vegetable), were fortified with selected pesticides by soaking them for 1 min in the pesticide mixed solution and then left for drying for 24 h.

2.2.6. Model Washing Process. Fruits and vegetables with implemented pesticides were washed with detergents with different talc particle sizes.

The cleaning performance was analyzed using an automatic washing tester for round fruits (cherry tomatoes and tangerines) and a scrub tester for long vegetables (cucumbers).

2.2.6.1. Automatic Test for Washing Round Fruits. Automatic tests for washing round fruits were performed using a Linitest device (Heraeus Group, Italy) (Figure S1a, Supporting Information). 0.50 ± 0.01 g of the detergent was applied to each cherry tomato and tangerine. The individual fruits were packed in a plastic bag and placed in a metal cup applied to each test. Different shear stresses and shear rates were applied to the sample, and the resulting rheogram was prepared to determine the rheological behavior.

2.2.6.2. Scrub Test for Washing Long Vegetables. The long vegetable (cucumbers) was washed in a TQC scrub abrasion and washability tester (TQC Sheen UK, Herefordshire, England), simulating cleaning actions. The testing device was a multitrack scrub tester with a sponge holder (Figure S1b, Supporting Information). The cucumber peel was removed and placed on a test bed in a tester. 0.50 ± 0.01 g of the detergent was applied to the sponge, and then the sponge was attached to the tool carrier. The holder’s weight was 671.75 g per sponge holder. The washing program consisted of 25 strokes over a double length of 80 mm, with a scrub speed of 20 strokes/min (1 stroke = one back and forth movement). No additional water was added during the wash test. After the wash test was completed, the cucumber peel was removed from the scrub tester, collected in a sieve, rinsed with 500 mL of tap water (20 °C, 20″N) with controlled flow (same stream, height), and then left for drying and used for further treatment.

The fruits and vegetables were dried, frozen, and stored in a freezer at ≤−18 °C until future preparation.

2.2.7. Sample Preparation. The deep-frozen sample was homogenized with dry ice using a laboratory knife mill (Cutter Mixer R5 Plus, Robot Coupe, France).

The whole contents of the laboratory mill were placed in separate, self-sealing plastic bags and stored for 24 h in a freezer at <−18 °C until all dry ice sublimated, and then extraction was performed.

2.2.8. QuEChERS Extraction. The extraction procedure for the determination of pesticide residues was based on the European Standard EN 15662:2008. 10.00 ± 0.1 g of homogenized fruits and vegetables was separately weighed into a 50 mL polystyrene centrifuge tube. An aliquot of 10 mL of acetonitrile was added to the sample. The PP centrifuge tube was closed tightly and shaken for 1 min automatically (BenchMixer XL multitube vortexer, Benchmark Scientific, USA). Subsequently, a buffer–salt mixture (4 ± 0.2 g of magnesium sulfate anhydrous, 1 ± 0.05 g of sodium chloride, 0.5 ± 0.03 g of Na citrate dibasic sesquihydrate, and 1 ± 0.05 g of Na citrate tribasic dehydrate) was added to perform a liquid–liquid partitioning step. The centrifuge tube was closed and shaken using the vortexer for 1 min. The extract obtained was centrifuged at >3000 rpm for 5 min (Universal 320R centrifuge, Andreas Hettich GmbH & Co, Tuttingen, Germany). After centrifugation, 6 mL of the sample extract supernatant was transferred to dispersive SPE 15 mL centrifuge tubes containing 150 mg of Supelclean PSA and 900 mg of MgSO_4_. The tube was shaken automatically for 30 s and centrifuged at >3000 rpm for 5 min. An aliquot of 0.5 mL of the purified sample extract was transferred to a new Eppendorf safe-lock tube and subsequently diluted with 0.4 mL of water, 0.05 mL of acetonitrile (+5% vol formic acid), and 0.05 mL of acetonitrile. The content was vortexed gently and filtered through a 0.22 μm Teflon filter, attached to a syringe, and directed into an amber high-performance liquid chromatography (HPLC) vial.

2.2.9. Assessment of Pesticide Content Using Reversed-Phase Chromatography Coupled with Tandem Mass Spectrometry (LC−MS/MS). The extract solutions were separated using a HPLC (Dionex UltiMate 3000 RS chromatograph, Thermo Fisher Scientific, Sunnyvale, CA, USA) system equipped with a reverse-phase precolumn and column (Synergi Fusion RP, 2.5 μm, 80 Å, 150 × 4.6 mm, Phenomenex) maintained at 25 °C. The mobile phase consisted of 0.1% (v/v) formic acid in water as solvent A and 0.1% (v/v) formic acid in acetonitrile as solvent B. The elution conditions applied were isocratic with 90% B for 6 min, a flow rate of 0.6 mL/min, and an injection volume of 10 μL.

The MS/MS detection was performed using a triple quadrupole mass spectrometer (4000 QTRAP, AB Scie, Framingham, MA, USA), equipped with an electrospray ionization (ESI) source working in positive-scan mode. The data were processed using Analyst ver.1.5.1.

Nitrogen was used as the curtain and collision gas.

The MS/MS instrument was operated in the multiple reaction monitoring (MRM) mode. The identification of selected compounds was done by molecular mass and fragment of anion entries of each individual compound and confirmed by MS^3 fragmentation. The protonated molecule of the
selected pesticide (precursor ion) generated in the ESI source was isolated by the first quadrupole by the mass/charge (m/z) ratio and subjected to collision-induced dissociation which occurs in the collision cell (second quadrupole). The resulting fragment ions (product ions) were separated according to their m/z ratio in the third quadrupole. MRM conditions were as follows: for boscalid, retention time, 3.9 min; parent ion, 343.1 Da; quantifying ion, 307 Da and qualifying ion, 140.1 Da. For acetamiprid, retention time, 3.4 min; parent ion, 223.0 Da; quantifying ion, 125.9 Da; and qualifying ion, 89.8 Da. For pyraclostrobin, retention time, 4.3 min; parent ion, 388.1 Da; quantifying ion, 194.0 Da; and qualifying ion, 163.2 Da.

2.2.10. Assessment of the Ability to Remove Pesticide Residues from the Surface of Fruits and Vegetables. Pesticide stock solutions (1000 mg/L) were used to prepare a working standard solution for the calibration curve. Five matrix-matched calibration samples were injected over the range from 0.001 to 0.2 mg/L. All standards were injected, and their corresponding peak responses were entered into the program to create a standard curve. Calculations for instrumental analysis were conducted using the software application Analyst 1.5.1. Weighting 1/x was used for all matrices. With no weighting, the slope of the line (curve) tended to be dominated by the highest point. When the weighting of 1/concentration (1/x) is used, the slope more closely approximates the majority of the points used to construct it. For individual pesticides, a curve using the peak area response and the concentrations of the calibration standards was generated. The pesticide concentration (µg/g = mg/kg) in fortified samples was calculated from a standard calibration curve using a Microsoft Excel spreadsheet. Cleaning performance was determined by the percentage of pesticide residue removal capacity. Data were expressed as the percentage of pesticide removal determined in extracts averaged over three measurements.

2.2.11. Statistical Analysis. All results in the study were expressed as the mean of three independent replicates (n = 3) ± standard deviation. Error bounds are presented in the figures. Classification techniques such as agglomerative hierarchical cluster analysis (dendrogram using Ward’s method with Euclidean distance) and principal component analysis (PCA) were used to interpret the obtained results. The calculations were performed using the software STATISTICA ver. 10. A correlation matrix was used to find a significant correlation between considered variables. Differences were considered significant when the correlation coefficient was greater than the absolute value of 0.4 and a p-value < 0.05.

3. RESULTS AND DISCUSSION

3.1. Development of Detergents for Fruits and Vegetables Containing Talc Particles. Formulations of detergents for washing fruits and vegetables using talc particles as an abrasive have been developed. Particular preparations differed from each other in the size of the particles used. In the first stage, work to create talcum particles with different grain sizes and reduced edge sharpness was carried out. Talc fractions of 50−125, 250−500, and 710−1000 µm designated as MT50, MS250, and MS710, respectively, were subjected to a tumbling process for 5 h until the talc particles lost their sharp edges, and then the individual fractions were sieved once more to remove undesirable particles.35,36 The process is schematically presented in the Supporting Information, Figure S2.

For the obtained fractions, particle size analysis was performed. Characterization of the shape of talc particles was carried out by SEM (Figure 1). Each fraction was found to contain at least 80 wt % particles with the size within the assumed range.

![Figure 1. SEM pictures of talc particles.](https://example.com/figure1.png)
were carried out at room temperature. In the first step, xanthan gum was dispersed in glycerin. Part of the water (75% of the total amount) was weighed in a separate container, and sodium citrate and sodium carbonate were dissolved therein. Thereafter, the resulting mixtures were combined and thoroughly mixed, taking care not to introduce air into the system. The remainder of the water (25% of the total amount) was placed in a separate container. Then, ethyl alcohol, benzyl alcohol, ethylhexylglycerin, tocopherol, disodium cocoyl glutamate, sodium cocoyl glutamate, and laureth-7 were added. The mixture was thoroughly mixed until a clear solution was obtained. All premixes were then combined and mixed for about 5 min until a homogeneous system was obtained. In the last stage, a weighted amount of talc particles was dosed and mixed until a homogeneous preparation was obtained. As a result, three prototypes of detergents for washing fruits and vegetables, with a variable size of abrasive particles, were created.

3.2. Detergent Characterization. The functionality of detergents is related to the appropriate combination of their quantitative and qualitative composition so that the finished products show satisfactory performance in the eyes of consumers. In their evaluation, consumers pay attention particularly to the characteristics related to the application of the detergent (appropriate viscosity and rheological properties) and its performance regarding washing properties. It is important to verify how the addition of talc particles affects the quality aspects of detergents related to their functionality. Parameters such as stability, viscosity, rheological properties, and washing properties related to pesticide residue removal efficiency were analyzed.

3.2.1. Stability. Testing the stability helps to ensure the high quality of the products and therefore safety of consumers. Organoleptic parameters (appearance, signs of separation, color, and odor) were checked in the mechanical loading test. No visual changes were noted for all investigated detergents. The products were found to be stable.

3.2.2. Rheological Behavior. Characterization of the rheological behavior of designed detergents is critical in a wide range of industries as it governs process efficiency, safety, and end-product quality. The rheological behavior of the obtained detergents was characterized. The rheogram of detergents is presented in Figure 2.

Table 1. Formulations of Prototypes of Detergents for Fruits and Vegetables

| name according to INCI nomenclature | MT50 | MS250 | MS710 | function |
|-------------------------------------|------|-------|-------|----------|
| laureth-7                           | 1.0  |       |       | primary surfactant |
| disodium cocoyl glutamate, sodium cocoyl glutamate | 0.5  |       |       | co-surfactants |
| sodium carbonate                    | 1.0  |       |       | pH regulator, a substance that improves detergency |
| ethyl alcohol                       | 5.0  |       |       | amphiphilic solvent, a substance that improves detergency and microbiological stability |
| sodium citrate                      | 1.0  |       |       | sequestrant, helps dissolve mineral impurities, supports the effect of preservatives |
| talc (particles 50−125 μm)          | 40.0 |       |       | abrasive substance |
| talc (particles 250−500 μm)         | 40.0 |       |       | |
| talc (particles 710−1000 μm)        | 40.0 |       |       | |
| benzyl alcohol, ethylhexyl glycerin, tocopherol | 0.5  |       |       | preservative |
| xanthan gum                         | 0.5  |       |       | viscosity modifier |
| glycerin                            | 1.5  |       |       | hydrophilic solvent, facilitates the dispersion of xanthan gum, counteracts crystallization of anionic surfactants |
| aqua                                | 49.0 |       |       | inactive filler |

Figure 2. Rheogram of detergents: (a) viscosity vs shear rate and (b) shear stress vs shear rate.
stress versus shear rate relationship curves are characteristic for Herschel–Bulkley fluids, also referred to as the yield power law model. To describe the rheological behavior of non-Newtonian fluids, the Herschel–Bulkley model is often used because it is a generalization of both the Bingham and power law models. The Herschel–Bulkley model describes fluids that exhibit yield stress and for which the shear stress tends to behave at a high shear rate like a power law. The model relates the shear stress \( \tau \) to the shear rate \( \dot{\gamma} \) as follows \(^{(1)}\)

\[
\tau = \tau_y + K\dot{\gamma}^n
\]

\( \tau_y \) is the yield stress, \( K \) is the consistency index, and \( n \) is the flow behavior index.

Detergents with paste consistency were obtained. Viscosity and shear stress increased with decreasing talc particle size. Comparison of the detergent rheograms also showed that an increase in talc particle size led to a decrease in yield point. As the talc particle size increased from 50 to 710 \( \mu \)m, the yield point decreased from 42.6 to 18.4 Pa and the plastic viscosity decreased by more than double. The obtained results indicated that the use of different talc particle sizes had a significant effect on the rheological behavior of the designed detergents. Scouring detergents in a paste form should have a high yield point and adhesion to the washed surfaces. The obtained results indicated that smaller talc particles were more desirable in the development of detergents in a paste form. In addition, the observed changes in the rheological behavior of the designed detergents with the change in talc particle have a significant impact on creating the quality of the final product and the efficiency of the detergent manufacturing process. Therefore, the work to create talcum particles with reproducible grain size and shape is very important.

3.3. Cleaning Performance. Washing of fruits and vegetables plays an important role in reducing pesticide residue levels. In this study, the effects of washing fruits and vegetables with designed detergents were examined. Cherry tomatoes, tangerines, and cucumbers were selected as the plant materials for this stage of the study. A known amount of pesticide standards most commonly used to protect the selected fruits and vegetables (the insecticide acetamiprid and two fungicides: boscalid and pyraclostrobin) were artificially applied to the selected plant materials under laboratory conditions. Then, the model washing process was applied to wash fruits and vegetables using designed detergents that differed in talc particle size. Fruit and vegetable samples were analyzed by LC–MS/MS before and after washing in order to determine the amount of individual pesticides. The effectiveness of detergents with different sizes of talc particles in removing selected pesticides from fruits and vegetables was calculated as follows

\[
\text{Effectiveness of pesticide residue removal [\%]} = \frac{\text{pesticide residues in unwashed material [mg/kg] } - \text{pesticide residues in washed material [mg/kg]}}{\text{pesticide residues in unwashed material [mg/kg]}} \times 100 \quad (2)
\]

The obtained results are presented in Figure 3.

The cleaning performance of designed detergents in removing selected pesticide residues from fruits and vegetables during their washing was based on the talc particles acting on the peel like gentle peeling. The effectiveness of pesticide residue removal varied with the size of the talc particles. In cherry tomatoes, the reduction of the investigated pesticide residues increased with decreasing particle size of the talc in detergents. For 50–125 \( \mu \)m talc particles, the residue removal efficiencies were 85, 81, and 75\% for boscalid, pyraclostrobin, and acetamiprid, respectively. For tangerines washed with detergents containing 50–125 \( \mu \)m of talc particles, 87, 87, and 75\% reductions of acetamiprid, pyraclostrobin and boscalid were calculated, respectively, while for cucumber, 58, 53, and 36\% of boscalid, pyraclostrobin, and acetamiprid were removed.

3.4. Statistical Analysis. A correlation matrix with one list of variables was used to find significant relationships between...
individual parameters. This compilation allowed us to observe that decrease in talc particle size caused an increase in the effectiveness of both boscalid and pyraclostrobin residue removal. Also, the amount of washed-out pyraclostrobin strongly positively correlated with removed boscalid quantity. In order to illustrate the relationship between the effectiveness of three pesticides removal from the surface of vegetables and fruits, chemometric analyses such as PCA and agglomerative hierarchical cluster analysis (AHC) were applied (Figure 4).

On the basis of the presented dendrogram (Figure 4a), it can be concluded that the degree of pesticide removal from tomatoes, tangerines, and cucumbers washed with detergents containing talc MT50 and MS250 is similar, while MS710 differed from them (p > 0.05) (orange, red, and green markings).

The cluster analysis technique proved to be helpful in the identification of detergents containing talc particles of sizes 50−120 and 250−500 μm, which removed similar quantities of considered pesticides from the surface of analyzed fruits and vegetables.

Next, PCA was performed to explain the differences between the concentration of removed pesticides from the surface of tomatoes, tangerines, and cucumbers using detergents containing talc of different particle sizes. The system of the two first principal components, PC1 and PC2, was used to present the results. Two main factors with eigenvalues higher than 1 explain over 98.8% of the data variance, while the first distinguishing factor (PC1) explains nearly 93.4% of it, and its eigenvalue of 2.1 indicates that it contains information originally explained by two variables used to describe the research object (Figure 4b). The factorial arrangement for the effectiveness of analyzed detergents containing different sizes of talc particles allowed for the identification of three groups, orange—tangerines, red—tomatoes, and green—cucumbers, washed with MT50 and MS250, which confirmed the observation in AHC similarity. A high degree of acetamiprid washout was responsible for these groupings of tangerines in −PC1 and −PC2 locations, while in the tomato group—the highest boscalid and pyraclostrobin removal (∼PC1 and +PC2). Completely different locations of the cucumber group (+PC1 and +PC2) resulted from the low removal of the analyzed pesticides from their surface.

4. CONCLUSIONS
Special talc-based scouring paste detergents for washing fruits and vegetables were developed, and their properties were studied. The detergents were tested for their ability to remove pesticide residues from fruit and vegetable surfaces. The results showed that the developed detergents were highly effective in removing pesticide residues during the fruit and vegetable washing process. The effectiveness of the washing detergents depended on the size of the talc particles. Detergents containing talc particles of 50–125 μm showed the most effective performance by providing greater coverage of the cleaned surface and thus better scrubbing efficiency. Furthermore, the top layer of the fruit peel was affected—the smaller particles were able to produce much shallower scratches, with more of them at the same time. A large number of shallow scratches promoted the effective reaching of the pesticides and, consequently, efficient pesticide removal. For fruits and vegetables with rougher peels, the finer particle size also allowed the particles to reach small cavities and crevices. Consequently, an increased ability to remove pesticides from washed fruit and vegetable surfaces was observed. Additionally, among the types of talc tested, particles with sizes in the range of 50–125 μm proved to be by far the most advantageous from the point of view of their application in detergents for washing fruits and vegetables. The highest pesticide removal capacity was obtained, and the viscosity of the detergents significantly increased. This feature allowed us to reduce the content of viscosity modifiers in the designed products without compromising the stability of the system. The developed washing agents provide an interesting and effective form of removing pesticide residues from fruit and vegetable surfaces for household applications.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01029.
Model washing process; washing machine for automatic test for round fruits and automatic scrub tester for washing cucumber peel, and schematic illustration of the talc particle production process (PDF)

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