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SYNTHESIS, CHARACTERIZATION OF DEVELOPED SILICA NANOPARTICLES AND NANO STRUCTURED ALUMINA AND STUDIES ON RESIDUES OF CERTAIN PESTICIDES IN AGRICULTURE PRODUCTS

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SUMMARY

Understanding the degradation of pesticides which affected by many different parameters and evaluation of pesticide residues are of crucial importance not only for a sound estimation of food risks, but also to improve pesticides application techniques, and to develop pesticides monitoring programs. Estimating the dissipation of pesticides and their corresponding half-life or decline time is important for estimating the risk to human health and to optimize pesticide application. Therefore, the present studies were undertaken to establish dissipation dynamics of selected pesticide, viz., azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin at recommended dose under Egyptian open field cucumber and strawberry. The studies also intended to assess the differences in rate of dissipation and to recommend Pre-harvest intervals (PHIs) based on maximum residue limits (MRLs).

A QuEChERS-based method for simultaneous determination of azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin in cucumber commodity fruits and strawberry commodity fruits was established and confirmed using high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS). Based on this method, the dissipation behaviors, residue distributions and dietary risk probability of these pesticides in cucumber and strawberry, were further investigated for food safety.

The initial deposits of azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin residues on cucumber were 1.22, 1.33, 0.435, 0.299, 0.668, 0.329 and 0.715 mg kg^{-1} and that in strawberry were 1.04, 1.08, 0.953, 1.02, 0.370, 0.535 and 0.620 mg kg^{-1} as a results of spraying the tested pesticides with its recommended single doses . Calculated initial residue level of picoxystrobin was slightly higher than that of the other tested pesticides in both crops (cucumber and strawberry).

The half- life time $t_{1/2}$ of azoxystrobin in cucumber was 2.39 days and in strawberry was 8.45 days, and of picoxystrobin in cucumber was 1.89 days and in strawberry was 5.37 days, and of pyraclostrobin in cucumber was 2.25 days and in strawberry was 4.98 days, and of pyridaben in cucumber was 2.52 days and in

strawberry was 2.50 days, and of spiroxamine in cucumber was 1.81days and in strawberry was 5.45 days, and of tebuconazole in cucumber was 2.40 days and in strawberry was 6.30 days and of trifloxystrobin in cucumber was 2.38 days and in strawberry was 6.18 days.

The prescribed EU-MRL for azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin residues on cucumber are 1.0, 0.01, 0.5, 0.15, 0.01, 0.6 and 0.3 mg kg^{-1}. The PHIs for azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin were 1, 14, 1, 3, 12, 1 and 3 days, respectively, for cucumber. The prescribed EU-MRL for azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin residues on strawberry are 60, 0.05, 0.1, 0.05, 0.05, 15 and 0.05 mg kg^{-1}. The PHIs thus calculated for the residues of azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin to reduce below MRL were 1, 24, 17, 11, 16, 1 and 23 days, respectively, for strawberry.

The estimation of the terminal residues for tested the pesticides, can be achieved upon treatment both of strawberry and cucumber plants the tested compounds marketed formulation with single specified doses and again with twice the recommended doses. Both of the two single and double levels were applied two and three times, at a separated period seven days interval in cucumber and fourteen days interval in strawberry between each treatments .

In cucumber samples harvested 3 days after the second and third foliar application of the recommended rates, residues of azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin were ranged at 0.173~0.256, 0.301~0.103, 0.089~0.357, 0.119~0.346, 0.229~0.106, 0.125~0.062 and 0.402~0.708 mg kg^{-1}, respectively. In cucumber samples harvested 7 days after the second and third foliar applications of the recommended rates, residues of azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin were ranged at 0.046~0.035, 0.021~0.059, 0.046~0.106, 0.025~0.135, 0.012~0.014, 0.012~0.011 and 0.036~0.373 mg kg^{-1}, respectively. When the tested pesticides formulations were sprayed at the overstated rate (two times recommended dose) twice and three times the final residue levels of azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin in/on cucumber were ranged at 0.543~0.236, 0.225~0.424, 0.162~0.295, 0.249~0.620, 0.434~0.418, 0.215~0.221 and 0.417~0.712 mg kg^{-1}, 3 days after the last treatment, respectively. When the tested pesticides were sprayed at double recommended dosage two and three times , the final residue levels of azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin in/on cucumber were ranged at 0.179~0.203, 0.011~0.143, 0.076~0.038, 0.065~0.131, 0.010~0.044, 0.022~0.043 and 0.261~0.395 mg kg^{-1}, 7-days after the last treatment respectively.

After the foliar applications of the recommended rate two and three times, residues of azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin in/on strawberry were ranged at 0.491~0.538, 0.751~0.955, 0.477~0.717, 0.363~0.592, 0.088~0.207, 0.197~0.283and 0.368~0.600 mg kg^{-1}, 3-days after the last treatment respectively. In strawberry samples harvested 14 days after the two and three foliar applications at the recommended rates, residues of azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin were ranged at 0.189~0.177, 0.128~0.170, 0.127~0.177, 0.141~0.102, 0.041~0.035, 0.079~0.047 and 0.127~0.111 mg kg^{-1}, respectively. In strawberry collected samples at the third day after the second and the third foliar treatment at the double rate i.e. two-folds authorised doses the calculated deposits of azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin were ranged at 0.762~0.808, 1.130~1.226, 0.727~1.263, 0.950~1.060, 0.287~0.582, 0.538~0.795 and 0.635~0.772 mg kg^{-1}, respectively. In strawberry samples harvested fourteen days after the second and the third foliar treatment at the double rate i.e. two-folds specified doses , the calculated deposits of azoxystrobin, picoxystrobin, pyraclostrobin, pyridaben, spiroxamine, tebuconazole and trifloxystrobin were ranged at 0.339~0.341, 0.333~0.259, 0.197~0.223, 0.432~0.300, 0.108~0.112, 0.185~0.156 and 0.236~0.081 mg kg^{-1}, respectively.

Health risk assessment studies were performed. Risk quotient (RQ) is among the most frequently used factors for pesticides residues risk assessment. Because of the higher residues level, RQ was determined as part of safety assessment. The results showed no significant potential risk to human health from the tested pesticide residue on cucumber and strawberry. Application of the pesticide following national GAP through conducting the supervised residue trials would provide the residue

amounts required for setting the MRL and supporting the risk assessment process. These results would be considered as important references for monitoring and assessing the quality safety of agricultural products and protecting consumer health.

Currently, nanoparticles have drawn great interest in water treatment, removing substantial part in water contaminants. In analogy for these newly emerging practices the present work has also meant to study the feasibility of using alumina and silica nanoparticles for removal of azoxystrobin from aqueous solution. The effects of experimental parameters, such as temperature of solution, adsorbent dosage, contact time and initial azoxystrobin concentration on the removal efficiency of azoxystrobin were studied. The morphology and special chemical characteristics of novel prepared nanoparticles was examined by the help of SEM, DLS, and XRD studies. The results revealed that, the percentage removal of azoxystrobin was directly proportional with the temperature and the removal percentage efficiency of both adsorbent is increased as the temperature was raised . The best temperature for the removal of azoxystrobin was 40 ºC. The optimum dose of both adsorbents to remove azoxystrobin was 50 mg. The results showed that, both adsorbent could be used for five-cycles of adsorption-desorption of azoxystrobin, which suggested that the synthesised nanoparticles shows good stability and performance. Finally, from our study we can concluded that the manufacturing nanoparticles considered as good and promise tools for adsorption removal of azoxystrobin from polluted water solution.