Conference Paper

A Qualitative Study of Residual Pesticides on Cotton Fibers

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Two different methods are utilized for this study. The first method covers the measurement of bioelectrical signals caused by enzymatic inhibition of acetylcholinesterase (AChE) for the detection of pesticides. Biosensor toxicity analyzer (BTA) was used for the testing and the monitoring of changes in bioelectrical signals caused by the interaction of biological substances, and residues were evaluated. The second method is based on measurement of the oxygen level caused by photosynthetic inhibition of residual pesticides by the interaction with green algae, Scenedesmus (Chlorophyta). Algaegrowth analyzer (AGA) equipped with miniature sensitive oxygen electrode, a light source and cover to model light and dark phases was used enabling us to follow the lifecycle of algae producing oxygen. The test, conducted under the guideline of faster analogy of DIN 863 toxicity test, algagrowth inhibition test (OECD TG 201) was and ISO standard (ISO: 8692). Two samples of cotton were analyzed. Cryogenic homogenization was carried out for sample pretreatment. Soxhlet extraction method (SOX) and ultrasound assisted extraction (USE) were used for extraction. Both methods show reasonable results and can successfully be utilized for the detection of residual pesticides on different types of cotton and especially to compare the classical conventional and organic cotton.

1. Introduction

Cotton has always been a major part of the textile industry and today provides almost 38% of the world textile consumption, second only to polyester, which recently took the lead [1]. Cotton production is highly technical and difficult because of pest pressures and environment, for example, drought, temperature, and soil nutritional conditions. The total area dedicated to cotton production accounts for approximately 2.4% of arable land globally, and cotton accounts for an estimated 16% of the world’s pesticide consumption [2]. Around 2.5 million tons of pesticides are used annually, and the number of registered active substances is higher than 500. Humans can be exposed to pesticides by direct or indirect means. Direct or primary exposure normally occurs during the application of these compounds, and indirect or secondary exposure can take place through the environment or the ingestion of food [3].

This is why development of natural biological methods of insect control was initiated. Cotton grown without the use of any synthetically compounded chemicals (i.e., pesticides, fertilizers, defoliants, etc.) is considered as “organic” cotton. It is produced under a system of production and processing that seeks to maintain soil fertility and the ecological environment of the crop [4].

Benzoyleureas, carbamates, organophosphorus compounds, pyrethroids, sulfonylureas, and triazines are the most important groups [5]. The organophosphates and carbamates are powerful inhibitors of acetyl cholinesterase [6]. They can irreversibly inhibit acetyl cholinesterase (AChE) which is essential for the function of the central nervous system [7], resulting in the buildup of the neurotransmitter acetylcholine which interferes with muscular responses and in vital organs produces serious symptoms and eventually death [8]. Inhibition of AChE by any xenobiotic compound is used as a tool for assessment of toxicity of some pesticides.
such as organophosphates and carbamates [9]. As the pesticide residue is a potentially serious hazard to human health, the control and detection of pesticide residue play a very important role in minimizing risk. Many methods have been developed in the last few years for the detection of pesticides. The most widely used methods are gas chromatography (GC), high-performance liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC-MS), immune assay, and fluorescence. However, these techniques, which are time consuming, expensive, and requiring highly trained personnel, are available only in sophisticated laboratories [10].

Biosensors based on the inhibition of acetylcholine esterase (AChE) have been widely used for the detection of OP compounds [11]. Electroanalytical sensors and biosensors provide an exciting and achievable opportunity to perform biomedical, environmental, food, and industrial analysis away from a centralized laboratory due to their advantages such as high selectivity and specificity, rapid response, low cost of fabrication, possibility of miniaturization, and ease of integration in automatic devices [12]. Electrochemical biosensors for measurement of these pesticides are based on the inhibition of AChE, and the inhibition degree is proportional to the pesticide concentration [13].

Assessment of human exposure to pesticides and other toxicants through biological monitoring offers one means to evaluate the magnitude of the potential health risk of these chemicals [14]. Algae occupy an important position as the primary producers in aquatic ecosystems, and they are the basis of many aquatic food chains. For this reason, they are used in environmental studies for assessing the relative toxicity of various chemicals and waste discharges [15].

The term algae refers to both macro algae and a highly diversified group of microorganisms known as microalgae. The number of algal species has been estimated to be one to ten million, and most of them are microalgae [16]. Algae are eukaryotic and predominantly aquatic, photosynthetic organisms. They range in size from the tiny flagellate *micromonas* that is 1 micrometer (0.000039 inch) in diameter to giant kelps that reach 60 meters (200 feet) in length [17].

Single celled microalgae are among the most productive autotrophic organisms in nature due to their high photosynthetic efficiencies and the lack of heterotrophic tissues [18]. The green pigment chlorophyll (which exists in three forms: chlorophyll a, b, and c) is present in most photosynthetic organisms and provides an indirect measure of algal biomass [19]. Even though all algae species combined represent only 0.5% of total global biomass by weight, algae produce about 66% of the net global production of oxygen on earth—more than all the forests and fields [20].

Algae possess a number of distinct physical and ecological features, and their ability to proliferate over a wide range of environmental conditions reflects their diversity [17, 20].

The action of toxic substances on algae is therefore not only important for the organisms themselves but also for the other links of the food chains [21]. Algal toxicity tests and life-cycle toxicity tests are increasingly being used in bioassay test batteries, and it has been observed in several studies that for a large variety of chemical substance algal tests are relatively sensitive bioassay tools [22, 23]. Thus, inhibition of photosynthetic performance could also be used as a tool to evaluate the presence of pollutants [15].

Keeping in mind the above-mentioned factors, the goal of the present work was to study two different methods for the detection of pesticides and hazardous compounds based on acetyl cholinesterase inhibition and the monitoring of changes in the oxygen level caused by the interaction of residual analytes and the green algae, *Scenedesmus* (Chlorophyta). Both methods are simple, fast, and more sensitive for pesticide determination with much lower detection limit.

## 2. Materials and Methodology

Two samples of Egyptian cotton Giza 86 (G86) and Pakistani cotton MNH 93 were collected from the cultivation season 2011/2012. Both varieties have classical conventional cotton and organic cotton. HPLC grade acetonitrile solvent was used for the extraction procedure. Green algae of the family Scenedesmaceae and genus *Scenedesmus* was arranged by Bvt Technologies, Czech Republic.

The determination of pesticides in samples at low concentrations is always a challenge. The main aim of any extraction process is the isolation of analytes of interest from the selected sample by using an appropriate extracting phase. The development of an appropriate sample preparation procedure involving extraction, enrichment, and cleanup steps becomes mandatory to obtain a final extract concentrated on target analytes. Cryogenic homogenization was carried out for all the samples, and Soxhlet extraction method along with ultrasonic extraction was used for extracting the analytes.

### 2.1. Principle of BTA

The target for many insecticides is an enzyme called acetyl cholinesterase (AChE) [24]. Acetyl cholinesterase’s (AChE) biological role is the termination of impulse transmissions at cholinergic synapses within the nervous system of the insects and mammals by rapid hydrolysis of the neurotransmitter acetylcholine. Pesticides block the catalytic activity of the active center, thus, acting as inhibitors of AChE. This results in the accumulation of acetylcholine in the synaptic membrane, which blocks the nerves from processing the signals properly [25].
Biosensor toxicity analyzer (BTA) works on the above-mentioned principle and monitors the activity of the inhibition of AChE with the help of sensors which are equipped with an enzymatic membrane of AChE enzyme which is immobilized.

It consists of two major parts, one of which is the microflow unit and the other is Bioanalyzer. The micro flow unit has the capillary arrangement which allows precise and constant flow of the liquid onto the active surface of the AChE sensor for a high level of repeatability and sensitivity in the measurements. The module has an integrated chamber in which the sensor can easily be placed or replaced as shown in Figure 1.

2.2. Principle of Algae Growth Analyzer. Algae growth analyzer is universal device enabling us to follow the lifecycle of algae or other biological objects producing oxygen. The device bears light source, exchangeable color filters, sensitive oxygen electrode, and cover to model dark phase as shown in Figure 2. It is controlled by Bioanalyzer potentiostat that allows user to program light and dark phases, measure, and evaluate the oxygen electrode response. The device provides faster analogy of DIN 863 toxicity test that takes about 1 hour.

Initially, calibration of the device is done with 1 gm Na₂SO₄ and 5 mL distilled water to consume all the oxygen inside the glass cell repeatedly for three times. Then, it is washed with distilled water for three times.

As all the resulted extracts were extracted by the solvent, acetonitrile, so as to ignore the impact of solvent on the communication of analytes with algae, this solvent was evaporated completely at room temperature, and then, the pure extracts were treated directly with 5 mL algae samples in Petri dishes. We allowed them to cultivate for one hour, and then, the samples were tested in algae growth analyzer.

3. Results and Conclusions
The results of the enzymatic inhibition are shown in Figure 3 for Giza classical cotton and organic cotton, respectively.
In these graphs, the response of current (nanoamperes) is on y-axis, and the time (seconds) is on x-axis.

It can be observed that although both classical and organic cotton samples show the change in the intensity of the current, but the organic cotton sample shows more response and more inhibition in case of Egyptian cotton, whereas in case of Pakistani cotton samples (Figure 4), the normal cotton shows more response and more inhibition as compared to the organic one.

Although the use of synthetic pesticides and sprays is prohibited in the cultivation of organic cotton, but the presence of these xenobiotic compounds indicates the improper storage, organic fields surrounded by the conventional cotton fields, or maybe some negligence in the organic cotton production line.

All the above-mentioned extracts were analyzed by AGA for duration of 30 minutes each. With the help of miniature oxygen electrode, we have obtained the oxygen production activity of the algae in presence of the extracts by recording the oxygen produced in medium.

The results of Giza cotton from Egypt were shown in Figure 5. There are differences in the oxygen production, but in each case the addition of extract increases the production of oxygen, whereas if we compare the classical and organic cotton, the stimulating agents in classical cotton are more, and this is the reason of increase of oxygen production. Also, it may be the possibility that the hazardous compounds in classical cotton are less than the organic one.

The results in Figure 6 contain the Pakistani classical and organic cotton. In this case, we can see that there are differences in the oxygen production with the addition of extracts, whereas if we compare the classical and organic cotton, the stimulating agents in organic cotton are more and this is the reason of increase of oxygen production.

In case of Giza cotton, the organic cotton shows the inhibitory effect on photosynthetic activity of the algae, whereas in the case of Pakistani cotton this inhibition is caused by the classical cotton.

This study is based on the development of two different methods for the detection of pesticides and hazardous
compounds based on acetyl cholinesterase inhibition and the monitoring of changes in the oxygen level caused by the interaction of residual analytes and the green algae, Scenedesmus (Chlorophyta).

Contrary to other sophisticated methods, acetyl cholinesterase inhibition test is an easier, faster, and cheaper method. It is a method that offers to different investigators an easy way to detect the presence of organo phosphorus and carbamate pesticides.

The results obtained with the laboratory algal test indicate a reasonable interaction of the analytes and the photosynthetic activity of the algae. Clearer picture of this interaction may be observed by prolonging these tests. Further research may be needed to verify the usefulness of the method presented here for the screening of pesticides on some more varieties of cotton of different regions.

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