



Review

A review of extraction, analytical and advanced methods for determination of pesticides in environment and foodstuffs

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ABSTRACT

Pesticides are widely applied to prevent unwanted pests from attacking crops and livestock which led to their access into the environment. Overuses of pesticides in environment are presence of pesticide residues and their metabolites that are causing serious detrimental effects on human health and all other living organisms. Several severe diseases (Cancer, chronic obstructive pulmonary disease, birth defects, infertility) and more damages of human health are associated with the exposure of pesticides. The maximum residue limits for pesticides have been regulated by the Codex Alimentarius Commission and European Union to protect human health. Thus, monitoring these compounds is extremely important to ensure that only permitted levels of pesticide are consumed. To date, several techniques have been developed for pesticide detection, from conventional analytical to advanced detection techniques. The conventional analytical methods are gas chromatography and high performance liquid chromatography coupled with various detectors involved a sample preparation step prior to further analysis. Advanced detection methods refer to the sensors development such as electrochemical, optical, piezoelectric and molecular imprinted polymer. In this review, we summarized and explained the available analytical and advanced methods for determination of pesticides compound in environment and foodstuffs. Also, pesticides classification and its toxicity, and available extraction methods are briefly discussed.

1. Introduction

Pesticides represented as substances or mixtures designated for destroying and mitigating any group of pests such as insects and plants. During the past decades, different types of pesticides had widely been used in agriculture for high yield productions. Applications of pesticides have secured almost one-third of crop production in the whole world. Pesticides have led to the improvement of food production to secure the demands of an ever increasing human population (Nsibande & Forbes, 2016). The significant impacts on controlling pests are beneficial to prevent hazardous diseases in agriculture crops.

The application of pesticides can be seen in non-agricultural areas such as industrial vegetation control (roadways, railroads), pest control in buildings, pets care or grass management. A wide application of pesticides is continuous increasing; there is no way to avoid them from getting contacted to the environment. To the extent of our concerns, the increasing trend in pesticide consumption is expected to continue for many years ahead in order to increase human population so the demand of food is countless. Furthermore, the world is now undergoing rapid urbanization which means less land will be allocated for farming

activity, so society is expected to produce high yield productions (Tankiewicz, Fenik, & Biziuk, 2011).

The rigorous pesticides usages have been criticized and blamed for resulting pest resistance (Pimentel et al., 1992; Widawsky, Rozelle, Jin, & Huang, 1998) human health problems (Kamel & Hoppin, 2004), and environment harm (Hao & Yang, 2013). After long time uses, pests will slowly develop resistance towards the pesticides. Hence, endless researches are carried out for more effective chemicals to fight the large groups of pests. Humans may be susceptible to pesticides via three ways (Yusà, Coscollà, & Millet, 2014): firstly, it can happen through diet or ingestion, this is the most important source of exposure to these chemicals. Secondly, through dermal contact, it has gained through the household use of pesticides. Lastly, it possibly occurs by means of inhalation of contaminated air that could be a closely connected exposure pathway, particularly for those are staying nearby the agriculture areas.

The applications of pesticides have rapidly increased mainly in agriculture thus they offer undisputed benefits in providing abundant of high quality vegetables with relatively low price. However, their excessive application may leave harmful residues which include metabolites and degradation products into the environment such as soil,

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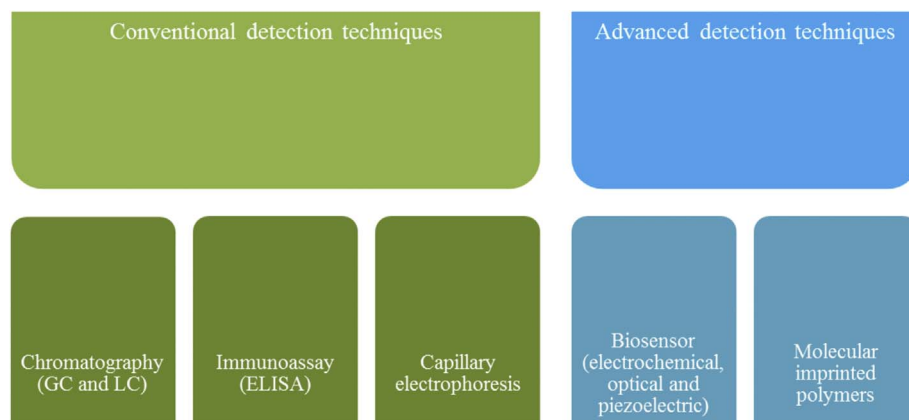


Fig. 1. Available detection techniques for pesticides.

water, plants and foods (Topuz, Özhan, & Alpertunga, 2005). The appearances of substantial amounts of their residues in those complicated matrices have become major issue and might have serious concerns regarding health and environment (Shamsipur, Yazdanfar, & Ghambarian, 2016). To date, several techniques have been exploited for determination of pesticides. Pesticides are conventionally detected by classical analytical methods such as gas and liquid chromatography, high performance liquid chromatography (Guan, Brewer, Garris, & Morgan, 2010; Ye, Wu, & Liu, 2009), enzyme-linked immunosorbent assays (Rekha, Thakur, & Karanth, 2000), and capillary electrophoresis (Hsu & Whang, 2009) (Fig. 1). Generally, these methods have high sensitivity and selectivity at low detection limits. However, these methods are limited with shortcomings such as complicated, laborious, costly instruments and high skilled-manpower. The second approach to determine pesticides via advanced methods in which based on sensors principles. Advanced methods offer several advantages including rapid, simple and low-cost operation, high sensitivity and selectivity, and on-site detection (Songa & Okonkwo, 2016). Zheng, Liu, Jing, Li, and Zhan (2015) have stated that the detection limits of sensor, particularly enzyme based biosensor so far cannot reach the same detection level as compare to traditional methods.

Therefore, the main objective of the present paper is to briefly discuss several available analytical and advanced methods for determination of pesticides in environment and food stuffs. Also, brief overview explained the pesticides classification and toxicity and available extraction methods.

2. Pesticides: classification and toxicity

Pesticides are classified based on target organism, origin and chemical structure. It can form in inorganic, synthetic (artificial as they are produced synthetically) or biological (bio-pesticides). Pesticides are widely classified into two major groups' viz A) chemical pesticides and B) biopesticides. A) Chemical pesticides are basically synthetic materials that directly kill or inactivate the pest. They are mainly classified as 1) insecticides, 2) herbicides, 3) fungicides, 4) rodenticide, 5) nematocides (Sharma, 2006). B) Biopesticides are pesticides derived from natural sources like animals, plants, bacteria, and certain minerals. For example, canola oil and baking soda have pesticidal applications and are considered biopesticides. Pesticides divided into four major families, namely as organochlorines, organophosphorus, carbamates and pyrethroids.

Organochlorines (OCs) pesticides are one of the most persistent chemicals that have high toxicity, lipophilicity and bioaccumulation. Moreover, OCs is found to be estrogenic, carcinogenic and resistance to environment degradation process (Taylor et al., 2013). OCs has long half-lives in tissues and it estimated that the range of half-life of OCs is about 10–30 years (Padrón, Ferrera, & Rodríguez, 2006). In Europe, North America and many countries of South America, OCs are banned

and no longer used in agriculture or domestic purposes. However, some other countries are still used of OCs until today but in a restricted limit, for example, DDT (half-life of 3–20 years) is used in dealing with malaria disease as it control the population of mosquitoes (Choi, Kang, Peng, Ng, & Wong, 2009). Although it has been phased out, their presence in the environment still can be recorded due to their great longevity (Tankiewicz et al., 2011). OCs have relatively stable and tend to bioaccumulate that transferred and exaggerated to higher trophic levels via food chain (Chung & Chen, 2011). It can also be transported at unlimited distances via air and water. Due to its high persistence in the environment and hazardous effects, OCs are withdrawn and replaced by other compounds.

Following the extreme toxicity occurred by OCs, it has been terminated and replaced with easy biodegraded compounds. For that circumstance, organophosphorus (OPs) and carbamates are definitely led for further uses. OPs pesticides are widely applied in agriculture industries globally. In 1942, the first invention of OPs was hexaethyl tetra phosphate (HETP) which used as an insecticide in agriculture sector (Tahara, Kubota, & Nakazawa, 2005). Currently, numerous OPs compounds can be found and used as insecticides besides as fungicides and herbicides. OPs commonly exist in the form of esters that simply can degrade. Apart from, they are less soluble in water; however, it dissolved in inorganic solvents and fats with good solubility. Carbamates are another class of pesticides which largely used in agriculture to protect crops against agriculture pests and household pests (Zhang, Arugula, Wales, Wild, & Simonian, 2015). As compared to OCs, these two pesticides (Ops and Carbamates) are preferred as they are best price, easy to obtained, low persistence in the environment (shorter half-life) and broad spectrum of utilization (wider applications), they are also capable to destroy large group of pests (Firdoz et al., 2010).

The similarity between the organophosphorus and carbamates are known as cholinesterase inhibitors. The inhibition based on their ability to prevent a key enzyme in central nervous system (CNS) of humans and insects, acetylcholinesterase (AChE) is notifying as a way of the toxicity mechanism. The inhibition of AChE will lead to the accumulation of acetylcholine (ACh) neurotransmitter at the synapse which later can damage the normal function of CNS. Although OPs and carbamates are reported as toxic substances, their toxicity is depending on the chemical structure of the pesticide (Dikshith, 1991). However, its toxicity is lower than OCs.

A broadly applied synthetic pesticide of Pyrethroids is derived from naturally occurred chrysanthemum esters that produced natural-existing chemicals, called as pyrethrins (Radford, Panuwet, Hunter, Barr, & Ryan, 2014). These pyrethrins possessed with pesticidal property and synthetic pyrethroids are invented which likely imitating the effective role of natural pyrethrins. The synthetic pyrethroids have stability and half-life longer of environment as compare to the natural form. Pyrethroids have drawn attractions and applied prevalently to crops and as household pests. They exhibit high selective insecticidal activity, non-

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