Review on Composite Based Materials as Analytical tools for Detection of Pesticides in Water and Food Samples

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Abstract**—**Organic pollutants like Organochlorine pesticide (OC) and Polychlorinated biphenyls (PCBs) are major environmental concern due to their persistence, long-range transportability, bio-accumulation and potentially adverse effects on living organisms. Much effort has been devoted during the last two decades to the development of faster, safer, more reliable and more sensitive techniques for their determination in water, feed, food, and in complex environmental matrices. This review article introduces recent analytical techniques used for detection of Organic pollutants like OC and PCBs in environmental and biota samples in field within time, space and compare with convention techniques like gas chromatography, liquid chromatography. Since convention technique was not found effective enough to deal with such specific problem, there is need to develop specific adsorbents which are efficient and economical enough to deal with such organic persistent pollutants.

Keywords**—**Pesticides, Organic Pollutants, Polychlorinated biphenyls (PCBs), Silica.

I. Introduction

THE world population is expected to cross 7 billion by the end of this century. With the increase in population, there is an ever growing need to feed the population, which can be achieved only by having bumper yield. This has necessitated the use of pesticides to protect crops and increase crop yields. However, presence of traces of these pesticides in the food supply cannot be avoided and the effect of long term exposure to these materials is not well understood. Interest in monitoring pesticide levels in soil, water and food matrices has risen with increased use of pesticides and the availability of highly sensitive analytical equipment. Pesticides tend to be active molecules that can be very challenging to analyze at trace levels particularly in sample matrices like food, water, air and soil. Environmental pollution by pesticides and other pesticide like compounds, polychlorinated biphenyls (PCBs) continue to be one of the most alarming challenges for sustainable development. These are considered to be persistent organic pollutants due to their long half lives [1]. Although PCBs are ubiquitous environmental contaminants that have been banned in most countries [2] but considerable amounts continue to cycle in the ecosphere. The consumers are exposed to pesticides and PCBs, in several food groups including fruits, vegetables, mutton, chicken, fish, egg and milk. However, extensive study on pesticides and PCBs residue in less fatty food and more fatty food like mutton, chicken, egg, fish and milk and their implications are lacking in India. Aulakh et al. [3] reported that, residues of pesticide are present despite complete prohibit on poultry muscle and egg in India. Likewise some scientists also found the residues of organophosphate and synthetic pyrethroids in addition to organochlorine compounds in seasonal vegetables from Haryana, India [4, 5]. India is the second largest producer of vegetables after China and accounts for 13.4 % of the world vegetable production and animal husbandry constitutes backbone of Indian farming, where animals are used as source of draft power as well as food in the form of milk, meat and eggs [6]. In India, 240 pesticides of various chemical groups are registered for the control of undesirable pests and weeds in food crops [7, 8]. More than 90% of the average human intake of PCBs originate from food, especially food of animal origin and bio accumulate in the food chain due to their lipophilicity and hence gets biomagnified in human beings [9]. As PCBs are stored mainly in the adipose tissues, these compounds can be transferred from mother to her newborn primarily via maternal milk and to some extent via the placenta [9,10]. In human populations exposed to PCBs, several authors have reported elevations in triglycerides [11, 12] and total cholesterol [13, 14] and occupationally exposed persons also noted elevations in rates of cardiovascular deaths [15, 16].

Hence, monitoring studies to know the actual status of contamination due to toxic pesticide residues and PCBs in various food commodities for the formation of legal guidance and for consumer satisfaction is necessary. There are different steps involved in the determination of pesticide residue as depicted in Figure 1.

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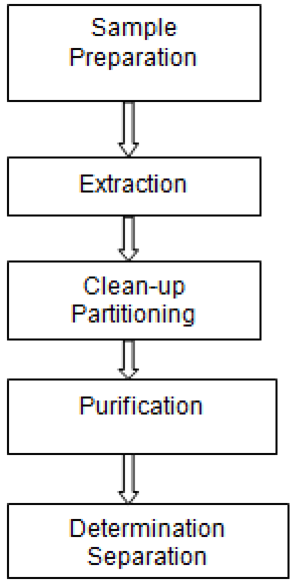

Further each step mentioned above, involves the following steps for pesticide analysis.

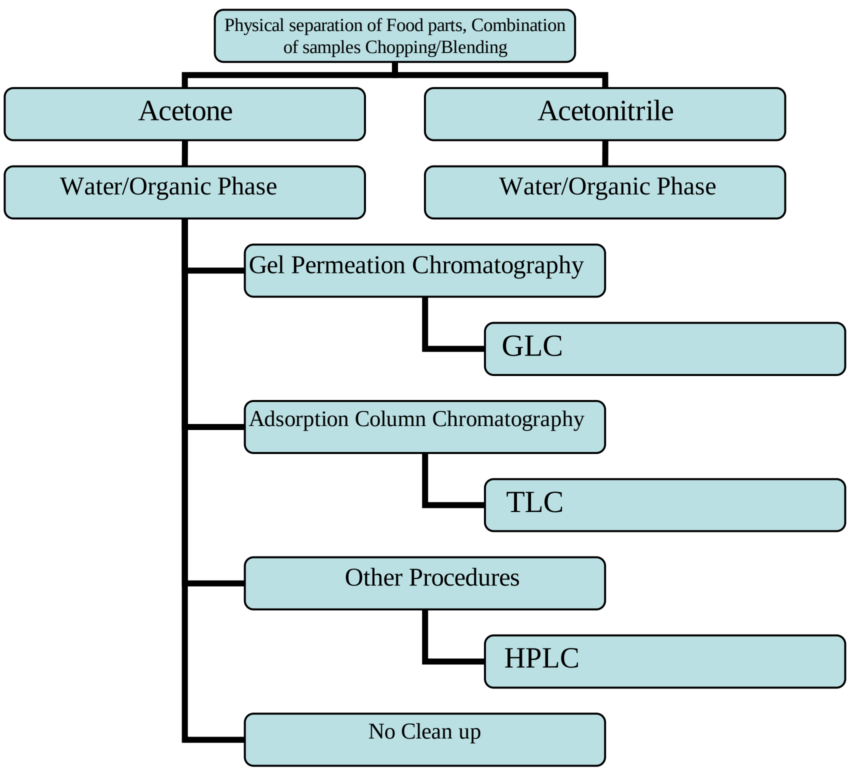

Fig 1: Steps involved in pesticide analysis [17]

Estimation of residual amounts of polychlorinated biphenyls (PCBs) in more fatty food like fish and milk requires the use of specific techniques for sample preparation as well as instrumental analysis which are time consuming, expensive and large volume of organic solvent utilised which are hazardous to humans and to the environment. In order to reduce such harmful effects, alternative technique were developed by many researchers. Sol-gel silica materials are able to entrap these pesticides through adsorption. Hence adsorption has been one of the techniques for detection of polluted water. It is not long back when activated carbon known to be more versatile adsorbents for pollutants. But convention technique was not found effective enough to deal with such specific problem. There is need to develop specific adsorbents which are efficient and economical enough to deal with such organic persistent pollutants. Hence synthesizing and using novel smart material is one of the stepping stone in technological advancement. Böttcher et al. [18] have used the sol-gel matrix as an alternative to biocide encapsulation. They prepared sol-gel composite films with controlled release properties. Raileanu et al. [19] had developed sol-gel composites to improve the release of the pesticide from the silica matrices. Choudhary et al. [20] have prepared SiO_2 sols using tetraethylorthosilicate as a source of SiO_2. The SiO_2 thin films were obtained using Dodecyl trimethyl ammonium bromide, (DTAB), Sodium Dodecyl Sulfate, (SDS) and Tween 20 (Tw 20) surfactants. They have reported that the SiO_2 thin films with SDS showed more surface roughness and water repelling ability when compared to DTAB and least with Tw 20. Kudo and Kudo 2006 [21],Tran and Nosaka 2006 [22], Chueh and Hsieh 2007 [23], Zhuang and Wang 2010 [24] have used silica and titanium oxide composite for analysis and degradation of toxic substances.It has been observed that the addition of SiO_2 to TiO_2 films not only permits an increase of in-time persistence of the photo-induced super-hydrophilicity[25], but also creates an extremely large surface area [26].Table 1**,** represents comparative study of novel composite materials developed for monitoring the concentration of pesticide like toxic compounds, mode of working and their potential benefit.

TABLE I
COMPARATIVE DATA OF COMPOSITE MATERIALS FOR MONITORING THE CONCENTRATION OF PESTICIDE, WITH MODE OF WORKING AND POTENTIAL BENEFIT

Composite materials	Mode of Detection	Substance/enzyme inhibitor	Potential benefit	Reference
Au nanoparticles	Amperometric Voltammetry	Carbaryl, carbofuran	Large effective surface area for enzyme immobilization	27
ZrO2 nanoparticles	Amperometric Voltammetry	Phoxim, malathion	Large effective surface area for enzyme immobilization	28
Quantum dots (QDs-CdTe)	Voltammetric	Phoxim, malathion	Luminescent fluorophores, possess size dependent properties	29
Carbon nanotubes SWCNTs MWCNTs	Amperometri Voltammetry	Monocrotophos	Unique surface area, conformation stability, high bioactivity and substrate biocatalyst interaction	30
CdS-decorated garphene nanocomposite	Amperometric	carbaryl	The high surface area favorable for immobilization of enzyme and have small band gap which is responsible for conducting the electrons with high efficiency	31
SiO_2	Surface adsorption	Monocrotophos	High visible transparency and hardness	32
TiO_2	Surface adsorption	Monocrotophos	UV protective effect	33

Detection techniques-old versus recently developed composite materials for detection of pesticides

The actual trend for detection of pesticides residue like pollutants in several different matrix was based on the use of liquid chromatography coupled to mass spectrometry techniques (LC-MS) and gas chromatography (GC) with selective detection as electron capture (ECD), flame photometric (FPD), nitrogen phosphorus (NPD) and thermal conductivity (TCD) detectors which represented the state of-the-art at the end of the last century. They are intended for lipophillic (in many cases obsolete) pesticides like most organochlorine (i.e. p,p'-DDT, aldrin, dieldrin, lindane). Moreover, the targeted compounds monitored by such methods sometimes are neither pesticides of toxicological relevance or the most commonly found in a particular sample. Also the existing methods need much time for sample preparation, as large amount of organic solvent is used and unable to monitor directly field sample. Table 2 shows a comparative study of old versus new analytical techniques developed with their potential benefit and drawback.

The new trends in pesticide residue analysis have been focused on the miniaturization of the sample preparation methodology, moving to the development of straightforward, faster, cost-effective, and environmentally friendly procedures, adaptable for routine use in laboratories as well as in field. The bibliographical survey covering the period 2010-2013 demonstrated that the predominant part of the recently developed nanostructured electrochemical biosensors for Organophosphorouss quantification make use of carbon nanotubes (CNTs) or gold nanoparticles (GNPs). Previous studies are revised and reported in the comprehensive reviews of Liu et al. [27] and Periasami et al. [28]. GNPs are extensively used in biosensors application, due to their biocompatibility, catalytic activity, excellent conductivity, and high surface area [29, 30]. Other composite materials modified devices for OPs determination were developed using functionalized graphene structures. It has been demonstrated that the acetylcholinesterase sensors based on graphene oxide, GNP-graphene oxide, and nanoparticles (NiO, Pt, SnO_2)-graphene nanocomposites show high electron mobility, catalytic activity, and sensitivity [31-35]. They were successfully applied for methylparathion, chlorpyrifos, malathion, and dichlorvos quantification.

TABLE II
COMPARATIVE ANALYSIS OF ANALYTICAL METHODS FOR MONITORING CONCENTRATION OF PESTICIDE RESIDUES

Analytical methods	Potential benefit	Drawback	References
Gas chromatography	Powerful technique for the determination of multipesticide residues	Complex Sample preparation procedure, time consuming, requires expensive equipment, only volatile compound can analyse	34
High performance liquid chromatography (HPLC)	Powerful technique for the determination of multi pesticide residues	Complex Sample preparation procedure, time consuming, requires expensive equipment	35
Thin layer chromatography	Very Simple operating procedure	Unable to quantify at ppm level	36,37
Capillary electrophoresis		Complex Sample preparation procedure, time consuming, requires expensive equipment	38
Mass spectrometry (MS)	Powerful technique for the determination of pesticide residues due to its robustness, and excellent sensitivity and selectivity	Complex Sample preparation procedure, time consuming, requires expensive equipment	39
Colorimetry	Fluorescence biosensor	Only possible in colour changing compounds	40
Immunoassays	Highly selectivity, sensitivity and reproducibility	They require corresponding antibodies	41
AChE electrochemical sensor	Based on acetylcholinesterase immobilized, selective and sensitive	Only organophosphorus pesticide can assay	42

II. CONCLUSION

This review addresses the recent trends in the development of composite based materials as analytical tool for detection of different class of pesticides like organophosphorus and organochlorine in food samples. The included examples demonstrate great potential of the carbon nanotubes and the gold nanoparticles, as well as of the emerging graphene structures, silica based composite materials. Current researches confirm that the adequate combination of nanomaterials, biological recognition events, and efficient electronic signal transduction result in biosensors with improved analytical performances, appropriate for the high sensitive determination of pesticide residue in difficult sample matrix.

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