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Bio-Sensor Kit for Detection of Quantity of Pesticides in Fruits and Vegetables

Pushkar Yadav[1], Pradyuman Singh[2], Priyesh Pandey[3], Bhuvnesh Chaturvedi[4]
[1]*Student,* [2]*Assistant Professor, Department of Computer science and engineering, Dronacharya Group of Institutions, Greater noida*

Abstract: Pesticides are majorly used in agricultural fields for crop protection but even after having agricultural benefits it also has negative acute toxic effects on human beings and environment.
Accumulation of these toxic substances in the living life cycle prove to be a source of diseases and causes of deaths if accumulated in higher concentration.
This research involves a method to detect the quantity of pesticides accumulate in our edibles which we consume, so as to ensure the quality of food we eat.
For this purpose, a colorimetry method can be used which is the application of beer-Lambert law (1) that measures the concentration of solute by measuring the loss of intensity of light which is passing through the solution.
Keywords: chromatography, carcinogenic, citrate-capped, catalyzed, transmittance

I. INTRODUCTION

In the case of pesticides "If little is good, a lot more will be better" has played havoc with human and other life forms thus their prompt and accurate analysis is a crucial matter of concern. Chromatographic techniques (HPLC, GC, etc.) are used for pesticide detection but these methods have various limitations so there is a need for methods which can detect these toxic compounds. Discussing about biosensors till date based on sensing element (enzyme based, antibody based, etc.) and type of detection method used (Electrochemical, optical, and piezoelectric, etc.), a number of biosensors have been developed for pesticide detection.

Keeping check on the usage of pesticides has become very important in recent years to sustain and maintain balance in life forms. Pesticides are inseparable to modern agriculture and used extensively to control attack of insects, fungus, and rodents or other diseases on crops; reduce the growth of weeds; boost agricultural productivity, thus increase crop yields; and reduce post-harvest losses.

During rainfall and downflow of water or due to absorption ability of soil these toxic substances enter into the food cycle through soil, air and water, which may deteriorate many life forms.

Common detection methods such as HPLC (High-Performance chromatography) and other spectroscopic methods have limitations on accuracy, time taken in detection process and other parameters. Hence, we can use the concept of colorimeter for detection of pesticide which itself is based on the concept of beer-lambert law (1).

II. RELATED WORK

Neelam Verma et al. [13] develop a method which detects the pesticides ranging from 10^{-6}–10^{-14} M having storage stability of 30–60 days.

Developed biosensors have been applied for the monitoring of pesticides in water, milk, vegetable and fruits. The response time of biosensors was found in the range of 2-20 min, and in some cases less than 1 min.

R. Montes F. et al. [14] constructed a method by means of EIS and CV techniques. Their study demonstrated the development of these electrochemical biosensors is based on the bio composites. Their optimized technique allows achieving lowest pesticide concentrations.

Narenderan S.T etal. [15] developed a new method for extraction and detection system for the pesticides residue analysis. Which is cost-effective and eco-friendly and detects a large number of pesticides residue in a single run.

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III. MEDICAL

As per the data from October 2019, 318 pesticides were registered in India, out of which 18 were extremely (Class-Ia) or highly (Class-Ib) hazardous according to toxicity criteria laid by WHO.

Total of 56 pesticides were carcinogenic and banned in other countries. Out of that 56, 20 pesticides are clearly harmful for children and cause blood cancer.

Some of the most common and hazardous pesticides which are used in India are:

A. Monocrotophos, class 1 pesticide (Acc. to WHO)[4].
B. Oxydemeton-methyl, class 1 pesticide (Acc to WHO)[4].
C. Acephate.
D. Profenophos.
E. Methyl Iodide.
F. BHC(β-Hexachlorocyclohexane) One of the most commonly used in India (represents almost 50% of volume in India), (Acc. to National Center for Biotechnology Information).
G. DDT (dichloro-diphenyl-trichloroethane), one of the most harmful pesticides used in India and was originally made to combat malaria.

The most important aspect to discuss is the consequences of pesticides on human health.
Basically, when considering health, we have found to bifurcate the health aspects in two main categories, namely:

1) *Acute:* Acute symptoms can be irritation of the nose and throat, skin burning, stinging and itching, rashes and blisters. Some common symptoms are nausea, dizziness and diarrhea. People who have asthma can have very severe reactions to pesticides.
2) *Chronic:* Cancer and other tumors are chronic symptoms, apart from that brain and nervous system damage, birth defects, infertility and other reproductive problems, damage to the liver. It takes several months or years for chronic symptoms to show their effect and thus makes it less traceable.

Speaking about the death toll related to pesticides, NCRB [(6)] states that,

1) 441,918 suicide cases were linked to pesticide usage in India between 1995 to 2015, of which almost 90.3% came from 11 of the 29 states (union territories excluded).
2) It is also estimated that deliberate ingestion of pesticides causes 370,000 deaths each year.
3) Apart from that about 385 million people, mainly farmers and agriculture workers, are poisoned by pesticides every year including 11,000 deaths per year. Of all the deaths, nearly 6,600 deaths per year occur in India.
4) This clearly means that almost 44% of the total worldwide farming population (that is around 860 million in total) are poisoned because of pesticide every year.

One of the most common threats is **cancer** due to high pesticide intake. In India **DDT** is used at a very high rate and due to this in most cases it causes Breast Cancer and quadruples the risk of getting it.
It is well known that farmers and their families are more affected by the use of pesticides than the whole general population. As a result, they experience higher rates of cancer.
When closely examining the data collected from **NCRB** we saw that most of the India cancer cases due to pesticides come from rural areas which are agricultural hubs like Punjab, Uttar Pradesh, Bihar.

IV. CHEMICAL

Pesticides are the chemical substances that are used to control pests. These chemical substances help farmers grow more food on less land by protecting crops from pests, diseases and weeds as well as raising productivity per hectare, even after its agricultural benefits some of the pesticides used by the farmers are harmful for human health.

Large number of pesticides are used across the world and India and if we categorize them
Organophosphate (OP), Organ carbamate (OC) and Organochlorine (OC) pesticides are most commonly used pesticides for agriculture and domestic use.

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Organophosphate (OP)	Organocarbamate (OC)	Organochlorine (OC)
Dichlorvos	Carbaryl	DDT(Dichloro-Diphenyl-Trichloroethane)
Methyl Parathion	Carofuran	BHC (Benzene hexachloride)
Monocrotophos	Carbosulfan	chlordane
Chlorpyrifos	Aldicarb	toxaphene
Phorate		
Profenofos		
Parathion		

[10] For colorimetric detection of pesticides, we need compounds which can give naked eye coloration in reaction with the solution containing pesticide, [9] AuNPs (citrate Gold Nanoparticles) and AgNPs (Silver Nanoparticles) are one useful for colorimetric detection. But since costing of a product is one the most important factor, due to which AuNPs is not a viable compound so [8]AgNPs is more useful. Five organophosphate and carbamate pesticides, including dimethoate, dipterex, carbaryl, chlorpyrifos and carbofuran, have been well-distinguished at desired concentrations. Twenty unknown pesticide samples have been successfully identified with an accuracy of 95%. Citrate-capped silver nanoparticles and acetylthiocholine were employed for the functionalization (catalyzed by acetylcholinesterase to form thiocholine) which induces the aggregation of AgNPs. As a result, the color of AgNPs in solution changes from bright yellow to pink.

V. DEVELOPMENT TOOLS USED

A. *Artificial Intelligence-Image Recognition*

To develop an automated device which can recognize fruit or vegetable through image recognition is a feature of a device that makes it acceptable and user friendly. For Image recognition Deep learning CNN method is used which can use any of the data sets of images for learning process such different data sets such: MINST, MS-COCO, ImageNet, Kaggle(a).

[2] Large-scale image recognition has become possible because of large public image databases such as ImageNet. Inception v3 is an open source architecture created by Google which uses approximately 1.2 million images. GoogleLeNet with an accuracy of almost 94.44% and with average error rate of 6.66% has the least error rate in image recognition among other competitive architectures, it has 22 layer deep convolutional neural network.

[2] A Raspberry Pi which operates as a regular computer but at very less cost and size. It is a great development platform for creating prototypes and is selected to replicate real scenarios in model. Raspberry Pi has 1GB RAM available and based on a 64bit Quad Core 1.2GHz CPU, it has two major CSI (Camera serial Interface) and DSI (Display serial Interface) for connecting a camera and display to show results. In terms of hardware requirements, the particular camera which is used for this project is Raspberry Pi camera module V2, the advantage of using this camera is that it provides easy and quick setup with raspberry pi without any external drivers, this camera uses ribbon cable to get connected with DSI (Display Serial Interface) of Raspberry pi. Raspberry Pi Display 7 multitouch used as digital display gets connected to the processor through adapter board which is responsible for power and signal conversion.

B. *Colorimetry (Spectrophotometry and Beer-lambert law)* [11][12]

Spectrophotometry may be defined as a method to calculate how much a chemical substance absorbs the light by exactly calculating the intensity of light, as soon as a beam of light passes through the taken solution. The fundamental principle of spectrophotometry is that every compound absorbs or spreads the light over a certain range of wavelengths. Since every chemical compound absorbs or transmits or reflects light(radiations) over a certain range of wavelengths, which can be used to determine the estimate of the concentration of solutions.

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A spectrophotometer estimates the amount of light(photons) absorbed after it passes through a certain solution, depending on the wavelength of the light source. A spectrophotometer has spectrometer which can produce a desired range of wavelength of light that is needed. This spectrometer component itself has a collimator which we can also say as a lens transmits a straight beam of photons that passes through a prism and split it into several component wavelengths which is called as a spectrum. Then a slit which acts as a wavelength selector transmits only the desired wavelengths, on the second hand it has a photometer to measure the quantity of photons that are absorbed and subsequently sends signals to digital display.

Note:(a) Dataset: https://www.kaggle.com/kritikseth/fruit-and-vegetable-image-recognition
Transmittance(T) can be related to intensity of light after it passes through the cuvette, transmittance is the fragment of light that passes through a certain solution or sample. Following equation can be used:

$$\textbf{Transmittance(T)} = I_t / I_o \quad (1)$$

$\mathbf{I_t}$, final light intensity.
$\mathbf{I_o}$, initial light intensity.

As Transmittance is related to absorption, which can be studied by the expression

$$\textbf{Absorbance(A)} = -\log(T) = -\log(I_t / Io) \quad (2)$$

Beer-lambert [(1)] sets a linear relationship between the absorbance of the concentration of a sample and the sample. This law can be applied when there is a linear relationship. The Law is given as:

$$A = \epsilon l c \quad [(1)] \quad (3)$$

A is the measure of absorbance,
ϵ (epsilon) is the molar absorptivity,
l is the length of path**,**
c is the concentration.
This concentration is the amount of solute in a solution which is responsible for coloration of solution that in case of pesticide detector kit is concentration of pesticide.

VI. CONCLUSION

Pesticides have become an integral part of the farming process over the years and helped farmers to protect their crops and increase the production per hectare, but due to health hazards caused by these chemical substances there should be some quantity check on their usage. So far, different approaches have been studied however colorimetry (Spectrophotometry) process seems to be a viable and accurate process, therefore detection of pesticides in edibles in a single kit(product) can be achieved by Image recognition of fruit or vegetable followed by naked eye color identification chemical test of that particular pesticide and then passing the known intensity light source through the solution and measure the light intensity of emitted light source from solution and calculate the concentration in solution by Spectrometer.
At the current stage (prototype stage) chemical identification tests are restricted to few pesticides using AgNPs (Citrated Silver Nanoparticles). Many studies have shown the use of AgNPs as colorimetric sensors, but the process is complex. In this context, our review summarizes the recent literature about whether pesticides detection with AgNPs (with different catalysts) can be employed for naked eye color detection and Spectrophotometry can measure the quantity of pesticides in edibles.
For future perspective, research to find a most accurate and viable compound which can give coloration for most pesticides in a single step reaction will undergo and moreover for automation of the device with Artificial intelligence (image recognition of edibles) and mechanical automated churner for preparing solution research will be kept on. Making an efficient kit will be a major concern for future researches thus replacing the spectrometer with a simple light sensor will be the centralized research point to reduce the cost of the kit to make it cost effective for users.

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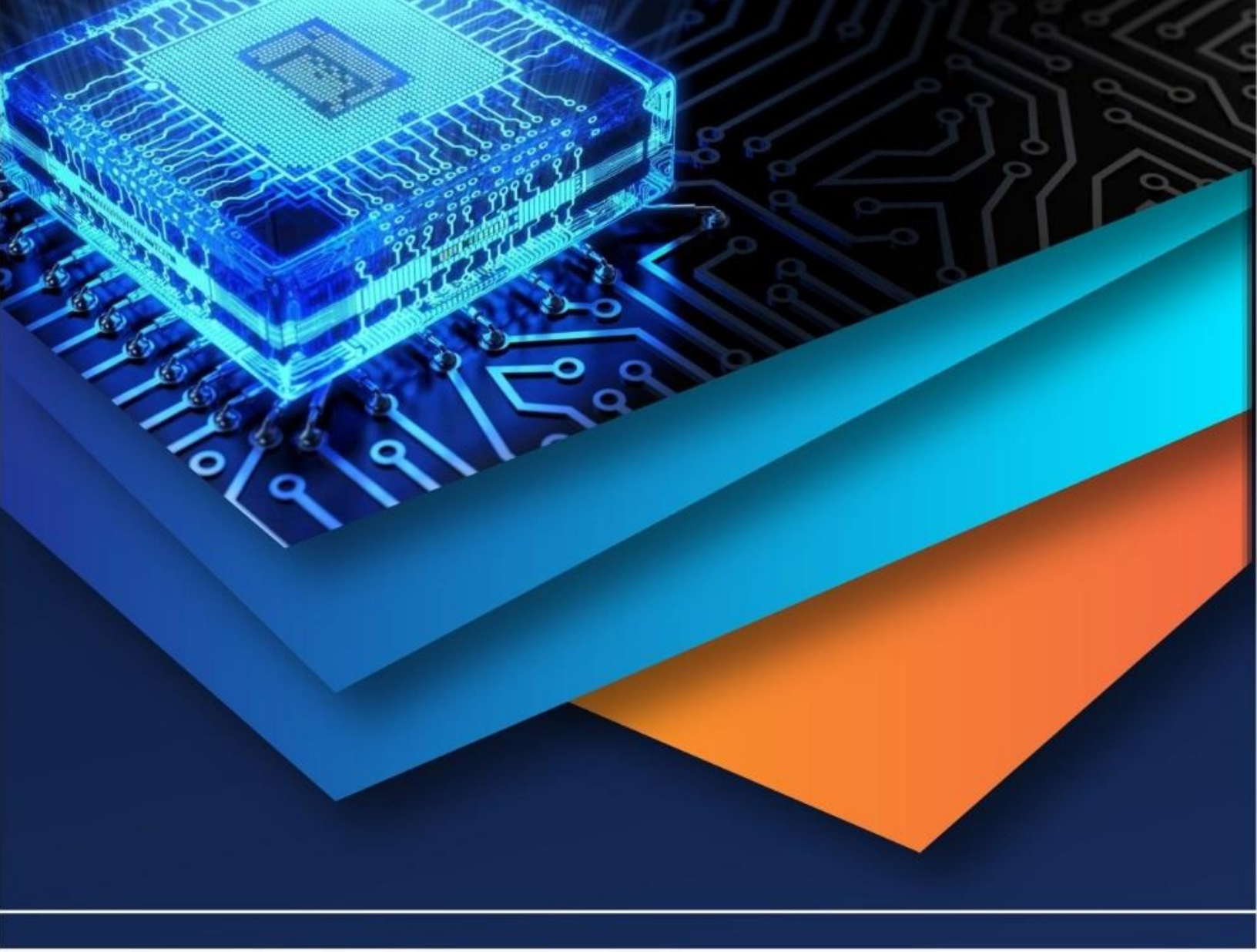

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