



REVIEW

Analytical Approaches for the Detection of Heavy Metals and Agrochemicals in the Environment Samples and their Recent Technologies

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At part per billion (ppb) concentrations, heavy metals and pesticides both pose a significant health risk. Over-ingestion of pesticides and heavy metals in the environment may cause various diseases and effects on human life. So, a systematic analysis for detecting and removing pesticides and heavy metals from the environment is required. This review provides a comprehensive study of the several analytical methodologies employed in the quantification of heavy metal ions and agrochemicals in environmental samples. Furthermore, the detrimental impacts of these substances on both human health and plant life are also discussed. Moreover, a concise overview of the latest developments in the design of nanomaterial-based sensors, specifically focusing on colorimetric and electroanalytical approaches. These sensors are utilized for the detection and analysis of heavy metals and pesticides. In addition, the information garnered from the study will improve the capability to detect and remove contaminants from environmental samples.

Keywords: Heavy metals, Agrochemicals, Nanoparticles, Analytical assay.

INTRODUCTION

Soil and water are the integral components of environment, playing a crucial role in the sustaining of living organisms by facilitating food production and supporting essential ecosystems. The biodiversity of the environment is comprised of several organisms, which provide antibiotics for better human health and the habitat of the organism is truly dependent upon the quality of soil for better growing media [1,2]. Both the soil and the water are mostly composed of inorganic and organic substances, respectively [3]. The presence of heavy metals in water and soil on their requirement and body system tolerance results a situation of toxicity. The developmental movement at the global level in past two decades has resulted in enormous industrial growth and increased consumers, this in turn further resulted in the accumulation of piles of organic and inorganic waste materials and biodegradability limits, besides geographical/neutral imbalance; ultimately polluting soil and water at source [4]. The environment is contaminated by heavy metals due to several factors such as human activities, industrial pollu-

tion sources like tanneries, chemical plants, wood preservation, electroplating industry, mining activities, *etc.* [5].

Heavy metals like lead (Pb), mercury (Hg), arsenic (As), cadmium (Cd), nickel (Ni), chromium (Cr), stannum (Sn), copper (Cu), vanadium (V), zinc (Zn), *etc.* are toxic in nature. The progress of the worldwide economy increases the contamination of heavy metals into the environmental components has gradually increased, consequential in the weakening of the environment [6-12]. Heavy metals easily pass in the food chain from the soil pollutant to it prefers the environment and living organisms [13]. The weathering process of some natural materials is parental source of heavy metals in the environmental components, which are trace (< 1000 mg/kg) and almost non-toxic. Now a days, the human activities slowly increase into environment affecting the geochemical sequence of heavy metals, most soil and water of rural and urban areas may be contaminated by higher concentration of single or more of the heavy metals is enough to originate dangers to human health as well as other species [14]. Historically, agriculture was the first major human influence on the environmental components.

The macro- and micro-nutrients are required for the growth and completion of the lifecycle of plants. If agricultural soil are lacking in the essential metals for crops growth, can be abounding by adding them into the soil or spraying directly into the crops leaves [15-20]. The fertilizers containing sufficient amount of N, P and K are regularly added to soil during farming for proper growth and development of crops. The fertilizers containing the essential elements for healthy crop growth can also have a trace amount of unwanted heavy metals such as Cd, Pb, *etc.*, which concentration is gradually increased into environmental components due to regular uses of fertilizer. The non-essential metals have no any physiological evidence to crops, these metals are toxic in nature, unintentionally inter into environment by using certain phosphatic fertilizers for farming by human [21].

In past, various pesticides were used heavily in food crops and plants contained significant amounts of metals, the United Kingdom approved only 10% of chemicals that contain Zn, Pb, Hg, Mn or Cu were used as pesticides. The mixture of copper sulphate and copper oxychloride called bordeaux were used as fungicide sprayer which contains majorly copper [22,23]. Arsenic and lead-containing pesticides were used to control pests in fruits [24], additionally, the concentration of Cu and Cr gradually increases due to extensive usage of pesticides [25]. The several biosolids generated from poultry, cattle and pig farming cause to the growth of Hg, Zn, Pb, As, Mo and Cd into the environmental components [26]. In the poultry industry, the health products especially meals of poultry contains mixture of metal ion such as As, Cu and Zn, therefore, the byproducts

of this industry can also enhance the concentration level of metal ion in the soil and other environmental compenents [27].

Impact on humans and plants: The study of diseases caused by soil contamination on human is a complex endeavor that attracts less attention to it, but according to the WHO listing, some soil pollutants *e.g.* Cd, Pb, Hg, Ni, Cu, As, pesticides and other chemicals show a great impact on human health [28-34]. Table-1 provides the possible sources of heavy metals and their effect of plants and humans.

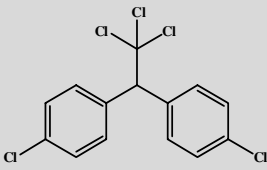
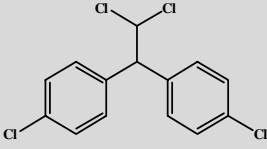
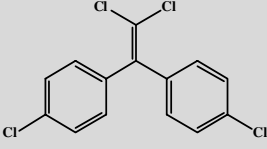
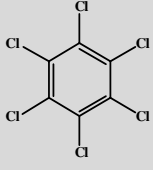
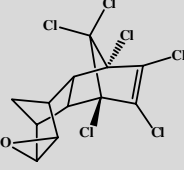
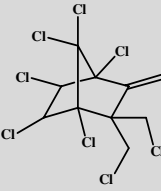
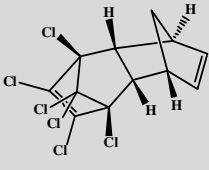
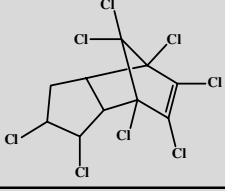
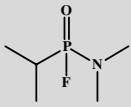
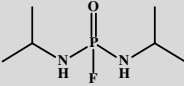
Pesticides are designed in that way to kill only the pests but their mechanism of action is still non-specific to one plant species. A report from WHO revealed that each year more than one lacs human beings are suffered from severe diseases caused by interaction with pesticides with a noticeable death rate [51]. When human being get exposer with amount of pesticides presnt in food materials can cause tumor, sugar, respiratory illnesses, neurological ailments, asthma, allergies, reproductive syndromes, hormone disturbance, oxidative stress and hypersensitivity [52,53]. Table-2 represent a comparise form of different classes of pesticides, structures and effect on humans and pests.

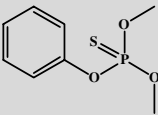
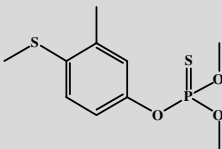
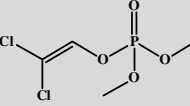
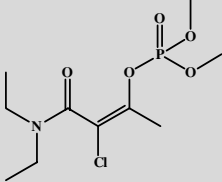
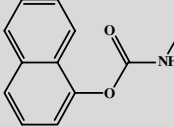
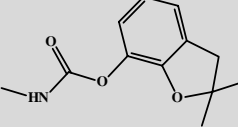
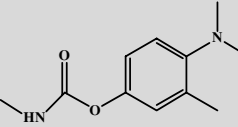
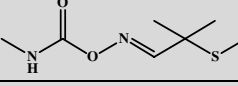
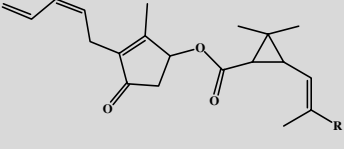
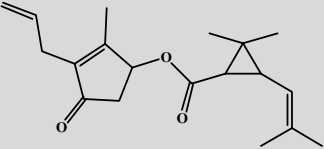
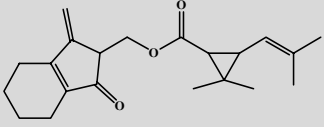
Detection and remediation of heavy metals and pesticides: Worldwide, about 8-9% of total disease is attributed by the minor molecules to pathogenic concentration of environmental contaminants. So, for the better environment and health the estimation of toxins is necessary [74,75]. For past few years, several techniques and equipment are being used for the detection of heavy metals and pesticides such as spectrophotometry [76,77], polarography [78], chromatography [79,80], FTIR-

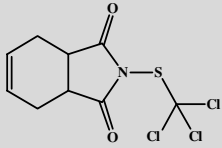
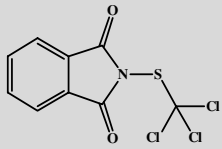
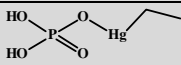

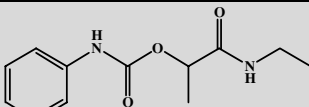
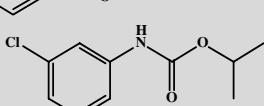
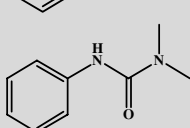
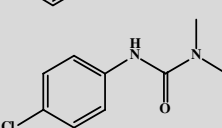
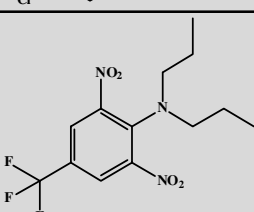
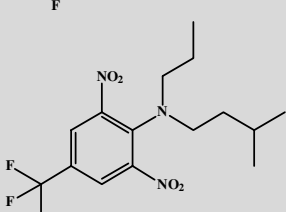
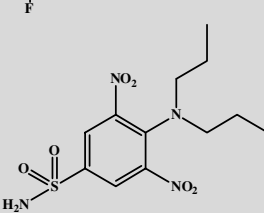
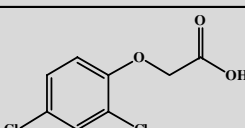
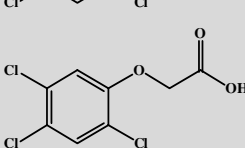
TABLE-1
SUMMARY OF POSSIBLE SOURCES OF HEAVY METALS AND THEIR EFFECT ON PLANTS AND HUMANS

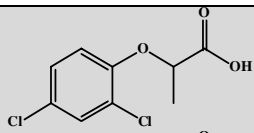
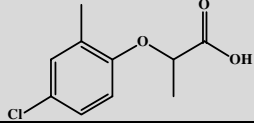
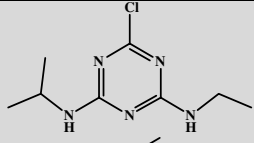
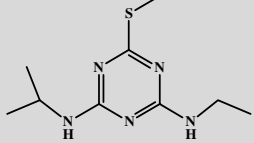
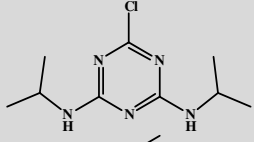
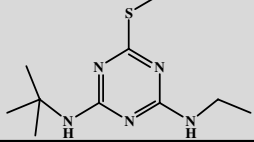
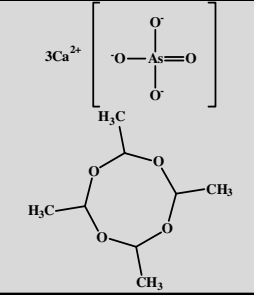
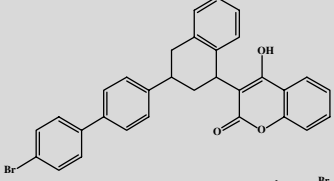
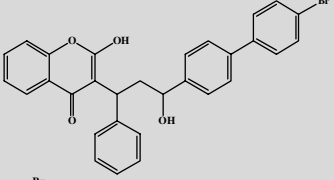
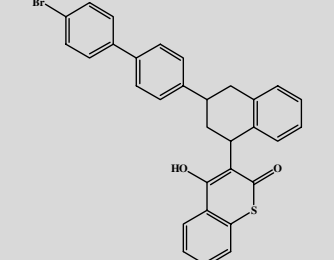
Heavy metals	Possible sources	Toxic effects on plants	Toxic effects on human health	Ref.
Cd	Electrodes, plastics, ceramics, glasses, polymers, steel, fertilizers, mining, smelting and refining	Increase oxidative stress, slowing photosynthesis and metabolism, affect root growth and seed germination, affect plant germination	Toxic effects on human health such as liver, kidney and bone density, cancer, cardiovascular disease and diabetic nephropathy.	[35-37]
Pb	Mining, smelting, gasoline, municipal sewage, paints	Affect overall growth and development, chlorosis, affects root growth, affect cell permeability, inhibited enzymatic activity and reduce mineral nutrition.	Central nervous sytem damage, hyperactivity, infertility, anorexia, high blood pressure, rensal damage, alzheimer disease	[38-40]
Hg	Coal, soda and wood industry, volcano outbreaks	Inhibiting electron transport causing damage of mitochondria, inhance oxidative stress, effect the cell permeability	Deafness, blindness, dizziness, dementia, infertility, gastric, kidney problem, memory loss, sclerosis, dysphasia	[41,42]
As	Minig, wood, battery, coal, petroleum, refineries industire, volcanoes	-	Brain damage, cardiovascular and respiratory disorders, conjunctivitis, dermatitis, skin cancer	[43,44]
Cu	Mining, electroplating biosolids, refining and smelting	Affect the cell membrane, cause oxidative stress, seed germination, affects root growth, DNA damage	Anemia, abdominal pain, diarrhea, liver damage, kidney damage, headache, nausea, metabolic disorders, vomiting	[45,46]
Ni	Forest fire, weathering, landfill, volcanic eruptions, steel, automobile, alloy, batteries, surgical instrument industries	Reduce plant growth, reduce photosynthetic activity, oxidative stress, affects on enzymatic and metabolic activity	Heart disease, dizziness, lung pain, skin disease, cancer, respiratory effects, headache, nausea, kidney damage	[47,48]
Cr	Electroplating industry, sludge, solid waste, tanneries	Affects on metabolic and enzymatic function, affects photosynthesis, affects physiological process, damage chloroplast, inhibit electron transport	Lungs related disease, diarrhea, headache, skin disease, emphysema, headache, itching, renal damage, liver damage, lung cancer, nausea and vomiting.	[49,50]

TABLE-2
SUMMARY OF DIFFERENT CLASS OF PESTICIDES, THEIR STRUCTURES, EFFECT ON HUMAN AND PEST

Class of pesticide	Chemical class of pesticide	Name of pesticide	Structure of pesticide	Effect on human	Effect on pest	Ref.
Insecticide	Organo-chlorines	Dichlorodi-phenyltrichloro-ethane (DDT)		Vomiting, tremors or shakiness, seizures and highly carcinogenic	Damaging nerve cells of insects	[54-56]
Insecticide	Organo-chlorines	Dichlorodi-phenyldichloro-ethane (DDD)		Cancer of the adrenal gland		
Insecticide	Organo-chlorines	Dichlorodi-phenyldichloro-ethylene (DDE)		Negative effect on serum and adipose tissue		
Insecticide	Organo-chlorine	Benzene hexachloride (BHC)		Seizures, ataxia, confusion and other central nervous system dysfunction.		
Insecticide	Organo-chlorines	Endrin		Convulsions, jerking of legs and arms, twitching facial muscles, sudden collapse, or even death		
Insecticide	Organo-chlorines	Toxaphene		Affect the central nervous system, liver and kidneys		
Insecticide	Organo-chlorines	Isodrin		Affect the nervous system, liver, kidneys and skin		
Insecticide	Organo-chlorines	Chlordane		Gastrointestinal distress and neurological symptoms, such as tremors and convulsions		
Insecticide	Organo-phosphates	Dimefox		Highly toxic Possible brain and central nervous system toxicant	Affect the central nervous system of insects causing them to death	[54,57-59]
Insecticide	Organo-phosphates	Mipafox		Neurotoxicity and paralysis		

Insecticide	Organo-phosphates	Methyl parathion		Aintness, blurry vision, chest pain, diaphoresis, vomiting and nausea, diarrhea, muscle pain, convulsions, comma and death	
Insecticide	Organo-phosphates	Fenthion		Nausea, headache, vomiting, faintness, muscular faintness, sleepiness, weariness, anxiety	
Insecticide	Organo-phosphates	Dichlorovas		Diarrhea, blurred vision	
Insecticide	Organo-phosphates	Phosphamidon		Toxic effect on lungs, neurons, myocardial <i>etc.</i>	
Insecticide	Carbamates	Carbaryl		Blurred vision respirator disorder	Damage the central nerous system of insects as Organo-phosphates [60,61]
Insecticide	Carbamates	Carbofuran		Hypertens ion vision defect, respiratory disorder	
Insecticide	Carbamates	Aminocarb		Affect the nervous system and lungs	
Insecticide	Carbamates	Aldicarb		Nausea, sweating, vomiting, headache	
Insecticide	Pyrethroids	Pyrethrin		The ringing of the ears, nausea, tingling of fingers and breathing problems and other nervous system problems	This pecticide break down easily with light and affect the growth of lice and other household pests [62,63]
Insecticide	Pyrethroids	Allethrin		Abdominal pain, dizziness, fatigue, palpitation, tightness in the chest and blurring of vision.	
Insecticide	Pyrethroids	Tetramethrin		Muscular pain, dizziness, nausea, fatigue, excessive salivation, muscle faintness, vomiting	

Fungicide	Phthalimides	Captan		Respiratory ailment	-	[64]
Fungicide	Phthalimides	Folpet		Upper and lower respiratory irritation		
Fungicide	Miscellaneous	Ethylmercuric phosphate		Neurological and psychiatric.	-	[65]
Fungicide	Miscellaneous	Methylmercury chloride		Affect the nervous system, dysarthria, ataxia, paraesthesia's		
Herbicide	Carbanilates	Carbetamide		Hypoglycaemia, anorexia	-	[66,67]
Herbicide	Carbanilates	Chlorpropham		Kidney and liver failure		
Herbicide	Carbanilates	Fenuron		Reproductive and development effects		
Herbicide	Carbanilates	Monuron		Moderately toxic to humans and a suspected carcinogen		
Herbicide	Toluidines	Trifluralin		Acute oral toxicity and dermal irritation, skin illnesses, lung problems and eye irritation	Increases the virulence of rust that attacks flax plants	[68]
Herbicide	Toluidines	Benfenin (benfuralin)		Skin, eye and respiratory irritations		
Herbicide	Toluidines	Oryzalin		Carcinogen, skin sensitization		
Herbicide	Phenoxy alkonates	2,4-Dichlorophenoxyacetic acid		Tachypnea, tachycardia, vomiting, leukocytosis, liver and kidney	-	[69]
Herbicide	Phenoxy alkonates	2,4,5-Trichlorophenoxyacetic acid		Nausea, renal injury, dizziness, headache, body pain, mytonia, hypotension hepatic injur		

Herbicide	Phenoxy alkonates	Dichloroprop		Reproductive disorder		
Herbicide	Phenoxy alkonates	Mecoprop		Low blood pressure, rooling		
Herbicide	Triazines	Atrazine		Kidney failure, congestive heart failure	-	[70,71]
Herbicide	Triazines	Ametryn		Liver damage and heart failure		
Herbicide	Triazines	Propazine		Reproductive toxicity, potential endocrine effects, mutagenicity, anemia		
Herbicide	Triazines	Terbutryn		Fate in humans and animals, carcinogenic effects		
Molluscicides	Miscellaneous	Calcium arsenate	$3\text{Ca}^{2+} \left[\begin{array}{c} \text{O}^- \\ \\ \text{O}-\text{As}=\text{O} \\ \\ \text{O}^- \end{array} \right]$	Skin dmage	-	[72]
Molluscicides	Miscellaneous	Metaldehyde		Neurotoxin and exposure result in vomiting, tremors, seizures and death.		
Rodenticide	Miscellaneous	Zinc phosphide	$\text{Zn}=\text{P}=\text{Zn}=\text{P}=\text{Zn}$	Liver and kidney failure, convulsion, delirium and coma may also occur.	Used as sðrav to control pests	[73]
Rodenticide	Miscellaneous	Brodifaco		Unexplained bleeding		
Rodenticide	Miscellaneous	Bromadiolone		Nose bleeds, bleeding gums, bloody urine, black tarry stools.		
Rodenticide	Miscellaneous	Difethialone		Ecchymoses, petechiae, frank-hemorrhage, pale mucous membranes, weakness, coughing.		

spectroscopy [81], gas chromatography-mass spectroscopy (GC-MS) [82-84], X-ray photoelectron spectroscopy (XPS) [83], inductively coupled plasma mass spectrometry (ICP-MS), HPLC, LC-MS [84,85], immunoassays [86], biorecognition elements [87], electrochemical detection [88], omics technologies [89], capillary electrophoresis [90], surface-enhanced Raman spectroscopy (SERS) [91] have been used for this drive. The advantages of these analytical instrument is its sensitivity, reproducibility and reliability, but also have several drawbacks like costly, time taking, difficult sample preparation and on site detection. Therefore, these drawbacks get attention towards the development of rapid and simple analytical approachses for analysis of trace level of pesticides in the environment and food [92].

Removal of soil pollutants like xenobiotic compounds, pesticides and metal ions is a worldwide problem because pollutants have a adverse effect on the living organisms, plants, ecosystems, agriculture, *etc.* [93]. So, the remediation and detection of pollutant is very essential [94]. In the contemporary era, there has been significant progress in the field of environmental restoration. There are five strategies, which are applicable for the removal of toxins from the environmental samples, *e.g.* (i) by separation, extraction and desorption methods; (ii) by phase separation, hydrocyclones, froth flotation and jig techniques; (iii) by thermal/chemical destruction; (iv) by biodegradation techniques; and (v) by biological mobilization or absorption [95].

Some of the remediation techniques are also used for the clean-up of soil such as isolation and containment, pyrometallurgical separation, chemical treatment, biochemical process, biosurfactant technology, mechanical separation, permeable treatment wall, electrokinetic remediation, phytoremediation, *in situ* remediations, soil washing, phytoextraction, leaching [96-100].

Nanoparticles as sensing probe: Nanoparticles are the particle with size ranges between 1-100 nm having with different shapes depending upon several factors including synthesis methods [101,102]. Several sensing approachses were developed based on different nanomaterials like silver, gold, carbon, graphene, *etc.* [103]. Recently, the chemical free synthesis of nanoparticles is preferred due to its cheap, safe and ecofriendly nature [104]. The issue of heavy metals and pesticides has emerged as a significant and crucial concern for researchers to address, moreover, this problem has substantial implications for social development. Recently, researchers and scientist focusing on some methodologies to monitor the environmental toxins [105]. But, the methods developed were expensive and very complex for analysis of environmental pollutant, hence nanoscience based methodology is now employed instead of these expensive techniques [106,107]. Nanosensors have several advantageous properties as compared to other traditional sensors with high precesion, accuracy, sensitivity, selectivity, stability, *etc.* [108].

Colorimetric sensor: This sensor is one of the most used sensing method for analysis of environmental samples such as water, soil, vegetables, *etc.* [109-113]. The basic mechanism of this method is the colour alteration after introduction of

analyte to the prepared nanoparicles as a sensing probe. The surface plasma coupling of nanoparticles and refractive index of media can affect the colour changes and aggregation process of nanoparticles. The aggregation of nanoparticles after the addition of anlyte is a basic step and aggregation cause colour changes in colorimetric based sensing probes [114]. The nanoparities based sensor is growing method for the analysis of environmental samples due to its several advantages like high accuracy, sensitivity, selectivity, precise and stable [115,116]. In recent times, the monitoring of environmental contaminants has been accomplished through the utilization of portable, cost-effective paper-based sensing approachses [117]. Maximum paper bridge device exploited the noble metallic nanoparticle that cost colouration have exchange with the contact of the pollutant on the paper sensor. The colour changed paper based sensor is further analyzed by different software such as ImageJ, which read the colour intensity developed on the paper sensor [118].

Colorimetric detection of pesticides: In the field of agricultural productivity, a wide array of agrochemicals, which often encompass substances such as pesticides and fertilizers, are frequently employed. Some part of these pesticide increases the pollution of the environment by leaching into the soil and water. Furthermore, when such chemicals get contact with humans by direct or indirect than it will affect the skin, lungs and other part of body. Hence, it is important to introduce an analytical method for sensitive and selective monitoring of pesticides [119]. Several colorimetric sensors have been reported for the identification of agrochemicals, wherein nanoparticles, enzymes, aptamers and other entities are employed in conjunction with heavy metals [120-125]. Kaur *et al.* [126] proposed a azo-coupling reaction mechanism for low limit detection (15 ppm) of carbryl pesticide. Alex *et al.* [127] developed 3D microfluidic paper-based analytical devices was fast for the estimation of paraoxon-ethyl pesticide by using cellulosic paper, since their surface contains negatively charged carboxyl group, which develops the robust electrostatic interaction with acetylcholine esterase (AChE). Hence, the value of the limit of detection is reduced in 3D microfluidic paper-based analytical devices.

Silver nanoparticles stabilized by tyrosine was synthesized by Weerathunge *et al.* [128], which have strong peroxidase-mimicing activity and this property is applied for the analysis of chlorpyrifos pesticides. Graphene quantum dots with gold nanoparticles (GQDs-AuNPs) as 3D paper was designed by several researchers [129-132] for monitoring the chlorpyrifos organophosphate pesticide with low limit of detection. This study revealed that the morphology of developed nanomaterials for colorimetric estimation can alter the limit of detection. The synthesized GQDs-AuNPs was uniform size and shape wound 12 nm was suitable for trace level detection of pesticide. So, these results are in good agreement with a previous report additionally some other reports as summeried in Table-3.

Colorimetric detection of heavy metals: Currently, metal ions such as Hg²⁺, Ni²⁺, Co²⁺, Cd²⁺, Cu²⁺, Pb²⁺, Al³⁺, Fe³⁺, As³⁺, and Cr³⁺ have become persistent pollutants in water, soil and many environmental constituents on the global scale [152-156].

TABLE-3
LINEAR RANGE AND LOD OF COLORIMETRIC DETECTION OF SOME PESTICIDES

Nanomaterial	Pesticides	Linear range (mol/L)	LOD (mol/L)	Ref.
IL@CoFe ₂ O ₄ NPs@MWCNTs	Fenitrothion	$2 \times 10^{-8} - 1.6 \times 10^{-4}$	1.35×10^{-8}	[133]
AuNPs/FcDr/rGO/GCE	Dichlorvos	$4.3 \times 10^{-7} - 2.1 \times 10^{-4}$	2.1×10^{-7}	[134]
NiO NPs	Carbofuran	$5 \times 10^{-6} - 3.05 \times 10^{-4}$	5×10^{-7}	[135]
GSH-Lac-AgNPs	Thiram	$1 \times 10^{-8} - 3 \times 10^{-6}$	3.0×10^{-9}	[136]
AgNPs-PHMB, AgNPs-PVP and AgNPs-BH ₄ ⁻	Thiram	$1 \times 10^{-7} - 1 \times 10^{-4}$	3.6×10^{-8}	[137]
AuNPs	Prothioconazole	3.8×10^{-9} to 5.8×10^{-8}	0.0011	[138]
Cu@AgNPs	Phenthoate	1.56×10^{-7} to 4.68×10^{-6}	4.68×10^{-8}	[139]
AgNP-BNCPs	4-Amino thiophenol and methomyl	1×10^{-7} to 1×10^{-3}	3.6×10^{-7}	[140]
CQDs-AgNPs	Carbaryl	9.9×10^{-10} to 9.9×10^{-8}	0.0 to 7.45×10^{-8}	[141]
AuNPs	Triazophos,	3.19×10^{-11} to 6.3×10^{-8}	2.23×10^{-11}	[142]
	parathion and chlorpyrifos	1.7×10^{-10} to 1.71×10^{-7}	3.08×10^{-11}	
AuNPs	Parathion-methyl, triazophos and phosmet	1.4×10^{-9} to 2.85×10^{-6} 3×10^{-9} and 1×10^{-8}	2.4×10^{-10} 0.026 ng cm ⁻² , 0.031 ng cm ⁻² and 0.032 ng cm ⁻²	[143]
AuNPs	Carbendazim	2.2×10^{-9} to 5.0×10^{-7}	2.2×10^{-9}	[144]
AuNP-SPCE	Imidacloprid	5.0×10^{-11} to 1×10^{-8}	2.2×10^{-11}	[145]
Citrate-Au NPs	Acephate, phenthoate, profenofos, acetamiprid, chlorothalonil, cartap	$1 \times 10^{-5} - 9 \times 10^{-5}$ $1 \times 10^{-8} - 1.5 \times 10^{-6}$ $1 \times 10^{-6} - 2 \times 10^{-4}$ $1 \times 10^{-9} - 1.5 \times 10^{-7}$ $1 \times 10^{-6} - 1 \times 10^{-3}$ $5 \times 10^{-8} - 1.5 \times 10^{-6}$	3.46×10^{-7} 3.0×10^{-9} 6.0×10^{-7} 6.24×10^{-10} 3.75×10^{-7} 1.7×10^{-8}	[146]
Imida-AgNPs	Paraquat	$2 \times 10^{-5} - 1.8 \times 10^{-4}$	6.27×10^{-6}	[147]
NFC/Au@AgNP	Thiram and paraquat	4.1×10^{-8}	2.9×10^{-7} and 1.7×10^{-7}	[148]
PSi-Pd NPs	Imidacloprid	-	1×10^{-9}	[149]
Ag@Au NPs	Profenofos, acetamiprid, carbendazim	-	5.6×10^{-12} 2.06×10^{-11} 3.19×10^{-11}	[150]
AuNPs	Dichlorvos, trichlorfon and paraoxon	-	1.4×10^{-5} 3.7×10^{-5} 2.6×10^{-5}	[151]

The identification and remediation of the heavy metals ion contamination are of significant importance. In recent times, considerable efforts have been focused to develop an on-site detection sensor for monitoring such contaminations [157]. These sensor have tremendous better analytical properties such as precise, accurate, low cost, rapid, on site, portable, *etc.* [158].

Recently, nanoscience and nanotechnology have developed, which has led to the emergence of new applications for nanomaterials. Technologies for ultrasensitive detection and imaging have also developed in the analytical sciences. Gold and silver based nanoparticles with colorimetric sensors are currently gaining increasing attention. As these nanoparticles have strong absorption of LSPR band associated to interparticle distance, colorimetric sensing methods provide the advantages of rapid, sensitive, cheap and smooth operatable [159,160].

A smartphone integrated portable colorimetric assay was developed by Motalebizadeh *et al.* [161] for the detection of As²⁺ using polydimethylsiloxane microfluidic kit. Moreover, an extract of mango-flower can be used as colorimetric sensor for monitoring of arsenic ions [162]. These two colorimetric

sensors have higher LOD 2.98×10^{-6} mol/L, 2.66×10^{-6} mol/L, respectively. In another method, Boruah *et al.* [163] developed glucose-functionalized gold nanoparticles as colorimetric approach towards detection of As³⁺ using with LOD 7.07×10^{-9} mol/L. The main region for good LOD is a strong chemical bond between hydroxyl(-OH) and arsenic ion (As³⁺).

For cadmium ions, a smartphone integrated colorimetric fluorescent paper strip was also developed by Wang *et al.* [164] for the quantitative estimation of Cd having a limit of detection of 3.33×10^{-8} mol/L. Sung & Wu [165] reported the colorimetric estimation of Cd(II) ions in lake water sample by using functionalized gold nanoparticles with a lower limit of detection.

Saenchoopa *et al.* [166] synthesized silver nanoparticles stabilized by γ -aminobutyric acid for the calorimetric detection of Hg²⁺ in the water sample having limit of detection is 2.37×10^{-6} mol/L and this value is higher compared to reported other nanomaterials. Graphene oxide/gold nanoparticles (GO/AuNPs) was synthesized by Tan *et al.* [167] for the detection of Hg²⁺ *via* with a lower limit of detection 3.8×10^{-10} mol/L. The Hg²⁺ have a property to sturdily binds with amino group of oligonucleotide to form T-Hg-T complex and the reaction solution

from GO/AuNPs-T-Hg-T complex still shows sturdy absorption at 655 nm [167]. So far, the colorimetric sensor has been used for the detection of heavy metals contamination, additionally the analytical parameters of these sensors are summarized in Table-4.

Electrochemical analysis: Electrochemical sensor belongs to the largest family of sensor, this consist with a transducer element known as electrode. An electrode is non-affected by internal solution due to protected by a selective membrane, which act as separating membrane between electrode and ionic solution [185-187]. Electrochemical sensors have a broad area from clinical treatments to food technology, it is a magnificent technique for real time and accurate measurement of different analytes [188]. The basic mechanism behind electrochemical sensing of any analyte is based on interaction between the electrode and the analyte, which generate an electric signals, this signals will further measure as qualitative as well as quantitative electric signals [189]. Several applications have been already reported for the electrochemical sensing probes like monitoring of the environmental pollutants, pharmaceutical, clinical diagnosis, *etc.* [190-193]. This technique have several analytical properties like rapid, reliable, effective sensing probe for monitoring the environmental pollutants [194]. The electro-analytical application is more powerful with modified electrode by nanoparticles, the properties like its sensitivity, high surface to volume ratio, rapidity, stability were increased [195].

Electrochemical detection of pesticides: The agricultural industry extensively employs various types of pesticides in order to maximize profits and achieve desired outcomes. Consequently, trace amounts of pesticides can be detected in the environmental components. So, the monitoring of pesticides by some developed nanosensor is important to reduce their toxicity for all living organisms [196,197]. Mogha *et al.* [198]

reported AChE biosensor which was based on the reduction of graphene by ZrO^{2-} used for the estimation of chlorpyrifos with a high limit of detection $1 \times 10^{-7} \mu M$. Different types of nanomaterials such as Au@MWCNTs/GCE, CuO NWs-SWCNTs hybrid nanocomposite, nano-MIP-CP electrode for the detection of dichlorvos, malathion, diazion are successfully accomplished [199]. Kamyabi *et al.* [200] developed an ultra-sensitive electrochemiluminescence platform that is based on ZnONPs/Ni-foam in the occurrence of $K_2S_2O_8$ as the robust co-reactant for detection of chlorpyrifos with a lower limit of detection *i.e.* of $9.5 \times 10^{-16} \mu M$. Several other colorimetric sensors have been used for the detection of other kind of pesticides with their analytical parameters are summarized in Table-5.

Electrochemical detection of heavy metals: The electrochemical method is one of most affective, rapid, portable, selective, cost -affective technique for simultaneous measurement of metal ion from the environmental samples [221-224]. Recently, new techniques such as screen printed electrodes, which are flexible, portable and disposable in nature are widely used as electrochemical detection of heavy metal ions [225]. Several Nowadays, the researchers and scientist developed a range of nanomaterials effectively been fabricated on papers by direct deposition or through screen printing [226]. For example, the magnetic nanoparticles like Fe_3O_4 fabricated by AuNPs was also helpful for monitoring of these heavy metal ions [227]. Similarly, glutathione coated magnetic nanoparticles ($GSH@Fe_3O_4$) for the electroanalytical measurement of heavy metals ions such as Pb^{2+} and Cd^{2+} ions with good lower detection limits $0.182 \mu g L^{-1}$ and $0.172 \mu g L^{-1}$, respectively has been reported [228]. Recently, $Fe_3O_4@Au$ -cystamine-thymine acetic acid based on the screen-printed electrode for the detection of arsenic (As^{3+}) and mercury (Hg^{2+}) ions are too reported [229].

TABLE-4
LINEAR RANGE AND LOD OF COLORIMETRIC DETECTION OF SOME HEAVY METALS

Nanomaterial	Heavy metal	Linear range (mol/L)	LOD (mol/L)	Ref.
GSH-AuNPs	Cd^{2+}	Maximum contamination level of 4.45×10^{-8}	1.88×10^{-8}	[168]
GNSs	Pb^{2+}	$0 - 1 \times 10^{-3}$	1.5×10^{-12}	[169]
AuNPs/Glu	As^{3+}	$2.6 \times 10^{-7} - 6.67 \times 10^{-6}$	7.4×10^{-8}	[170]
AuNPs/Glu	Pb^{2+}	$9.6 \times 10^{-8} - 4.82 \times 10^{-6}$	3.7×10^{-8}	[170]
(Ag@rGO)	Cr^{4+}	$1 \times 10^{-7} - 2.52 \times 10^{-5}$	3.1×10^{-8}	[171]
AgNPs LSPR	Pb^{2+}	$2.4 \times 10^{-9} - 4.8 \times 10^{-8}$	$0.64 \pm 0.04 \mu g/L$	[172]
TiO_2 NPs	Cu^{2+}	1×10^{-8} to 1.25×10^{-5}	2.51×10^{-9}	[173]
NDTM-AuNPs	Pb^{2+}	$0 - 3.0 \times 10^{-8}$	3.5×10^{-7}	[174]
AuNPs	Cd^{2+}	$2.0 \times 10^{-7} - 1.70 \times 10^{-6}$	1.0×10^{-7}	[175]
Au-NPs-PVA-Cy	Cu^{2+}	9.74×10^{-8} to 3.27×10^{-6}	2.1×10^{-8}	[176]
Au@Ag NPs	Hg^{2+}	-	1.0×10^{-10}	[177]
AuNPs	Co^{2+}	0.05 to 1.6×10^{-5}	4.0×10^{-10}	[178]
AuNPs@MB	As^{3+}	1.3×10^{-8} to 4×10^{-7} and 4×10^{-7} to 1.3×10^{-6}	2.40×10^{-9}	[179]
AuNPs-(EK)3	Ni^{2+}	$5 \times 10^{-6} - 5.0 \times 10^{-5}$	4.8×10^{-6}	[180]
ChI-AgNPs	Hg^{2+}	1×10^{-7} to 2×10^{-4}	2.7×10^{-6}	[181]
AgCu-BNPs	Hg^{2+}	$1 \times 10^{-9} - 1 \times 10^{-4}$	9.0×10^{-9}	[182]
Molybdenum oxide nanomaterial-based three-input logic gate	Sn^{2+}	$1 \times 10^{-6} - 1.4 \times 10^{-4}$	2.75×10^{-8}	[183]
AgNPs	As^{3+}	1.3×10^{-8}	1.33×10^{-8}	[184]

TABLE-5
LINEAR RANGE AND LOD VALUES FOR THE DETECTION OF SOME PESTICIDES

Nanomaterial	Pesticides	Linear range (mol/L)	LOD (mol/L)	Ref.
AuNP-SPCE	Imidacloprid	$5 \times 10^{-11} - 1 \times 10^{-8}$	2.2×10^{-11}	[201]
screen-printed carbon electrodes(SPCE)	Imidacloprid	$5 \times 10^{-11} - 1 \times 10^{-8}$	2.4×10^{-1}	[202]
h-CNT- μ Ps/Nafion/GCEs	Parathion	$3 \times 10^{-7} - 2 \times 10^{-5}$	9.2×10^{-8}	[203]
Carbon electrode modified with platinum doped silica	Chlorpyrifos-methyl	$1.2 \times 10^{-9} - 6.2 \times 10^{-8}$	7.0×10^{-11}	[204]
Nd-UiO-66@MWCNT	Paraoxon	$7 \times 10^{-10} - 1 \times 10^{-7}$, $1 \times 10^{-9} - 1.2 \times 10^{-7}$	4.0×10^{-11}	[205]
SWCNT-ZnPc hybrid material	Methyl parathion, deltamethrin, chlorpyrifos and Spinosad	$2.45 \times 10^{-9} - 4.0 \times 10^{-8}$	1.49×10^{-9}	[206]
ELP-OPH/BSA/TiO ₂ NFs/c-MWCNTs	Parathion	Up to 3.64×10^{-5}	1.0×10^{-8}	[207]
ZnO NPs/SPCE	Chlortoluron	$1 \times 10^{-9} - 1 \times 10^{-7}$	4.7×10^{-10}	[208]
Au-SPEs	Paraoxon	Up to 1.4×10^{-4}	7.26×10^{-6}	[209]
PCz/CRGO	Imidacloprid	$3 \times 10^{-5} - 2 \times 10^{-4}$	4.4×10^{-7}	[210]
MIP/GN modified glassy carbon electrode	Imidacloprid	$5 \times 10^{-7} - 1.5 \times 10^{-5}$	1×10^{-7}	[211]
Nanosilver Nafion [®] /nanoTiO ₂ Nafion [®] modified glassy carbon electrode	Imidacloprid	$1 \times 10^{-6} - 5 \times 10^{-6}$	9.3×10^{-7}	[212]
AG/Au-NPs	Hydrazine	Up to 9.36×10^{-4}	5.7×10^{-10}	[213]
AuNPs/GO-SPCE	Carbofuran	$1 \times 10^{-6} - 2.50 \times 10^{-4}$	2.2×10^{-7}	[214]
Gd ₂ S ₃ /RGO	Carbofuran	$1 \times 10^{-9} - 1.38 \times 10^{-3}$	1.28×10^{-8}	[215]
3DG-Au/GCE	Carbaryl	$4 \times 10^{-9} - 3 \times 10^{-7}$	1.2×10^{-9}	[216]
Au NPs/Mo ₂ C/Mo ₂ N	chlorpyrifos	0 to 1.14×10^{-6}	1.0×10^{-10}	[217]
ZrP/GO	fenitrothion	$8 \times 10^{-9} - 2.6 \times 10^{-5}$	1.0×10^{-9}	[218]
g-C ₃ N ₄ -CTAB/CPE	Amino-triazole and linuron	$3 \times 10^{-7} - 4.5 \times 10^{-5}$	6.4×10^{-8}	[219]
GO@Ce-doped TiO ₂ NPs	Methyl parathion	$2 \times 10^{-9} - 4.83 \times 10^{-5}$	1.6×10^{-9}	[220]

TABLE-6
ANALYTICAL PERFORMANCE OF SOME ELECTROCHEMICAL SENSOR FOR THE DETECTION OF HEAVY METALS

Nanomaterials	Heavy metals	Linear range (mol/L)	LOD (mol/L)	Ref.
Fe ₃ O ₄ @Au NPs/MGCE	Ag ⁺	$1.17 \times 10^{-7} - 1.77 \times 10^{-5}$	59×10^{-9}	[230]
MCPE/Fe ₃ O ₄ /DA/DTPA	Cu ²⁺	$5.0 \times 10^{-9} - 1.0 \times 10^{-4}$	2.1×10^{-9}	[231]
MCPE/Fe ₃ O ₄ /DA/DTPA	Pb ²⁺	$1.0 \times 10^{-9} - 5.0 \times 10^{-8}$ and $5.0 \times 10^{-7} - 1.0 \times 10^{-3}$	8.2×10^{-9}	[231]
MnFe ₂ O ₄ /Au/GCE	As ³⁺	–	44.9×10^{-9}	[232]
Fe ₃ O ₄ @TiO ₂ @NG@Au@ETBD/GCE	Pb ²⁺	$4 \times 10^{-13} - 2 \times 10^{-8}$	7.5×10^{-13}	[233]
Bi/Fe ₂ O ₃ /Gr	Zn ²⁺	$1.5 \times 10^{-8} - 1.5 \times 10^{-6}$	1.68×10^{-9}	[234]
RGO-Fe ₃ O ₄ /SPE	As ³⁺	$2.6 \times 10^{-8} - 4.0 \times 10^{-6}$	1.3×10^{-9}	[235]
Fe ₃ O ₄ @Au	Ag ⁺	$1.0 \times 10^{-8} - 1.5 \times 10^{-7}$	3.4×10^{-9}	[236]
MnFe ₂ O ₄ /GO/GCE	Pb ²⁺	$2.0 \times 10^{-7} - 1.1 \times 10^{-6}$	0.08×10^{-6}	[237]
GSH@Fe ₃ O ₄ /MGCE	Pb ²⁺	$2.4 \times 10^{-9} - 4.82 \times 10^{-7}$	8.78×10^{-10}	[228]
GSH@Fe ₃ O ₄ /MGCE	Cd ²⁺	$4.4 \times 10^{-9} - 8.89 \times 10^{-7}$	1.5×10^{-9}	[228]
Fe ₃ O ₄ @PANI/MGCE	Cd ²⁺	$1 \times 10^{-9} - 9 \times 10^{-4}$	0.3×10^{-9}	[238]
MWCNT-Fe ₃ O ₄ /eggshell-CPE	Cd ²⁺	$2.66 \times 10^{-11} - 2.22 \times 10^{-9}$	2.1×10^{-1}	[239]
Bi ₂ O ₃ /Fe ₂ O ₃ @GO/GPE	Cd ²⁺	$5.5 \times 10^{-11} - 1.03 \times 10^{-8}$	9.56×10^{-13}	[240]
Au/ZIF67	Hg ⁺	$4.9 \times 10^{-9} - 1.24 \times 10^{-7}$	2.49×10^{-10}	[241]
GO-Fe ₃ O ₄ -PAMAM/GCE	Pb ²⁺	$1.9 \times 10^{-9} - 5.79 \times 10^{-7}$	6.2×10^{-10}	[242]
Fe ₃ O ₄ /MWCNTs/LSG/CS/GCE	Cd ²⁺	$8.8 \times 10^{-9} - 1.779 \times 10^{-6}$	6.9×10^{-10}	[243]
Fe ₃ O ₄ /F-MWCNTs/NF/GCE	Cu ²⁺	$5.0 \times 10^{-7} - 3.0 \times 10^{-5}$	0.02×10^{-9}	[244]
Fe ₃ O ₄ /F-MWCNTs/NF/GCE	Hg ²⁺	$5.0 \times 10^{-7} - 2.0 \times 10^{-5}$	0.05×10^{-9}	[244]
Au NPs/Fe ₃ O ₄ /GCE	As ³⁺	$1.33 \times 10^{-10} - 1.33 \times 10^{-8}$	4.90×10^{-12}	[245]

Table-6 shows the analytical performance of some electrochemical sensors for the detection of heavy metals.

Conclusion

The current study aims to report the potential origins of harmful heavy metals and pesticides, as well as their adverse

effects on human health and plant life. The present study reveals that the levels of potentially toxic heavy metals and pesticides in ambient samples exhibit a significant elevation, demanding regular monitoring and assessment. In these circumstances, the different nanomaterials based analytical approaches are developed. This study explores various methodologies for dete-

cting and mitigating the presence of certain heavy metals and pesticides in diverse samples. This work presents a comprehensive overview of the latest advancements in the field of nanomaterial based simple colorimetric and paper-based colorimetric chemical sensors. This overview might prove useful to researchers working on the nanomaterial-based chemical sensors for the detection of a wide range of analytes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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