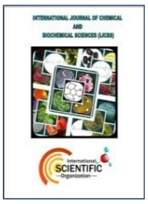
International Journal of Chemical and Biochemical Sciences
(ISSN 2226-9614)

Journal Home page: www.iscientific.org/Journal.html



Plant growth regulators (PGRs): Providing modern solutions to conventional agricultural problems

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Abstract

Rapid increase in global population is a constant threat to the food security all over the world. The only way to cope with the ever increasing demands of food crops and aromatic medicinal plants is to modernize the conventional agricultural practices. The use of cost efficient, effective and environmentally benign plant growth regulators (PGRs) appears to be the most appealing option for the modulation of plant growth. The plant growth regulators (PGRs) work by altering the physiological traits and enhancing the plant's response towards biotic and abiotic stresses. This review article basically discusses the role of plant growth regulators (PGRs) in enhancing the yield of essential oil and major secondary metabolites of aromatic medicinal plants. The data is summarized for some selected plant growth promoters (PGPs) (such as (a) sodium nitropheno-late (b) 28-homobrassinolide (c) 1-nephthylacetamide (d) oxalic acid and (e) hymexazol) and plant growth inhibiters (PGIs) (such as (a) chlormequat chloride (b) maleic hydrazide (c) daminozide (d) ethephon and (e) tetcyclacis). However, some major problems in the use of plant growth regulators (PGRs) include photodegradation, thermal degradation, cytotoxic effects and excessive leaching of applied chemicals that can be overcome by using nanotechnology. In the last section of review article, some advanced spectroscopic techniques (such as Fourier transform infrared spectroscopy (FTIR), Lased induced breakdown spectroscopy (LIBS), Atomic absorption spectrometry (AAS), Scanning electron microscopy (SEM), Thermal gravimetric analysis (TGA) and X-ray diffraction (XRD)) are mentioned to study the complete chemical composition and surface properties of plant growth regulators (PGRs).

Keywords: Plant growth regulators, sodium nitrophenolate, chlormequat chloride, LIBS, TGA

Full length article **Corresponding Author*, e-mail: farwa668@gmail.com

1. Introduction

The conventional agricultural practices face many challenges in fulfilling the rapidly increasing food demands of growing global population. Therefore, significant improvements in old agricultural practices are needed to ensure the high quality nutrition for living beings [1]. The adequate food production and proper cultivation of aromatic medicinal plants can only be made possible by increasing the percentage of arable land area. The use of environmentally benign plant growth regulators (PGRs) is one of the most appealing options in order to modulate the plant growth and development. The plant growth regulators (PGRs) are the chemical substances having specific formulations, capable of modifying the physiological traits and promoting the improved stress responses of plants towards external stimuli. These plant growth regulators (PGRs) can improve the nutritional profile and maximize the production of crops, by overcoming the genetic problems and biotic and abiotic stresses of plants [2]. Some conventionally used plant hormones or plant growth regulators (PGRs) include auxins, cytokinins, paclobutrazol, mepiquat chloride, brassinolide and many structural analogues. The excessive utilization of plant growth regulators (PGRs) in agriculture came to the limelight within past two decades as their benefits were understood by the local growers and poor farmers. Unfortunately, the growth of the PGR market may be constrained by a lack of innovation at a time when an increase in demand for new products will require steady innovation and discovery of novel, cost-competitive, specific, and effective PGRs [3]. Therefore, the present review article discusses the biosynthetic pathways involving the production of essential oils and menthol contents in aromatic medicinal plants with special emphasis on *Mentha arvensis* L. The second major part summarizes the data on some selected plant growth promoters (PGPs) (such as sodium nitrophenolate, 28-homobrassinolide, 1-nephthylacetamide, oxalic acid and hymexazol) and plant growth inhibiters (PGIs) (such as chlormequat chloride, maleic hydrazide, daminozide, ethephon and tetcyclacis). The third part of review article includes the problems associated with the use of plant growth regulators including photodegradation, thermal degradation and cytotoxic effects and leaching potentials. Some of the advanced characterization techniques are also mentioned at the end of review article.

2. Biosynthesis of essential oils in plants

In almost all the aromatic plants of kingdom plantae, secondary metabolites are produced for the purpose of (i) formation of ozone of troposphere (ii) formation of fine aerosol particles (iii) quenching of ozone (iv) thermo-tolerance of plants (v) attracting the insects for the purpose of pollination and dispersion of seeds (vi) plant to plant signaling and (vii) protection against the foreign invaders and pathogens. Essential oils are one of the most important phytochemicals and secondary metabolites of plants, having natural aroma and high volatility under all conditions of temperature and pressure. These volatile organic compounds usually originate from three types of chemical compounds including the (a) isoprenoids (b) fatty acid derivatives and (c) phenolic compounds. Essential oils are highly complex in their chemical composition due to the presence of diverse class of compounds like phenylpropanoids, sesquiterpenoids, and monoterpenoids. In all aromatic plants, essential oils are synthesized by two natural and highly complex biochemical pathways, involving the chains of enzymatic reactions. For the biosynthesis of essential oils in plants, isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP) are the two major and universal precursors. These compounds are produced by two possible pathways (i) plastidic and enzymatic 1-deoxy-D-xylolose-5-phosphate (DXP) pathway, commonly termed as the 2-C-methylerythritol-4-phosphate (MEP) pathway and (ii) the cytosolic enzymatic mevalonic acid (MVA) pathway. In different parts of cell, prenyl diphosphate synthases immediately condenses into the dimethylallyl diphosphate (DMAPP) and isopentenyl diphosphate (IPP), for the further conversion into prenyl diphosphates. The prenyl diphosphate is a basic substrate for the synthesis of fernesyl diphosphate (FPP) and geranyl diphosphate (GPP). All the major constituents of the essential oils are final products of terpenoids, and are ultimately formed by the complex group of enzymes also known as terpene synthases (TPS) [4]. The detailed mechanism of the synthesis of essential oils in plants is shown in (Fig.1).

3. Biosynthesis of menthol in *Mentha arvensis* L.

The epidermal tissues of the plants contain two different types of trichomes named as (a) simple trichomes (STs) and (b) glandular secreting trichomes (GSTs). The STs are also known as "non-glandular trichomes" and they are directly associated with the gene expressions, involved in the biosynthesis of glucosinolate, flavonoid and anthocyanin. The glandular secreting trichomes (GSTs) significantly influence the water retention, pollinator attraction, pest resistance and pathogen defence of the plants, depending upon the phytochemical secretions. These GSTs plays an important role in synthesis of natural products in aromatic plants. In case of *Mentha arvensis* L., special "peltate glandular trichomes" are found on the aerial parts of plant, and directly involved in the secretions of essential oils. In this plant, eight radially distributed secretory cells are located on the young stalk and also embedded in the basal cells. These cells produce the essential oils, involving the number of complex biochemical reactions, as per the mechanism shown in (Fig.2) [5].

4. Plant growth regulators (PGRs)

A diverse group of naturally occuring or synthetically produced larger complex organic compounds, having significant influence on the growth parameters and secretions of secondary metabolites, specifically essential oil contents of ornamental and medicinal aromatic plants are termed as plant growth regulators (PGRs) [6]. The plant growth regulators (PGRs) are considered to be highly proficient elicitors for the stimulation of production of secondary metabolites in plants [7]. Sometimes, plant growth regulators (PGRs) are confused with natural plant hormones, but there are certain differences in both these chemicals. The plant growth regulators (PGRs) are specific agrochemicals that are mostly produced synthetically and applied to the plants to enhance the required phytochemicals and secondary metabolites through modification of biochemical pathways, while the natural plant hormones directly influence the different physiological processes of plants [8]. The production of secondary metabolites in plants is believed to be stimulated under stressful environmental conditions, and thus application of plant growth regulators (PGRs) is the most probable option to enhance the essential oil contents, more specifically menthol contents of *Mentha arvensis* L. [9].

4.1. Plant growth promoters (PGPs)

Plant growth promoters (PGPs) are mostly synthesized and transported through the vascular system of plants, but any change in external environment can lead to the modification of cellular response. The living cells of plants try to balance the externally applied plant growth promoters (PGPs), either through up-regulation or down-regulation, depending upon the extent of change in the surrounding environment. Therefore, targeted delivery of the nanostructured plant growth promoters (PGPs) can ensure the expected developmental responses [10], through increased efficiency of plant growth promoters (PGPs) and highly controlled delivery of nutrients with the minimum usage [11]. According to the European Biostimulant Industry Council

(EBIC), "biostimulants" are the chemical substances that stimulate the natural processes of plants to (i) increase the quality of crops (ii) tolerate the abiotic stresses and (iii) enhance the nutrient uptake efficiency [12]. The effects of sodium nitrophenolate, 28-homobrassinolide, 1-nephthylacetamide, oxalic acid and hymexazol on the essential oil contents and growth characteristics of different aromatic and non-aromatic plants are compiled in table 1.

4.2. Plant growth inhibitors (PGIs)

Salt stress, acute water shortage, high temperature, saline conditions, insect attacks and harsh environmental conditions can significantly increase the release of secondary metabolites in plants [13]. Therefore, application of growth retardants or plant growth inhibitors (PGIs) not only reduces shoot elongation, but also improves the chemical composition of essential oils in aromatic medicinal plants. The plant growth inhibitors (PGIs) can be classified into two major groups (i) chemicals inhibiting the biosynthesis of gibberellic acid (GA) and (ii) chemicals releasing the ethylene based compounds. Until now, four different types of plant growth inhibitors (PGIs) have been used including (a) 16,17-Dihydro-GA_5 and all the structurally related compounds that acts like gibberellic acid (GA) using dioxygenases (b) structurally similar compounds of 2-oxoglutaric acid that generally involves in the catalysis of series of biochemical reactions, resulting in formation of gibberellic acid (GA) (c) nitrogen containing heterocyclic compounds that are capable of blocking cytochrome P_{450}-dependent monooxygenases, involved in the oxidation of ent-kaurene into ent-kaurenoic acid and (d) onium compounds that block the ent-kaurene synthase and cyclases copalyl-diphosphate synthase, directly involved in metabolism of gibberellic acid (GA) [14]. The effects of chlormequat chloride, maleic hydrazide, daminozide, ethephon and tetcyclacis on the essential oil contents and growth characteristics of different aromatic and non-aromatic plants are compiled in table 2.

5. Importance of nanotechnology in agriculture

The use of nanotechnology and nano-scale formulations can significantly alter the global agricultural canvas, by providing effective solutions, for a number of agriculture-related-problems. Nanoparticles act as a bridge in between atomic/molecular structures and their bulk counterparts, and thus are known to have great scientific interest. Over the past few decades, huge amount of work has been carried out on the use of nanotechnology in agriculture, emphasizing its number of applications in this sector [11-15-17]. The use of nano-carriers for the application of plant growth regulators (PGRs) can ensure the slow delivery and sustained release of bioactive components, thereby avoiding their supra-optimal levels. In addition to this, nano-formulations can improve the solubilizing potentials of plant growth regulators (PGRs) by protecting them from photodegradation, thermal degradation, and biodegradation [18-21].

Nanomaterial engineering is considered to be a major cutting-edge-track of the recent scientific researches, supporting the development of advanced agricultural techniques, through providing a larger specific surface area, essentially required for the sustainable development of agricultural system [11-22-23]. Nanotechnology not only decreases the uncertainty, but also helps in the management of agricultural production, as an effective alternative to the conventionally used agricultural technologies. The innovations in agro-nanotechnology offer the short term solutions for a number of agricultural problems, being faced in the modern system of agriculture [11]. Nano-encapsulations have full potential to increase the bioavailability, improve the sustained delivery of applied chemicals and enable the targeted supply of bioactive components, as compared to micro-encapsulations [24-25].

Therefore significant improvements and continuous developments are ultimately required for the production of nanoparticles, having potential applications in the modern environmental and agricultural systems [26]. In case of conventional agricultural practices, the agrochemicals are mostly applied to the crops using broadcasting and foliar sprays. These types of systems enable the small amount of agrochemicals to reach at the actual target, resulting in the supply of doses much lower than the effective concentrations of agrochemicals required for the proper growth and development of plants. Most of the agricultural loses are mainly due to the microbial degradations, hydrolytic reactions, photolysis and leaching of applied agrochemicals [27-28]. In order to ensure the environmental friendly agricultural practices, recent developments are required in the synthesis of nanotechnology based herbicides, pesticides, fungicides, fertilizers, and plant growth regulators (PGRs) [22].

The use of nanoparticles in the modern system of agriculture is highly advantageous due to the effective delivery of agrochemicals at the targeted location, mainly because of the larger surface area, high mass transfer rate and easy attachment of applied chemicals [29]. One of the major difficulties in the use of plant growth regulators (PGRs) is rapid degradation on exposure to the number of environmental factors such as high temperature and intense light, resulting in the loss of natural activity. Another major advantage of the use of nanotechnology in the agriculture is to provide the nanoscale materials, capable of enhancing the bioactivity and stability of bioactive agents, along with the significant reduction in harmful environmental consequences. Therefore, encapsulation of bioactive agents can improve the physiochemical characteristics, and avoid the excessive leaching. Nanotechnology also ensures the maximum bioavailability and minimum wastage of agrochemicals, making it safer for the environment [19].

The controlled release of agrochemicals is a "permeation-regulated-transfer" of bioactive ingredients from the source reservoir to the targeted surface, for maintenance of predetermined concentrations of agrochemicals, for a specific period of time. Some major objectives of the use of nanotechnology in agriculture are (i) high reliability of entire process (ii) improved safety of environment (iii) prolonged efficacy (iv) negligible side effects, and (v) very effective treatments [30-31]. Over the past few decades, much literature has been published regarding the use of plant growth regulators (PGRs) and their nano-encapsulations on different aromatic and non-aromatic plants, but all these methods and processes are quite prolonged or time consuming, inexpensive or cost inefficient, energy consuming, and uses high-tech instruments, making it unfit for the local growers and poor farmers. Therefore, most of these processes are only restricted to the scientific researches and peer reviewed articles, and cannot be commercialized properly. Some nano-structured plant growth regulators (PGRs) and their methods of preparation with complete reaction conditions are mentioned in table 3.

6. Factors affecting the plant growth regulators (PGRs)

6.1. Photodegradation

Photodegradation of plant growth regulators (PGRs) and other agrochemicals is one of the major challenges faced by global agriculture. The amount of solar radiations required for the photolysis of plant growth regulators (PGRs) mainly depends on the ultraviolet absorption profile of plant growth regulators (PGRs), emission spectrum of sunlight, and chemical composition of surrounding media. The minimum amount of energy required to break the chemical bonds of plant growth regulators (PGRs) generally ranges from 70 kcal/mol to 120 kcal/mol, corresponding to the wavelength of sunlight in the range of 250 to 400 nm. Therefore, the solar radiations reaching towards the surface of ground are very important in determining the photodegradation profiles of plant growth regulators (PGRs) and pesticides. The intensity of solar radiations decreases up to 10% by passing through the atmosphere and reaching towards the troposphere. At the wavelength ranging from <290 to >295 nm, most of the solar radiations are absorbed by the layer of ozone, prior to reaching the surface of ground. Therefore, all the solar radiations near the ground surface exhibit the wavelengths ranging from 440 to 460 nm, and its ability to cause the photodegradation in plant growth regulators (PGRs) becomes only 5 to 6% of the total degradation intensity [32].

The absorption of sunlight by any material is known to have number of photo-physical pathways, involving the complex system of interactions. According to Franck–Condon principle, solar radiations passing through the plant growth regulators (PGRs) causes molecular excitations, due to the interactions in between sunlight and electric field of plant growth regulators (PGRs), at the timescale of femtoseconds, without showing any change in the molecular geometry of the agrochemical. As per the Stark–Einstein rule, single photon can excite only one molecule of the agrochemical, with the probability of excitation in the lowest excited state (S_1), which further involves number of photo-physical processes. Usually, it has been observed that the molecules of plant growth regulators (PGRs) exhibit ultraviolet-visible spectrum at wavelength >290 nm, due to the presence of aromatic substituted moieties. In some cases, plant growth regulators (PGRs) are known to contain the unsaturated bonds and lone pairs of electrons of carbamoyl or carbonyl groups, thus showing the $n\rightarrow\pi^*$or $\pi\rightarrow\pi^*$ transitions upon irradiation [33].

According to the recent photo-physical studies, there are only three possible pathways for the excitation of a molecule from lower energy level to higher energy states (Fig.3) (i) non-radiative internal conversion (IC) system (ii) emissions due to fluorescence and (iii) intersystem crossing (ISC) to reach up to the excited triplet state (T_1). In first pathway, all excited molecules are relaxed from the higher vibrational levels to the S_1 state within 10^{12} sec^{-1}, followed by the decay towards the lower electronic energy states within 10^6 to 10^{12} sec^{-1}. In the second pathway, all the excited molecules undergo radiative deactivation through fluorescence, and fluorescence spectra is found similar to the absorption spectrum caused by the Franck–Condon principle, but with the shift towards the red colour. The duration of florescence ranges from few nano-seconds to few micro-seconds, due to the transitions in between similar energy states. In third pathway, spin-forbidden process ($S_1\rightarrow T_1$) is followed with the help of (a) emission of phosphorescence and (b) radiationless deactivation. In $S_1\rightarrow T_1$ process, the duration of phosphorescence generally ranges from few milliseconds to 10^2 sec [34-35].

In the higher energy state, all the excited molecules can cause different types of chemical reactions, unless their total energy contents are lost by the emission of light and release of heat. There are two possible forms of photochemical reactions such as (a) "direct photolysis" and (b) "indirect photolysis". In the case of direct photolysis, photochemical reactions takes place by the absorption of light energy, while in case of indirect photolysis, the chemical reactions of ground state molecules are preceded by the excitation with other excited molecules and photochemical species. The direct photolysis is also termed as "quenching" or "photosensitization" and indirect photolysis is the "photo induced reaction with reactive oxygen species" [32]. Some recent photodegradation studies of plant growth regulators (PGRs) and other agrochemicals are compiled in table 4.

6.2. Thermaldegradation

Thermaldegradation of plant growth regulators (PGRs) and other plant nutrients significantly limit the agricultural output and overall productivity of aromatic plants. Therefore, thermal stability of agrochemicals plays an important role in determining the shelf-life, longterm utilization and efficiency of plant growth regulators (PGRs). Thermal analysis (TA) is used to study the kinetic properties, thermo-physical characteristics, total char contents and decomposition temperature of agricultural chemicals, by measuring the change in mass with respect to change in temperature. The temperature range usually varies from -150 to 1600°C depending upon the nature of sample and the type of information required. For the preparation of novel metal based nano structured plant growth regulators (PGRs), all temperature ranges including the degradation temperature must be known, for heating up to specific level. Many techniques have conventionally been used in thermal analysis (TA) such as (i) pressurized thermogravimetric analysis (PTGA) (ii) dilatometry (DIL) (iii) laser flash analysis (LFA) (iv) evolved gas analysis (EGA) (v) dielectric thermal analysis (DEA) (vi) differential thermal analysis (DTA) (vii) dynamic mechanical analysis (DMA) (viii) thermo mechanical analysis (TMA) (ix) differential scanning calorimetry (DSC) and (x) thermogravimetric analysis (TGA) [36].

All these techniques are based on variations in temperature with respect to change in (a) PTGA–change in mass as a function of pressure (b) DIL–change in volume (c) LFA–change in thermal conductivity and thermal diffusivity (d) EGA–change in chemical composition of final gaseous products (e) DEA–change in loss factor and dielectric permittivity (f) DTA–difference in temperature (g) DMA–change in damping and mechanical stiffness of analyte of interest (h) TMA–change in dimensions and deformations (i) DSC–difference of heat and (j) TGA–change in mass. Among all these methods, TGA is the most sensitive and highly recommended method for the agricultural chemicals, to study the change in structure and composition of final product. It involves the heating of plant growth regulators (PGRs) till its degradation point, with gradual increase in temperature. Similarly, DSC is another important thermodynamic tool for direct estimations of change in heat energy with the regular increase or decrease in temperature. DSC is capable of measuring the heat capacity, specific heat, energy of precipitation, oxidation induction time, crystalline phase, transition temperature, energy of reaction, melting temperature, glass transition temperature, latent heat of melting and heat of fusion [36]. Some recent data on the thermal degradation of plant growth regulators (PGRs) and other agrochemicals is listed in table 5.

6.3. Leaching potential

Nitrogen, phosphorous and potassium are the critical elements essentially required for the increased forage production, improved fertility, and higher crop yield. However, the build-up of surplus agricultural nutrients for increased forage demands can lead to the leaching of nutrients, thereby causing the economic losses, wastage of nutrients and significant harm to environment. This type of nutrient leaching can cause the soil degradation, water contamination, air pollution, and eutrophication involving the loss of nutrients through the surface water. The air pollution is caused by the emissions of greenhouse gases, more specifically ammonia and carbon dioxide. Some additional environmental problems include all the concerns regarding the sustainability of diminishing phosphorous resources from soil [37-38].

Similarly, plant growth regulators (PGRs) plays an important role in development of effective responses in plant as a result of abiotic stresses [39]. The plant growth regulators (PGRs), pesticides, herbicides, fungicides and various other agrochemicals are found to persist in the environment for relatively long period of time, with the capacity of bioaccumulation through food web. These agrochemicals, specifically organochlorine pesticides can directly affect the human health and surrounding environment. The extent of persistence of agrochemicals and their harmful consequences mainly depends on the (i) toxicity of compound (ii) type of formulation (iii) amount of chemical applied (iv) their mode of application and (v) mobility/incorporation in environment. Some agrochemicals also acts as an "endocrine disruptors" that alter the functions of endocrine system [40].

Leaching, degradation and adsorption are some of the key processes, having significant influences on the fate of agrochemicals in soil. Some important processes like (i) plant uptake (ii) assimilation by microorganisms (iii) water runoff (iv) soil erosion (v) volatilization (vi) diffusion and (g) leaching are mainly responsible for the movements of agrochemicals in environment. Leaching can be defined as downward displacement of agrochemicals in soil by passing through the unsaturated zone and finally reaching towards groundwater, thereby causing contamination in the natural water resources. Irrigation water and excessive rain is mainly responsible for leaching and its rate is highest for the persistent compounds, being used in the area of high precipitation and low temperature. The extent of leaching depends on the nature of agrochemical, type of soil, rate of volatilization, crop-root uptake, method of application and type of organisms inhibiting the soil [38]. Leaching of some important agrochemicals is compiled in table 6.

6.4. Cytotoxic effects

The 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) assay is a colorimetric method for the measurement of metabolic activity of living cells. It is mainly based on the natural ability of "nicotinamide-adenine-dinucleotide-phosphate" (NADPH) dependent oxidoreductase enzymes of the cells to completely reduce the soluble MTT reagent (light yellow) into insoluble formazan crystals (dark purple) (Fig.4). Therefore, MTT assay measures the viability of living cells as it converts the "water soluble tetrazolium compound" into "water insoluble formazan crystals" with the help of mitochondrial dehydrogenases. In this cytotoxic assay, sodium dodecyl sulfate, acidified ethanol and dimethyl sulfoxide are used to dissolve the insoluble formazan crystals and to get the coloured solution [41].

The obtained coloured solution shows maximum absorption at the wavelength ranging from 500 to 600 nm, by using the UV-Vis spectrophotometer. The MTT reagent is taken up by the living cells through endocytosis and immediately reduced into formazan crystals, by using the endosomal, lysosomal and mitochondrial enzymes, inside the cellular compartments. However, living cells can dramatically be damaged by complete metabolism of MTT reagent, as it can activate the "apoptosis-related-factors" including the caspase-3 and caspase-8, resulting in the leakage of cellular components [42]. The cytotoxic effects of various *Mentha* species on different cell lines are compiled in table 7.

7. Advanced characterization techniques

The physical properties and chemical reactivity of nanomaterials is quite different from their bulk counterparts mainly due to high "surface-to-volume ratio" and "peculiar morphological characteristics". Preparation of nanomaterials is still under the developmental stages, and so the analytical methods, used for the complete characterization of nanoparticles (NPs). The size and shape are the two major parameters mostly considered for the improved reactivity of nanoparticles (NPs). Up till now; there are no standard protocols to study the chemical composition and crystal structure of nanoparticles (NPs). Thus, credible and robust methods of measurements for the nanoparticles (NPs) can enhance the commercial scale utilization of nanomaterials. Some major challenges faced by the nanotechnology includes (i) interdisciplinary nature of nanotechnology (ii) lack of proper reference materials (iii) improper calibration of analytical tools (iv) difficult sample preparation and (v) complex interpretation of obtained spectra. Therefore, manufacturing of nanoparticles (NPs) require highly reliable quantification methods for the characterization of nanoparticles (NPs) [43]. Some of the major characterization techniques for the nano structured plant growth regulators (PGRs) are discussed in detail in the table 8.

7.1. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is an effective method and important tool for the measurement of absorption of electromagnetic radiations, mainly in the mid infrared (IR) region of electromagnetic spectrum. This region of electromagnetic spectrum generally ranges from 4000 to 400 cm^{-1}. The absorptions in this region are based on changing dipole moment and vibrations of IR active molecules. In the IR spectra, positions of bands are mainly relevant to the nature and strength of bonds, and functional groups present in the analytical samples. This type of spectroscopy provides valuable information about the molecular structures and complex interactions in between different functional groups [43].

7.2. Laser induced breakdown spectroscopy (LIBS)

Laser induced breakdown spectroscopy (LIBS) is an emerging analytical technique, used for the *in-situ* elemental analysis of various organic, inorganic and organometallic compounds. This technique is based on the emission spectroscopy [44] and thus measures the spectral emissions of different elements, in the plasma generated by high energy laser. LIBS have been used for elemental analysis since past few decades due to the easy sample preparation, simultaneous multi-element detection, and rapid responses [45]. LIBS require the minimum pretreatment of samples, produces no unwanted byproducts, and generates the spectra based on excitations and de-excitations of species at specific wavelength [44].

7.3. Atomic absorption spectrometry (AAS)

Atomic absorption spectrometry (AAS) is another useful analytical technique used for the elemental analysis of metallic compounds. Generally, this technique can be employed with the help of three different atomization processes like chemical vapor generation atomic absorption spectrometry (CVG-AAS), electrothermal atomization atomic absorption spectrometry (ETAAS) and flame atomic absorption spectrometry (FAAS). The selection of appropriate method depends on the chemical nature of analytical sample and physical state of major chemical constituents. For the direct determination of analyte of interest in the solid and liquid samples, AAS requires some specific modifications in the basic instrumentations, to ensure the reliability of results and obtained informations [46].

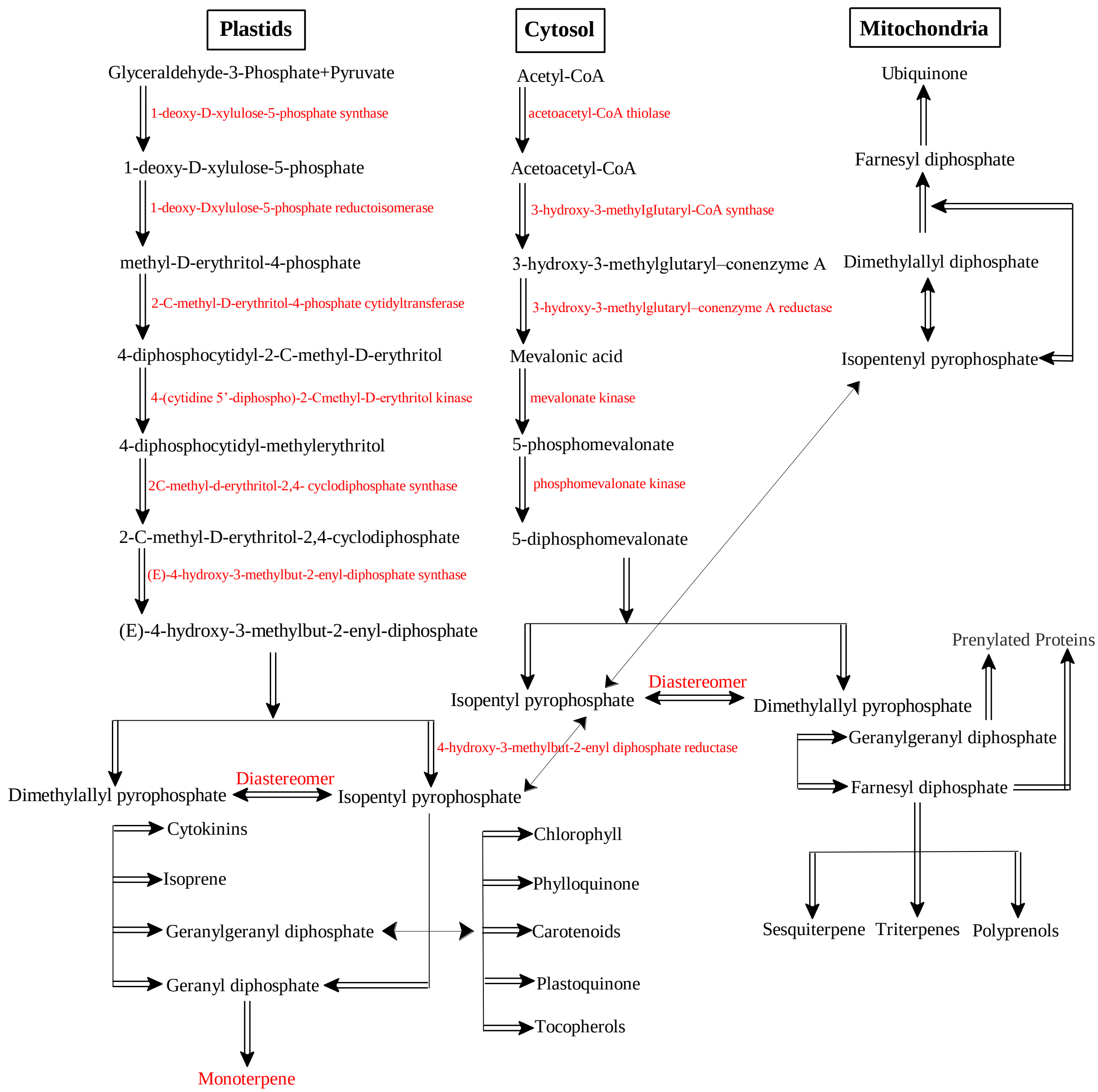


Fig.1: Biosynthetic pathway of essential oil in plants [4]

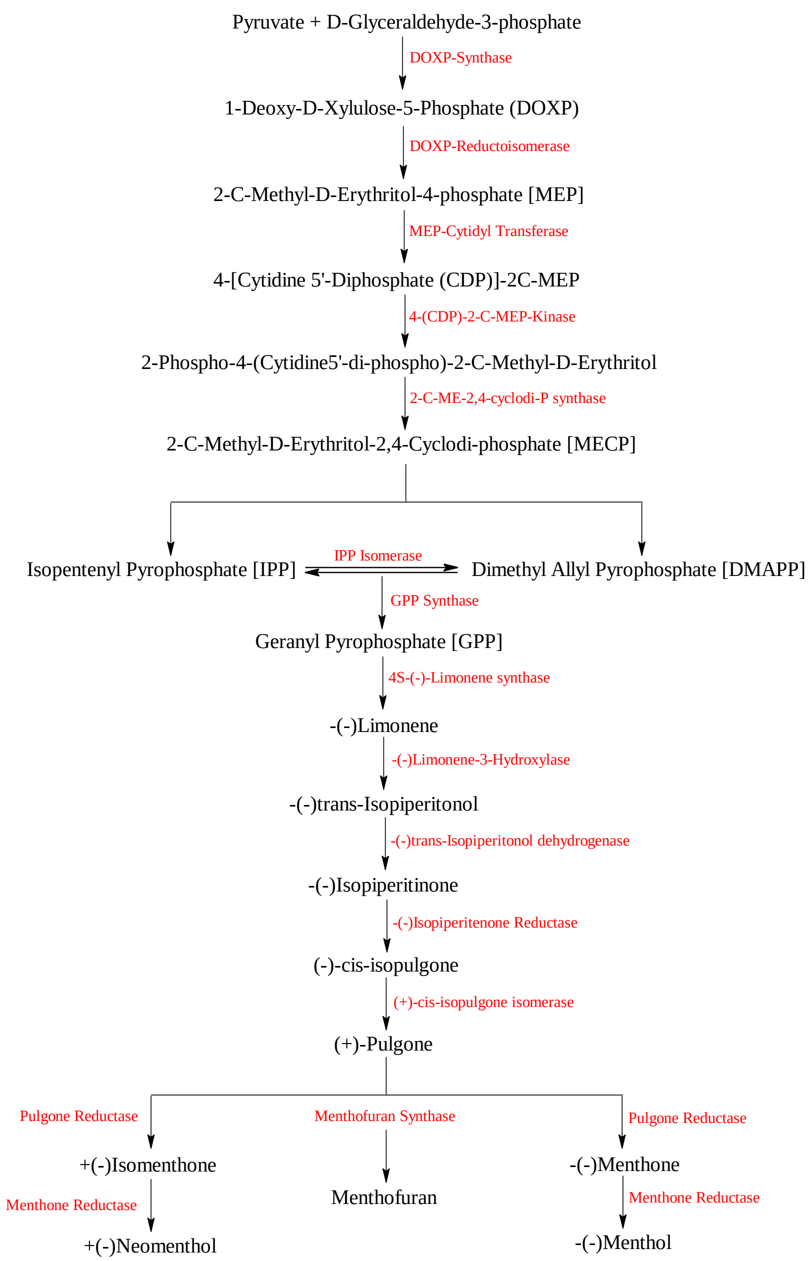


Fig.2: Biosynthesis of secondary metabolites of *Mentha arvensis* L. [5]

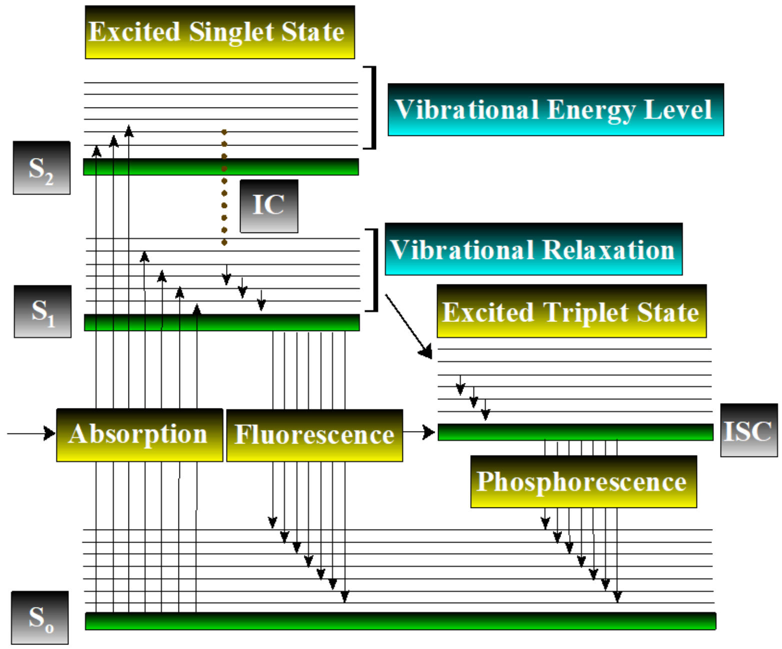


Fig.3: Jablonski diagram showing different photo-physical pathways [33]

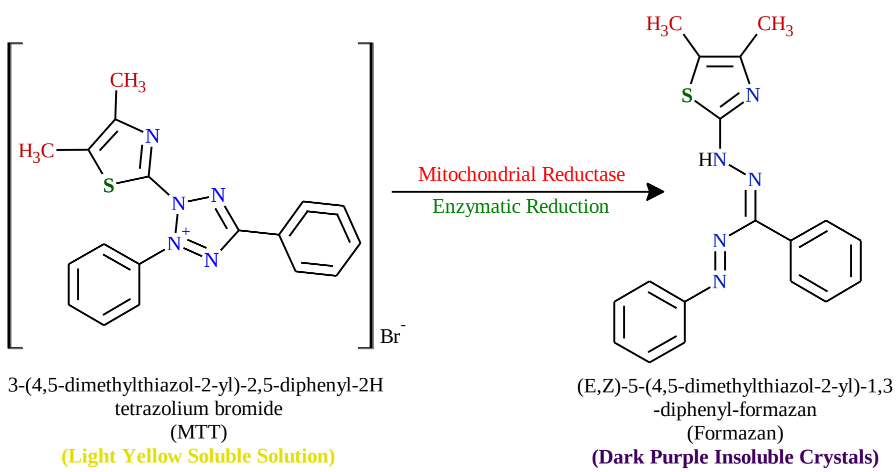
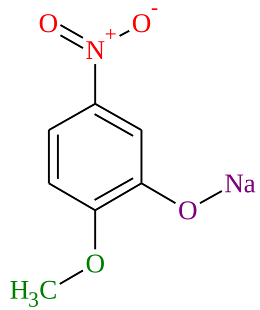
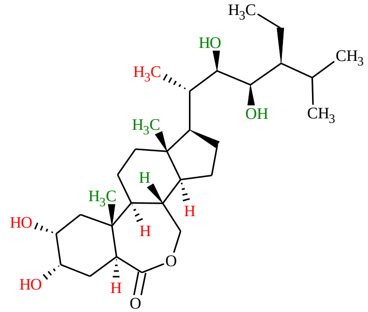
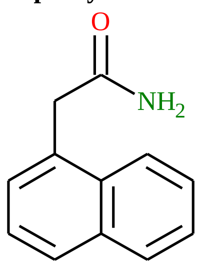
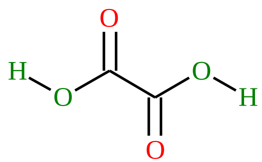


Fig.4: Biochemical conversion of MTT reagent into formazan crystals [49]

Table 1: Effects of PGPs on essential oil contents and growth parameters of different plant species

Sr. No	Plant species/Type of study	Name of chemical applied	Effects on essential oil contents/Miscellaneous effects	Effects on other growth attributes/Additional properties	References
			Sodium nitrophenolate 		
1	*Amaranths hypochondriacus* L.	Sodium nitrophenolate in compound form	Significant decrease in concentration of cadmium from highly polluted land area due to the excessive grown plants	Improved enzymatic potentials of catalases in leaves and higher biomass yield and chlorophyll contents in grains	[50]
2	Barley fodder	Atonik	Use of hydroponic solution for barley as a basic growth media, instead of soil	Hydroponic solution improved the dry matter, acid detergent fibre, neutral detergent fibre, crude protein, crude fat and crude fibre contents	[51]
3	*Mentha piperita*	Atonik also known as Asahi SL	Significant increase in essential oil percentage	Marked increase in herbage yield of plant	[52]
			28-Homobrassinolide 		
1	*Mentha arvensis* L.	28-homobrassinolide	Significant increase in percentage of major secondary metabolites such as menthyl acetate, menthone and menthol in essential oil	Higher carotenoids, flavonoid and chlorophyll contents with significant increase in fresh and dry weight of	[53]

				plants, lead area index and height of mint	
2	*Mentha arvensis* L.	28-homobrassinolide	Appreciable increase in percentage of menthyl acetate, l-menthone, isomenthone and menthol contents	Significant improvement in rate of photosynthesis, stomatal conductance and overall biomass yield	[54]
3	*Mentha arvensis* L.	28-homobrassinolide	High percentage of isomenthone, menthyl acetate, menthol and l-menthone	Significant improvements in herbage yield and physiological characteristics	[55]
1-Naphthylacetamide 					
1	Photodegradation and photocatalytic potentials	2-(1-naphthyl) acetamide	Characterization of plant growth regulator by using liquid chromatography electrospray ionization tandem mass spectrometry	Plant growth regulator and potential pesticidal compound	[56]
2	Studies involving the photo-stabilization	2-(1-naphthyl) acetamide	Two types of spectroscopic techniques (i) absorption spectroscopy and (ii) fluorescence spectroscopy	Encapsulation of plant growth regulator in the envelop of β-cyclodextrin for the photo-stabilization	[57]
3	Photo-physical characterization of plant growth regulator	2-(1-naphthyl) acetamide	Time resolved spectroscopy and steady state spectroscopy	2-(1-naphthyl) acetamide is a synthetic plant growth regulator which mimic the functioning of natural indole auxin	[58]
Oxalic acid 					

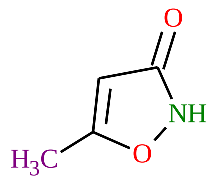
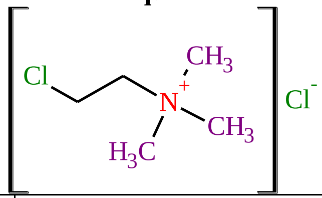
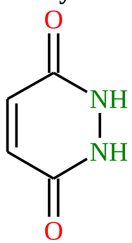
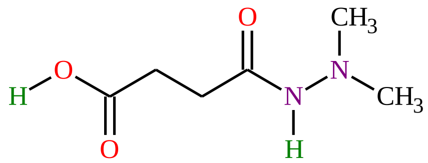
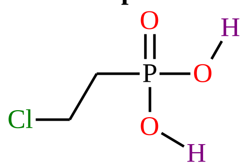
1	Tomato fruit	Oxalic acid	Significant improvements in gene expressions and advancements in oncological studies	Marked improvements in defense responses, cellular processes, metabolic stresses, phosphorylation and oxidation reduction reactions along with enhanced chilling tolerance	[59]
2	Shoots of Bamboo Plant (*Phyllostachys prominens*)	Oxalic acid	Improved post-harvest management and quality of plant material with marked increase in chilling responses	Enhanced membrane integrity, reduced respiration, retarded lignification process, decreased losses of sugar contents, inhibited enzymatic browning and decreased disease incidences	[60]
3	Pomegranate fruit	Oxalic acid	Improved chilling tolerance and better post-harvest quality of fruits	Remarkable increase in total phenolic contents, catalase activity and antioxidant potentials	[61]
Hymexazol 					
1	Increased pesticidal activities with negligible process losses	Hymexazol	Synthesis of hymexazol-graphene oxide-polydopamine based nano-composites	A known plant growth regulator and a potential antifungal compound	[62]
2	Preparation of host-guest-inclusion-complexes using hymexazol	Hymexazol	Significant growth promoting effects and pronounced antifungal activities	Mycelial growth of fungal strains is reduced by the exogenous application of hymexazol in complex form	[63]
3	Estimation of antifungal potentials of hymexazol-linked-chitosan derivatives	Hymexazol	Synthesis of hymexazol-linked-chitosan derivatives	Hymexazol has been proved as a potential antifungal agent for number of medicinal aromatic plants against *Gibberella zeae* CGMCC$_{3.42}$ and *Rhizoctonia solani* CGMCC$_{3.28}$	[64]

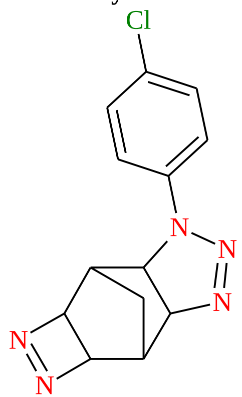
Table 2: Effects of PGIs on essential oil contents and growth parameters of different plant species

Sr. No	Plant species/Type of study	Name of chemical applied	Effects on essential oil contents/Miscellaneous effects	Effects on other growth attributes/Additional properties	References
Chlormequat chloride 					
1	Baby primrose plant (*Primula forbesii*)	Chlormequat chloride	Chlormequat chloride possesses growth retarding effects	Reduction in new leaf growth, short height of plants, increased number of floral whorls and significant reduction in length of peduncle	[65]
2	*Mentha arvensis* L.	Chloromequat chloride (also named as cycocel)	The damaging effects of cycocel are further ameliorated under the water stressed conditions	Significant improvements in peroxidase activities and percentage of essential oil and menthol contents with slight reduction in biomass yield	[66]
3	Japanese mint/Wild Mint/Corn mint (*Mentha arvensis* L. var. Piperascens Mal.)	Chlormequat chloride	The exogenous application of chlormequat chloride can reduce the harmful consequences of acute water shortage in plants	Significant increase in sugar contents, peroxidase activities and menthol contents of essential oil with slight reduction in essential oil percentage, herbage yield and moisture contents	[67]
Maleic hydrazide 					
1	Cucumber (*Cucumis sativus*)	Maleic hydrazide	The application of maleic hydrazide reduced the plant height as it acts as a potential herbicide and a known plant growth retardant	Higher chlorophyll contents of plant leaves, increased biomass production, improved sex modifications, higher fruit yield and enhanced fruit settings	[68]

2	Fenugreek (*Trigonella Foenum-Graecum* L.)	Maleic hydrazide	Specific gene mutation, growth retarding effects and higher herbicidal potentials	Significant improvements in seed quality and morphological characteristics with reduced seed germination and pollen fertility, and lower chlorophyll contents	[69]
3	Chrysanthemum (*Dendranthema grandiflorum*)	Maleic hydrazide	The combination of maleic hydrazide and potassium showed very positive effects on floral quality of plants	The application of maleic hydrazide maximizes dry and fresh weight of flowers, plant height and number of leaves, along with the introduction of early flowering in plants	[70]
Daminozide 					
1	*Ruellia brittoniana*	Daminozide	Significant increase in chlorophyll contents of leaves and reduction in overall plant growth	Daminozide caused significant decrease in plant height, internodal length, leaf area index, and dry weight of roots, stems and leaves	[71]
2	Fennel (*Foeniculum vulgare*)	Alar (also known by different trade names such as N-dimethyl amino succinamic acid, SADH, Alar 85, B-995, B-9 and daminozide)	Exogenous application of alar decreased the fenchone percentage and increased the anethole contents in essential oil of plant	Remarkable increase in essential oil contents and seed production in fennel	[72]
3	*Mentha piperita*	Daminozide	Decreased concentration of menthone and menthol, and increased percentage of isomenthone and neoisomenthol in peppermint	Significant increase in essential oil contents and remarkable improvements in overall biomass yield	[73]
Ethephon 					
1	Winter wheat (*Triticum aestivum* L.)	Ethephon	Ethephon caused appreciable increase in plumpness of basal internodes, wall thickness, breaking strength and internodal diameter	Improved internodal characteristics and higher lignin contents	[74]

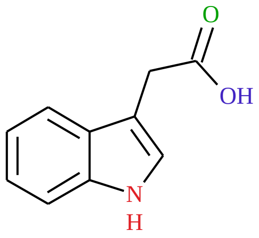
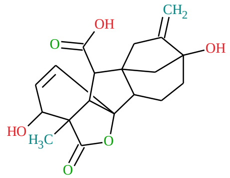
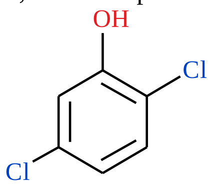
2	Field mint (*Mentha arvensis* L.)	2-chloroethyl phosphonic acid	Negative correlation between herb yield and essential oil contents of *Mentha arvensis* L., with significant improvements in percentage of menthone in essential oil	Significant reduction in biomass yield and height of plants, indicating the strong growth retarding effects	[75]
3	*Mentha piperita*	Ethephon	The essential oil of *Mentha piperita* showed significant increase in isomenthone and neoisomenthol, and marked decrease in menthone and menthol percentage of essential oil	Ethephon is a known plant growth retardant that reduces essential oil contents and biomass yield of plants	[73]

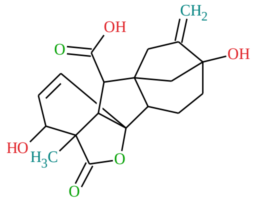
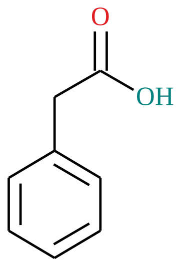
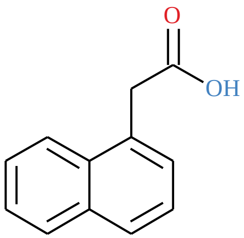
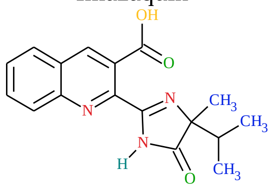
Tetcyclacis



1	Potato (*Solanum tuberosum* L.)	Tetcyclacis	The plant growth regulator acts as herbicide and inhibit the growth of stolon by lowering the level of gibberellins	The tuber stimulating effects are caused by the potential plant growth retardant	[76]
2	Fenugreek (*Trigonella foenum-graecum* L.)	Tetcyclacis	Tetcyclacis acts as norbornanodiazetine plant growth retardant which decreases the sapogenin contents in roots of Fenugreek	Better accumulation of cholesterol and 14α-methyl sterols contents with reduced growth of seedlings, shoots and roots	[77]
3	Moth bean (*Vigna aconitifolia* (Jacq.) Marechal cv. Jaadia)	Tetcyclacis	Reduced the high temperature induced lipid oxidation in beans and acts as potential herbicide	It makes the plants resistant towards heat shock by decreasing the oxidative potential of ascorbic acid and enhancing the catalytic potentials of catalase and peroxidase	[78]

Table 3: Nanostructured PGRs, their methods of preparation and reaction conditions

Sr. No	Plant species/Type of study	Name of PGR/Agrochemical	Type of NPs prepared	Method of preparation	Detailed mechanism/Reaction conditions	Characterization techniques	References
1	Crocantela variety from lettuce seedlings	Indole-3-acetic acid 	Chitosan based nanoparticles	Ionic gelation by using sodium tri-poly-phosphate	Chitosin based nanoparticles were prepared by dispersive agitation followed by ultrasonication and centrifugation. The indole-3-acetic acid was loaded by continuous stirring through ultrasonication followed by centrifugation and magnetic agitation for 24 hours	Dynamic light scattering (DLS), polydispersity index (PDI), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and infrared (IR) spectroscopy	[79]
2	*Solanum lycopersicum*	Gibberellic acid 	Nano alginate/chitosan and nano chitosan/tripolyphosphate containing gibberellic acid	Process of colloidal dispersion	Preparation of nano chitosan/tripolyphosphate containing gibberellic acid using vigorous stirring with the help of peristaltic pump	Dynamic light scattering (DLS), atomic force microscopy (AFM) and nanoparticle tracking analyses (NTA)	[80]
3	Efficiency of removal of plant growth regulator from contaminated aqueous solution	2,4-dichlorophenol 	Zinc metal-organic framework having 2-aminoterephthalic acid and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene	The process of sonication facilitated by ultrasound	Preparation of single crystal zinc metal-organic framework having 2-aminoterephthalic acid and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene followed by controlled crystal growth using sonochemical process	Thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET), Infrared spectroscopy, X-ray diffraction (XRD) and Scanning electron microscopy (SEM)	[81]
4	Seeds of *Phaseolus vulgaris* L.	Gibberellic acid	Alginate/chitosan and chitosan/tripolyphosphate based nano-formulations	The process of gelation and ionotropic pre-gelation	Preparation of alginate/chitosan nanoparticles using ionotropic pre-gelation and encapsulation of gibberellic acid using chitosan/tripolyphosphate	Zeta potential and poly dispersity index (PDI)	[19]

					based nano-formulations aided by gelation method		
5	Controlled release of plant growth regulators	Phenylacetic acid 	Preparation of polysaccharide beads from xylan, cellulose nanocrystals, starch, cellulose powder and beads of alginate reinforced with kaolin clay modified with polyethylenimine	Slow entrapment of phenylacetic acid in complex network of cellulose	Preparation of polysaccharide beads by homogeneous suspension using crosslinking agent, followed by drying (48 hours) and soaking in solution of phenylacetic acid (48 hours)	Energy dispersive spectroscopy (EDS), Ultraviolet-visible (UV–Vis) spectroscopy, Scanning electron microscopy (SEM) and Tensile testing (TT)	[82]
6	Wheat seeds	1-Naphthylacetic acid 	Conjugated nanospheres of 1-naphthylacetic acid and silica	The covalent crosslinking reactions followed by hydrolyzation and poly-condensation process	Conjugation of 3-aminopropyltriethoxysilane and 1-naphthylacetic acid through covalent cross-linking and hydrolyzation in the presence of tetraethyl orthosilicate to form 1-naphthylacetic acid and silica nano-spheres	High performance liquid chromatography (HPLC), Scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and UV–Vis spectroscopy	[83]
7	Preparation of nano-formulations of herbicide	Imazaquin 	Encapsulation of imazaquin using starch and chitosin beads reinforced with alginate	The method of external gelation	Starch/alginate beads and chitosan/alginate beads were prepared by extrusion of beads in calcium chloride followed by starch gelatination at 75°C	Fourier transform infrared (FTIR) spectroscopy, Scanning electron microscopy (SEM) and Differential scanning calorimetry (DSC)	[84]

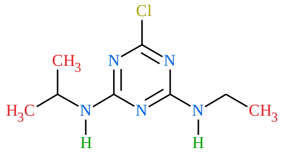
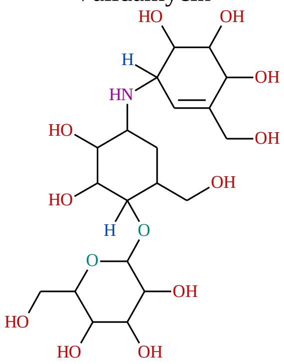
8	Preparation of herbicides based nanoformulations	Atrazine 	The microspheres of poly(hydroxy-butyrate-co-hydroxy-valerate) loaded with atrazine	Microspheres were prepared by solvent evaporation method and emulsification process	Solubilization of atrazine with poly(hydroxy-butyrate-co-hydroxy-valerate) in the presence of polyvinyl alcohol followed by heating, evaporation and centrifugation of nano-suspensions	Ultraviolet (UV) spectrophotometry and Scanning electron microscopy (SEM)	[85]
9	Water soluble pesticides showing controlled release and slow delivery of bioactive compound	Validamycin 	Silica based porous hollow nanoparticles loaded with validamycin	Loading of agrochemical using supercritical fluid method	Use of sol-gel method for the preparation of hollow silica nanoparticles by heating upto 353 K followed by adsorption of validamycin at 40 MPa for 5 hours	High performance liquid chromatography and ultra-violet spectrophotometry, Transmission electron microscope (TEM), Thermo-gravimetry-differential thermal analysis/differential scanning calorimetry (TG-DTA/DSC), Infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS)	[86]

Table 4: Photodegradation studies of PGRs and other agrochemicals

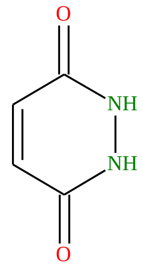
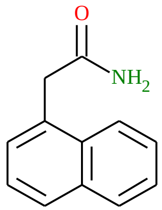
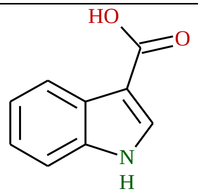
Sr. No	Name of agrochemical and category	Molecular structure	Photosensitizers	Techniques/Apparatus	Experiments conducted	References
1	Maleic hydrazide (Herbicide)		Humic acid and vitamin B_2/Riboflavin	The steady state fluorescence by using Spex Fluoromax spectrofluorimeter and absorption measurements using Hewlett Packard 8452A diode array spectrophotometer	Time resolved phosphorescence detection, continuous photolysis and laser flash photolysis	[87]
2	2-(1-naphthyl) acetamide (Plant growth regulator)		Rose Bengal	Liquid chromatography-mass spectrometry-mass spectrometry (LC/MS/MS), High performance liquid chromatography-mass spectrometry-mass spectrometry (HPLC/MS/MS), Ultraviolet–Visible spectroscopy and Liquid chromatography-mass spectrometry (LC/MS)	Assessment of hydrogen peroxide free radical formation and nanosecond laser flash photolysis	[88]
3	Indole-3-carboxylic acid (Plant growth regulator)		The reference sample contains haricot bean	Ultraviolet–visible spectroscopy using Beckman instrument (model: 3600) and photochemical reactor containing an oriel light source equipped with (i) tungsten-lamp and (ii) oriel power supply box, with a magnetic agitator and (iii) a quartz cell placed at 60 cm from the lamp	Determination of half-life, rate constants, caulogenesis, rhizogenesis and photodegradation kinetics	[89]

Table 5: Thermaldegradation studies of PGRs and other agrochemicals

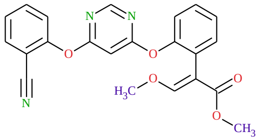
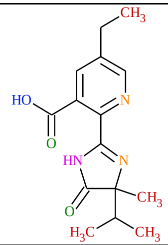
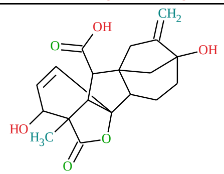
Sr. No	Name of agrochemical and category	Molecular structure	Type of nanoparticle	Technique of thermal analysis used	Instrumental specifications and processing conditions	References
1	Azoxystrobin (Fungicide)		Metal organic framework containing porous iron based nano-structures	Thermal gravimetric analysis (TGA)	Thermal gravimetric analysis was performed by PerkinElmer Pyris Diamond having 20 mL/min and 30 mL/min flow rate of nitrogen for sample and reference. All readings were taken using nitrogen steam having a heating rate of 10°C/min to 550°C at the end	[90]
2	Imazethapyr (Herbicide)		Biopolymeric beads containing alginate cellulose mixture	Thermal gravimetric analysis (TGA)	Thermal gravimetric analysis was performed by Shimadzu Analyzer (model: DTG60, Japan) with scanning rate: 10°C/min in nitrogenous atmosphere and flow rate: 20 mL/min with a temperature ranging from 25 to 600°C	[91]
3	Gibberellic acid (Plant growth regulator)		Chitosan/tripolyphosphate and alginate/chitosan polymeric beads	Differential scanning colorimetry (DSC)	Chitosan/tripolyphosphate and alginate/chitosan polymeric beads were characterized by differential scanning colorimetry using aluminum cups with a constant flow rate of nitrogen (50 mL/min) and heating from 20 to 350°C	[19]

Table 6: Leaching potentials of PGRs and other agrochemicals

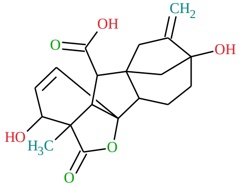
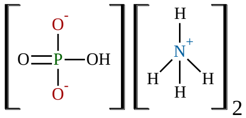
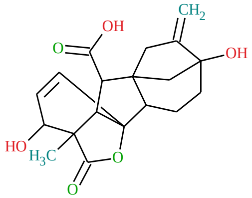
Sr. No	Name of agrochemical and category	Molecular structure	Type of nanoparticle	Encapsulation efficiency	Technique used and instrumental specifications	References
1	Gibberellic acid (Plant growth promoter)		Nano alginate-chitosan and nano chitosan-tripolyphosphate having gibberellic acid	Entrapment efficiency of nano chitosan-tripolyphosphate is 90% and nano alginate-chitosan is 100%	Ultrafiltration membranes were used with the dense cellulosic network with the approximate pore size of 30 kDa followed by quantitative analysis of entrapped gibberellic acid through high performance liquid chromatography	[80]
2	Diammonium hydrogen phosphate (Phosphorous fertilizer)		The superabsorbent composites containing starch and alginate	Almost 80% release of diammonium hydrogen phosphate from dense network of superabsorbent composites after 30 days of treatment	The standard curve of pure diammonium hydrogen phosphate drawn by using high performance liquid chromatography at 20:80 volume/volume methanol to water ratio. Separation was achieved by a thin column at the flow rate of 1 mL/min at 30°C followed by the ultraviolet-visible (UV-Vis) spectrophotometric detection at 254 nm	[92]
3	Gibberellic acid (Plant growth regulator)		Alginate-chitosan and chitosan-tripolyphosphate	The encapsulation efficiency of 50 µg/mL solution was found to be 100%	Analysis of prepared solution using ultrafiltration device having cellulosic membrane (pore size: 30 kDa) followed by centrifugation for 30 minutes. The filtrate was analyzed by high performance liquid chromatography for the quantification of residual hormone, not associated with the NPs	[19]

Table 7: Cytotoxic effects of different *Mentha* species

Sr. No	Plant material or type of NPs	Type of cell line used	Cytotoxic assay and detailed process	Probable outcomes of research	References
1	*Mentha arvensis* L. (A rich source of rosmarinic acid fraction)	Hepatocellular carcinoma in $HepG_2$ cells of human beings	The MTT cytotoxic assay was performed by using $HepG_2$ cell line by treating with rosmarinic acid rich fraction of *Mentha arvensis* L. The entire setup was kept in the incubator for 24 hours	The results obtained confirmed the anticancer potential of rosmarinic acid by G_o/G_1 phase arrest and synchronizing the ERK2, Bax and Bcl-2 mRNA expressions, resulting in apoptosis of severe hepatocellular carcinoma	[93]
2	*Mentha spicata* essential oil	Breast adeno-carcinoma MCF-7 cell line, kidney carcinoma A498 cell line, ductal breast epithelial tumor T47D cell line, renal cell carcinoma Caki cell line, EBV-negative Burkitt's lymphoma BJAB cell line, , prostate adenocarcinoma PC-3 cell line, colon adeno-carcinoma Caco-2 and epithelial carcinoma HeLa cell line	The MTT cytotoxic assay was performed by dissolution of dimethyl sulfoxide in essential oil along with the analyte of interest, followed by the incubation at 37°C for the period of 48 hours	The obtained results showed that the essential oil of *Mentha spicata* possesses enough potential to neutralize the free radical species of cancerous cells, thereby acting as an anti-cancer agent through reversal of tumorigenesis. These processes helps to avoid the deleterious effects of chemotherapy	[94-95]
3	Synthesis of green silver nanoparticles using *Mentha arvensis* L.	MDA-MB-231 and MCF7 cells	The survival rate of treated and untreated cells were studied by MTT cytotoxic assay by the use of fluorescence activated cell sorting through fluorescence microscopy	The results obtained by the MTT cytotoxic assay showed that the nanoparticles exhibited far better cytotoxic effects against breast cancer with increase in the population of G_1 cells. Hence, these nanoparticles can preferably be used as they are non-mutagenic and least toxic in nature	[96]

Table 8: Characterization techniques for nanostructured PGRs, nanofertilizers and other agrochemicals

Sr. No	Name of plant/Type of sample/Purpose of analysis	Name of PGR/Type of Agrochemical	Instrumental specifications	Probable outcomes/Obtained results	References
Fourier transform infrared (FTIR) spectroscopy					
1	Cherry tomatoes	Glyoxylic acid monohydrate, 1-naphthaleneacetic acid, indole-3-butyric acid and indole-3-propionic acid	IR spectra were recorded by using an ona Vertex70 FTIR spectrometer (provided by Bruker, Karlsruhe, Germany) in the range of 500 cm^{-1} to 4000 cm^{-1}	Among all the peaks obtained in FTIR spectra, the stronger peaks at 3384 cm^{-1} represents −OH group, 1816 cm^{-1} and 1630 cm^{-1} represents C=C stretching vibrations, 1736 cm^{-1} represents C=O and 1069 cm^{-1} represents the C−O−C stretching vibrations	[97]
2	Plant based tissues, fruits and vegetables	2,4-dichlorophenoxyacetic acid, 1-naphthaleneacetic acid, indole-3-butyric acid and indole-3-acetic acid	FTIR spectra were obtained by using the FTIR spectroscopy through NICOLET IS10 instrument	The spectral peaks at 3596 cm^{-1} and 2927 cm^{-1} indicates the presence of methacrylic acid and β-cyclodextrin, while the peaks at 1731 cm^{-1} represents C=O stretching vibration, 1636 cm^{-1} represents O−H deformation, 1149 cm^{-1} represents O−C(O)–C bonds and the peaks at 2989 cm^{-1}, 2957 cm^{-1}, 1458 cm^{-1}, and 1387 cm^{-1} indicates the other stretching vibrations	[98]
3	Solid phase magnetic adsorbents based on β-cyclodextrin	Tebuconazole, uniconazole, paclobutrazol, atrazine, 2,4-dichlorophenoxyacetic acid, 1-naphthaleneacetic acid, simazine, 4-chlorophenoxyacetic acid, and 4-fluoro-phenoxyacetic acid	The FTIR spectrums were obtained through a Tensor 37 (Bruker spectrometer company, Germany)	The characteristic peak at 578 cm^{-1} represents Fe–O–Fe, 1082 cm^{-1} and 3420 cm^{-1} indicates Si–O–Si and O–H stretching vibrations, 1628 cm^{-1} represents bending vibration of N–H, 3500–3300 cm^{-1} shows stretching vibration of N–H, and 1716 cm^{-1} and 1388 cm^{-1} represents the stretching vibration of C=O and bending vibration of O–H groups	[99]
Laser induced breakdown spectroscopy (LIBS)					
1	Seaweed	Fertillizers based on seaweed	LIBS spectra was obtained by a Nd:YAG laser (wavelength 1064 nm, pulse duration 6ns, Litron Lasers, Rugby, United Kingdom)	Stronger emission lines were obtained for strontium, sodium, potassium, calcium, magnessium, and manganese, and some trace elements like silicon (at 288.15 nm and 390.53 nm) and iron (at 382.04 nm, 375.82 nm, 374.95 nm, 374.83 nm, 374.56 nm, 373.71 nm, 373.49 nm and 371.99 nm)	[45]
2	Quick method of identification of potassium, nitrogen and phosphorous	Fertillizers	The LIBS spectra was generated by a Q-switched Nd:YAG pulsed laser with the following specifications (ICE450, 1064 nm, 6 ns pulse duration, Big Sky Laser Technologies, Morgan Hill, CA, USA with an alternative name of Quantel Laser	The strong characteristic lines of the elemental phosphorus were found to be at 255.5 nm, 255.3 nm, 253.6 nm, 253.4 nm, 215.4 nm, 214.9 nm and 213.5 nm, elemental potassium at 769.9 nm, 766.5 nm and 404.7 nm, and elemental nitrogen at 871.8 nm, 871.2 nm, 870.3 nm, 862.9 nm, 859.4 nm, 856.7 nm, 746.8 nm, 744.2 nm and 742.4 nm	[100]

3	Estimation of potassium in fixed concentration nutrient media	Fertillizers based on biochar	The calcium and potassium were analyzed by Q-switched Nd:YAG laser, capable of emitting at 1064 nm (Quantel, Big Sky Laser, Ultra 50) and operating at maximum energy of 50 mJ with a repetition rate up to 20 Hz and a pulse duration of 20 ns, thereby creating the laser spot diameter of about 0.5 mm	The LIBS spectra showed the strong peaks for calcium-I at 431.86 nm, 430.25 nm, 428.94 nm and 428.30 nm, and for potassium-I at 404.64 nm	[101]
			Atomic absorption spectrometry (AAS)		
1	Trace metal determination in soil	Complete environmental analysis of contaminated soil samples	For the elemental analysis, a flame atomic absorption spectrometer (model: AAnalyst 700, PERKIN ELMER-SCIEX) was used in acetylene/nitrous oxide flame and air/acetylene flame for determination of aluminium and cadmium, cupper, nickle and zinc	The traces of metallic elements in soil samples were successfully extracted by the "ultrasound-assisted-extraction" method, using hydrochloric acid, hydrofluoric acid and nitric acid. Among all the acids, hydrofluoric acid proved to be the most efficient solvent for the extraction of zinc, nickle, cupper, cadmium and aluminium to be analyzed by the atomic absorption spectrometry	[102]
2	Qualitative and quantitative determination of cadmium in oyster and water samples	Solid-phase and magnetic micro-extraction technique by using $CoFe_2O_4$ nanoparticles	For the analysis of cadmium in given sample, a Perkin Elmer Instruments (Norwalk, CT, USA) with the model AAnalyst 200 flame atomic absorption spectrometer was used	As a result of complete elemental analysis by atomic absorption spectrometry, it was confirmed that the amount of cadmium in the experimental water samples and oyster samples was in the range of 2.75 μg/L to 4.8 μg/L and 4.6 mg/kg to 7.8 mg/kg, respectively	[103]
3	Trace metal analysis in organic fertillizers	Assessment of zinc, lead, nickle, manganese, copper, chromium, cobalt and cadmium in organic fertilizers	For the determination of trace metals, a Varian Spectra 220 (model: Mulgrave, Australia) flame atomic absorption spectrometer was used in a sequential mode, equipped with the deuterium background corrector and multi-element hollow cathode lamp	During this experiment, nitric acid, hydrofluoric acid and hydrochloric acid were used for the solvent extraction of trace metals from analytical samples. Among all these variables, hydrofluoric acid proved to be best for the extraction of traces of metals due to the high dissolution potential. Thus extracted metals were analyzed by the atomic absorption spectrometry	[104]
			Scanning electron microscopy (SEM)		
1	Synthesis of novel PGRs based on the potential derivatives of dehydroamino acids followed by the	1-methyl-3-methylamino-maleimide, Z-isomer of potassium salt of 2-amino-3-methoxycarbonylacrylic acid	The surface morphology and particle size of the nano-structured PGRs were studied by scanning electron microscopy (FE-SEM,	The results obtained by the SEM analysis showed that the wet encapsulations of PGRs do not have significant effects on the overall particle size. The size of wet beads ranged from 1706.07 μm to 2120.64 μm and dry	[105]

	encapsulation inside the biopolymeric beads	and 2,3-dehydroaspartic acid dimethyl ester	model: JSM-7000F, Jeol Ltd., Japan)	beads ranged from 745 µm to 810 µm. The surface of dried nanoparticles was quite rough and wrinkled	
2	Fabrication of biochar based nanocarriers for sustained release of nano-herbicides	2,4-dichlorophenoxyacetic acid	Some morphological characteristics and elemental analysis of the encapsulated nano-herbicide was done by a VEGA 3 TESCAN, scanning electron microscope (SEM), coupled with EDAX for the dual functions	As per the data obtained by SEM analysis, the hydrodynamic particle size of the nano-encapsulated herbicide was around 256.5 nm which indicates the high loading capacity, enhanced herbicidal efficiency, better penetration potential, controlled release and sustained delivery of agrochemical, leading towards the sustainable developments	[106]
3	Synthesis of nano-structured tricyclazole (Fungicide)	Tricyclazole	To study the topological properties, to determine the particle size and to assess the morphological characteristics of nano-fungicide, scanning electron microscopy (model: Zeiss Evol8) was used with the variable magnification ranges using the sputtering coater and electron beam released by electron gun	As per the conventional approximations, smaller particle size of agrochemicals enhances the rate of dissolution, lower the leaching of chemicals, enhances the surface area and improves the penetration potential. Highly magnified images of SEM indicated the different shapes of tricyclazole leading to the agglomeration of particles and formation of nano-clusters. The particle size distribution of nano-tricyclazole is found to be in the range of 60 nm to 95 nm	[107]
Thermal analysis (TA)					
1	Preparation of encapsulated chitosin based pesticidal formulations for slow release of spinosad by coprecipitation	Spinosad (Pesticide)	Differential scanning calorimeter (model: Shimadzu, DSC-60 Plus, Japan) was used having a temperature range of 30°C to 400°C with 10°C/min increase in temperature, and TGA curves were obtained by TGA/DSC simultaneous thermal analyzer (model: Discovery, SDT 650, USA) with temperature range of 30°C to 600°C at the rate of 10°C/min increase in temperature	The prepared chitosin based encapsulating structure of nanoparticles showed the initial volatilization of potentially adsorbed water at the temperature range of 50°C to 230°C, rapid weight loss at temperature range of 230°C to 312°C and relatively slow weight loss at temperature range of 312°C to 430°C. Similarly, spinosad loaded encapsulated nanoparticles showed the rapid weight loss at the temperature range of 230°C to 312°C, indicating the significant improvements in thermal stability of prepared nano-formulations. The decomposition temperature is around 312°C to 600°C	[108]
2	Synthesis of ecofriendly corncob biochar based nano-composites to ensure the sustained delivery of agricultural chemicals	Biochar (Nano-fertilizer)	Thermal analysis was performed by using the TGA/DSC (Model: SDT-Q600, Germany) in order to check the thermal stability of prepared nano-formulations	In the TGA curves, first peak at 147.52°C showed the rapid weight loss due to higher moisture contents, second peak at 335.13°C indicated gradual weight loss and third peak at 481.25°C represented pyrolytic degradation of sample with the release of methane, carbon monoxide and carbon dioxide	[109]
3	Preparation of a novel brassinosteroid modified	Brassinosteroid (Growth regulating hormone)	DSC was performed by a PerkinElmer Differential Scanning	The results obtained by the DSC/TGA curves showed that major endothermic processes mainly relevant to	[110]

	polyethylene glycol micelles for targeted delivery of agrochemical		Calorimeter Pyris 1 (PerkinElmer, Inc., Waltham, MA, USA) and TGA curves were obtained by Netzsch TG 209 C Iris system	the melting of prepared nano-formulations are in the range of 38°C to 64°C while exothermic processes including the pyrolytic degradations are in the range of 225°C to 300°C with weight loss up to 98%	
X-ray diffraction (XRD)					
1	Synthesis of interpenetrating dense polymeric networks of hydrogels potentially integrating natural soil colloids via covalent cross-linking of polyacrylamide and ionic crosslinking of alginate	Hydrogels integrated with natural soil colloid – a potential carrier for slow release of agrochemicals	For the XRD analysis of prepared hydrogels and colloidal soil particles, the samples were analyzed at diffraction angles ranging from 2° to 70° with the help of x-ray diffractometer (model: D8 Advance, Bruker) with CuKα radiation (at λ=0.1548 nm) at 40 kV and 40 mA	In the XRD pattern, several sharp lines were obtained indicating the multiple mineral elements of the soil colloides. Some phase peaks of pure hydrogels in XRD pattern were relatively broad, indicating the poor crystallinity of hydrogel matrix. In case of hybrid hydrogels, 7.5 wt% of the soil colloids were identified, indicating the presence of soil colloids inside the dense polymeric network	[111]
2	Preparation of biocompatible chitosin based nanoparticles loaded with spinosad and permethrin	Permethrin and spinosad – two potential pesticides for proper insect pest management	For the powdered XRD analysis of nano-structured pesticides, model: Panalytical's X'Pert Pro was used by taking 2 g of finely powdered sample on a glass slide having uniform layer of nanoparticles	The XRD pattern of nano-formulations exhibited a strong characteristic peaks at 20° indicating the purely crystalline nature of chitosan. On the other hand, the broad peaks of loaded chitosan nanoparticles indicate the amorphous nature and incoherent scattering of x-rays. The results showed that crosslinking destroyed the crystalline structure of loaded chitosin nanoparticles	[112]
3	Preparation of carboxymethyl cellulose based nanocomposites for slow release of basic nutrient elements by fertillizers and water retention in soil	Nitrogen-phosphorous-potassium (NPK) (Fertilizer)	The XRD patterns of cellulosic nanoparticles were obtained by using a Siemens D500 x-ray diffractometer (model: Siemens AG, Karlsruhe, Germany) with a CuKα radiation in a 2θ range of 2° to 70° angle	The peak at 22.5° confirmed silica, peaks at 37°, 36°, 32°, 29°, 25° and 23° confirmed urea, peaks at 49°, 47°, 46°, 34°, 31°, 24° and 17.5° confirmed potassium dihydrogen phosphate and peaks at 69°, 62°, 60.5°, 58.5°, 51.5°, 45°, 38.5°, 34°, 29°, 23° and 17.5° confirmed ammonium dihydrogen phosphate in the given samples	[113]

7.4. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) has widely been used to determine the shape and surface morphology of nanoparticles (NPs) in various disciplines all over the world. SEM is regarded as the most effective method for the analysis of organic and inorganic samples, having particle size in the micrometer (µm) and nanometer (nm) range. The extent of magnification of some modern SEM instruments can reach up to 300,000x and even 1000000 in producing the images for a wide range of samples. SEM works with energy dispersive x-ray spectroscopy (EDS) for qualitative and semi-quantitative results. Together, both these techniques can produce the basic information about chemical composition of scanned samples [47].

7.5. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) is one of the most important types of thermal analysis (TA), capable of providing the valuable informations regarding the change in mass and chemical composition of prepared nanoparticles (NPs). In this method, nanomaterials are heated up to degradation temperature and their components are decomposed and vaporized with the passage of time. The loss of mass with the change in temperature is recorded with the help of TGA device, and quantity, type and mass of prepared nanoparticles (NPs) are determined by comparing it with the starting material. In the case of "micro-thermogravimetric analysis" (µ-TGA), the amount of sample generally varies in between one nano-gram to one micro-gram, thereby improving the detection limit of conventional TGA up to great extent [43].

7.6. X-ray diffraction (XRD)

In the x-ray diffraction (XRD), scattering of x-rays is used to elucidate the crystallinity of crystalline and semi-crystalline materials. The scattering of x-rays by periodic arrangement of atoms, give rise to the definite diffraction patterns, thereby providing the qualitative imaging of atomic arrangements inside the crystal lattice. In case of powder x-ray diffraction (P-XRD), both the precursors and end products can simultaneously be characterized with complete qualitative representation of micro-structural behaviours. This method is quite convenient as compared to the single crystal XRD that requires individual crystal for analysis. In addition, XRD is the non-destructive method for crystallographic determination of a crystal [48].

8. Conclusions

The use of cost effective and environmentally benign plant growth regulators (PGRs) is the most preferred option in modern agriculture. Plant growth regulators (PGRs) not only enhance the biomass yield, essential oil percentage and amount of major secondary metabolites, but also improve stress responses and environmental resistance in plants. However, long duration of sunlight, high temperature and cytotoxic nature of plant growth regulators (PGRs) can cause severe damage to plants and environment. The excessive leaching of agrochemicals not only pollutes the natural water reservoirs, but also damages the life quality of aquatic animals. Therefore, use of nanotechnology holds great potential in this regard. Nano encapsulated and polymeric plant growth regulators (PGRs) ensure the controlled release, long persistence and targeted delivery of applied chemicals to plants. Hence, nanotechnology can work wonder to increase the production of food crops and essential oil contents of aromatic medicinal plants.

References

[1] F. Nadeem, M.A. Hanif, I.A. Bhatti, R.W.K. Qadri. (2022). Improved Spectrophotometric Method for Fast and Accurate Quantitative Determination of Menthol in Essential Oils. Food Analytical Methods. 15(6): 1575-1580.

[2] W. Rademacher. (2015). Plant growth regulators: backgrounds and uses in plant production. Journal of Plant Growth Regulation. 34(4): 845-872.

[3] C. Rodriguez-Furlán, G. Miranda, M. Reggiardo, G.R. Hicks, L. Norambuena. (2016). High throughput selection of novel plant growth regulators: Assessing the translatability of small bioactive molecules from Arabidopsis to crops. Plant Science. 245: 50-60.

[4] R. Rehman, M.A. Hanif, Z. Mushtaq, A.M. Al-Sadi. (2016). Biosynthesis of essential oils in aromatic plants: A review. Food Reviews International. 32(2): 117-160.

[5] P. Tiwari. (2016). Recent advances and challenges in trichome research and essential oil biosynthesis in Mentha arvensis L. Industrial crops and products. 82: 141-148.

[6] Y. Sajjad, M.J. Jaskani, M. Asif, M. Qasim. (2017). Application of plant growth regulators in ornamental plants: a review. Pakistan Journal of Agricultural Sciences. 54(2).

[7] K. Jamwal, S. Bhattacharya, S. Puri. (2018). Plant growth regulator mediated consequences of secondary metabolites in medicinal plants. Journal of applied research on medicinal and aromatic plants. 9: 26-38.

[8] P.J. Davies, The plant hormones: their nature, occurrence, and functions. In *Plant hormones*, Springer: 2010; pp 1-15.

[9] N. Sangwan, A. Farooqi, F. Shabih, R. Sangwan. (2001). Regulation of essential oil production in plants. Plant growth regulation. 34(1): 3-21.

[10] D.K. Verma, S. Srivastava, P.P. Srivastav, B. Asthir, Nano Particle Based Delivery System and Proposed Applications in Agriculture. In *Engineering Practices for Agricultural Production and Water Conservation*, Apple Academic Press: 2017; pp 363-386.

[11] Y. Shang, M. Hasan, G.J. Ahammed, M. Li, H. Yin, J. Zhou. (2019). Applications of nanotechnology in plant growth and crop protection: a review. Molecules. 24(14): 2558.

[12] A. Przybysz, H. Gawrońska, J. Gajc-Wolska. (2014). Biological mode of action of a nitrophenolates-based biostimulant: case study. Frontiers in Plant Science. 5: 713.

[13] T. Isah. (2019). Stress and defense responses in plant secondary metabolites production. Biological research. 52(1): 39-63.

[14] K. Grossmann, Plant growth retardants: their mode of action and benefit for physiological research. In *Progress in plant growth regulation*, Springer: 1992; pp 788-797.

[15] M. Lv, Y. Liu, J. Geng, X. Kou, Z. Xin, D. Yang. (2018). Engineering nanomaterials-based biosensors for food safety detection. Biosensors and Bioelectronics. 106: 122-128.

[16] Y.W. Chen, H.V. Lee, J.C. Juan, S.-M. Phang. (2016). Production of new cellulose nanomaterial from red algae marine biomass Gelidium elegans. Carbohydrate polymers. 151: 1210-1219.

[17] R. Prasad, A. Bhattacharyya, Q.D. Nguyen. (2017). Nanotechnology in sustainable agriculture: recent developments, challenges, and perspectives. Frontiers in microbiology. 8: 1014.

[18] A.d.E. Santo Pereira, H.C. Oliveira, L.F. Fraceto. (2019). Polymeric nanoparticles as an alternative for application of gibberellic acid in sustainable agriculture: a field study. Scientific reports. 9(1): 7135.

[19] A.E. Santo Pereira, P.M. Silva, J.L. Oliveira, H.C. Oliveira, L.F. Fraceto. (2017). Chitosan nanoparticles as carrier systems for the plant growth hormone gibberellic acid. Colloids and Surfaces B: Biointerfaces. 150: 141-152.

[20] R. Yang, C.-F. Xiao, Y.-F. Guo, M. Ye, J. Lin. (2018). Inclusion complexes of GA3 and the plant growth regulation activities. Materials Science and Engineering: C. 91: 475-485.

[21] A. Pereira, I. Sandoval-Herrera, S. Zavala-Betancourt, H. Oliveira, A. Ledezma-Pérez, J. Romero, L. Fraceto. (2017). γ-Polyglutamic acid/chitosan nanoparticles for the plant growth regulator gibberellic acid: Characterization and evaluation of biological activity. Carbohydrate polymers. 157: 1862-1873.

[22] D.G. Panpatte, Y.K. Jhala, H.N. Shelat, R.V. Vyas, Nanoparticles: the next generation technology for sustainable agriculture. In *Microbial Inoculants in Sustainable Agricultural Productivity*, Springer: 2016; pp 289-300.

[23] X. He, H. Deng, H.-m. Hwang. (2018). The current application of nanotechnology in food and agriculture. Journal of food and drug analysis.

[24] M.R. Mozafari, J. Flanagan, L. Matia-Merino, A. Awati, A. Omri, Z.E. Suntres, H. Singh. (2006). Recent trends in the lipid-based nanoencapsulation of antioxidants and their role in foods. Journal of the Science of Food and Agriculture. 86(13): 2038-2045.

[25] V. Suganya, V. Anuradha. (2017). Microencapsulation and nanoencapsulation: A review. Int. J. Pharm. Clin. Res. 9(3): 233-239.

[26] H. Cheng, K. Klasson, T. Asakura, Q. Wu In *In Nanotechnology: Delivering on the Promise Vol. 2*, ACS Symposium Series, Am. Chem. Soc, 2016; 2016; pp 233-242.

[27] R. Nair, S.H. Varghese, B.G. Nair, T. Maekawa, Y. Yoshida, D.S. Kumar. (2010). Nanoparticulate material delivery to plants. Plant Science. 179(3): 154-163.

[28] H. Yang, M. Xu, R.T. Koide, Q. Liu, Y. Dai, L. Liu, X. Bian. (2016). Effects of ditch-buried straw return on water percolation, nitrogen leaching and crop yields in a rice–wheat rotation system. Journal of the Science of Food and Agriculture. 96(4): 1141-1149.

[29] V. Ghormade, M.V. Deshpande, K.M. Paknikar. (2011). Perspectives for nano-biotechnology enabled protection and nutrition of plants. Biotechnology advances. 29(6): 792-803.

[30] A. Mihou, A. Michaelakis, F. Krokos, B. Mazomenos, E. Couladouros. (2007). Prolonged slow release of (Z)-11-hexadecenyl acetate employing polyurea microcapsules. Journal of applied entomology. 131(2): 128-133.

[31] A. Roy, S.K. Singh, J. Bajpai, A.K. Bajpai. (2014). Controlled pesticide release from biodegradable polymers. Central European Journal of Chemistry. 12(4): 453-469.

[32] T. Katagi, Photodegradation of pesticides on plant and soil surfaces. In *Reviews of environmental contamination and toxicology*, Springer: 2004; pp 1-78.

[33] R. Šípoš, J. Šima. (2020). Jablonski Diagram Revisited. Revista Cubana de Física. 37(2): 125-130.

[34] C. Chen, H. Ou, R. Liu, D. Ding. (2020). Regulating the photophysical property of organic/polymer optical agents for promoted cancer phototheranostics. Advanced Materials. 32(3): 1806331.

[35] Y. Zhang, B.A. Lorsbach, S. Castetter, W.T. Lambert, J. Kister, N.X. Wang, C.J. Klittich, J. Roth, T.C. Sparks, M.R. Loso. (2018). Physicochemical property guidelines for modern agrochemicals. Pest management science. 74(9): 1979-1991.

[36] N. Saba, M. Jawaid, M. Sultan, Thermal properties of oil palm biomass based composites. In *Lignocellulosic Fibre and Biomass-Based Composite Materials*, Elsevier: 2017; pp 95-122.

[37] O. Publishing. (2008). Environmental performance of agriculture in OECD countries since 1990. Organisation for Economic Co-operation and Development: pp.

[38] M.A. Hanif, F. Nadeem, I.A. Bhatti, H.M. Tauqeer. (2020). Environmental Chemistry: A Comprehensive Approach. Wiley: pp.

[39] N. Khan, A.M. Bano, A. Babar. (2020). Impacts of plant growth promoters and plant growth regulators on rainfed agriculture. PLoS ONE. 15(4): e0231426.

[40] G. Pérez-Lucas, N. Vela, A. El Aatik, S. Navarro, Environmental risk of groundwater pollution by pesticide leaching through the soil profile. In *Pesticides-use and misuse and their impact in the environment*, IntechOpen: 2018.

[41] N. Nga, T. Ngoc, N. Trinh, T. Thuoc, D. Thao. (2020). Optimization and application of MTT assay in determining density of suspension cells. Analytical Biochemistry. 610: 113937.

[42] S. Rekha, E. Anila. (2019). In vitro cytotoxicity studies of surface modified CaS nanoparticles on L929 cell lines using MTT assay. Materials Letters. 236: 637-639.

[43] S. Mourdikoudis, R.M. Pallares, N.T. Thanh. (2018). Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties. Nanoscale. 10(27): 12871-12934.

[44] A. Jabbar, B. Rehman, M. Iqbal, R. Ahmed, S. Mahmood, M.A. Baig. (2020). Elemental Analysis of Plants Cultivated in Saline Soil by Laser-Induced Breakdown Spectroscopy (LIBS). Analytical Letters. 1-15.

[45] Q. Lin, P. Yin, Y. Duan, Y. Wang, L. Zhang, X. Wang. (2020). Quantitative multiple-element simultaneous analysis of seaweed fertilizer by laser-induced breakdown spectroscopy. Optics Express. 28(10): 14198-14208.

[46] S.L. Ferreira, M.A. Bezerra, A.S. Santos, W.N. dos Santos, C.G. Novaes, O.M. de Oliveira, M.L. Oliveira, R.L. Garcia. (2018). Atomic absorption spectrometry–A multi element technique. TrAC Trends in Analytical Chemistry. 100: 1-6.

[47] A. Mohammed, A. Abdullah In *Scanning electron microscopy (SEM): A review*, Proceedings of the 2018 International Conference on Hydraulics and Pneumatics—HERVEX, Băile Govora, Romania, 2018; 2018; pp 7-9.

[48] A. Rajeswari, E.J.S. Christy, S. Gopi, K. Jayaraj, A. Pius, Characterization studies of polymer-based composites related to functionalized filler-matrix interface. In *Interfaces in Particle and Fibre Reinforced Composites*, Elsevier: 2020; pp 219-250.

[49] V. Kuete, O. Karaosmanoğlu, H. Sivas, Anticancer activities of African medicinal spices and vegetables. In *Medicinal Spices and Vegetables from Africa*, Elsevier: 2017; pp 271-297.

[50] S. Sun, X. Zhou, X. Cui, C. Liu, Y. Fan, M.B. McBride, Y. Li, Z. Li, P. Zhuang. (2020). Exogenous plant growth regulators improved phytoextraction efficiency by Amaranths hypochondriacus L. in cadmium contaminated soil. Plant Growth Regulation. 90(1): 29-40.

[51] H.W. Al-Juthery, J.T. Al-Fadhly, E. Ali, R. Al-Taee. (2019). Role of some nanofertilizers and atonikin maximizing for production of Hydroponically-grown barley fodder. International Journal of Agricultural and Statistical. 15(2): 565-570.

[52] B. Kołodziej. (2008). The effect of drip irrigation and Asahi SL application on peppermint yield and quality. Herba Pol. 54(4): 43-50.

[53] M. Naeem, T. Aftab, M. Idrees, M. Singh, A. Ali, M.M.A. Khan, M. Uddin, L. Varshney. (2017). Modulation of physiological activities, active constituents and essential oil production of Mentha arvensis L. by concomitant application of depolymerised carrageenan, triacontanol and 28-homobrassinolide. Journal of EssEntial oil rEsEarch. 29(2): 179-188.

[54] M. Naeem, M. Idrees, T. Aftab, M.M. Alam, M.M.A. Khan, M. Uddin, L. Varshney. (2014). Employing depolymerised sodium alginate, triacontanol and 28-homobrassinolide in enhancing physiological activities, production of essential oil and active components in Mentha arvensis L. Industrial Crops and Products. 55: 272-279.

[55] M. Naeem, M. Idrees, M.M. Alam, T. Aftab, M.M.A. Khan. (2012). Brassinosteroid-mediated enrichment in yield attributes, active constituents

and essential oil production in Mentha arvensis L. Russian agricultural sciences. 38(2): 106-113.

[56] E.S. Da Silva, M. Sarakha, H.D. Burrows, P. Wong-Wah-Chung. (2017). Decatungstate anion as an efficient photocatalytic species for the transformation of the pesticide 2-(1-naphthyl) acetamide in aqueous solution. Journal of Photochemistry and Photobiology A: Chemistry. 334: 61-73.

[57] E.S. Da Silva, H.D. Burrows, P. Wong-Wah-Chung, M. Sarakha. (2014). β-Cyclodextrin as a photostabilizer of the plant growth regulator 2-(1-naphthyl) acetamide in aqueous solution. Journal of Inclusion Phenomena and Macrocyclic Chemistry. 79(3-4): 329-336.

[58] E.S. Da Silva, P. Wong-Wah-Chung, M. Sarakha, H.D. Burrows. (2013). Photophysical characterization of the plant growth regulator 2-(1-naphthyl) acetamide. Journal of Photochemistry and Photobiology A: Chemistry. 265: 29-40.

[59] P. Li, F. Yin, X. Zheng. (2020). Microarray analysis of gene expression profile induced by pre-storage application of oxalic acid in tomato fruit under chilling stress. EUROPEAN JOURNAL OF HORTICULTURAL SCIENCE. 85(4): 232-241.

[60] J. Zheng, S. Li, Y. Xu, X. Zheng. (2019). Effect of oxalic acid on edible quality of bamboo shoots (Phyllostachys prominens) without sheaths during cold storage. Lwt. 109: 194-200.

[61] S. Ehteshami, F. Abdollahi, A. Ramezanian, A.M. Dastjerdi, M. Rahimzadeh. (2019). Enhanced chilling tolerance of pomegranate fruit by edible coatings combined with malic and oxalic acid treatments. Scientia Horticulturae. 250: 388-398.

[62] Y. Tong, L. Shao, X. Li, J. Lu, H. Sun, S. Xiang, Z. Zhang, Y. Wu, X. Wu. (2018). Adhesive and stimulus-responsive polydopamine-coated graphene oxide system for pesticide-loss control. Journal of Agricultural and Food Chemistry. 66(11): 2616-2622.

[63] Y. Fan, R.H. Gao, X. Xiao, Z. Tao. (2018). Inclusion complexes of hymexazol with three different cucurbit [n] uril: preparation, and physicochemical and antifungal characterization. Israel Journal of Chemistry. 58(3-4): 466-471.

[64] Y. Li, Y. Qin, S. Liu, P. Li, R.e. Xing. (2017). Preparation, characterization, and antifungal activity of hymexazol-linked chitosan derivatives. Chinese Journal of Oceanology and Limnology. 35(5): 1079-1085.

[65] M. Zhang, J. Yang, H. Pan, B.J. Pearson. (2020). Dwarfing Effects of Chlormequat Chloride and Uniconazole on Potted Baby Primrose. HortTechnology. 30(5): 536-543.

[66] M. Priti, A. Farooqi. (2009). Response of different cultivars of Japanese mint (Mentha arvensis) under water stress and chloromequat chloride treatment. Journal of Eco-friendly Agriculture. 4(2): 135-138.

[67] P. Mathur, A. Farooqi, S. Sharma. (2005). Ameliorative effect of chlormequat chloride on water stressed cultivars of Japanese Mint (Mentha arvensis). Indian Journal of plant physiology. 10(1): 41.

[68] M.D. Sarkar, M. Moniruzzaman, M.S. ALAM, M.J. Rahman, R.N.R. QUAMRUZZAMAN, S. SUBRAMANIAM. (2019). GROWTH, SEX EXPRESSION AND NUTRIENT COMPOSITION OF CUCUMBER (CUCUMIS SATIVUS) AS INFLUENCED BY MALEIC HYDRAZIDE. Pak. J. Bot. 51(1): 117-123.

[69] N. Hassan, R.A. Laskar, A. Raina, S. Khan. (2018). Maleic hydrazide induced variability in fenugreek (Trigonella foenum-graecum L.) cultivars CO1 and Rmt-1. Res Rev J Bot Sci. 7(1): 19-28.

[70] N. Zeb, M. Sajid, A.M. Khattak, I. Hussain. (2015). Effect of potassium and maleic hydrazide on growth and flower quality of chrysanthemum (Dendranthema grandiflorum). Sarhad Journal of Agriculture. 31(4): 210-216.

[71] M. Nurhazwani, A. Yahya, R. Shairul Izan. (2018). Growth Performance of Ruellia brittoniana as Affected by Daminozide Concentrations. Plant Productivity and Environmental Conservation. 25: 93-97.

[72] A. Arafa. (2017). Seed Yield and Essential Oil Composition of Fennel Plant as Affected by Ethrel and B-9 Application. Journal of Plant Production. 8(7): 755-758.

[73] N.E. El-Keltawi, R. Croteau. (1986). Influence of ethephon and daminozide on growth and essential oil content of peppermint and sage. Phytochemistry. 25(6): 1285-1288.

[74] I. Ahmad, M. Kamran, Z. Guo, X. Meng, S. Ali, P. Zhang, T. Liu, T. Cai, Q. Han. (2020). Effects of uniconazole or ethephon foliar application on culm mechanical strength and lignin metabolism, and their relationship with lodging resistance in winter wheat. Crop and Pasture Science. 71(1): 12-22.

[75] A.A. Farooqi, S. Sharma. (1988). Effect of growth retardants on growth and essential oil content in Japanese mint. Plant Growth Regulation. 7(1): 39-45.

[76] I. Dragićević, R. Konjević, B. Vinterhalter, D. Vinterhalter, M. Nešković. (2008). The effects of IAA and tetcyclacis on tuberization in potato (Solanum tuberosum L.) shoot cultures in vitro. Plant Growth Regulation. 54(3): 189-193.

[77] C. Cerdon, A. Rahier, M. Taton, Y. Sauvaire. (1995). Effects of tetcyclacis on growth and on sterol and sapogenin content in fenugreek. Journal of Plant Growth Regulation. 14(1): 15-22.

[78] A. Upadhyaya, T.D. Davis, N. Sankhla. (1991). Heat shock tolerance and antioxidant activity in moth bean seedlings treated with tetcyclacis. Plant Growth Regulation. 10(3): 215-222.

[79] A. Valderrama, J. Lay, Y. Flores, D. Zavaleta, A.R. Delfín. (2020). Factorial design for preparing chitosan nanoparticles and its use for loading and controlled release of indole-3-acetic acid with effect on hydroponic lettuce crops. Biocatalysis and Agricultural Biotechnology. 101640.

[80] A.d.E. Santo Pereira, H.C. Oliveira, L.F. Fraceto. (2019). Polymeric nanoparticles as an alternative for application of gibberellic acid in sustainable agriculture: a field study. Scientific reports. 9(1): 1-10.

[81] R. Abazari, G. Salehi, A.R. Mahjoub. (2018). Ultrasound-assisted preparation of a nanostructured zinc (II) amine pillar metal-organic framework as a potential sorbent for 2, 4-dichlorophenol adsorption from aqueous solution. Ultrasonics sonochemistry. 46: 59-67.

[82] M. Li, M.A. Tshabalala, G. Buschle-Diller. (2016). Formulation and characterization of polysaccharide beads for controlled release of plant growth regulators. Journal of Materials Science. 51(9): 4609-4617.

[83] M. Ao, Y. Zhu, S. He, D. Li, P. Li, J. Li, Y. Cao. (2012). Preparation and characterization of 1-naphthylacetic acid–silica conjugated nanospheres for enhancement of controlled-release performance. Nanotechnology. 24(3): 035601.

[84] L.A. Nnamonu, R. Sha'Ato, I. Onyido. (2012). Alginate reinforced chitosan and starch beads in slow release formulation of imazaquin herbicide—preparation and characterization.

[85] F.A. Lobo, C.L. de Aguirre, M.S. Silva, R. Grillo, N.F.S. de Melo, L.K. de Oliveira, L.C. de Morais, V. Campos, A.H. Rosa, L.F. Fraceto. (2011). Poly (hydroxybutyrate-co-hydroxyvalerate) microspheres loaded with atrazine herbicide: screening of conditions for preparation, physico-chemical characterization, and in vitro release studies. Polymer bulletin. 67(3): 479-495.

[86] F. Liu, L.-X. Wen, Z.-Z. Li, W. Yu, H.-Y. Sun, J.-F. Chen. (2006). Porous hollow silica nanoparticles as controlled delivery system for water-soluble pesticide. Materials research bulletin. 41(12): 2268-2275.

[87] A. Pajares, M. Bregliani, W. Massad, J. Natera, C. Challier, L. Boiero, M. Montenegro, N.A. García. (2014). On the natural fate of maleic hydrazide. Kinetic aspects of the photochemical and microbiological degradation of the herbicide. Journal of Photochemistry and Photobiology B: Biology. 135: 48-54.

[88] E.S. Da Silva, P. Wong-Wah-Chung, H.D. Burrows, M. Sarakha. (2013). Photochemical Degradation of the Plant Growth Regulator 2-(1-Naphthyl) acetamide in Aqueous Solution Upon UV Irradiation. Photochemistry and photobiology. 89(3): 560-570.

[89] D. Sarr, A. Coly, S.E. Douabalé, A. Tine, S. Traoré, N. Diallo. (2003). Photodegradation kinetics of some indolecarboxylic acids and their regulation effects on plant growth (groundnut and haricot bean). Talanta. 60(2-3): 571-579.

[90] Y. Shan, L. Cao, B. Muhammad, B. Xu, P. Zhao, C. Cao, Q. Huang. (2020). Iron-based porous metal–organic frameworks with crop nutritional function as carriers for controlled fungicide release. Journal of Colloid and Interface Science. 566: 383-393.

[91] A.B. Nörnberg, V.R. Gehrke, H.P. Mota, E.R. Camargo, A.R. Fajardo. (2019). Alginate-cellulose biopolymeric beads as efficient vehicles for encapsulation and slow-release of herbicide. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 583: 123970.

[92] S.W. Phang, L.T. Sin, S.-T. Bee, J.Y. Low, T.-T. Tee. (2018). Release behaviour study on controlled-release phosphorous fertilizer encapsulated by starch-alginate superabsorbent composite. J. Eng. Sci. Technol. 13: 82-94.

[93] C. Jerard, B.P. Michael, S. Chenicheri, N. Vijayakumar, R. Ramachandran. (2019). Rosmarinic Acid-Rich Fraction from Mentha arvensis Synchronizes Bcl/Bax Expression and Induces Go/G1 Arrest in Hepatocarcinoma Cells. Proceedings of the National Academy of Sciences, India Section B: Biological Sciences. 1-8.

[94] S.K. Bardaweel, B. Bakchiche, H.A. Alsalamat, M. Rezzoug, A. Gherib, G. Flamini. (2018). Chemical composition, antioxidant, antimicrobial and Antiproliferative activities of essential oil of Mentha spicata L. (Lamiaceae) from Algerian Saharan atlas. BMC Complementary and Alternative Medicine. 18(1): 201.

[95] S.K. Bardaweel, K.A. Tawaha, M.M. Hudaib. (2014). Antioxidant, antimicrobial and antiproliferative activities of Anthemis palestina essential oil. BMC Complementary and Alternative Medicine. 14(1): 297.

[96] P.P. Banerjee, A. Bandyopadhyay, S.N. Harsha, R.S. Policegoudra, S. Bhattacharya, N. Karak, A. Chattopadhyay. (2017). Mentha arvensis (Linn.)-

mediated green silver nanoparticles trigger caspase 9-dependent cell death in MCF7 and MDA-MB-231 cells. Breast Cancer: Targets and Therapy. 9: 265.

[97] M. Wang, Y. Han, F. Qiao, H. Yan. (2020). Improved Solid-Phase Extraction for Simple, Sensitive, and Efficient Determination of Trace Plant Growth Regulators in Cherry Tomatoes by High-Performance Liquid Chromatography. Journal of Agricultural and Food Chemistry. 68(31): 8447-8454.

[98] C. Wang, C. Ding, Q. Wu, X. Xiong. (2019). Molecularly Imprinted Polymers with Dual Template and Bifunctional Monomers for Selective and Simultaneous Solid-Phase Extraction and Gas Chromatographic Determination of Four Plant Growth Regulators in Plant-Derived Tissues and Foods. Food Analytical Methods. 12(5): 1160-1169.

[99] J. Chen, S. Cao, M. Zhu, C. Xi, L. Zhang, X. Li, G. Wang, Y. Zhou, Z. Chen. (2018). Fabrication of a high selectivity magnetic solid phase extraction adsorbent based on β-cyclodextrin and application for recognition of plant growth regulators. Journal of Chromatography A. 1547: 1-13.

[100] W. Sha, J. Li, W. Xiao, P. Ling, C. Lu. (2019). Quantitative analysis of elements in fertilizer using laser-induced breakdown spectroscopy coupled with support vector regression Model. Sensors. 19(15): 3277.

[101] C.P. de Morais, A.I. Barros, M.A. Bechlin, T.V. Silva, D.S. Júnior, G.S. Senesi, M.S. Crespi, C.A. Ribeiro, J.A. Gomes Neto, E.C. Ferreira. (2018). Laser-induced breakdown spectroscopy determination of K in biochar-based fertilizers in the presence of easily ionizable element. Talanta. 188: 199-202.

[102] D.C.C. da Silva Medeiros, F. Piechontcoski, E.R.L. da Rocha Watanabe, E.S. Chaves, S.D. Inglez. (2020). Fast and effective simultaneous determination of metals in soil samples by ultrasound-assisted extraction and flame atomic absorption spectrometry: assessment of trace elements contamination in agricultural and native forest soils from Paraná-Brazil. Environmental Monitoring and Assessment. 192(2): 111.

[103] F.d.S. Dias, M.E.P. Guarino, A.L.C. Pereira, P.P. Pedra, M.d.A. Bezerra, S.G. Marchetti. (2019). Optimization of magnetic solid phase microextraction with CoFe2O4 nanoparticles unmodified for preconcentration of cadmium in environmental samples by flame atomic absorption spectrometry. Microchemical Journal. 146: 1095-1101.

[104] L.S. Teixeira, H.P. Vieira, C.C. Windmöller, C.C. Nascentes. (2014). Fast determination of trace elements in organic fertilizers using a cup-horn reactor for ultrasound-assisted extraction and fast sequential flame atomic absorption spectrometry. Talanta. 119: 232-239.

[105] K. Vlahoviček-Kahlina, S. Jurić, M. Marijan, B. Mutaliyeva, S. Khalus, A. Prosyanik, M. Vincekovic. (2020). Synthesis, Characterization and Encapsulation of Novel Plant Growth Regulators (PGRs) in Biopolymer Matrices.

[106] M.E.A. Abigail. (2019). Biochar-based nanocarriers: fabrication, characterization, and application as 2, 4-dichlorophenoxyacetic acid nanoformulation for sustained release. 3 Biotech. 9(8): 317.

[107] N. Venugopal, N. Sainadh. (2018). Synthesis and characterization of Nano-tricyclazole-A systemic fungicide. Materials Today: Proceedings. 5(8): 16807-16813.

[108] G.-B. Li, J. Wang, X.-P. Kong. (2020). Coprecipitation-based synchronous pesticide encapsulation with chitosan for controlled spinosad release. Carbohydrate polymers. 249: 116865.

[109] A. Lateef, R. Nazir, N. Jamil, S. Alam, R. Shah, M.N. Khan, M. Saleem. (2019). Synthesis and characterization of environmental friendly corncob biochar based nano-composite–A potential slow release nano-fertilizer for sustainable agriculture. Environmental Nanotechnology, Monitoring & Management. 11: 100212.

[110] J. Pérez Quiñones, O. Brüggemann, J. Kjems, M.H. Shahavi, C. Peniche Covas. (2018). Novel brassinosteroid-modified polyethylene glycol micelles for controlled release of agrochemicals. Journal of Agricultural and Food Chemistry. 66(7): 1612-1619.

[111] Q. Zhang, G. Yu, Q. Zhou, J. Li, Y. Feng, L. Wang, Y. Tang, Y. Peng. (2020). Eco-friendly interpenetrating network hydrogels integrated with natural soil colloid as a green and sustainable modifier for slow release of agrochemicals. Journal of Cleaner Production. 122060.

[112] A. Sharma, K. Sood, J. Kaur, M. Khatri. (2019). Agrochemical loaded biocompatible chitosan nanoparticles for insect pest management. Biocatalysis and Agricultural Biotechnology. 18: 101079.

[113] A. Olad, H. Zebhi, D. Salari, A. Mirmohseni, A.R. Tabar. (2018). Slow-release NPK fertilizer encapsulated by carboxymethyl cellulose-based nanocomposite with the function of water retention in soil. Materials Science and Engineering: C. 90: 333-340.