GREEN SYNTHESIS OF PHOTOCATALYTIC NITROGEN NANOPARTICLES AND ITS APPLICATION ON PADDY: A REVIEW

CHITTIMOTHU SURESH BABU

Faculty, Dept of Agronomy,

Bharatiya Engineering Science & Technology Innovation University, Andhra Pradesh, India.

Abstract:
Green synthesis of nitrogen nanoparticles. Catalysis is a phenomenon where a reaction is taken through an alternative pathway involving lesser energy. Thus, it has an energy saving dimension implicit in its definition. This thesis involves the study of catalysts, synthesized by the solution combustion method. The fuel required for the newline combustion is aqueous extract obtained from the leaves of selected plants which gives added credence to the ecofriendly aspirations that dominated our work. A series of ceria based nano sized catalyst materials, pure and modified using rare earth metal oxides, transition metal oxides and a non-metallic substance have been synthesized by the above method. The catalysts have then been newline characterized for their composition, crystallinity, morphology, surface properties, thermal stability etc. The prepared catalysts were subsequently evaluated for their catalytic and photocatalytic efficacy. The photocatalytic potential of the catalysts was evaluated on the degradation studies of two dyes Malachite Green (MG) and Congo Red (CR) under visible light and one antibiotic drug ciprofloxacin (CIP) under UV light. The catalysts were found to show good photocatalytic efficiency all the three substances mentioned above. The catalytic efficiency was evaluated on two chemical reactions. One, the reduction of 4- nitrophenol to 4-aminophenol and the other, the synthesis of compounds of Biginelli reaction. To achieve maximum reduction the experimental conditions for the catalyst were optimized. Biginelli reaction involves the condensation of ethyl acetoacetate, benzaldehyde and urea in presence of modified ceria catalysts to form dihydropyrimidines. The reaction was performed with different catalysts and the one which gave the best yield was selected for further optimization of other reaction conditions. Employing the optimized conditions, a set of different dihydropyrimidinone derivatives were synthesized by varying the precursor aldehydes and ketones. the study conducted on Green synthesis of nitrogen nanoparticles and its application on paddy.

Keywords: Green synthesis, nitrogen, nanoparticles, paddy

Introduction

The process of green synthesis of nitrogen, catalysis also affects the state of our global environment. Automobiles use catalytic converters to treat exhaust. The metals platinum and palladium facilitate the chemical conversion of noxious gases to more inert forms, greatly decreasing the environmental impact of combustion engines. Probably the most important impact of catalyst is on life itself. All the important biochemical reactions are catalyzed by molecules called enzymes. Most enzymes are proteins which catalyze specific reactions within cells. Some examples include polymerases, which synthesize DNA and RNA, peptidases, which digest protein, and ATP synthases, which produce energy for the many different cell activities. While catalysts can be broadly classified into homogeneous and heterogeneous catalysts, heterogeneous catalysts possess distinct advantages over their homogeneous counterparts. Heterogeneous catalysis refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. A good number of heterogeneous catalysts are metals and metal oxides in their pure form as well as in combined forms. A wide range of methods are available for synthesizing catalyst systems. These methods differ in the time of preparation, cost and eco-friendliness. A systematic study on the various preparative techniques will throw light on the relative merits of the different methods of catalyst preparation. **Nanoparticles**

Nanoparticles are ultrafine particles that exist on the nanometer scale. One nanometer is one-billionth of a meter. Nanoparticles have mechanical, optical and chemical properties that are markedly different from the bulk counterparts that make them exciting materials to work with. Nanotechnology has become one of the most exciting fields of research in the last few decades. The importance of nanoparticles became apparent when it was realized that the physical and chemical properties change considerably when particles assume a size in the nano dimensions as compared to the bulk. Nanoparticles are composed of three layers. The outer layer is usually made up of small molecules, metal ions, surfactants or polymers. This layer could be functionalized. The second layer is called the shell layer and is different from the core layer in many respects. The innermost layer is called the core layer and makes up the central portion of the nanoparticle. Nanoparticles can be classified as carbon-based nanoparticles, metal nanoparticles, ceramic, semiconductor, polymeric and lipid based. While various methods are available for the synthesis of nanoparticles, all these methods can be broadly categorized into two methods. The two broad approaches to the synthesis of nanoparticles are, a) Top-down approach and b) Bottom-up approach. However, based on the method of operation, reaction conditions and protocols adopted, several methods of synthesizing nanoparticles are available within the two broad domains mentioned above. Solution combustion, sol- gel, hydrothermal synthesis and precipitation method are all the names of the various synthetic methods available 4 by which metal oxide nanoparticles can be synthesized, all of which are in the domain of bottom-up approach. Due to their versatile properties, scientists from various domains have been attracted to this field of nanomaterial research. As a result, nanomaterials find applications in a variety of fields like a) drugs and medications, b) environment and pollution abatement c) catalysis d) manufacturing and materials e) electronics f) energy harvesting g) mechanical industries etc. As catalysts, nanomaterials have proven to be versatile and often more efficient than their bulk counterparts. The physical aspects of nanoparticles like, size, agglomeration type, surface properties and coating etc. are the aspects that determine the efficiency of the catalyst at the nano dimensions.

Plant as nanofertilizers

With an increasing emphasis on green and sustainable processes being the order of the day, it is important for us to look at synthetic routes that are ecofriendly and yet economical. The secondary impacts on the preparative/ manufacturing processes on human health and the environment at large must be investigated. Some synthetic methods in the bottom-up protocol use toxic substances, while some of them produce harmful substances during synthesis. On the other hand, top-down methods involve the usage of a large amount of energy. Of late researchers have been experimenting with a variety of green reducing agents for synthesizing catalysts. These materials are biocompatible, nontoxic, ecofriendly and yet economical. Plant materials have been used with good results to synthesize catalysts. Though the exact mechanism by which these materials work or the influence that the different components that make up the plant material exert is not yet clear, it is speculated that the presence of various substances like amino acids, phenolics, sugars etc. act as reducing agents in the synthesis.

Review of Literature

A. A. Hassan, 1Dina M. Salama (2019) Green Synthesis of Nanofertilizers and Their Application as a Foliar for Cucurbita pepo L. The implementation of nanofertilizers in agriculture is the purpose in specific to decrease mineral losses in fertilizing and raises the yield during mineral management as well as supporting agriculture development. Hence, this experiment was conducted in Shebin El-Kom, El-Monifia governorate, Egypt, during two seasons 2017 and 2018 to study the effect of micronutrient oxide nanoparticles of zinc, iron, and manganese, as well as combination between these oxides as a foliar application on the growth, yield, and quality of squash plants. The obtained results showed that the spraying of manganese oxide nanoparticles on the plants led to the best vegetative growth characteristics, also, the characteristics of the fruits, yield, and the content of photosynthetic pigments. On the contrary, the content of organic matter, protein, lipids, and energy gave the highest value in squash fruits that have been sprayed with iron oxide nanoparticles.

Howra Bahrulolum1†, Saghi Nooraei1 (2021) Green synthesis of metal nanoparticles using microorganisms and their application in the agrifood sector. The agricultural sector is currently facing many global challenges such as climate change, and environmental problems such as the release of pesticides and fertilizers, which will be exacerbated in the face of population growth and food shortages. Therefore, the need to change traditional farming methods and replace them with new technologies is essential, and the application of nanotechnology, especially green technology is considerable promise in alleviating these problems. Nanotechnology has led to changes and advances in many technologies and has the potential to transform various felds of the agricultural sector, including biosensors, pesticides, fertilizers, food packaging and other areas of the agricultural industry. Due to their unique properties, nanomaterials are considered as suitable carriers for stabilizing fertilizers and pesticides, as well as facilitating controlled nutrient transfer and increasing crop protection. The production of nanoparticles by physical and chemical methods requires the use of hazardous materials, advanced equipment, and has a negative impact on the environment. Thus, over the last decade, research activities in the context of nanotechnology have shifted towards environmentally friendly and economically viable ‘green’ synthesis to support the increasing use of nanoparticles in various industries. Green synthesis as part of bioinspired protocols, provides reliable and sustainable methods for the biosynthesis of nanoparticles by a wide range of microorganisms rather than current synthetic processes. Therefore, this feld is developing rapidly and new methods in this feld are constantly being invented to improve the properties of nanoparticles. In this review, we consider the latest advances and innovations in the production of metal nanoparticles using green synthesis by diferent groups of microorganisms and the application of these nanoparticles in various agricultural sectors to achieve food security, improve crop production and reduce the use of pesticides. In addition, the mechanism of synthesis of metal nanoparticles by diferent microorganisms and their advantages and disadvantages compared to other common methods are presented.

Metal oxides as homogeneous catalysts

Metals and their oxides play a significant role in heterogeneous catalysis. Metal oxides are an important class of inorganic materials that possess unique and characteristic properties that find varied applications such as sensors, fuel cells and catalysis. They make up an important class of heterogeneous catalysts where they are prepared from their nitrates, hydroxides or carbonates through calcination. The main characteristics of metal oxides that make them so important in catalysis are their oxidation state, redox properties and the coordination environment of the atoms at the surface. Metal oxides possess both electron transfer properties as well as surface polarizing abilities. These properties enable oxides of metals to be good catalysts in both redox as well as acid-base catalytic environments. The redox properties of metal oxides are crucial in enabling them to oxidize toxic materials, degrading dyes as well as other environmentally significant reactions. Due to the larger size of the oxide anions, the surfaces of metal oxides usually terminate with the oxide anions exposed. This leads to a loss of symmetry and coordination in the metal cations. This factor along with the presence of defects on the surface of metal oxides plays an important role in determining the catalytic efficacy of metal oxide catalysts. Metal oxide catalysts have been popular since the 1950s when they were found to catalyze many important oxidation and acid-base reactions. Metal oxide catalysts find applications in petrochemical, pharmaceutical and fine chemical industries. The applications of metal oxide catalysts span a wide spectrum of areas like photocatalysis, pollution abatement, selective and total oxidation etc.,

Need of the study

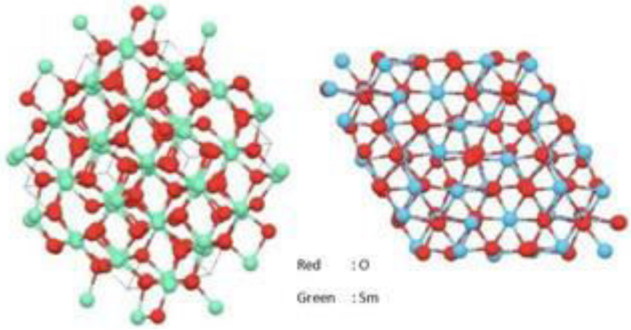
Even though ceria is one of the most studied rare earth metal oxide for its heterogeneous catalytic applications, the number of studies on synthesizing ceria nanoparticles using green protocol is limited. Moreover, the modified ceria nanoparticles synthesized by the phytogenic method have not been studied for degradation of dyes, ciprofloxacin drug or 4-nitrophenol. All the above-mentioned studies are significant from the environmental point of view. The degradation studies and synthetic applications have not been done using the supported ceria catalysts proposed to be synthesized. The conditions required for maximum degradation must be explored using Box Behnken Design of the RSM. This tool optimizes the conditions for utilizing chemicals and energy to obtain the best results in the studies we have conducted. Thus, RSM will shed light on the most efficient conditions for the different reactions to be studied.

Metal oxides

Rare earth metal oxides are a group of compounds that have closely related properties and show a variety of typical behavior. Their properties differ from those of transition metals as their 4f orbitals are shielded by 4d, 5s and 5p electrons. This aspect imparts unique properties to the rare earth elements. Most of them are paramagnetic, strongly basic and show refractory properties with melting points above 2000 C. Rare earth metal oxides have been finding several applications in recent years, notably in the field of catalysis. Materials obtained from rare earth elements find a place in daily applications starting from cosmetics to particle accelerators. In the field of catalysis, rare earth oxides are recognized for their selectivity and catalytic efficacy. Most notable among them is their application in converting methane into higher hydrocarbons through oxidative coupling. This process has enabled the utilization of the vast reserves of natural gas. As mentioned earlier, most rare earth metal oxides have refractory properties and this makes them excellent support materials for other catalysts. Unsurprisingly, we encounter several instances where they function as catalytic support for many catalysts

Cerium Oxide

Cerium is the first member of the lanthanide series. It is also the most abundant of the rare earth elements and is found to the extent of 0.0046 % by weight on the earth's crust. In recent years cerium and its oxides have received a lot of attention for a variety of applications. This is indicated by the large number of publications in scientific journals that appear on ceria. Cerium is a rather unique lanthanide by showing a variable electronic structure. While other lanthanide elements are most stable in the trivalent state, cerium in its +4 state is the most stable. This particular property enables the easy separation of cerium from other rare earth elements. However, cerium does exist in the +3- oxidation state as well and very small energy separates these two states. Thus, cerium exists in two oxidation states, +3 and +4 and it not uncommon for cerium to switch between the two oxidation states. Ceria (CeO_2), the most stable oxide of cerium offers a lot of scope for application in the field of catalysis. Ceria a pale-yellow solid exists in the fluorite structure (CaF_2). It has a face-centered cubic structure (FCC) with a space group Fm3m as shown in Figure 1.2, throughout the entire temperature range from room temperature to the melting point. Each cerium cation is found coordinated to equivalent oxygen anions at the corner of a cube and each anion is tetrahedrally coordinated by four cations. While ceria possesses special and unique properties that make it attractive as a catalyst, its properties can be significantly improved by combining it with other materials, metallic and nonmetallic. Ceria is a very good support material, it prevents sintering at high temperatures and stabilizes the dispersed state. Modification of Cerium oxide: Samarium belongs to the lanthanide series of elements. Samarium oxides possess high thermal stability and are used in glass, solar cell, nanoelectronics, resistance- based gas sensors, capacitors, semiconductor applications etc. While the oxides of lanthanide series elements are relatively less explored for their catalytic properties, it is especially so for Samaria. Samarium oxide (Sm_2O_3) is a high dielectric oxide with a density of 8.43 gcm^{-3}. Crystal structure of Sm_2O_3 is given. It is a refractory ceramic which is used for temperature control and shielding in nuclear piles. It also finds other applications like capacitors and sensors due to its high permittivity. The element samarium is quite abundant and has some unique applications. It is a good reducing agent for single electron transfer reactions. Samarium oxide catalysts have been used in the oxidation of alkanes. However not much has been explored with respect to the nano particles of samarium oxideApparently, the photogenerated holes in Ag_2O have a strong oxidation power to oxidize the lattice O^{2-} in Ag_2O. It is expected that if the photogenerated holes in Ag_2O can transfer to other electron donors (such as organic substances) before oxidizing the lattice O^{2-} and the photogenerated electrons are captured by O_2 before reducing lattice Ag^+, it is possible to keep the stability of Ag-O-Ag in Ag_2O under light irradiation. The photo decomposition process of Ag_2O can be balanced by the relative instability of AgO and the binding energy of each Ag cluster relative to the excitation energy. This indicates that Ag_2O has a great potential to be used as a stable and highly efficient photocatalyst for decomposition of organic contaminants under visible-light irradiation. Green synthesis of nanoparticles: With an increasing emphasis on green and sustainable processes being the order of the day, it is important for us to look at synthetic routes that are ecofriendly and yet economical. The secondary impacts on the preparative/ manufacturing processes on human health and the environment at large must be investigated. Some synthetic methods in the bottom-up protocol use toxic substances, while some of them produce harmful substances during synthesis. On the other hand, top- down methods involve the usage of a large amount of energy. Of late researchers have been experimenting with a variety of green reducing agents for synthesizing catalysts. These materials are biocompatible, nontoxic, ecofriendly and yet economical. Plant materials have been used with good results to synthesize catalysts. Though the exact mechanism by which these materials work or the influence that the different components that make up the plant material exert is not yet clear, it is speculated that the presence of various substances like amino acids, phenolics, sugars etc. act as reducing agents in the synthesis. Schematic representation of the green synthesis of nanoparticles Solution combustion synthesis (SCS) is a process wherein an oxidizer, typically a nitrate and a fuel are dissolved in distilled water and placed in a preheated muffle furnace at temperatures around 500 °C, a schematic representation of the processes done in the solution combustion synthesis is



given in Figure 1.9. The water solution boils, foams and subsequently burns with a glowing flame with temperatures reaching up to 1350 □C. Typically this process yields a fluffy and voluminous solid along with the liberation of large amount of gases. SCS is a self- sustained process and the heat source comes from the reactions taking place during combustion. SCS may be considered as a specific type in a more general process called self-propagating high-temperature synthesis (SHS). However, SCS differs from other forms of combustion synthesis in the following three aspects. Firstly, the initial components of SCS are mixed in aqueous solution at the molecular level, SHS uses powders and are mixed

at the microlevel. Secondly, in the SCS. the product formation reaction can be different compared to the heat generation step. For example, heat is generated by the burning or oxidation of the organic fuel components while the products formed are mainly metal oxides. In the SHS, the synthesis and the heat generation reactions are one and the same. Thirdly the SCS process generates a large volume of gaseous byproducts which lead to a significant expansion of the solid product with a decrease of temperature after the reaction. These make the solid product porous and finely dispersed. The last-mentioned factor is 13 significant in the synthesis of nanoscale powders. In summary we can say that SCS is a complex self-sustained chemical process taking place in a homogeneous solution of precursors. SCS begins with several thermally coupled exothermic reactions involving dehydration and thermal decomposition of the homogeneous solution which culminates in the formation of at least one solid product and a large volume of gases. This is a versatile method that can be used to synthesize a large number of nanoscale materials including oxides, metals, alloys etc. that find several applications. A mere preparation of new catalyst or employing a different technique does not make it a novel catalyst. The true challenge would be in employing environmentally benign processes, to study the different ways of preparing catalyst supports, exploring ways to add active sites to the existing catalyst, immobilizing a pre-formed active site, adding a precatalyst and synthesizing a new site on the surface.

Application Based Materials

Ever since scientists at Ford Motor Company reported the unique capability of ceria to store and release oxygen back in 1976, ceria has attracted a lot of attention and CeO2 has found extensive use in automotive exhaust catalysis. The ability of ceria to reduce carbon monoxide and nitric oxide is still unsurpassed. Further, ceria finds applications in diverse fields like medicine, biotechnology/environmental chemistry, solid oxide fuel cells, solar cells, photocatalysis, sensors and in oxygen pumps apart from finding minor applications like sunscreen lotions and polishing agents Photocatalysis the solar energy we receive from the sun is limitless, clean and renewable. The amount of energy available is more than all the energy we need. The challenge, however, is in storing and converting it to a usable form. With the amount of natural energy resources running out and with increasing environmental concerns, it is imperative to tap into the boundless energy that is streaming down from the sun. Photocatalysis offers such an opportunity. Photocatalysis has been successfully used to produce energy as well as for pollution abatement. Semiconductor photocatalysis using metal oxide is a process where light is absorbed by the catalyst resulting in the formation of electrons and holes which can then be conveyed to other chemical species at the surface of the photocatalyst. The electron can be transferred to an acceptor if the redox potential of a molecule is lesser than the conduction band of the photocatalyst whereas the hole can be transferred to the molecule if its redox potential is greater than the valence band of the photocatalyst. Several metal oxides have been used as semiconductor photocatalysts, even though TiO2 and ZnO continue to be the most studied. Photocatalysts are generally non-selective but their properties can be tuned by doping, mixing to form composites etc. Semiconductors (e.g., TiO2, ZnO, Fe2O3, CdS, and ZnS) can act as sensitizers for light-induced redox processes due to their electronic structure which is characterized by a filled valence band and an empty conduction band. When a photon with an energy of h matches or exceeds the bandgap energy (Eg), of the semiconductor, an electron, e-, is promoted from the valence band (VB) into the conduction band (CB), leaving a hole (h

+) behind. Excited-state conduction-band electrons and valence-band holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbe

on the semiconductor surface or within the surrounding electrical double layer of the charged particles. In the absence of suitable electron and hole scavengers, the stored energy gets dissipated very fast. Today, considering the large number of industries we have, the problem of pollutants is grave. Dealing with these pollutants is a big challenge. While many physical, chemical, biological and electrochemical methods are available to cope with these pollutants, photocatalysis is a very attractive proposition for its ability to operate under ambient conditions, simplicity and cost-effectiveness. Photocatalysis offers a convenient and ecofriendly way of dealing with these 15 pollutants. Photocatalysis enables the decomposition of the harmful pollutants into smaller fragments through a process of oxidation- reduction. The fragments are usually water and carbon dioxide, though, at times, other less harmful products are also produced. Many industries like textile, paper, leather, polymer and pharmaceutical industries make use of a large number of dyes and these find their way into the wastewater generated from these industries. These dyes are generally non-biodegradable, toxic and some are even carcinogenic. Photocatalysis might remediate this problem of dyes in wastewater.

Dyes are persistent industrial pollutants. Most of these dyes are mostly organic in nature. Many of them are toxic, non- biodegradable and some are even carcinogenic. They are used in a number of industries like textile, paper, leather, food, cosmetic and polymer industries. These dye substances ultimately reach the water bodies and unsurprisingly they are found in dangerous levels in surface and underground water systems. It is very important to remove these from the environment without leaving any harmful residues. While degrading and detoxifying dyes, care should be taken to incorporate eco-friendly methods. Several methods have been used to degrade dyes. Methods, both physical and chemical, have been employed in the last few decades and these include the usage of penetrating radiations like gamma radiations, coagulation–flocculation, oxidation and electrochemical methods. While Titania and ZnO systems have been extensively used as photocatalysts, ceria and modified ceria have some distinct advantages as a photocatalyst. The unique oxygen storage capacity and desirable band edge positions have enabled ceria to be used to remediate several harmful dyes. Ceria and its modified forms have been used in degrading dyes like Sudan red, Congo red, Malachite green, Rhodamine B, Methylene blue, Tryphan blue etc.,

Degradation of Ciprofloxacin Drug The presence of antibiotic residues in wastewater is becoming a major environmental problem. Ciprofloxacin and tetracycline are the main culprits. Antibiotics are being used extensively for human and livestock use. These antibiotics do not get metabolized completely and get excreted mostly in their pharmacologically active forms. These pollutants find their way into the domestic wastewater and from there onto water bodies where they cause considerable damage to the environment. All around the world, water bodies and wastewater treatment plants are found to have an alarming level of antibiotic residue in them. Many methods, physical, chemical and biological have been tried out to remediate the problem due to antibiotics. Of all the methods mentioned above, semiconductor-based photocatalysis promises to be an attractive option. This method uses only solar light and therefore is not expensive. Thus, this method is at once efficient, eco-friendly and economical. Fluoroquinolone antibiotics are one of the most extensively used with limited side effects. Ciprofloxacin (CIP) is one such antibiotic belonging to the fluoroquinolone (FQ) family. CIP is found in relatively high concentrations in municipal and domestic wastewaters. FQs possess a stable quinolone ring and this makes the compound quite stable and therefore, is resistant to high temperatures and hydrolysis. Advanced oxidation processes, sorption on soil and sedimentation are other viable processes that could remove FQs from the environment. But these methods, however, involve usage of chemicals for treatment and therefore may not be eco- friendly. FQs possess functional chromophore groups that are capable of absorbing solar radiation. Therefore, degradation of FQs using UV light in the presence of a suitable photocatalyst is potentially a convenient, economical and eco-friendly way to remove them from the environment, notably from water bodies. Reduction of 4- Nitrophenol 4-nitrophenol (4-NP) is an important chemical used extensively as a precursor in the manufacture of pesticides, explosives, pharmaceuticals and synthetic dyes. The highly soluble and stable nature of 4-NP causes it to accumulate in soil and groundwater for a very long time, posing an environmental hazard. 4-NP is also resistant to chemical and biological oxidation due to the strong electron-withdrawing effect of the nitro group ($-NO_2$) on the aromatic ring, thereby enhancing its stability. The use of nanomaterials as a catalyst is a viable method for hydrogenating reduction of 4-NP to 4-aminophenol (4-AP) by $NaBH_4$ and thereby to remove 4-NP from the environment. In contrast to 4-NP, its reduced product, 4-AP has lower toxicity and is used in pharmaceutical industries for the manufacture of analgesic, antipyretic and other drugs. Biginelli Reaction Biginelli reaction was discovered in 1891 by the Italian chemist P. Biginelli. It is a multicomponent reaction that yields 3,4- dihydropyrimidones from aldehydes, urea and β-keto esters in a one-pot operation. The reaction is promoted by Brønsted and Lewis acids, organocatalysts, ionic liquids or microwave heating and generally works well with non- enolizable aromatic and heteroaromatic aldehydes. Conversely, Biginelli reactions with aliphatic aldehydes are more challenging with lower yields due to side reactions of the aldehydes. Dihydropyrimidine derivatives show many medicinal properties such as calcium channel blocking, antiviral and antibacterial activities and are an effective scaffold for subsequent additions. In 1893, Petro Biginelli reported the first synthesis of 3,4-dihydropyrimidin-2(1H)- one (DHPM) of type 4 by a very simple one-pot condensation reaction of an aromatic aldehyde, β-ketoesters and urea under strongly acidic conditions. However, this protocol often provides only low to 18 moderate yields of the desired target molecules. In recent years, interest in these compounds has increased rapidly, mainly due to the apparent structural similarity of DHPMs to the well-known dihydropyridine calcium channel modulators of the Hantzsh type. Several alkaloids containing the dihydropyrimidine core unit, exhibiting interesting biological properties, have been isolated from marine sources. Among these, the combine and batzelladine alkaloids were found to be potent HIVgp-120-CD4 inhibitors. The scope of this pharmacophore has been increased further by the identification of the 4-(3- hydroxyphenyl)-2-thione derivative (±)-4i called monastol as a novel cell-permeable lead molecule for the development of anticancer drugs. Due to the importance of the Biginelli reaction products, much work on improving the yields and reaction conditions has been actively pursued.

Response surface methodology (RSM) is a kind of effective method to optimize process conditions and it can determine the influence of various factors and their interactions on the indexes under investigation (response value) during an experimental operation. It can be used to fit a complete quadratic polynomial model through central composite experiment and present a more excellent experiment design and result expression. Response surface methodology (RSM) is a collection of mathematical and statistical techniques for empirical model building. By careful design of experiments, the objective is to optimize a response (output variable) which is influenced by several independent variables (input variables). An experiment is a series of tests, called runs, in which changes are made in the input variables in order to identify the reasons for changes in the output response. Generally, the structure of the relationship between the response and the independent variables is unknown. The relationship between the response and the factors that affect the response yields the surface. Regression models are used for the analysis of the response, as the focus now is on the nature of the relationship between the response and the factors rather than identification of the important factors. The first step in RSM is to find a suitable
19 approximation to the true relationship. The most common forms are low-order polynomials (first or second- order). While using RSM for the studies, it is vital that we choose the right design of experiment (DOE). In simple terms, DOE is the experimental points where the response should be determined. The most common DOEs are as follows: Full three-level factorial design, Central composite design (CCD), Doehlert design and Box–Behnken design (BBD). By choosing the appropriate DOE, we can build a good response surface and the prediction can be sharpened.

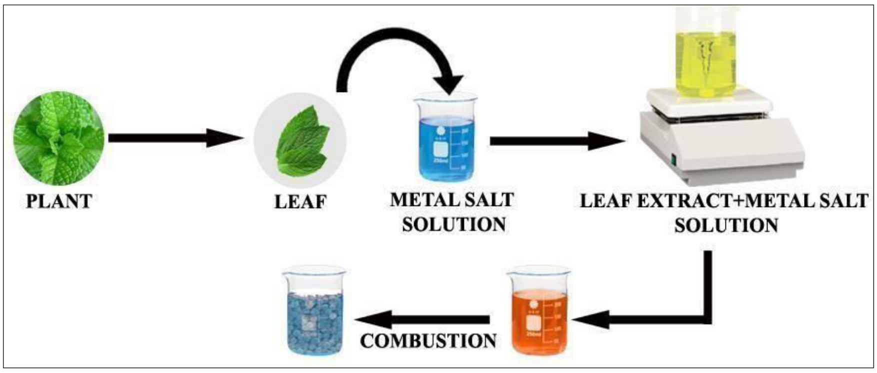


Fig 2: Schematic representation of the green synthesis of nanoparticles

Solution combustion synthesis (SCS) is a process wherein an oxidizer, typically a nitrate and a fuel are dissolved in distilled water and placed in a preheated muffle furnace at temperatures around 500o C. schematic representation of the processes done in the solution combustion synthesis is given in Figure 1.9. The water solution boils, foams and subsequently burns with a glowing flame with temperatures reaching up to 135oC. Typically, this process yields a fluffy and voluminous solid along with the liberation of large amount of gases. SCS is a self-sustained process and the heat source comesfrom the reactions taking place during combustion. SCS may be considered as aspecific type in a more general process called self-propagating high-temperaturesynthesis (SHS). However, SCS differs from other forms of combustion synthesis in the following three aspects. Firstly, the initial components of SCS are mixed in aqueous solution at the molecular level, SHS uses powders and aremixed at the microlevel. Secondly, in the SCS. the product formation reaction can be different compared to the heat generation step. For example, heat is generated by the burning or oxidation of the organic fuel components while the products formed are mainly metal oxides. In the SHS, the synthesis and the heatgeneration reactions are one and the same. Thirdly the SCS process generates a large volume of gaseous byproducts which lead to a significant expansion of thesolid product with a decrease of temperature after the reaction. These make the solid product porous and finely dispersed. The last-mentioned factor is significant in the synthesis of nanoscale powders. In summary we can say that SCS is a complex self-sustained chemical process taking place in a homogeneous solution of precursors. SCS begins with several thermally coupled exothermic reactions involving dehydration and thermal decomposition of the homogeneous solution which culminates in the formation of at least one solid product and a large volume of gases. This is a versatile method that can be used to synthesize a large number of nanoscale materials including oxides, metals, alloys etc. that find several applications [18, 19]. A mere preparation of new catalyst or employing a different technique does not make it a novel catalyst. The true challenge would be in employing environmentally benign processes, to study the different ways of preparing catalyst supports, exploring ways to add active sites to the existing catalyst, immobilizing a pre- formed active site, adding a pre- catalyst and synthesizing a new site on the surface.

Table 1: Design and results of response surface experiments for 4-NPreduction

Run Order	Conc of 4-NP (mM)	Amount of catalyst (mg)	Time (min)	Amount of NaBH4 (mg)	Reduction of 4-NP (%)	FITS
1	0.0625	15	8	20	66.95	71.154
2	0.0625	15	8	50	84.42	80.598
3	0.0625	10	1	20	12.97	0.683
4	0.0625	5	15	35	60.32	58.165
5	0.0625	5	8	50	62.69	60.678
6	0.1	10	1	35	20.26	26.781
7	0.025	15	8	35	90.73	90.535
8	0.0625	10	8	35	78.17	78.1

						70
9	0.1	10	8	20	80.12	81.728
10	0.025	10	8	50	84.85	85.226
11	0.025	10	8	20	63.79	68.478
12	0.1	10	8	50	68.26	65.556
13	0.1	5	8	35	80.54	76.560
14	0.0625	5	1	35	23.74	25.865
15	0.1	15	8	35	86.14	81.955
16	0.0625	10	8	35	78.17	78.170
17	0.0625	15	1	35	14.95	19.090
18	0.025	5	8	35	74.39	74.400
19	0.0625	5	8	20	63.53	69.544
20	0.0625	10	15	20	86.82	82.593
21	0.025	10	1	35	28.23	27.681
22	0.1	10	15	35	71.57	74.311
23	0.025	10	15	35	84.16	79.831
24	0.0625	10	1	50	32.99	33.041
25	0.0625	10	15	50	42.7	50.811
26	0.0625	10	8	35	78.17	78.170
27	0.0625	15	15	35	86.61	86.470

Most investigations have examined the influence of one single parameter. However, as other parameters may have a significant impact on the experimental results, it is pertinent to investigate the impact of one parameter vis-a-vis another parameter. The significance of the interaction between the variables was recorded (F-value), indicating that the results from the model hada good fit. The P-value of the model indicates that this model could describethe relationship between the response and independent variables. Results obtained for analysis of variance are tabulated. The F-value of 28.56indicates that the model is significant. The significance of each term is

evaluatedaccording to the P- value. A P-value less than 0.05 indicates the term is significant and the model term is insignificant if the value is more than 0.10. The R2 of 0.9709 and R2 (adj) value of 0.9369 indicate adequate precision of this model. Itis important that a good R2 value be closer to 1 and it indicates a better correlationbetween experimental and predicted responses.
The Box-Behnken design is a response surface methodology (RSM) design that requires only three levels to run an experiment. In the Box–Behnken design, the number of experiments required to be performed is given by equation (1.1) $N = 2(k - 1) + C0$ (1.1) where N is the number of experiments required to be performed, C0 is the number of center points, k is the number of variables. Experiments are run at different factor values, called levels. Each run of an experiment involves a combination of the levels of the factors that are being studied. It is a special 3-level design because it does not contain any points at the vertices of the experiment region. The points are shown .. This design has advantages, especially when the points on the corners of the cube represent level combinations that are 20 very expensive, impossible to test or practically inconceivable. an example of a Box-Behnken design with three factors. BBD is done for three levels of variables that are evenly spaced. Ferreira *et al*. have discussed the uses and application of BBD in the various fields of chemistry for optimizing the results and procedures. Once the experimental design is selected, the variables should be chosen with care. Prior knowledge about the processes, a good literature survey, limitations of the instrumental methods being used and required number of preliminary experiments to be performed will all go a long way in making RSM a very valuable tool to optimize processes.

Conclusion

The most significant conclusions that can be arrived at from this study can be listed out as follows. Plant or paddy extracts can effectively be used to prepare ceria and modified ceria nonmaterial's for catalytic and photo catalytic applications using the solution combustion synthesis. Modification of the nanomaterials was done using transition, inner transition metal oxides and g-carbon nitride. The paddy extracts were obtained from the plants Spinacia oleracea and Piper betle make good materials as fuels in the solution combustion synthesis. The ceria and modified ceria show a cubic fluorite crystalline structure. Modification of ceria support with other metals oxides have resulted in a good synergistic effect between ceria and metal oxides that led to enhanced activity of the catalysts and the formation of a robust reusable catalyst. The synthesized materials show good photocatalytic properties as evidenced from their ability to degrade the two dyes Malachite green and Congo red under visible light illumination and the antibiotic drug Ciprofloxacin under UV irradiation. Reduction of 4- nitrophenol using sodium borohydride can be effectively catalyzed using the materials synthesized. These catalysts can be used to synthesize the pharmacologically significant dihydropyrimidine compounds by the Biginelli reaction. Box Behnken Design of the Response Surface Methodology can be a good tool to optimize the variables for best results. There was a good agreement in the results predicted by the Minitab 18 software for statistical analysis and the experimental values, thus validating the applicability of RSM for optimization studies.

References

1. Aneggi E, Boaro M, Colussi S, de Leitenburg C, Trovarelli A. Ceria-Based Materials in Catalysis: Historical Perspective and Future Trends. 1st ed. Handbook on the Physics and Chemistry of Rare Earths. Elsevier B.V, 2016.
2. Rattanaphra D, Soodjit P, Thanapimmetha A. Synthesis, characterization and catalytic activity studies of lanthanum oxide from Thai monazite ore for biodiesel production. Renew Energy,2019:131:1128- 1137. doi: 10.1016/j.renene.2018.08.066.

3. Khan K, Saeed I, Khan. Nanoparticles: Properties, applications and toxicities. Arab J Chem. 2017. doi: 10.1016/j.arabjc.2017.05.011.
4. Charbgoo F, Ahmad M, Darroudi M. Cerium oxide nanoparticles: green synthesis and biological applications. Int J Nanomedicine,2017:12:1401-1413. doi: 10.2147/IJN.S124855.
5. Ramachandran M, Subadevi R, Sivakumar M. Role of pH on synthesis and characterization of cerium oxide (CeO2) nanoparticles by modified co-precipitation method. Vacuum,2019:161:220-224. doi: 10.1016/j.vacuum.2018.12.002.
6. Nandigama, N. C. (2021). Advancing Underwater Image Segmentation through Pix2Pix Generative Adversarial Networks. Research Journal of Nanoscience and Engineering, 5(1), 20–25. https://doi.org/10.22259/2637-5591.0501004
7. Kannan SK, Sundrarajan M. A Green Approach for the Synthesis of a Cerium Oxide Nanoparticle: Characterization and Antibacterial Activity. Int J Nanosci,2014:13:1-7. doi: 10.1142/S0219581X14500185.
8. Hernández S, *et al*. Insights into the sunlight-driven water oxidation by Ce and Er-doped ZrO2. Front Chem,2018:6:368-398. doi: 10.3389/fchem.2018.00368.
9. Gao W, Wen D, Ho JC, Qu Y. Incorporation of rare earth elements with transition metal-based materials for electrocatalysis: a review of recent progress. Mater Today Chem,2019:12:266-281. doi: 10.1016/j.mtchem.2019.02.002.
10. Wang Y, O'Connor D, Shen Z, Lo IMC, Tsang DCW, Pehkonen S, *et al*. Green synthesis of nanoparticles for the remediation of contaminated waters and soils: constituents, synthesizing methods, and influencing factors. J Clean Prod,2019:226:540-549. doi: 10.1016/j.jclepro.2019.04.128.
11. Charan Nandigama, N. (2024). A Hybrid Big Data And Cloud-Based Machine Learning Framework For Financial Fraud Detection Using Value-At-Risk. International Journal of Research and Analytical Reviews, 11(3). https://doi.org/10.56975/ijrar.v11i3.324899.
12. Nandigama, N. C. (2023). Enhanced Fingerprint Recognition system using hybrid Feature Fusion with Deep learning and Machine learning Optimization. Research Journal of Nanoscience and Engineering, 6(1), 9–15. https://doi.org/10.22259/2637-5591.0601003.