GREEN SYNTHESIS OF MOLYBDENUM OXIDE NANOPARTICLES CHARACTERISATION AND ITS APPLICATIONS

Dissertation submitted to the JSS College of Arts, Commerce and Science
In
partial fulfillment for the award of

MASTER OF SCIENCE
IN
CHEMISTRY
By

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PARENTS AND MY LECTURERS.

DECLARATION

I hereby declare that the dissertation entitled "Green synthesis of molybdenum oxide nano particles characterisation and its applications" submitted to the JSS College of Arts, Commerce and Science for the partial fulfilment of the degree Master of Science in Chemistry is the result of my own study and was composed independently by me under the guidance of ***Dr.MahadevaSwamy M****, Assistant Professor, PG Department of Chemistry, JSS College of Arts, Commerce and Science, Ooty Road, Mysuru, and that it has not formed the basis for the award of any degree, diploma, associate ship, fellowship or other similar title.*

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Shashank P

Place: Mysuru

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INTRODUCTION

In the last few decades, transition metal oxides have attracted the research community in great deal due to their diversified applications. Among them, molybdenum oxide has been found to be one of the most fascinating materials due to its unique structural, optical, electrical, and mechanical properties and multidirectional applications such as gas sensing, photo catalysis, field emission (FE), capacitors, resistive switching, solar cells, light emitting diodes, hole transport materials, etc. Molybdenum is a Block D, Period 5 element, while oxygen is a Block P, Period 2 element in the periodic table. Molybdenum does not occur naturally as a free metal on Earth. Molybdenum Oxide is a wide bandgap material whose bandgap varies from insulating MoO_3 (≈3.2 eV) to more conducting MoO_{3-x} to semi-metallic MoO_2 (≈2.55 eV). Molybdenum oxide exists in several phases such as MoO_3 (orthorhombic, monoclinic, and hexagonal), Mo_4O_{11} (monoclinic and orthorhombic), Mo_5O_{14} (tetragonal), Mo_8O_{23} (monoclinic), Mo_9O6 (monoclinic), and MoO_2 (monoclinic) depending upon the oxygen concentration and the oxidation state (+6, +5, +4 and +2) of Mo. The commonly used molybdenum oxide, MoO_3, have three different polymorphs and these are:

i) A thermodynamically most stable orthorhombic structure(a -MoO3)
ii) A metastable monoclinic structure (β-MoO3) and
iii) A metastable hexagonal structure (h-MoO3).

Molybdenum oxide nanoparticle, also known as molybdenum trioxide nanoparticle, is a fine light blue powder composed primarily of MoO3 particles with diameters of 100nm or less generally.

Due to high melting point, high chemical and thermal stability, and metallic conductivity, monoclinic MoO_2 has attracted much attention in the research community.Looking to its high chemical stability, quick oxidation-reduction process, easy nonmetric sized particles preparation procedure, we selected molybdenum oxides as viable candidates. Mo exists in three oxidation states and thus can readily participate in redox reactions and exhibits interesting metallic electrical conductivity. Hence, the nanostructured molybdenum oxide particles (MoOx NPs) could act as efficient electron redox mediators, contributing to theelectrochemical sensing of some biological compounds such as dopamine. MoOx NPs are widely used in lithium ion batteries, capacitors and gas sensors, while their application in bio-sensing is still limited. Different types of MoO_2 morphologies such as nanoparticles, hollow spheres, sheets, large scale nanowires, and nano stars have been synthesized via diversified

techniques such as hydrothermal reaction, thermal evaporation, solution-based reactions, and hydrogenation processes. Molybdenum dioxide is also an unusual transition metal oxide because of its high metallic-like electrical conductivity, which is associated with its mixed interatomic bonding and a relatively high density of states at the Fermi level. The existence of free electrons in this region enhances the catalytic activity of Mo^{4+} in MoO_2, unlike that of Mo^{6+} in MoO_3, where all the valence electrons of the metal are covalently bonded to neighbouring oxygen atoms. The metallic conductivity of MoO_2 makes it a material of interest for many applications, including catalysis. Most recently it has been studied as a possible anode for lithium-ion batteries.

Different morphologies of MoO_3 nanostructures (NSs) such as nanoribbons, nanobelts, nanorods, nanowires, nanotubes, and nanosheets are prepared by various physical and chemical methods. Different techniques are deployed to synthesize MoO_3 NSs successfully such as chemical vapor deposition (CVD), thermal evaporation, e-beam evaporation, pulsed laser deposition, sputtering, hydrothermal, molecular beam epitaxy (MBE), and van-der-Waals epitaxy.

MoO_3 is a promising candidate to realize applications in electronic, photo-catalytic, gas sensor, biological activity, electrochromic, photochromic, lithium-ion batteries etc., owing to its tunable properties. It is an n-type wide band gap semiconductor with three crystal structures (i) orthorhombic(a-MoO_3) which is thermodynamically stable, (ii) metastable hexagonal (h-MoO_3) and (iii) monoclinic (m-MoO_3). Orthorhombic (a-MoO_3) phase is widely studied by researchers because it gives out many applications. Molybdenum oxide nanoparticles can be synthesized through various methods like hydrothermal, microwave irradiation, co-precipitation, sono-chemical, flame synthesis, sol-gel etc. Among these methods, co-precipitation is a simple and cost-effective method capable producing large quantity of yield. There are many influencing synthesis parameters like acid or base, PH, surfactant, source material, annealing temperature etc., which could change the property of the bulk material significantly.

Environmental factors like temperature, humidity, light, etc. have to be monitored and controlled for various applications and industry including medical, food, agriculture, and others [1–3]. There is vast research going on in sensor development for accurate monitoring of the environmental parameters. The goal of this research is to develop sensing devices with higher accuracy, robustness, sensitivity, stability, small size, and fast response. Humidity is

one factor among these that involves detection of physical molecules and is one of the toughest to sense and control. This is why research on development of high end humidity sensors is much larger when compared to other mentioned parameters. Different researches focus on improving one or two of the many parameters in humidity sensors while compromise the remaining ones. That can be useful for a target specific application for example the detectable range is important in long term environmental sensors [4] but the response time and sensitivity are not very crucial. in case of medical applications, the response and recovery times are crucial [5] but the range can be compromised. Researchers are implementing various techniques, materials, and mechanisms to improve the desired parameters of the humidity sensors. Different structures and transduction techniques including interdigitated transducers [6–8], surface acoustic waves [9–11], field effect Transistors [12–14], and other structures [15–17] and techniques [18–20] have been reported in previous works. Capacitive and resistive sensors have been among the major research techniques because of their cheaper and easier fabrication [21–23] but their results are not very promising to be used for high end applications. To improve the performance, difference materials including ceramics, oxides, polymers, and composites have been used [24–26] achieving improved performance. Most humidity sensors comprise of a single sensing layer that can be among any of the categories mentioned above but in most cases, the response of the sensors is non-linear that is not ideal for wide range of applications and high accuracy and repeatability [27–29]. Bi-layered films have been implemented successfully to improve certain parameters with some compromise on parameters like response time[17,30] and detection range [31,32] and others not achieving any prominent improvements [33].

2D materials are in limelight these days for electronic devices. 2D materials possess unique chemical, electrical, and physical properties that canbehelpfulinmany different applications including sensing devices. 2D flakes of transition metal di-chalcogenides (TMDs) have been used for various sensing applications including gas sensing, bio-sensing, photo-sensing, etc.[34–38]. Transition metal carbides (TMCs) have been used in their MXene phase mostly in catalysis, energy storage devices, and biosensors [39–42]. Molybdenum carbide (Mo2C) is one of the most famous TMCs and has been used in its various forms and phases in applications including immunosensing [43], catalysis [44–46], semiconductors [47], CO absorption [48], etc. Large scale 2D Mo2C is synthesized usually by selective etching [49], nano-casting [50], and CVD [51]. In this work, we report on mechanically exfoliating the bulk -Mo2C in to smaller particles and 2D flakes and employ it in application of humidity

sensing. The adopted method of wet grinding can produce a mixture of smaller chunks of bulk -Mo2C along with dispersed exfoliated 2D flakes. Thin films of the resulting material possess high surface area to volume ratio and improved electrical and chemical properties that can be utilized in humidity sensing devices and other applications. Different polymer composites and bi-layer structures have been used with Mo2C for the fabrication of humidity sensors.

High-performance gas sensing technology is a key issue in the 4th industrial revolution due to the importance of the detection of invisible variations in the ambient environment.1,2 Gas sensors can be utilized in various applications including breath analysis for patients, smart home systems, industrial safety, air pollution tracking, and alcohol testing.3,4 The technology used in devices such as infra-red (IR) gas sensors,5 quartz crystal microbalances,6 surface acoustic wave devices,7 gas chromatographs,8 colorimetric sensors,9 and solid-state sensors10 has been used in the development of gas sensors. Among these, solid-state sensors based on charge variations of conductive channel materials have shown much promise for next generation gas sensing technology due to their low-power operation, integrated circuit (IC) possibility, and multichannel operation, which are key requirements of internet-of things (IoT) sensors.11 Various sensing materials for solid-state sensors have been explored, including metal oxide semiconductors (MOS), monolayer-capped metal nanoparticles, metal nanowires, conducting polymers, carbon nanomaterials, and two-dimensional (2D) materials. For example, MOS, including SnO_2, ZnO, TiO_2, WO_3, and CuO, have been widely investigated as channel materials due to their high sensitivity and easy production.12,13 In addition, 2D materials including graphene, transition metal dichalcogenides (TMDs), boron/ carbon nitrides, and black phosphorus (BP) have been considered as potential chemical sensing materials due to their unique layer-dependent electrical properties, maximum surface-to-volume ratio, and various active sites (e.g., at vacancies, edges, basal planes, and defects).14–16 However, despite intensive efforts in this field, the development of channel materials with high electrical conductivity and long-term stability as well as high sensitivity is still very limited for their practical application as solid-state gas sensors, which should be operated with low power, low noise and excellent ambient stability

In this paper, we report transition metal carbides (TMCs) as gas sensing channel materials. TMCs such as Mo2C, W2C, WC, TaC, and NbC are a large family of materials that combine the unique properties of ceramics and metals.17 During the carburization reaction, generally,

new bonding (Mo–C) is formed at interstitial sites by inserting carbon atoms into unoccupied sites in the molybdenum crystal structure. Our approach for TMCs as sensing channel materials is based on several unique features, which are as follows: □rst, the TMCs have rich density of states (DOS) near the Fermi level compared to the parent metal.18,19 This is because the metal lattice expands and the distance between metal atoms increases during the formation of interstitial TMCs, which would result in a broadening of the metal d-band.20 Accordingly, this high DOS near the Fermi level of TMCs can lead to the strong surface adsorption of chemical analytes due to active surface charge interactions.21 Second, the TMCs show very high electrical conductivity similar to pure metals, indicating that they can lead to low-power operating devices with significantly low baseline resistance levels.22,23 Finally, the interstitial carbides of TMCs have excellent physical and chemical stability: high melting temperature (e.g. the melting points of tantalum carbide and hafnium carbide are among the highest known of all materials), high resistance to oxidation, and superior ambient stability.24,25 Accordingly, this superior physical/ chemical stability can lead to the realization of a gas sensor that is highly stable at ambient conditions and has long-term stability, which is difficult to achieve with other sensitive sensing materials including carbon nanomaterial's, 2D materials and MOS. Overall, these strong and unique features of TMCs will be helpful for achieving highly sensitive gas sensing performance accompanied by low-noise and low-power operation, and long-term stability.

Literature Review

Caleb A. Ellefson et.al. Molybdenum dioxide (MoO_2) is a transition metal oxide with unusual metal-like electrical conductivity and high catalytic activity toward reforming hydrocarbons. This review covers the synthesis techniques used to fabricate MoO_2 in a variety of morphologies and particle sizes. Processing from molybdenum ore and reduction from MoO_3 are also covered, with emphasis on reduction mechanisms and kinetic considerations. Discussions of various solution-based and gas phase synthesis techniques shed light on strategies to achieve various unique morphologies, which leads into a brief discussion of Nano scale MoO_2. Nano scale MoO_2 is of interest for important technological applications including catalysts for partial oxidation of hydrocarbons, solid oxide fuel cell anodes, and high-capacity reversible lithium ion battery anodes

S. Muthamizh1 et.al. Molybdenum oxide nanoparticles were prepared by Solid state synthesis. The MoO3 nanoparticles were synthesized by using commercially available ammonium heptamolybdate. The XRD pattern reveals that the synthesized MoO3 has orthorhombic structure. In addition, lattice parameter values were also calculated using XRD data. The Raman analysis confirm the presence of Mo-O in MoO3 nanoparticles. DRS-UV analysis shows that MoO3 has a band gap of 2.89 eV. FE-SEM analysis confirms the material morphology in cubes with nano scale.

Molybdenum oxide nanoparticles were synthesized by simple solid state reaction. The structure of the MoO3 nanoparticles was characterized by XRD, and Raman spectroscopy. Optical property was investigated using DRS-UV spectroscopy. The morphology of the MoO3 was confirmed by FE-SEM and the EDAX spectrum shows the absence of impurity.

Memoon Sajida et.al.A high performance humidity sensor for environmental and health monitoring has been fabricated using various combinations of molybdenum carbide (Mo2C) with polyacrylamide (PAM) and polyvinyl alcohol (PVA). The humidity sensing properties of pure Mo2C were compared with those of its composites with PAM and PVA. The response curves and working principle were investigated and novel bi-layered sensors were then fabricated to achieve highly linear and stable response for a wide range of humidity sensing (0% RH to 90% RH). The sensors having a bi-layer combination of Mo2C with PAM

give a linear response with a sensitivity of 775 /%RH and excellent repeatability. The working mechanism of the sensors allow them to be used with frequency response conversion read-out circuits and the results ascertain their linear and stable behavior. The response-time and recovery-time of the sensors were measured that gave average values of ~1 s and ~2.5 s respectively for the composites and ~1.8 s and 2.3 s for the bi-layer configuration. The sensors are aimed to replace low performance complex and expensive sensors in the market for environmental and health monitoring applications.

As a conclusion, it can be stated that the humidity sensor fabricated using Mo_2C, a transition metal carbide, combined with PAM polymer in bi-layer configuration show excellent sensitivity, stability, and response curve linearity. The tunable linear curve shape can be explained with using a two stage sensing mechanism for low and high humidity levels using the top and bottom layers respectively. The fast response and recovery times and a stable and linear frequency response output makes the sensors ideal to be used as high end but cheap commercial sensors for environmental and health monitoring. The materials used in this experiment are quite cheap and the fabrication methods used are all printed and mass production compatible allowing commercialization of the devices with minimal cost and very high accuracy. The reported sensors are ideal solution for general purpose and application specific humidity sensing

Taotao Lianget.al. There are great challenges to fabricate a highly selective and sensitive enzyme-free biomimetic sensor. Herein for the first time a unique nanostructure of porous molybdenum carbide impregnated in N-doped carbon (p-Mo2C/NC) is synthesized by using SiO2 nanocrystals-templating method and is further used as an enzyme-free electrochemical biosensor toward highly selective, sensitive detection of H2O2, of which the limit of detection, dynamic detection range and sensitivity accomplish as 0.22 μM 0.05-4.5 mM and 577.14 $\mu A\ mM^{-1}\ cm^{-2}$, respectively, and are much superior to the non-porous molybdenum carbide impregnated in N-doped carbon (Mo_2C/NC). The sensor is also used to monitor H_2O_2 released from A549 living cells. This work holds a great promise to be used to monitor the presence of H_2O_2 in biological research while offering an important knowledge to design a highly selective and sensitive biomimetic sensor by synthesizing a porous catalyst to greatly improve the reaction surface area rather than conventionally only relying on dispersing the catalyst material into porous carbon substrate

Soo-Yeon Choet.al. Herein, we present a demonstration of the usability of the chemical sensing properties of transition metal carbides (TMCs) as gas sensing channels. Two phases of nanostructured molybdenum carbide (a-MoC1x and b-Mo_2C) with high porosities were perfectly synthesized by a temperature-programmed reduction (TPR) method, and they showed distinct metallic characteristics due to different density of states (DOS) localization status. The molybdenum carbide sensors showed novel gas sensing characteristics which have not been shown by previous typical sensing materials: predominantly, an unprecedentedly high signal-to-noise ratio (SNR) with the ability to detect the ppb levels of NH_3 and NO_2 was achieved, which is attributed to a combination of high electrical conductivity and superior catalytic properties. In addition to high sensitivity, unlike previous channel materials, the molybdenum carbide sensors showed very high ambient stability. The electrical conductivity and sensing performance are well preserved for half-year ambient exposure without any oxidation or degradation of channel materials, due to the good corrosion resistance and low chemical reactivity of molybdenum carbides. In addition, a versatile gas sensing response is observed according to the crystal phase of molybdenum carbides due to the distinct DOS of a-MoC1x and b-Mo_2C. We believe that this observation of new chemical sensing materials can shed light on the superior potential of TMCs for highly sensitive and stable low-power operating internet-ofthings (IoT) sensors. In addition, owing to their ultra-high chemical stability and high melting temperature, TMCs can be utilized as channel materials for sensors in harsh operating conditions.

Solid-state gas sensors having very high sensitivity and superior ambient stability were developed using molybdenum carbides. Due to the unique material characteristics of molybdenum carbides, i.e. a combination of high metallic conductivity and rich DOS near the Fermi level, highly sensitive gas sensing responses to various analytes were observed with an ultra-high SNR. A-MoC1x and b-Mo2C showed distinct sensing behaviour, response direction, and amplitudes due to different metallic characteristics, and this was further proved by DOS calculation using DFT. In addition, the electrical conductivity and sensing performance are well preserved for half-year ambient exposure without any oxidation or degradation of channel materials due to the good corrosion resistance and low chemical reactivity of molybdenum carbides. We believe that this highly sensitive TMC material with an ultra-high SNR and stability has the potential to serve as a channel material for low-power operating IoT sensors. With ultra-high chemical stability and high melting temperature, TMCs can be utilized as channel materials for sensors in harsh operating conditions.

Rudzani Sigwadi1et.al. Stable and high surface area zirconium oxide nanoparticles have been synthesised by means of the hydrothermal method. The Brunner–Emmett–Teller results show that a high surface area of 543 m^2 /g was obtained in the hydrothermal process, having a high porosity in nanometre range. The hydrothermal method was applied at 120 °C by using an autoclave with a Teflon liner at an ambient pressure for 48 h. High-resolution scanning electron microscopy shows the different morphologies of zirconia nanoparticles, which could be categorised as one-dimensional and zero dimensional, as they had a high crystallite orientation, which was also confirmed by the X-ray diffraction (XRD). The mixture of two types of cubic phases in one sample was obtained from XRD and confirmed by the zirconia nanostructure, showing the stable phase of fluorite, which has full cubic symmetry (Im-3m), and also an Arkelite zirconia nanostructure, showing the stable phase of fluorite, which has full cubic symmetry (Fm-3m). The XRD results also show the different structure orientations of face-centred cubic and body-centred cubic in one sample.

The hydrothermal method was found to be the suitable method to synthesise a high surface area zirconia, as confirmed by BET results which reveal a high specific surface area of 543 m2 /g and pore volume of 0.5 cm^3 /g. The XRD results indicate the pure cubic Nano crystalline phase of zirconia, with the different structure orientations of FCC and BCC in one sample. High-resolution SEM images of ZrO_2 nanoparticles confirm the presence of Nano spheres and nano bars. Moreover, the EDAX spectra show the highest value of zirconia (Zr (51.5%)) and oxygen (O (32.0%)) elements that represent the presence of zirconia and oxygen in the synthesised sample. Furthermore, the TGA/DTG results show the improvements in thermal stability with little degradation. This is very important in the modification of Nafion membrane for fuel cell application, as it will enhance the thermal stability of the membrane. The zirconia nanoparticles maintain a rectangular shape with good cycling and reversibility stability at the scan rate of 100 mV s^{-1} . The CV rectangular shape reveals the ideal capacitive behaviour, with the increased redox peak current, due to the transfer of electrons. The Nyquist plots of 2 M $NaNO_3$ and KCl electrolytes have higher electric conductivity at lower and higher frequency. However, the Nyquist plots of 2 M $NaNO_3$ are higher than those of 2M KCl electrolytes, which may be due to its higher electrical conductivity. It can be concluded that ZrO_2 nanoparticles composited in Nafion membrane can be considered a promising electrolyte in the application of fuel cell.

Caleb A. et.al. Molybdenum dioxide (MoO2) is a transition metal oxide with unusual metal-like electrical conductivity and high catalytic activity toward reforming hydrocarbons. This

review covers the synthesis techniques used to fabricate MoO2 in a variety of morphologies and particle sizes. Processing from molybdenum ore and reduction from MoO3 are also covered, with emphasis on reduction mechanisms and kinetic considerations. Discussions of various solution-based and gas phase synthesis techniques shed light on strategies to achieve various unique morphologies, which leads into a brief discussion of nanoscale MoO2. Nanoscale MoO2 is of interest for important technological applications including catalysts for partial oxidation of hydrocarbons, solid oxide fuel cell anodes, and high-capacity reversible lithium ion battery anodes.

Molybdenum dioxide exhibits growing potential for a number of applications. It can be synthesized in several highly specific morphologies by a variety of techniques. MoO_2 is easily obtained by reduction of MoO_3 by hydrogen or other reducing gases above 450 ^{0}C. Studies also found success making a wide variety of MoO_2 and MoO_3 products by solution-phase and gas-phase approaches. Several of these studies seek high surface area products for application in lithium ion battery anodes. Other groups have recently used MoO_2 as a catalyst for partial oxidation logistics of fuels such as biodiesel, gasoline, and Jet-A. In an extension of this research, MoO_2 is being tested as an anode material for direct-fueled solid oxide fuel cell anode that is resistant to coking and sulfur poisoning.

Juan Li,a,et.al. There are great challenges to fabricate a highly selective and sensitive enzyme-free biomimetic sensor. Herein for the first time a unique nanostructure of porous molybdenum carbide impregnated in N-doped carbon (p-Mo_2C/NC) is synthesized by using SiO2 nanocrystals-templating method and is further used as an enzyme-free electrochemical biosensor toward highly selective, sensitive detection of H_2O_2, of which the limit of detection, dynamic detection range and sensitivity accomplish as 0.22 μM, 0.05-4.5 mM and 577.14 μA mM−1 cm−2 , respectively, and are much superior to the non-porous molybdenum carbide impregnated in N-doped carbon (Mo_2C/NC). The sensor is also used to monitor H2O2 released from A549 living cells. This work holds a great promise to be used to monitor the presence of H2O2 in biological research while offering an important knowledge to design a highly selective and sensitive biomimetic sensor by synthesizing a porous catalyst to greatly improve the reaction surface area rather than conventionally only relying on dispersing the catalyst material into porous carbon substrate.

In summary, a porous Mo_2C catalyst was prepared by onestep pyrolysis of $(NH_4)_6Mo_7O_2$, melamine and SiO_2 to fabricate a sensitive, selective and stable p-Mo_2C/NC sensor toward

H_2O_2 detection for the first time. The H_2O_2 sensor displays a high sensitivity (577.14 μA mM^{-1} cm^{-2}), good selectivity and excellent stability/reproducibility. The excellent biomimetic performance can be attributed to the porous Mo2C catalyst rather than conventionally relying on only catalyst dispersing in a porous substrate for a large reaction surface area. This work holds great promise for a biomimetic sensor to be used in biological research, while offer scientific lights on how designing high-performance enzyme-free biomimetic sensors from both chemistry and physics.

Objectives

- To get extract out of the medicinal plant from Soxhlet's method.
- To synthesis MoO_3nanoparticle by sol-gel method.
- To use Eco-friendly green approach technique.
- Characterization (XRD, EDS, SEM, FTIR& Elemental Mapping)
- To study the Applications such asOxidation of Kinetics to determine the rate

- To study the comparison between Macro and Nano metal Oxides such as ZnO, MoO_2 etc.

- To study the antimicrobial activities for different bacteria's such as E coli, S sabrinus etc.

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Chapter-2

Materials and methods:

- Leucasaspera medicinal plant.
- Doubled distilled water.
- Soxhlet's apparatus
- Ammonium molybdatetetrahydrate.
- Silica crucibles & muffle furnace.

Preparation of Leucas aspera plant leafExtraction

The preparation of extraction, we were collected Leucas aspera medicinal plant Leaves which are collectively known as medicinal leaves. All were collected from in and around areas of Mysuru, Karnataka, India. The Leucas aspera medicinal plant were picked up from well growned plants and trees, wash away with double distilled water to eliminate any contaminations, ground the leaves in mortar and introduced into a round bottomed flask mixed with 100 ml of distilled water to connect the succelet operator at 80° C for 3 hours for the extraction from the seven major medicinal plants. After 3 hours cool the round bottom flask at room temperature and filter through filter paper and collect the filtrate in a glass container and kept in cold place.

Sample and extract preparation:

The fresh leaves of Leucasaspera were washed gently to remove dust particles and dried and shaded place at room temperature (22-25^{0}C). Thereafter the leaves were pulverized using a mortar. The plant material was plate in a Soxhlet's apparatus for continual solvent extractions. Water was employed as a solvent for the extraction. The temperature of the apparatus was set at 90-95 ^{0}C and the extraction lasted for approximately 3 hours. The resultant extract was filtered using Whatman filter paper and preserved in airtight container until further use.

Synthesis of MoO_3nanoparticles using Sol gel method:

Nanoparticles were synthesized using eco-friendly sol-gel method:

Today, various methods such as sol-gel method (solution method), vapour phase compression method, mechanical alloying method or collision with high-energy pellets, plasma method, and electrochemical methods are used for the production and synthesis of nanoparticles. Although all the mentioned methods have the ability of producing large volumes of nanomaterial, the sol-gel method has a higher popularity and industrial application than other existing methods [1–5]. Due to its unique properties and characteristics, this method is capable of producing high qualityNanoparticles of the same size on an industrial scale [6–8]. .is method is capable of producing two or more types of nanoparticles simultaneously, meaning that alloy products are synthesized in one step by mixing two or more metal (or metal oxide) precursors in certain proportions [9–11]. Of course, there are other methods such as plasma method and electrochemical methods that have the ability of synthesizing alloy products in one step, but their main difference with solgel method is the industrial scale of sol-gel method [12–15]. In addition, the sol-gel method makes it possible to make highly homogeneous composites with very high purity (99.99% purity) [16–20].

Another advantage of this method compared to conventional methods is the lower temperature of the process in it, so that the production of metal and ceramic nanomaterial with this method is possible in the temperature range between 70 and 320°C [21–24]. .e other methods mentioned produce nanomaterial in the temperature range of 1400–3600°C [25–28].

Synthesis of MoO_3 nanoparticles

Using the extract of Lucas aspera as fuel. Ammonium molybdatetetrahydrate of (3.089g) was mixed with (2, 4, 6 ml) of Leucasaspera extract in a silica crucible, the above crucible was heated on a hot plate with continuous stirring for solidification (to form gel like consistency). The solid was then cooled in a room temperature. Before starting the combustion process, the muffle furnace was heated to 495 ± 5 ^{0}C. Thereafter, the sample was taken in clay crucible and then placed in the preheated muffle furnace for about 3-5min to evoparate off all the water content and to ensure proper drying of the precursor materials and then they were subjected for calcination at temperature 500 ± 5 ^{0}C (with the aid of a long tongs). to attain purity i.e., to eliminate all the unwanted organic matrix present in it.Calcination of the

mixture was done for about 3 hrs. This yielded fine, grey green MoO_3 which was stored in airtight container.

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Chapter-3

Characterization:

The prepared MoO_3 NP was done characterisation, to confirm the material size, shape surface properties and surface volume. In this study we done scanning electron micrographs (SEM) analysis, Elemental analysis (EDX), X-ray diffraction studies and Uv-visible studies. In SEM analysis was done for prepared nano-adsorbent of MoO_3. It shows structural morphology and shape of the prepared MoO_3 nanoparticles, in elemental analysis was shows the elemental composition of the prepared MoO_3NPs and in the case of XRDof specific shape and structure of prepared compound was measured with ambient atmosphere at 30° C by theX'pert Pro diffractometer (Cu-Ka radiation, λCu = 1.5148 Å). The Ag_2O NPs was degassed under vacuity at 300° C for 3 h before the measurement.The effective absorption study was estimated by UV–vis spectrophotometer (Agilent cary 60 UV–visible spectrophotometer).

Scanning Electron Micrograph (SEM):

The present scanning electron micrographs (SEM) analysis of bio mediatedMoO_3 NPs shows the effectiveness and its ability towards antimicrobial activity as displayed in the following figure. The MoO_3 NPselemental analysis showed the smoothening effect, it was revealed that there is no impurities are present in the sample.

Elemental analysis (EDX):

Energy dispersive X-ray spectroscopy (EDX) is an analytical method for analytical or chemical characterization of materials. EDX systems are generally attached to an electron microscopy instrument such as transmission electron microscopy (TEM) or scanning electron microscopy (SEM). EDX is based on the emission of a specimen characteristic X-rays. A beam of high energy charged particles (electrons or protons) are focused into the investigated sample. An electron from a higher binding energy electron level falls into the core hole and an X-ray with the energy of the difference of the electron level binding energies is emitted. EDX analysis gives a spectrum that displays the peaks correlated to the elemental composition of the investigated sample. In addition, the elemental mapping of a sample can be created with this characterization method.

Energy-dispersive X-ray spectroscopy (EDX) is used to analyze the elemental composition of solid surfaces. X-ray emission is stimulated by the irradiation of the surface with a high energy beam of charged particles or a focused X-ray beam. Excitation of the electronic structure of an atom can produce an X-ray emission, the energy signature of which is a unique characteristic of each element. Therefore a "fingerprint" or "signature" spectrum can be obtained allowing element identification via comparison with reference spectra. Electron microscopes often contain the instrumentation to perform EDX analysis, as the technology required to generate a high energy beam of charged particles, i.e., electrons, is already present. Electron energy-loss spectroscopy (EELS) requires the use of electrons with much lower energies than EDX, typically a beam of 100–1000 eV energy. These electrons are detected upon their reflection from a surface, and the loss of energy due to their interaction with the surface material is used to determine information regarding its chemical structure.

X-ray diffraction studies (X RD):

The X-ray diffraction patterns of MoO_3nanoparticles with different hardening temperatures are revealed in Fig.3. The synthesizedMoO_3 NPssample displayed less crystallinity structure due to low-temperature synthesis[19]. The regular particle phase and size discovery of materials were estimated by X-ray diffraction (XRD) configuration using X'pert Pro diffractometer (Phillips, Cu-Ka radiation, λCu = 1.5148 Å) employed at 30 mA and 40 kV recorded in the 2λ range between 10° and 90° (scan rate 1° min−1).The point establishment and important morphologies of bio mediated synthesisof Silvernanoparticleswere categorisedby PXRD peaks as shown in figure-3. The sharp fine peaks of MoO_3 NPsnano particle shows the fine crystal-like particles. On the other hand, the extreme intensity of the deflection points were witnessed in the plane (101) and its familiar crystalline dimensions of the MoO_3 NPsnanoparticles were found to be 25-28 nm calculated with Scherer's formula (Eq.3). Similarly, other parameter considerations such as micro-strain, displacement density and Strain were analysedby means of the subsequent expressions (eq.4, 5, 6).

$$D = \frac{k\lambda}{\beta \cos\theta} \text{-------(3)}$$

$$\varepsilon = \beta \cos\frac{\theta}{4} \text{-------(4)}$$

$$\delta = \frac{1}{D2} \text{-------(5)}$$

$$\sigma = \varepsilon Y \text{-------(6)}$$

Where, β is full width half maxima of the peak, D is crystal size, λ is X-ray wavelength. Lesser the constituent dimension of MoO_3 NPsnanoparticle illustrate the greater the micro straining and lesser displacement compactness in place of fine crystallineparticles.

Elemental Mapping:

An element map is an image showing the spatial distribution of elements in a sample. Because it is acquired from a polished section, it is a 2D section through the unknown sample. Element maps are extremely useful for displaying element distributions in textural context, particularly for showing compositional zonation.

One can use either an EDS or WDS system to produce an element map. Either way, the image is produced by progressively rastering the electron beam point by point over an area of interest. Think of an element map as a pixel by pixel (bitmap) image based on chemical elements. Resolution is determined by beam size, and relative response of each element is determined by how long the beam dwells on each point (and of course the actual concentration). Greater distinction can be made by longer analysis, but at the cost of time.

In many cases, adequate element maps can be acquired by EDS systems. This is typically a faster approach, but sacrifices resolution and detection limits. The best element maps are acquired using a WDS system on an electron microprobe, but the trade-off in using the spectrometers is longer acquisition time.

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Chapter-4

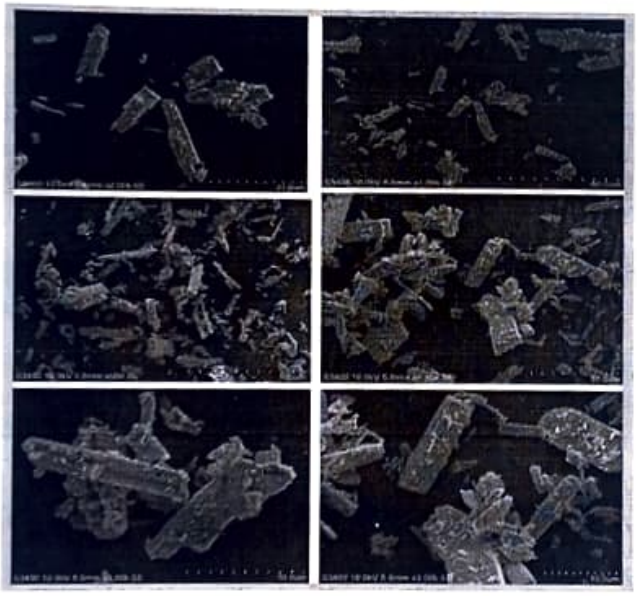
4.1 Results and Discussion

4.1.1 Scanning Electron Micrograph (SEM):

SEM(Scanning electron microscopy):

1.The SEM images generally shows the typically appearance of the given nano particle, it uses electrons instead of light to form an image.

2.The SEM images of synthesized molybdenum oxide is presented in the figure(1-6).



3. The electron beam energy was adjusted between 8-10k.

4.The SEM images of molybdenum oxidenano particles shown in thefigure are similar to elongated rectangular structure.

5.The particles of molybdenum oxide nano materials are quite freely arranged, they are not too clumsy or agglomerated in nature.

6.The size of the nano materials are ranging from around 200 to500 nanometer in size (figure 5).

7. By looking at the SEM images we can say that the the shape of the molybdenum is not uniform its quite irregular in nature.

8.the synthesized Mo oxide particles does not contain any porous structure in the crystals.

9.The structure of particles are quite sharp/pointed, edgy, rectangular, narrow, and crystal like in appearance.

10. The picture are scaled from 10-100micrometer magnification scale range.

4.1.2 Energy dispersive X-ray spectroscopy (EDX):

EDX STUDIES

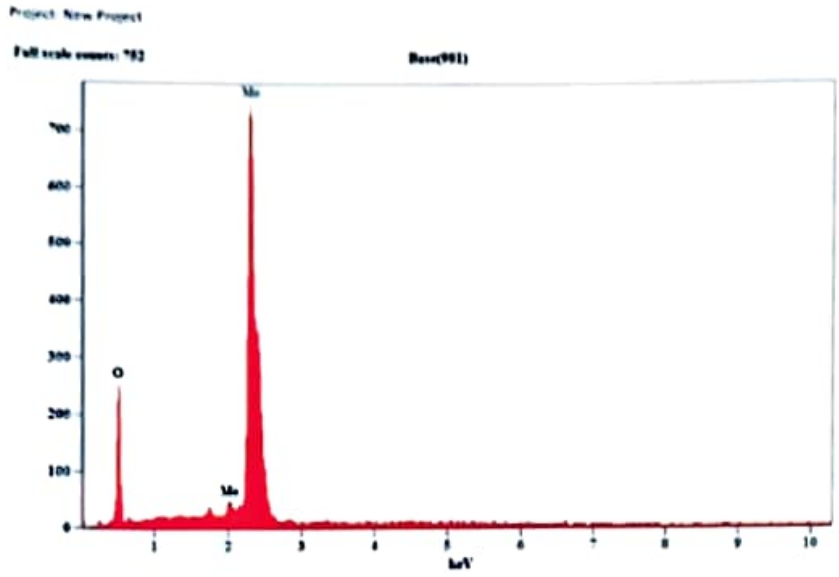
1.Energy-dispersive X-ray spectroscopy (EDS, EDX, EDXS or XEDS), sometimes called energy dispersive X-ray analysis (EDXA or EDAX) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample.

2.Applications include materials and product research, troubleshooting, deformulation, and more.

3.The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analysed. Elemental mapping of a sample and image analysis are also possible.

4.As we can see in the above EDX graph the largest peak of the molybdenum nanoparticles can be seen at the range of 752.

5.At the x-axis it can be seen at 2.4-2.5kew whereas in y-axis it can be seen at 752 .



6.The peaks obtained in this spectrum confirms the presence of Mo and O.

7.By this EDX analysis we can say that solution combustion method is capable of synthesizing high purity of a molybdenum oxide nanoparticle.

4.1.3 X-ray diffraction studies (XRD):

XRD STUDIES

XrDis treated as the chemical fingerprint for every crystalline material. The particle size analysis from XrD analysis obtained for the prepared molybdenum oxide nanoparticles is revealed in.

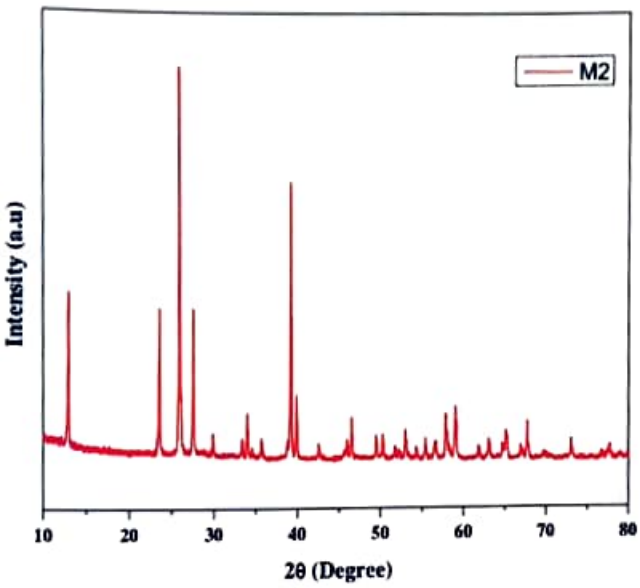
1.The atomic planes of a crystal cause an incidental beam of x-ray to interfere with one another as the leave the crystal. The phenomenon is called x-ray diffraction.

2.The x-ray diffraction is non-destructive technique used to understand the crystalline phase, different polymeric forms and structural properties of the material.

3.The XRD graph is the plot of dihedral angle (2θ) in x-axis against intensity in y- axis.

4.The x-ray pattern of Molybdenum oxide nanoparticles synthesized using "LEUCAS ASPERA" leaf extract with different concentration.

5.The XRD peak positions were consistent with molybdenum oxide and sharp peaks of XRD indicates the crystalline structure.



6.The presence of diffraction peaks at 12.5°,24 °, 26°, 26.5° and 39° were well assigned to (020), (110), (040), (021), (060) planes in XRD indicates the formation of pure monoclinic structure of molybdenum oxide nanoparticles.

7.The strong intensity and narrow width of molybdenum oxide diffraction peaks indicates the resulting products were highly crystalline in nature.

8.By using Debye Scherrer formula, we can calculate average crystalline size of the nanoparticles.

$$B(2\theta) = K\lambda / L \cos\theta$$

where, L is the average size of the crystal

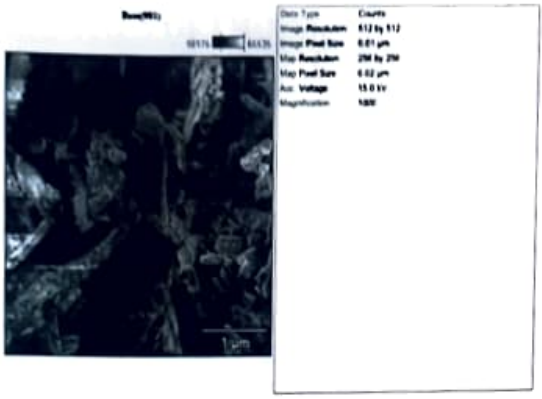
λ is the wavelength of radiation.

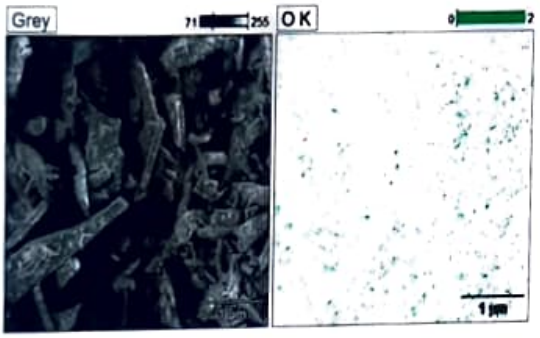
K is the Scherrer constant.

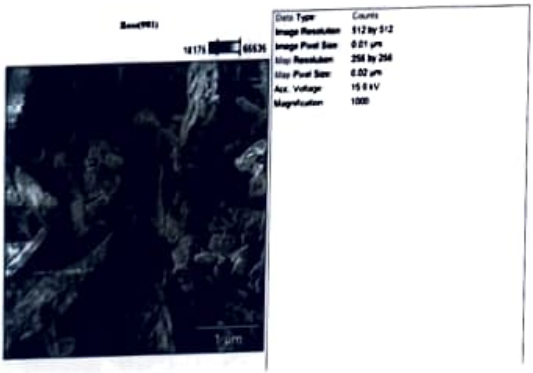
9. XrD data can provide useful information and also help correlate microscopic observation with the bulk sample.

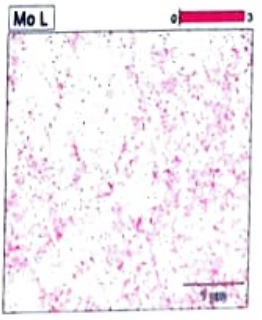
10.XrD has wide range applications such as structure of crystals, polymer characterization, state of anneal in metals and determination of cis-trans isomerism.

4.1.4 Elemental mapping:









4.2 Kinetics Study between Macro and Nano Metal Oxide

KINETICS OF PHOTODEGRADATION OF INDIGOCARMINE USING ZnO nano, macro & Mo nano particles.

Aim: To study the kinetics of photodegradation of indigocarmine using Zno and Mo oxide nano particles as photocatalyst and determination of state constant.

Introduction: over past many decades dyes have been posing potential environmental hazards as their manufacturing involves a variety of organic chemicals. Some of which are carcinogenic , therefore the present experiments focus on the ability of UV light and Solar energy to destroy indigocarmine organic dye through photo associated catalytic degradation.

INSTRUMENT REQUIRED-UVlight,calorimeteror spectrophotometer .

CHEMICALS REQUIRED- indigocarmine solution(0.001),zincoxide and molybdenum oxide(solid),25ml volumetric flask.

PROCEDURE-

1. Weigh accurately 0.3g of powdered zinc oxide and molybdenum oxide in to each one of the six different 25ml volumetric flask.

2. Pipette out 1.25ml of 0.001M IC solution make up with distilled water.

3. Irradiate the above solution in UVlight %T at different intervals of time i.e 0,10,20,30,.....60 min at lamda max =610nm.

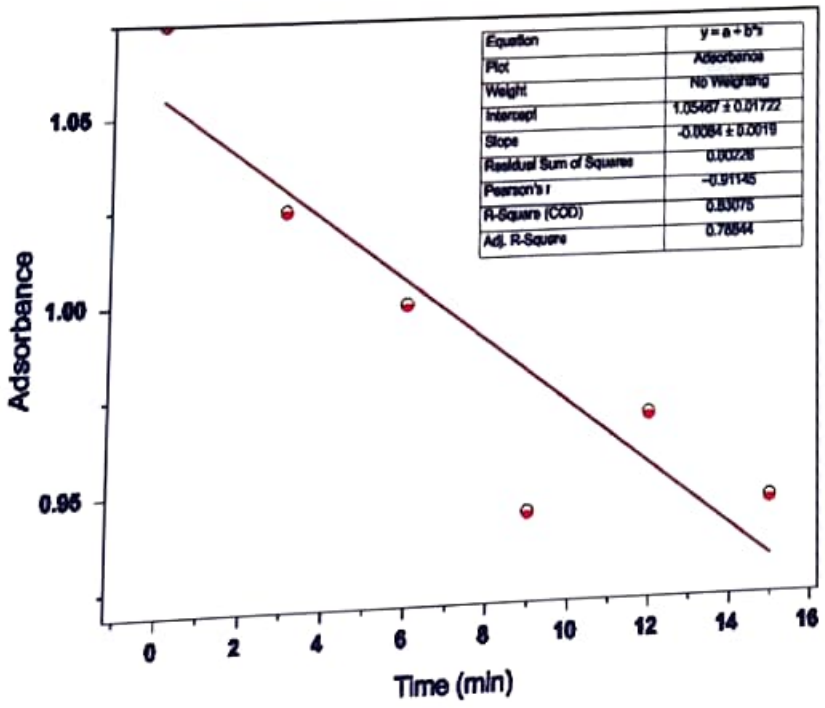
4. Plot a graph of absorbence v/s time from the slope of the linear plot calculate the rate constant(k).

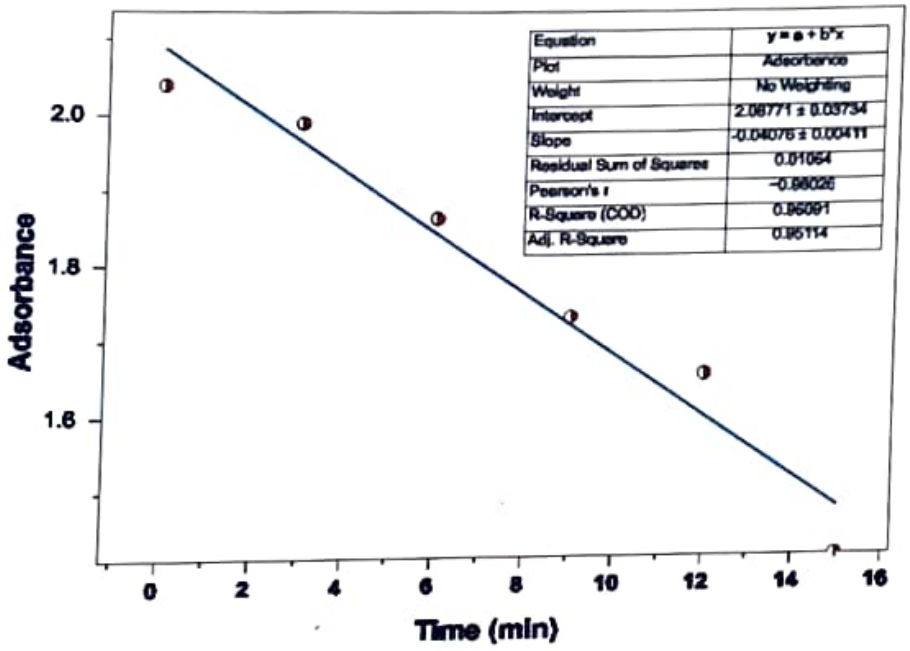
K=2.303*slope /60

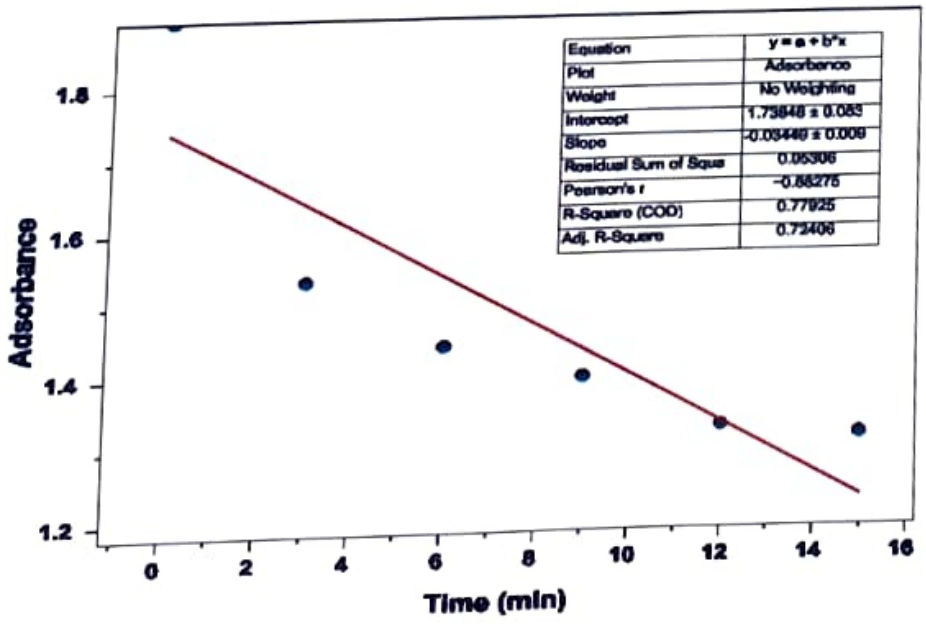
5.Repeat the experiment with 0.5g and 0.7g of zinc oxide and molybdenum oxide nano particles and compare the rate constant with 0.3g zinc and molybdenum oxide nano particles.

Recorded absorbence using uv spectrophotometry in 610nm wavelength for zinc oxde nanoparticles.

TIME	ABSORBENCE		
	0.03	**0.05**	**0.07**
0	1.075	2.04	1.895
3	1.024	1.99	1.530
6	0.998	1.864	1.437
9	0.942	1.732	1.391
12	0.967	1.654	1.320
15	0.944	1.412	1.306




Equation y = a + b*x
Plot Adsorbance
Weight No Weighting
Intercept 2.08771 ± 0.03734
Slope -0.04076 ± 0.00411
Residual Sum of Squares 0.01064
Pearson's r -0.88026
R-Square (COD) 0.96091
Adj. R-Square 0.95114
Adsorbance
2.0
1.8
1.6
0
2
4
6
8
10
12
14
16
Time (min)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Weight No Weighting
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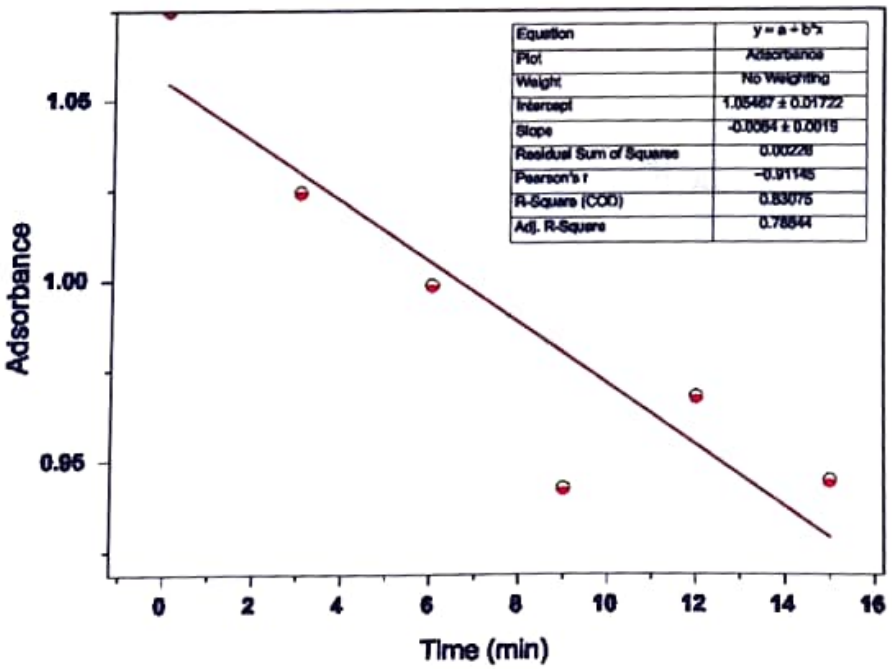
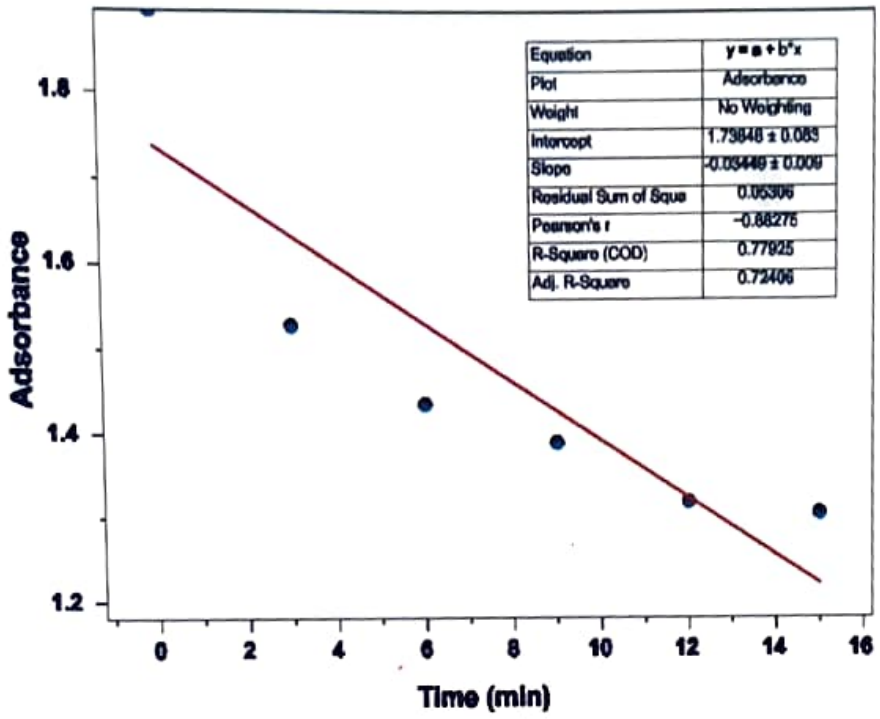
Slope -0.03446 ± 0.009
Residual Sum of Squa 0.05306
Pearson's r -0.88275
R-Square (COD) 0.77925
Adj. R-Square 0.73406
Adsorbance
1.8
1.6
1.4
1.2
0
2
4
6
8
10
12
14
16
Time (min)

Recorded absorbence using uv spectrophotometry in 610nm wavelength for molybdenum oxide nanoparticles.

TIME	ABSORBENCE		
	0.03	**0.05**	**0.07**
0	1.260	1.651	2.06
3	1.114	1.502	1.82
6	1.041	1.410	1.74
9	1.017	1.368	1.62
12	0.986	1.326	1.56
15	0.973	1.319	1.50

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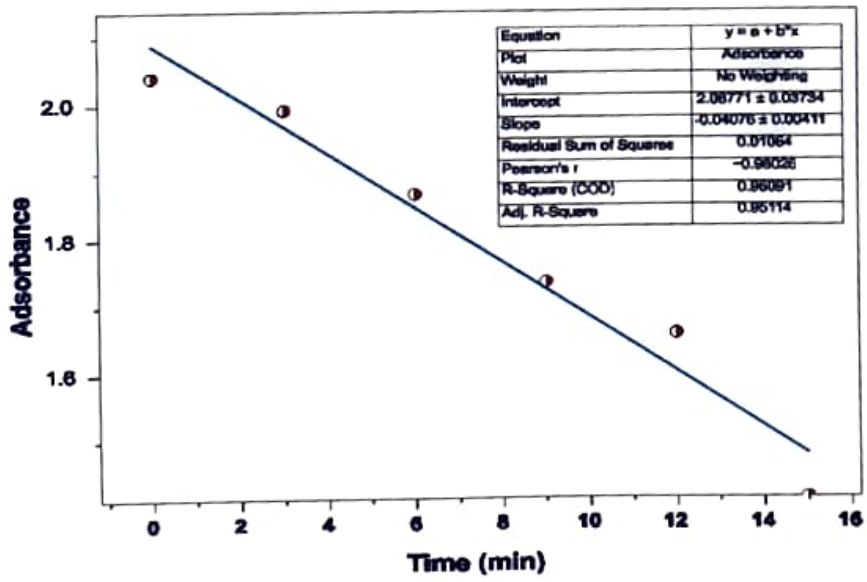
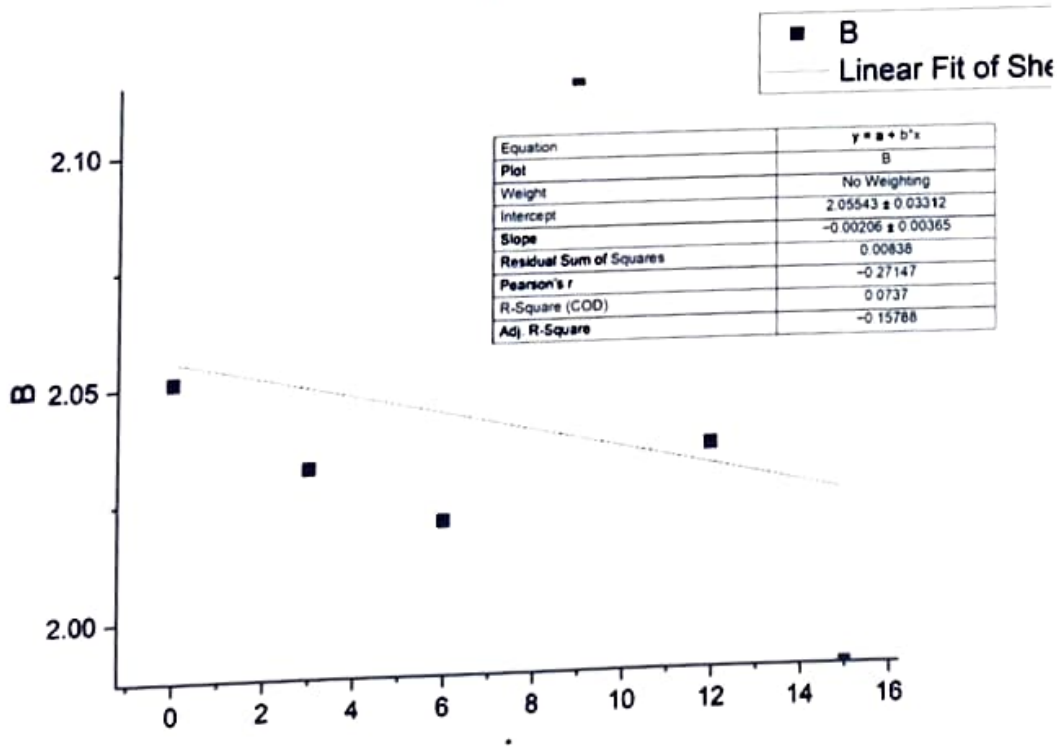
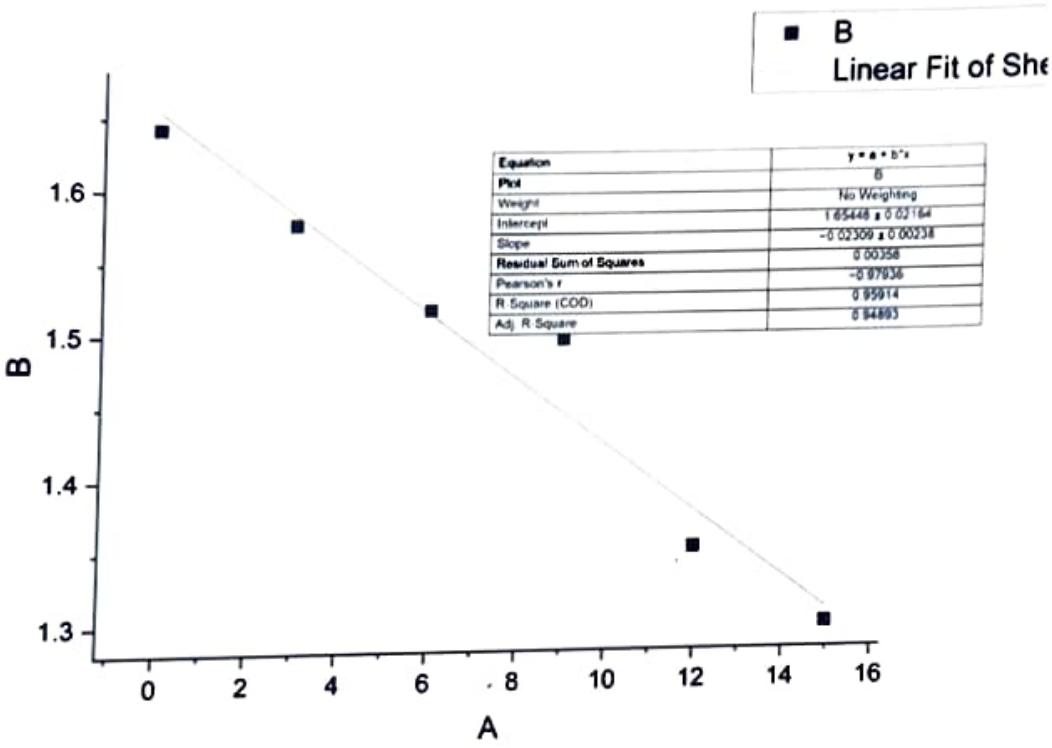
Plot Adsorbance
Weight No Weighting
Intercept 1.79848 ± 0.085
Slope -0.05449 ± 0.009
Residual Sum of Squa 0.05306
Pearson's r -0.88275
R-Square (COD) 0.77925
Adj. R-Square 0.72406
Adsorbance
1.8
1.6
1.4
1.2
0
2
4
6
8
10
12
14
16
Time (min)


Equation y = a + b*x
Plot Adsorbance
Weight No Weighting
Intercept 2.08771 ± 0.03734
Slope -0.04076 ± 0.00411
Residual Sum of Squares 0.01064
Pearson's r -0.98026
R-Square (COD) 0.96091
Adj. R-Square 0.95114
Adsorbance
2.0
1.8
1.6
0
2
4
6
8
10
12
14
16
Time (min)

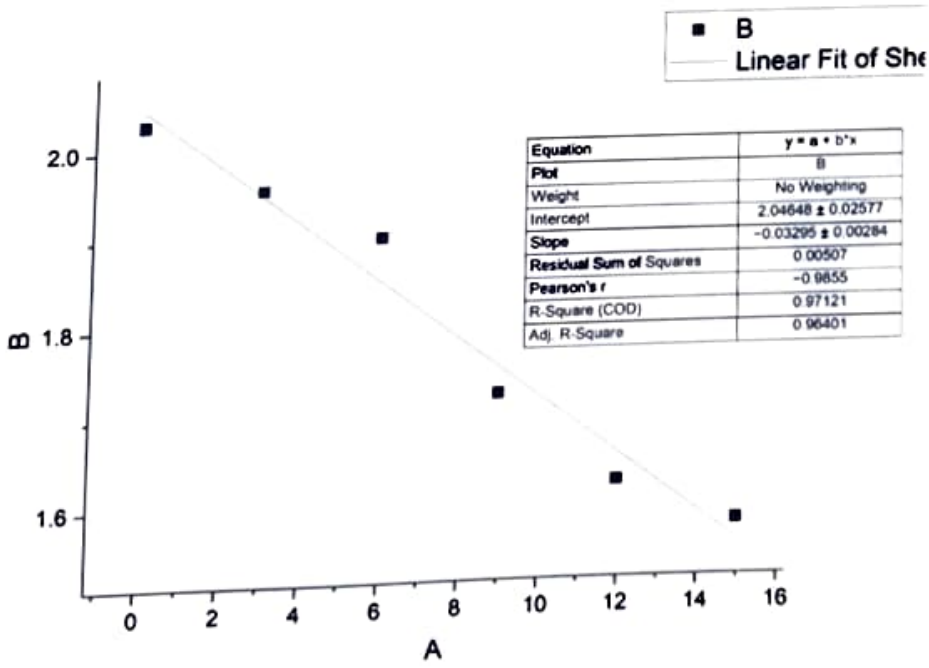
Recorded absorbence using uv spectrophotometry in 610nm wavelength for zinc oxde macroparticles.

TIME	ABSORBENCE		
	0.03	**0.05**	**0.07**
0	2.051	2.030	1.643
3	2.032	1.954	1.578
6	2.020	1.898	1.519
9	2.115	1.720	1.498
12	2.035	1.620	1.352
15	1.987	1.575	1.298





Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	1.65448 ± 0.02164
Slope	-0.02309 ± 0.00238
Residual Sum of Squares	0.00358
Pearson's r	-0.97936
R Square (COD)	0.95914
Adj. R Square	0.94893



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	2.04648 ± 0.02577
Slope	-0.03295 ± 0.00284
Residual Sum of Squares	0.00507
Pearson's r	-0.9855
R-Square (COD)	0.97121
Adj. R-Square	0.96401

4.2.1 Calculation

1. **0.001M Indigo carmine solutions:**

0.001*50*466.36/1000 = 0.023g

From graph of zinc oxde nanoparticles

K1 = 0.00307

K2 = 0.00171

K3 = 0.00107

K1>K2>K3

From graph of molybdenum oxide nanoparticles.

K1 = 0.00376

K2 = 0.00080

K3 = 0.00061

K1>K2>K3

From graph of zinc oxide macroparticles.

K1 = 0.00042

K2 =0.00027

K3 =0.00019

K1>K2>K3

4.3 Anti bacterial activity study of Molybdenum oxide nano particles.

Antibacterial activity

The pure cultures obtained were revived and maintained in nutrient agar at 37°C.The microorganisms were cultured in nutrient broth at 37°C over night.

Determination of antibacterial activity by disk-diffusion method

The test organisms were subculture using nutrient agar medium. The tubes containing sterilized medium were inoculated with the respective bacterial strain. After incubation at 37°C ±1°C for 18 hours, they were stored in a refrigerator. The nutrient agar medium was sterilized by autoclaving at 121°C for 15 min. Into each sterilized petriplate, was poured about 25 ml of nutrient agar medium [1]. The plates were left at room temperature aseptically to allow the solidification. After solidification, the appropriate bacterial cultures were inoculated over the surface of the agar using glass beads. The discs of each compounds was placed individually on nutrient agar medium with fresh bacteria respectively. Each test compound was dissolved in sterile water. Each test compound were added separately in the plates were kept undisturbed for at least 2 hours in a refrigerator to allow diffusion of the solution properly into nutrient agar medium. Petri dishes were subsequently incubated at 37±1 ^{0}C for 24 hours. After incubation, the diameter of zone of inhibition surrounding each of the dishes was measured with the help of an antibiotic zone reader.

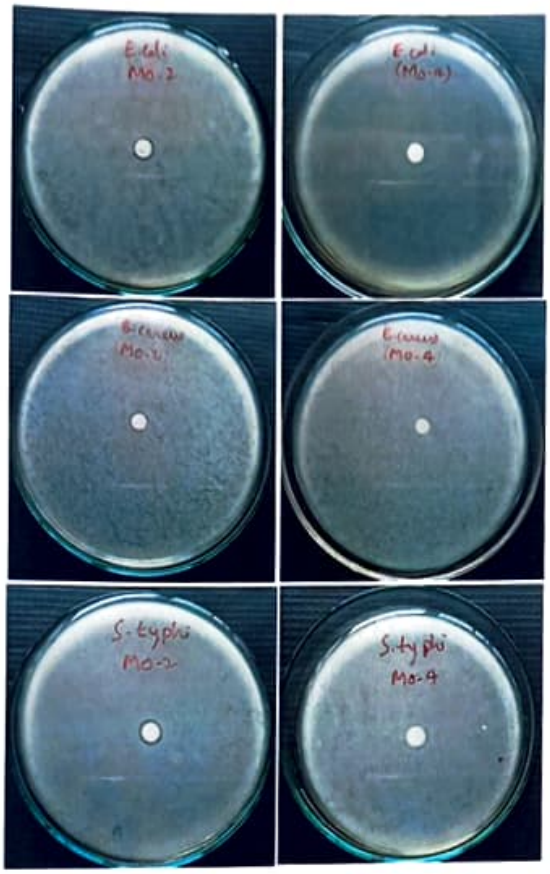


Fig-1 Anti bacterial activity of test compounds *against*

E.coli, B. cereus and S. typhi

The antibacterial activity of Mo nanoparticles was tested against the three different bacteria like *Escherichia coli*, *Bacillus cereus,* and *Salmonella typhi*. The diameter (mm) of the inhibition zone as depicted in Fig.1 and also tabulated in Table 1. Antibacterial activity of Mo nanoparticles was observed in *E.coli and S.typhi.* Mo nanoparticles did not show any zone of inhibition in *B.cereus*. Mo-4 nanoparticles showed more antibacterial activity when comparison to Mo-2 nanoparticles.

Table- Antibacterial activity of Mo nanoparticles

Sl.no		*E coli*	*B cereus*	*S typhi*
1	**MO-2**	**7.27 ± 0.21**	nil	**7.5 ± 0.50**
2	**MO-4**	**8.4 ± 0.53**	nil	**8.4 ± 0.53**

(Diameter of the inhibition zone in mm at 200 µg of Sample)

4.4 Conclusion

MoO_3 is a promising candidate to realize applications in electronic, photo-catalytic, gas sensor, biological activity, electrochromic, photochromic, lithium-ion batteries etc., owing to its tuneable properties. It is an n-type wide band gap semiconductor with three crystal structures (i) orthorhombic (a-MoO_3) which is thermodynamically stable, (ii) metastable hexagonal (h-MoO_3) and (iii) monoclinic (m-MoO_3). Orthorhombic (a-MoO_3) phase is widely studied by researchers because it gives out many applications. Molybdenum oxide nanoparticles.

Nanoparticles synthesized by using medicinal plant extract and calcined at 530∘ C for 3 h were MoO3 (MOLYBDINUM OXIDE). This review highlights the recent developments in molybdenum nanoparticle synthesis by plant either in the form of extracts or as it is. While physical and chemical methods of synthesis are more common, several eco-friendly and economically feasible synthesis protocols have also been developed, in some cases even by employing unused plant parts such as peels and leaves. As-synthesized nanoparticles have been successfully implemented in the fields of medicine and environmental remediation. However, the enormity of future research scope in this field cannot be accentuated enough.

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