

SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF ADIPIC ACID AND THIOUREBASED TEMPLATE MEDIATED COMPLEXES DOPED WITH METAL(II)SULPHATES

Priyashree Sindhu¹, Monika Chahar^{1*}, Sushila Singhal², Namita Gandhi²

¹ Department of Chemistry ,BMU , Rohtak , Haryana

¹ Baba Mastnath University , Asthal Bohar -124021, Rohtak , India

² Deshbandhu College,Kalkaji-11019 ,University of Delhi , India

Corresponding Author : chaharmonika507@gmail.com , sushilasinghal1@gmail.com

Abstract- In the presence of ethanol, the template-mediated synthesis of compounds that took place under mild circumstances was accelerated up. This was accomplished by homogeneously combining thiourea with adipic acid (AC) on a heated plate using a water condenser to form crystals. Investigations utilising as in-depth examinations using FTIR, UV-VIS, and SEM were carried out on the reaction in order to validate the growth of crystals.. The FTIR spectra indicated the existence of a broad variety of distinct functional groups despite the dramatic drop in their total number. The "UV-Vis" spectra show that the crystal possesses high absorption between 295-310 nm throughout a broad range, encompassing the visible and near-IR regions of the spectrum.

Keywords: template-mediated, thiourea, FTIR,UV-VIS,SEM.

1) Introduction:

Thiourea ligands and the metal complexes of these ligands exhibit a wide variety of biological actions, including but not limited to the following: anticancer [3, 4], antimicrobial [4, 5], antibacterial [6, 6], antifungal [7, 8], antimalarial [8, 9], and antituberculosis [10.] Numerous investigations on benzoyl-substituted thioureas and other ligands that are similar to those that are coordinated to metals have been carried out [9]. These ligands are often coordinated to the metal through the elements of sulphur and oxygen, which ultimately results in the formation of a six-membered ring structure [10]. They are able to form coordination complexes with one another in order to organise metal centres as either neutral ligands or anionic ligands [11]. The increasing demand for innovative, functional, and intelligent materials which are useful in several spheres and disciplines by minimal adjustments/ improvisation with their synthesis based on the novel and if possible green techniques are the ultimate research, beneficial to the society and environment. One such molecule in nature and which is even prepared synthetically is porphyrin. It has so many advantages that its mimics have also been prepared. It is involved in various functions like photosynthesis, mimicking superoxide dismutase, catalyzing halide oxidation reactions, applicability in organic solar cells, artificial photosynthesis, targeted drug delivery systems, sensors, optoelectronic materials, photodynamic therapy, photocatalysts, coordinating with different elements in its cavity, fluorescent probes for detecting heavy metal ions, for example, mercuric ion Hg^{2+} , acting as one of the constituents in clathrates/host-guest complexes are few of the favors it has on the mankind. This list is not complete because it has

multifaceted characteristics which are tunable through different functionalization of the outer boundary and metals that it bounds.

According to the findings of a number of studies, the antibacterial activity of some compounds is enhanced when the compounds are complexed with copper. [Citation needed] There have only been a few of studies done on aromatic diamines, such as 1,2-Bis[N'-(2,2-dimethylpropionyl) thioureido]cyclohexane[12] and 1,2-bis(N'-2methoxybenzoyl thioureido)-4-nitrobenzene"[13]. [12] and [13] are the references for the two studies, respectively.

The current inquiry focuses on adipic acid and thiourea (TA), an analogue of compound crystal, and uses the high-dilution approach to analyse the results.

The powder FTIR, UV-vis, SEM, analyses were performed on the generated crystal [14].

2) Experimental: Synthesis of Adipic and Thiourea based Template mediated complexes doped with metal (II) sulphates

Step I

In order to produce TA, also known as thiourea adipic acid, a technique known as the dilution principle method was applied, and the thiourea needed to be dissolved in the least quantity of water feasible before proceeding. This solution was brought to room temperature, and 50 millilitres of ethanol and 2 grams of adipic acid were added to it while it was being stirred constantly. After this step was complete, very little amounts of ethanol were added while the mixture was continually stirred. After that, place the mixture in a flask that has a circular bottom and a water condenser on a hot plate and keep it at a temperature between 70 and 80 degrees Celsius for 10 to 14 hours. After that, a white crystalline solid was produced, and after that, it was washed with distilled water numerous times before being kept in an air oven at a temperature of 45 degrees Celsius. Ethanol was then used in a process that involved progressive evaporation as part of the recrystallization procedure for the chemical that had previously been manufactured [15].

The product is a solid that melts at a temperature of 162 degrees Celsius and is of the same name as the material that was manufactured. It is possible to dissolve it with water. 88 is the percentage that represents the yield of the chemical when it is measured.

Step II

In order to continue working on it, we react it with heavy metals[16].

I made the decision to go with lead sulphate, also known as Pb(II) sulphate and PbSO₄.

All of the chemicals that were utilised in the experiment were of sigma grade, and no additional purification was done before using them.

Every one of the solutions was prepared using de-ionized or double-distilled water.

"Pb(II) sulphate given by Mumbai, India (minimum assay 99 percent) were created from the solution containing 200 mg/L as both the stock solution and one of the test solutions. Subsequent dilutions were made at the following concentrations: 150 mg/L, 100 mg/L, 50 mg/L, and 10 mg/L. The ph of the solution was 5.0, and this value did not shift significantly after being diluted. The acidity of heavy metal (Pb(II)sulphate)solutions was modified by the addition of drops of 0.1 M HNO₃ and 0.1 M NaOH solutions in order to conduct tests at a

range of varied pH values. The synthesised compound AATU, with an average weight of 2.00 grammes, was mixed with 100 millilitres of an aqueous heavy metal solution in a bath shaker maintained at a fixed temperature for a predetermined amount of time while rotating at a constant speed of 200 revolutions per minute"[17].

After this step, the mixture was filtered, and the EDS was used to analyse what was left behind. The equation used to determine the amount of mass contained in AATU's heavy metals was eq-1.

$$Q = \frac{C_0 - C_e}{M} \dots\dots\dots 1$$

"Where C_0 and C_e are the concentrations of heavy metal in mg/L before and after adsorption for the time in minutes, and M is the quantity of adsorbent in grammes that was used for 1 litre of heavy metal solution. The amount of adsorption, expressed as a percentage, may be calculated using equation 2".

$$\text{Adsorption\%} = \frac{C_0 - C_e}{C_0} * 100 \dots\dots\dots 2$$

"All the batch studies were performed in triplicate within error of $\pm 0.5\%$. To investigate the effect of various operational parameters like pH, temperature etc. The following experimental conditions were opted for different batch experiments (Table-1)"[18].

Results & Discussion

FTIR Study of Adipic Acid and Thiourea Acid

At a frequency of 2960.75, the chemicals that have been created experience ν_{NH} stretching vibrations. At a frequency of 1566 cm^{-1} , aromatic stretching vibrations may be observed in the compounds that have been produced[19-22]. At a frequency of 734 cm^{-1} , the stretching vibration denoted by the symbol $\nu_{C=S}$ takes place. 1570 cm^{-1} is the frequency at which the absorption band caused by δ_{NH} out of plane bending occurs. The three different forms of NH_2 group coming out of tautomeric form are indicated by the vibrations that were observed at 3588 cm^{-1} , 3568 cm^{-1} , and 2960 cm^{-1} respectively[23-26]. At 1044 cm^{-1} , the ν_{C-N-C} structure is seen. This provides a positive indication of the substitution occurring on thiourea and adipic acid as well as the creation of the chemical. The bending vibration of the NH_2 molecule is the source of the prominent peaks that can be detected at a frequency of 1,701 cm^{-1} . The stretching mode denoted by "C-C" varies in intensity at a frequency of 926 cm^{-1} . IR representation signals that were drawn using the origin programme. The "C-C-N" stretching mode, which can be noticed in the spectrum, is the cause of the enormous peak that was detected at 734 cm^{-1} [27-28].

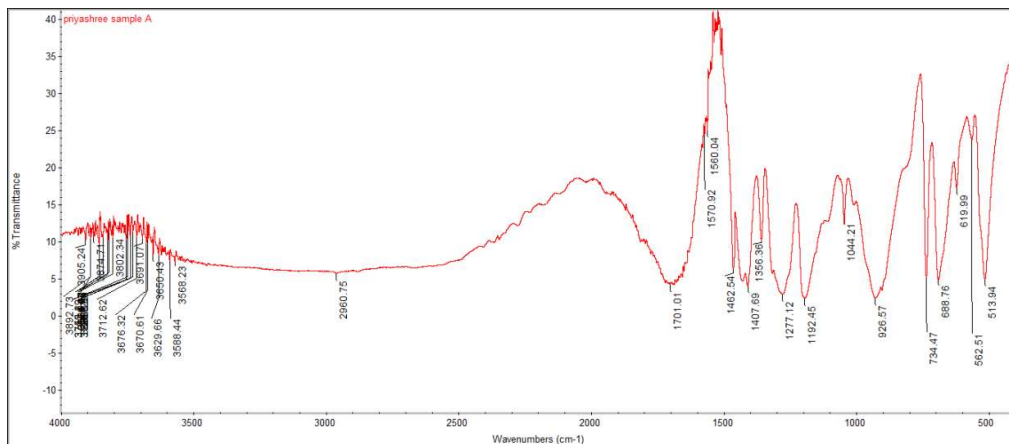
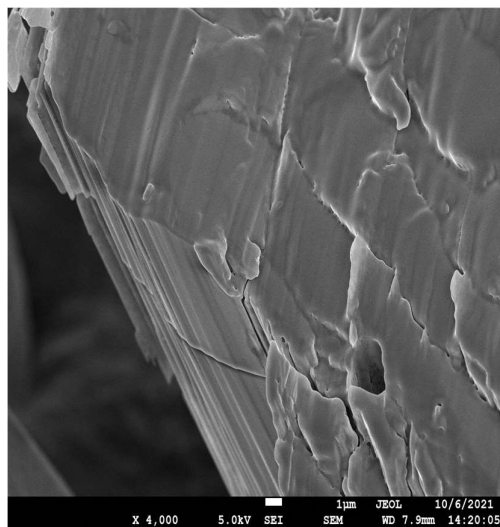


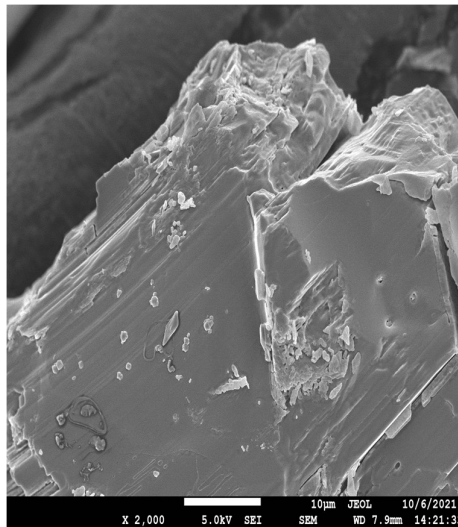
Figure: The FT-IR Spectrum of AATU(adipic acid thiourea doped compound)

SEM Study

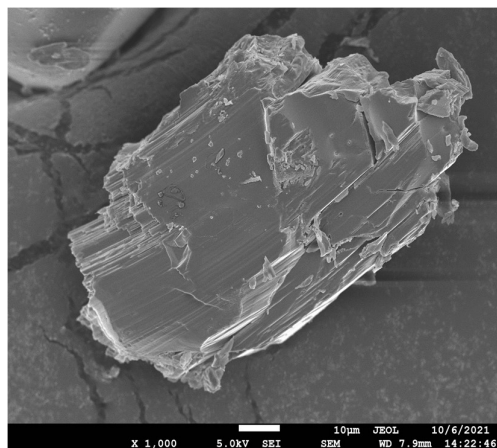
SEM surface investigation of crystal, the morphology of AATU was analysed using SEM, and SEM photographs available with a variety of magnifications and scales were used for the analysis. Crystals appear to have smooth surfaces when viewed at a magnification of 4000 and a scale of 10 micrometre. In addition, the magnifications and scales that are presented below show how the visible differences may be seen. (2) This image was taken at a magnification of 2,000 and 100 micrometer. (3) Using a scale of 10 microns and a magnification of one thousand. (4) This image was taken at a magnification of 500 and a scale of 10 micrometres[29].



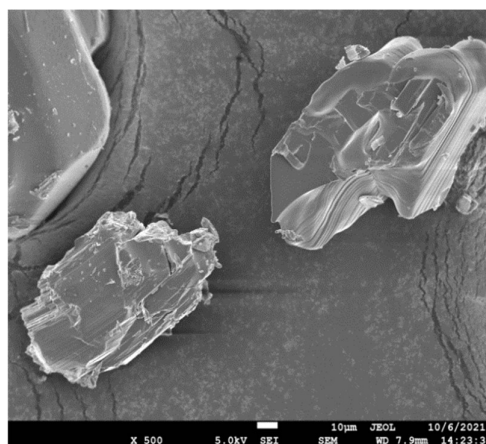
a)



b)



b)



d)

Figure SEM Micrograph of Synthesized Adipic acid and Thiourea Acid showing different magnifications before absorption

UV-Vis Spectrophotometry

Benzene ring transitions were observed using UV-visible spectrophotometry, which was utilised to describe the molecule that was produced. These transitions were ascribed at the wavelength of 295 nm [30]. Additionally, there are two carboxyl groups that are ortho to each other. In the instance of the C = S group, the transition that occurred at a wavelength of 305 nm was referred to as n^* , whilst the Dd transitions occurred at a wavelength of 410 nm[31].

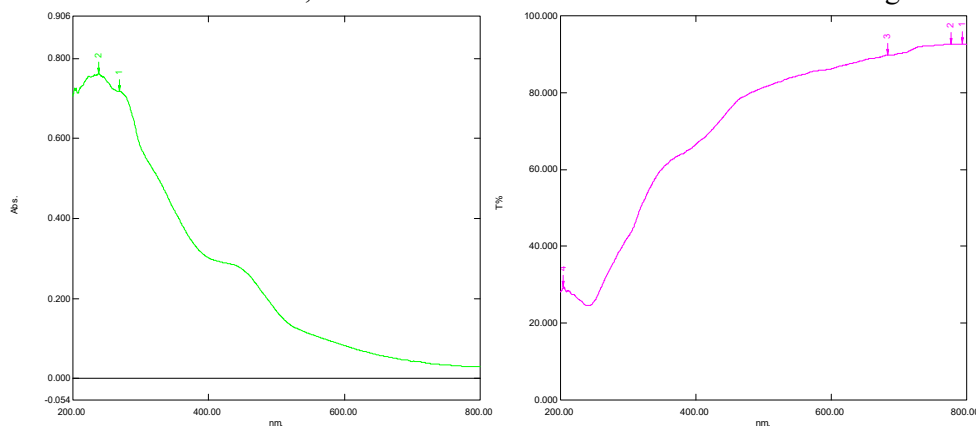


Figure Absorbance and Transmissions of spectral analysis

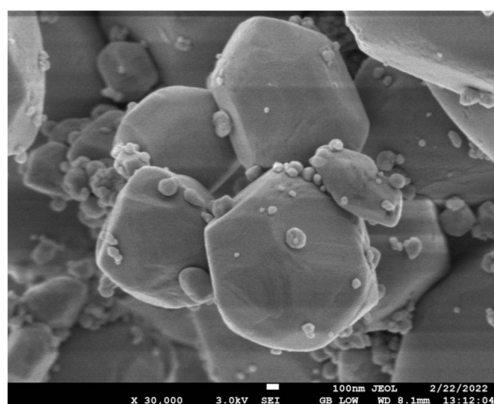
Applications

The continuous growth of environmental pollutants as a result of accelerated industrial development and rising needs of human beings have led to a serious concern among present-day scientists. Determining the use of synthetic compounds in a variety of fields is necessary in order to address this issue. Despite this, the idea of a clean and green environment requires a comprehensive understanding of the many forms of pollution (air, water and soil)[32].

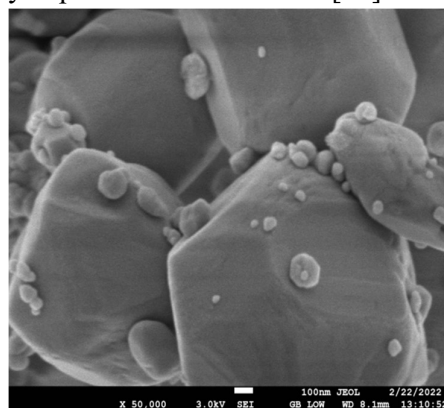
Sem

The SEM micrograph of the template mediated doped compounds of thiourea and adipic acid with heavy metals sulphates at a magnification of x 50,000 before to adsorption are displayed

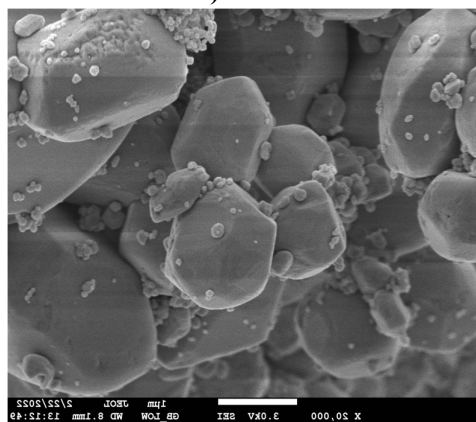
in the figure below, and the subsequent surface assimilation of metals is shown in the figure below at different orientations using SEM analysis[33]. There are noticeable changes to the surface morphology of the compounds as well as the creation of discrete aggregates on the doped compound surface following metal removal via adsorption showing that the biomaterial surface following metal removal via adsorption. Figure showing that the doped compound was an assemblage of fine particles (needle like structure due to crystalline nature and like cavities due to templates) but irregular. The particles were found to be of various dimensions consisting of steps and kinks on the external surface. Interaction of doped compound with heavy metals has resulted in the formation of flake -like shiny deposition on its surface [34].



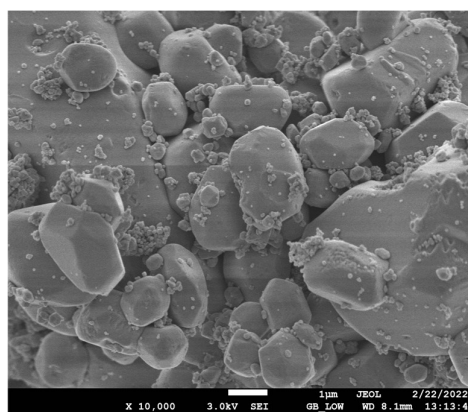
a)



b)



c)



d)

bacterial pathogens and even commensal species, this scenario is becoming an increasingly problematic one. "In-vitro antimicrobial susceptibility testing is performed with the intention of providing a reliable prediction of how an organism is likely to respond to antimicrobial treatment when it is administered to an infected host. These types of epidemiological monitoring data give a foundation upon which to select the most appropriate empirical treatment (fine line therapy) and to identify the appearance and/or propagation of resistant bacterial strains or resistance determinants in various species of bacteria" A measure of a microbe's level of vulnerability to antimicrobial drugs. The choice of a methodology is determined by a variety of considerations, including those pertaining to practicability, adaptability, automation, affordability, repeatability, accuracy, and individual preference.

Reference Strains recommended by the CLSI for AST profiling-

Bacterial strains

Escherichia coli

Bacillus subtilis

Pseudomonas aeruginosa

Broth dilution method

"The broth dilution methods are used for the purpose of determining the minimal inhibitory concentration (MIC), which is typically expressed in units of micrograms per millilitre or milligrammes per litre and refers to the lowest concentration of the antimicrobial that inhibits the visible growth of the bacterium being tested. The purpose of these methods is to determine the lowest concentration of the antimicrobial that inhibits the growth of the bacterium. The method that is known as broth dilution entails conducting an experiment in which a suspension of bacteria is tested against varying concentrations of an antimicrobial agent in a liquid medium that has been predetermined and documented". The optimal or suitable concentration of the bacteria is determined in advance. Either tubes with a minimum capacity of 2 millilitres, which are referred to as microdilution, or microtitration plates with even smaller volume capacities can be used to carry out the broth dilution technique (microdilution). The minimum inhibitory concentration (MIC) is the concentration at which the growth of the bacteria is no longer inhibited, and it is located at a point that is between the lowest test concentration that has this effect and the next lower test concentration. The "real" MIC is the concentration at which the growth of the bacteria is no longer inhibited. It is possible to think of MIC determinations that are carried out with the help of a dilution series as having an inherent variance of one dilution as a result. These determinations are carried out in accordance with standard protocols. The antimicrobial ranges that are employed should comprise not only the necessary quality control reference species, but also the interpretation criteria (susceptibility, intermediate, and resistance) for a specific bacterium/antibiotic combination. The antimicrobial susceptibility dilution procedures appear to be more quantitative and easier to repeat than the agar disk/well diffusion methods. Because of this, it is absolutely vital for these sorts of laboratories to make use of quality control organisms (for more information on this subject, see below), as doing so will guarantee the correctness and standardisation of the processes that they carry out.

Test protocol

“Within 15 minutes of the inoculum being standardised to 0.5 Macfarland, add 1 ml of the adjusted inoculum to each tube containing 1 ml of an antimicrobial agent in the dilution series (along with a positive control tube containing only broth), and mix well. This should be done so that each tube contains 1 ml of the adjusted inoculums”.

In an incubator containing ambient air, incubate the tubes that have been injected under the right conditions.

When defining the growth end points, it is helpful to compare the amount of growth that occurred in the growth tubes that contained the antimicrobial agent to the amount of growth that occurred in the growth tubes that served as controls and did not include any antimicrobial agent.

Preparation of inoculum

1. To make the inoculum, begin by first producing a broth suspension. Next, execute secondary inoculation on a culture that has been growing in the nutrientbroth for at least one full overnight cycle.

2. Make any necessary modifications to the suspension in order to get a turbidity that is comparable to a turbidity standard of 0.5 Mcfarland. The product that was developed is a suspension that has around one to two times 10⁸ colony forming units (CFU) per millilitre.

3. Using a card with a white backdrop and black lines for contrast, compare the inoculum tube and the 0.5 McFarland standard.

1. 4.Dilute the appropriate inoculum suspension in broth as soon as possible, preferably within 15 minutes of finishing the preparation.

2. 5.The method for preparing the culture to be tested is consistent, however the preparation method differs depending on the culture.

Preparation of 0.5 MacFarland standards

1.0.5ml of 1%BaCl₂ and99.5 ml of 1% H₂SO₄ mixed to prepare 0.5 MacFarland.

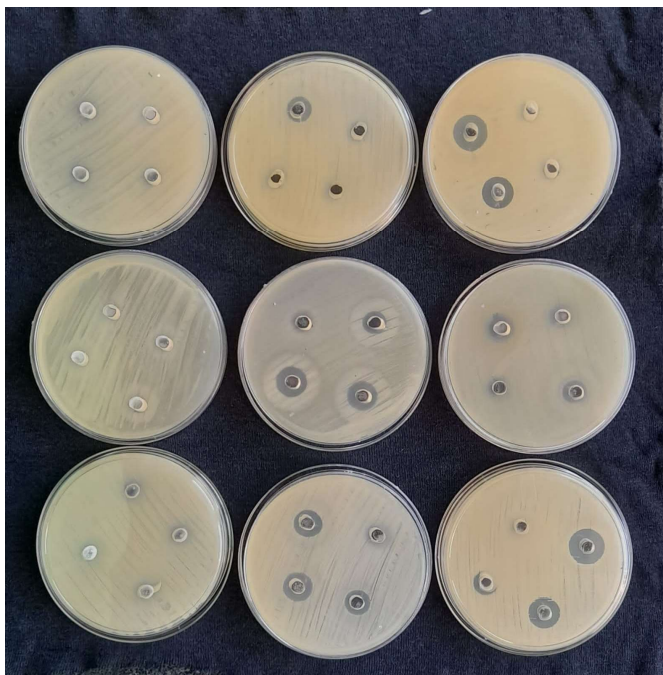
2.0.5 Macfarland =1.5*10⁸ CFU/ml

Specific growth conditions for microbial isolates [36].

For bacterial isolate nutrient broth/agar is used and incubation conditions are 37°C for 14-16 hours.

AATU at conc.	E.coli	Stephlococcus	pseudomonas
CompdCu,25	15	27	23
50	20	20	20
75	25	26	27
100	30	30	30
CompdNi,25	-	23	21
50	-	26	22
75	-	24	20
100	-	27	23
CompdZn,25	-	18	15
50	-	17	13

75	-	24	27
100	-	29	28



Conclusion:

This research work includes the investigation and interpretation between newly synthesized compound with high dilution principle method i.e.doped compound of thiourea and adipic acid(TA) and different anions of heavy metal sulphates.i decide to go with lead sulphate inos(Pb(II) sulphate).The structure of the doped crystal analysed by X-Ray diffraction at 2theta upto 80.All the functional groups in the synthesized compound confirms by the FT-IR specxtroscopic analysis. The good transmittance window is shown by the UV-Vis spectra, and the lower cut-off is discovered to be as low as 305 nm, which enables frequency conversion to the UV-region. The study by the SEM shows that the surface of the crystal can be seen at microlevel magnification at 500, 1000, 2000, and 4000X, which demonstrates that it is possible to add more molecules and grow into a larger crystal. For the purpose of its application with lead sulphates, scanning electron microscopy (SEM) analysis performed after absorption at micro magnifications of 10,000 and 20,000 X demonstrates the presence of a layer of adsorption of heavy metal (Pb(II)Sulfates), the percentage of which is confirmed by EDX..

For the further applications,we examined antimicrobial study with E.coli,stephlococcus and pseudomonas at different concentration value at 25,50,75 and 100 ppm which shows the higher inhibition and act as good antibacterial agent against growth of bacteria. On the basis of the physiochemical characterisation of the synthesised compounds and the biological evaluation of these compounds, the following findings have been obtained. Because of the template effect, the final product is more likely to have a cyclic than an acyclic structure. The hot plate with water condenser technique of synthesis produces a larger yield of product in a shorter amount

of time in comparison to the usual thermal approach. This may be owing to the rate at which the reaction is accelerated. This approach was discovered to be beneficial to the environment.

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