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SYNTHESIS OF TEMPLATE MEDIATED DOPED COMPOUNDS THIOUREA WITH SUCCINIMIDE AND ITS APPLICATION WITH HEAVY METAL SULPHATES

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Abstract:

A novel template-mediated compound crystal called succinimide thiourea has been synthesised, and the high-dilution principle method has been used to successfully produce single crystals of high optical quality. A method that may be used for some macrocyclization processes is known as the High Dilution Principle. For the purpose of characterising the generated crystal, powdered single crystal XRD, SEM, FT-IR, UV–vis, and NMR were used. The powder XRD revealed both the crystalline structure as well as the many reflection planes present in the material. Under magnifications of 500, 100000, 15000, and 20000, a scanning electron microscope (SEM) was utilised to assess the elemental content of the particles as well as their shape. FT-IR spectra provided conclusive evidence for the existence of several vibration modes associated with functional groups. We were able to acquire a peak in the crystal's absorption between 200 and 400 nanometers, as shown by the UV–Vis spectra, which suggest that the crystal has extremely good absorption over the whole visible and near infrared area spectrum.

Keywords: structural investigation, Thiourea, High Dilution Principle, UV-VIS-IR,SEM,XRD,NMR

INTRODUCTION

The research paper titled "Template mediated synthesis of macrocycles containing succinimide and thiourea-applications to pharmaceutics, photosystems, and environment" is largely self-explanatory and was developed to address issues concerning pharmaceuticals, photovoltaic systems, and environmental contamination [1,2]. The challenges that frequently arise while using medications to treat cancer include the drugs' poor water solubility and the toxicity that they cause to healthy tissues[3 ,4]. As a result, a tailored drug-delivery system is required in order to resolve these concerns and achieve greater therapeutic results. Today, reducing environmental pollution has become an extremely difficult task due to the fact that the negative impacts of pollution are already manifesting themselves in the form of diseases in humans, animals, and the environment itself [5,6]. There is a great deal of worry over the hazardous heavy metals that are released into water bodies and soil by businesses such as the chemical, electrical, and metallurgical ones; as a result, there is a need for techniques for their assessment and removal[7] . Second, since volatile organic compounds, which when broken down produce harmful gases, are linked to a wide variety of adverse health consequences, ranging from irritation of the conjunctiva to cancer, detecting them is of the highest significance in order to determine their quantity[8, 9]. These kinds of macrocycles have the potential to be very effective at removing metals that have favourable ligational properties. The need to find new sources of energy has pushed humankind to investigate methods of collecting solar energy, such as photosynthesis. Since this is the case, there is a demand for synthetic photosynthesis, which may be satisfied by conjugated macrocycles such as porphyrin [10, 11].

1. Because it contains both a carbonyl group and a methylene group, succinimide exhibits a high level of chemical reactivity while being readily accessible.
2. The number of hydrogen bonds donated by succinimide is one, while the number of hydrogen bonds accepted is two.
3. The complexity score of succinimide is 105.
4. The chemical thiourea is a planar structure.
5. The spacing between the C=S bonds is 1.71 angstroms.

The C-N pi bond is responsible for weakening the C-S bond. There are two different tautomeric forms of thiourea, although the thione form is the one that is more common in aqueous solutions [12]. For this reason, crystals of succinimde and thiourea have been analysed in great detail by a number of different researchers in order to determine their properties. Methods such as thermal analysis, XRD analysis, microscopic analysis, and spectral analysis are all extremely helpful for characterisation[13,14]. As a result, several writers have utilised these methodologies for the purpose of characterising a variety of materials.

The current work focuses on the formation of a single crystal of succinimde thiourea (STU), which is an analogue of succinimide and is grown using the High Dilution Principle approach[15].

Powder XRD, FT-IR, UV-VIS-IR, SEM, and NMR analyses were performed on the generated crystal.

EXPERIMENTAL:

Synthesis and High Dilution Principle methodology

Ethanol was used to dissolve Succinimide and Thiourea both of which were of the AR grade from Sigma-Aldrich. In order to cultivate crystals of high quality, it is very necessary to get the purity level up to an acceptable level. In the current investigation, the thiourea and succinimide salt that is available in the marketplace was dissolved in ehanol and then further purified through the process of repeated recrystallization. The material that had been recrystallized was then used to prepare the saturated solution. The resultant solution was filtered, and then it was allowed to evaporate at room temperature (32 degrees Celsius) while the conditions were optimised in order to produce crystals using the slow evaporation method. The process of spontaneous nucleation results in the formation of needle-like crystals. After a very lengthy period of time, about ten days, single crystals of high optical quality are collected.

Characterization details

Physiochemical characterization

The synthesised compound of TS was placed in deuterated DMSO and subjected to 1H and 13C nuclear magnetic resonance (NMR) spectroscopy using a Buker 500 MHz spectrometer. Powder XRD patterns of the crystalline powder samples of succinimde and thiourea were recorded using a Rigaku MiniFlex2 goniometer with the attachment of a standard sample holder. The scanning mode was set for a 2 range that was between 10-80 degrees, and the scan speed was.02 degree per minute. After mounting the chosen crystal on the goniometer, optical alignment was carefully performed on the crystal. The grown crystal's unit cell parameters "were indexed by using the first 25 reflections that were collected within the range of 9*- Q 11*. Using the w-2Q scan technique, a total of 998 unique reflections were gathered at an angle of 2* Q _25* between the hkl limits of 0 h 6,-1, k 15,0 1 17. The software programmes CAD-4 Express[28] and Xcad4[29] were utilised in order to refine the cells and perform data reduction on the X-ray images. The crystalline structure of TS was solved by the direct technique utilising the SHELXS-97 program[30], and anisotropic refinement was done for the location of atoms that were not hydrogen utilising the SHELXL-97 program[30]. All of the locations of the hydrogen atoms were locked in place, and they were given permission to ride on the atoms to which they were linked. Molecular images of the TS crystal structure were created with the help of the software programmes ORTEP-3 for Windows[31] and Mercury3.8[32]". The information on the crystal and the details of its structural refinement were presented in the graph shown below.

The geometrical properties of certain chosen hydrogen bonds were used in order to get the FT-IR spectra of the compounds succinimde and thiourea. In order to capture an FT-IR spectrum with the KBr pelletization process, a Shimadzu IRAffinity-1S FTIR spectrometer was utilised. The spectrum was captured at a resolution of 0.5 cm-1 throughout the frequency range of 4000 to 400 cm-1. For the purpose of recording the spectrum, a Nd:YAG laser with a wavelength of 1064 nanometers that was fitted with a "BRUKER RFS27 standalone FT-Raman spectrometer was utilised. Utilizing a spectrophotometer of the Varian,Cary 5000 model, we were able to capture the UV-Vis optical transmission spectrum within the region of 200-400 nm". The Field emission scanning electron microscope JSM-7610 Fplus was utilised for the SEM study that was carried out. In order to make the sample conduct electricity, the surface of the crystal was covered with a very tiny layer of carbon.

Results and Discussion

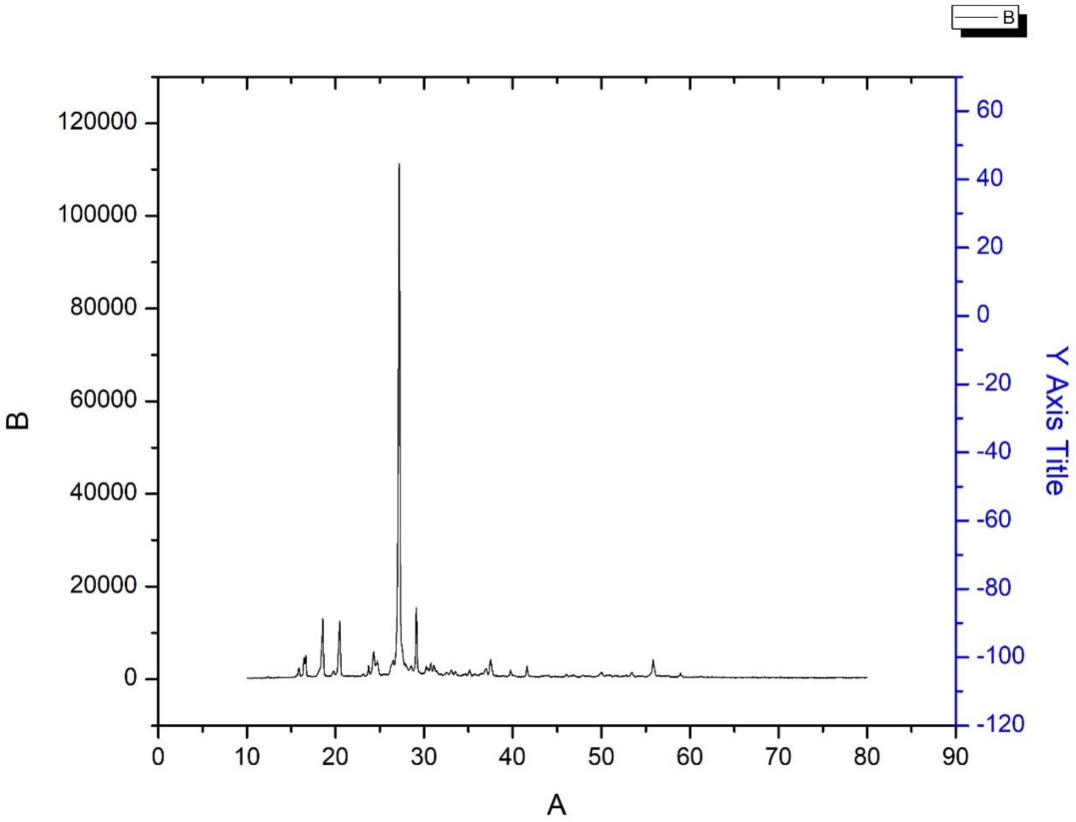
XRD

The purpose of the powder XRD investigation was to provide evidence that each of the samples consisted of a single phase. Table 1 provides a summary of the XRD data for both succinimide and thiourea, while tables 2 and 3 include the XRD patterns for each compound. When crystals are organised, clearly defined Bragg peaks will appear at certain 2 theta angles. This indicates that the crystals are ordered.

We found the "d" spacing and the hkl values for notable peaks in the spectrum, and we compared them with data from the international centre for diffraction data (ICDD).

Doping the crystals with succinimide causes just a very tiny shift in the parameters of the unit cell, which leads one to believe that the crystals maintain practically their original single-phase structure.

The findings of well-defined diffraction peaks at certain 2theta attest the crtysatalline character of the crystal, as well as its high level of purity.

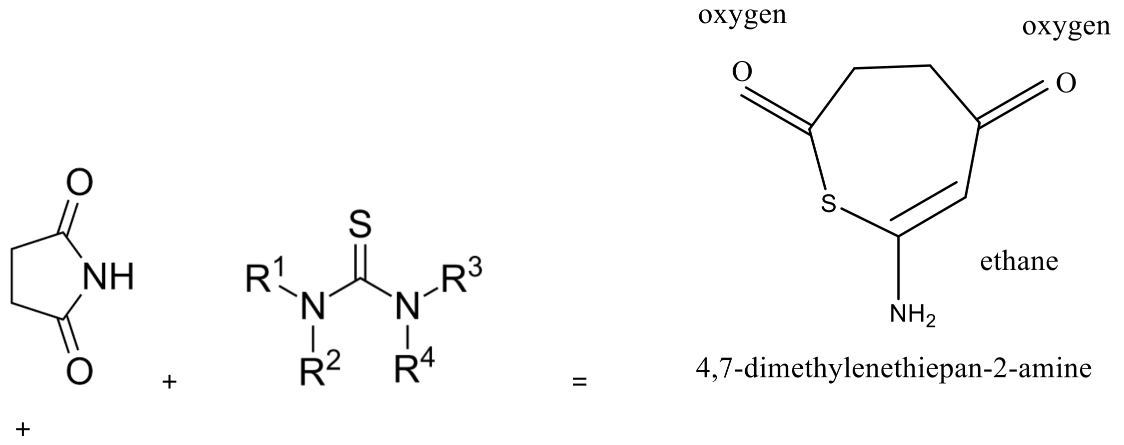


FT-IR spectral studies

The FT-IR spectra of succinimide and thiourea are shown in FIG.> The primary contributors to the formation of the FT-IR spectra of STU are the internal vibrations of the functional groups.

Table 1 Comparison of FT-IR spectra of Succinimide and succinimide thiourea

Succinimide bands/cm_1	Thiourea	Thiourea Succinimide (TS) bands /cm-1	Assignments
3454		3650	Amine N-H stretch
3157		3197	Alkenyl C-H stretch
3080	3000		OH
2924	2960		NH stretching
1829		1836	Conjugated
1783		1604	Conjugated
1772		1743	C=O stretch
1697	1570		C = O stretching
1464	1356	1307	CH bending vibrations
1418	1407		NH bending
1397	1277		CN assymetric
650	688		C = S rocking

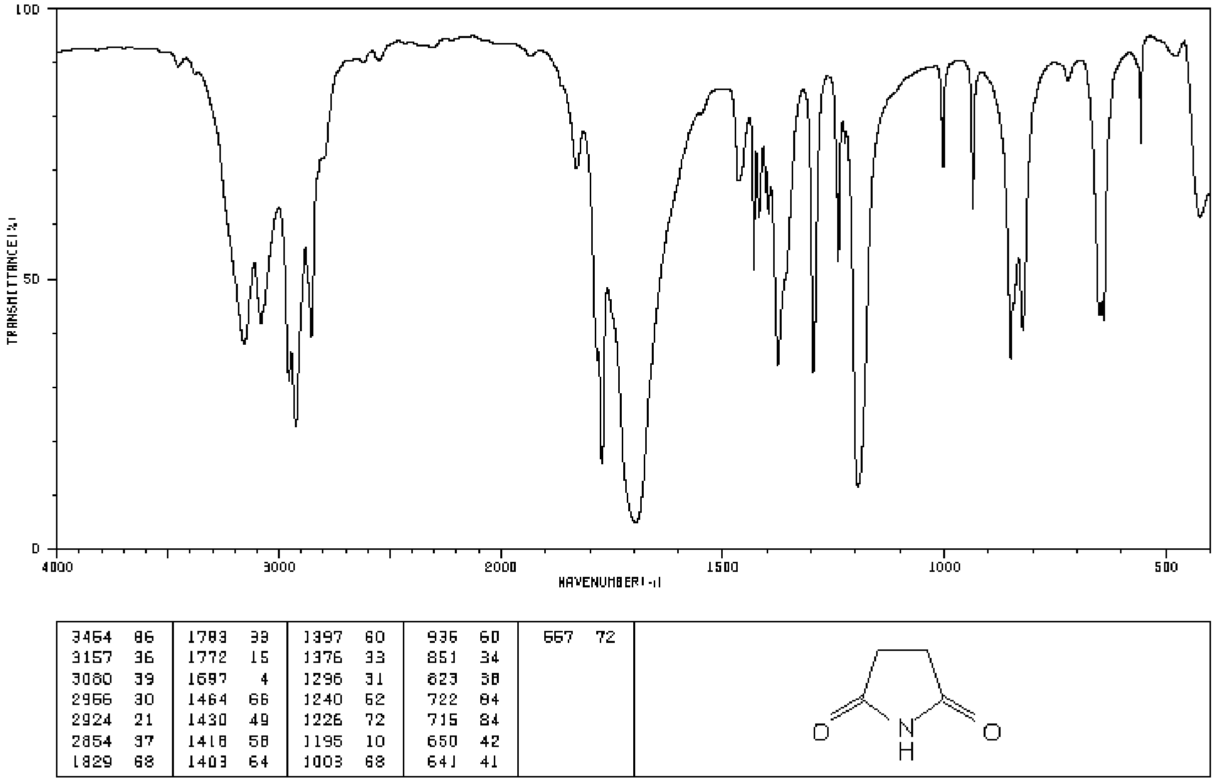


4,7-dimethylenethiepan-2-amine

HIT-NO=823 | SCORE= ( ) | SDBS-NO=1410 | IR-NIDA-62921 : NUJOL MULL

SUCCINIMIDE

$C_4H_5NO_2$



3464	86	1783	33	1397	60	936	60	667	72
3157	36	1772	15	1376	33	851	34		
3080	39	1697	4	1296	31	823	38		
2966	30	1464	66	1240	62	722	84		
2924	21	1430	49	1226	72	715	84		
2854	37	1418	58	1195	10	650	42		
1829	68	1403	64	1003	68	641	41		

Fig 2. Graph of succinimde IR spectrum before template synthesis

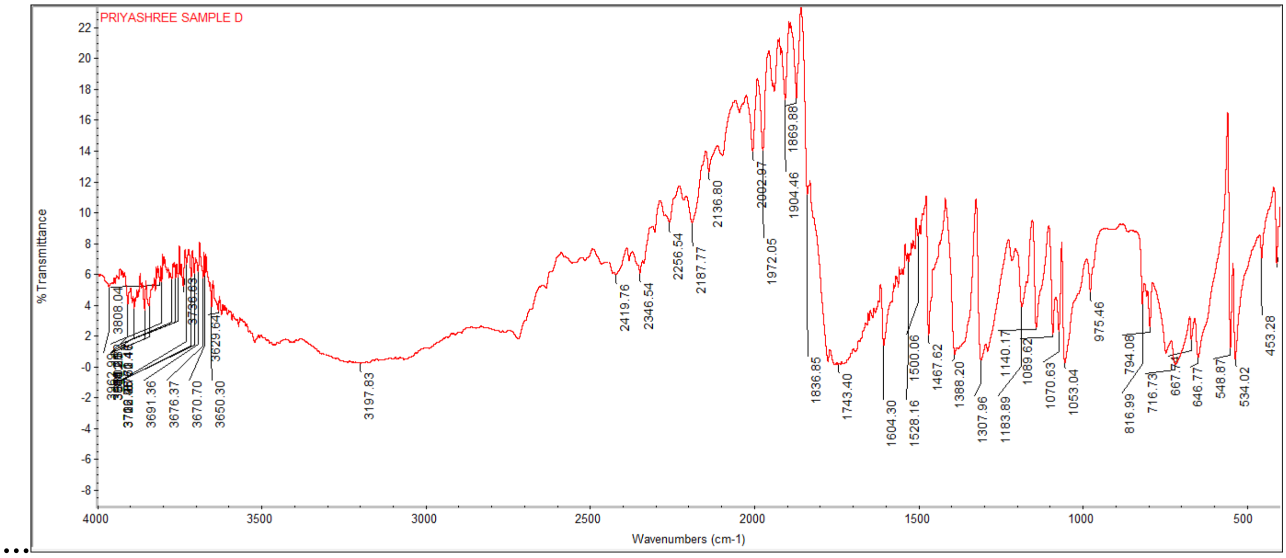


Fig. 3 showing Succinimide and theorem peaks; after template mediated synthesis.

When looking at succinimide and thiourea succinimde, we can see that the initial stages of the compound's decomposition begin at 255 and 280 nanometers, respectively. Because these breakdown temperatures are higher than 80 degrees Celsius, succinimde and succinimde thiourea do not contain any water that is capable of crystallisation.

"NMR spectral analysis"

"The synthesized compound of TS was characterized by1H and 13C NMR spectral technique to determine its molecular structure in an effective manner, and the spectrum that corresponds to this structure is displayed below. The existence of a number of protons in TS compound, including exchangeable protons, is demonstrated beyond a reasonable doubt by the 1H NMR spectra. The appearance of a single signal at a delta of 3.7ppm can be attributed to the protons that are coupled to the succinimde moiety at a level of 8.52ppm. A triplet and multiple signals occurred at delta 2.02ppm The presence of C- and C- protons of the glutaric acid moiety, respectively, corresponds to an amount of 4.82 ppm, as shown. The creation of a co crystal of the TG compound is evidenced by the emergence of a singlet signal at a concentration of 8.52 ppm, which may be attributed to the presence of four numbers of protons in amine groups connected to the theorem moiety. 1H NMR (300MHz,DMSO-D6)delta. When we use the chem draw to determine the value, we discover that there are 7 and 6 diastereotopic at 2.85 ppm, and there are 7 and 6 diastereotopic at 2.00 ppm".

The 13C NMR spectrum demonstrates, beyond a shadow of a doubt, the presence of four carbon peaks, which match to the TS molecule ("both thiourea and glutaric acid moieties are in symmetric nature")

The existence of a thiourea moiety in TS molecule is plainly confirmed by the appearance of a signal at 52.1ppm that corresponds to a thiocarbonyl unit.

Remaining peaks occur at 48.8ppm owing "to the aliphatic carbons connected to the succinimde moiety" which has definitely confirmed the molecular structure of the TS molecule. The signal at delta 156.3ppm is ascribed to the 1-ethylene.

13C "NMR(75 MHZ,DMSO-D6)delta 184.36,174.66,33.30,20.51".

Vibrational analysis

"FTIR spectral studies were pwrformed to identify the internal vibrational thiourea and succinimde molecules.thiourea and succinimide were linked viaintermolecular hydrogen bonds which have been confirmed by weak intensity peak appeared at 3197cm-1 in FTIR spectrum".

"Thiourea"

"Thiourea included two amines (NH2) groups, and one may anticipate seeing their asymmetric and symmetric stretching vibrations, respectively, in the ranges of 3350-3200cm-1 and 3300-3080cm-1. A faint intensity peak could be seen at 3312 cm-1 for the asymmetric stretching vibration of the NH2 group, which was IR active. It was determined that the symmetric stretching vibration of the NH2 group was responsible for the appearance of a faint intensity peak at 3215 cm-1 in both the FTIR and FT-Raman spectra. The most recognisable vibrations of thiourea are the asymmetric and symmetric stretching of N-C-N. These vibrations often exist in the ranges of 1380-1300 cm-1 and 1190-1140 cm-1, respectively [60]. It was determined that the asymmetric stretching mode of N-C-N was responsible for the appearance of a faint intensity peak at 1379cm-1 in both the FTIR and FTRaman spectra. The symmetric stretching vibration of the N-C-N group was found with modest intensities in the FTIR and FT-Raman spectra, respectively, at 1180 cm-1 and 1167 cm-1. The area between 1625 and 1505 cm-1 is where the deformation vibration of the NH2 group is most prominent The FTIR and FT-Raman spectra of the TG compound both showed a faint intensity peak corresponding to this vibration at 1624 cm-1. This peak was observed in the FTIR spectrum. Both the FTIR and the FTRaman spectra obtained from the TG compound exhibited medium to strong intensity peaks at 1411 cm-1, which corresponded to the C=S stretching vibration".

UV-Vis spectral analysis

"To find out the optical absorption range of STU crystal, the UV-VIS spectra of succinimide and succinimde theorem were used. When the absorption is monitored from longer to shorter wavelength, absorption with lower cut-off wavelength below 300 for STU<which is sufficient for synthesis and the transmittance of the crystal, is about 90%in the entire visible and infrared region".The lower cut-off wavelength and the optical transparency area may be determined by optical transmittance spectral analysis, which is a highly useful technique for gaining information about produced crystals. "A broad optical transmittance analysis and a

lower cut-off wavelength than 300 nm are two characteristics that an effective NLO material should have. As can be seen in the illustration, the results of the experiment showed that TS crystal had an excellent optical transparency, with an efficiency that was greater than 65 percent within the range of 225-800 nm. The C-N stretching vibration of the thiourea molecule was attributed to the sudden appearance of a dramatic reduction in the transmittance spectrum above 800 nm. In a surprising turn of events, TS demonstrated a low cut off wavelength of 225 nm".

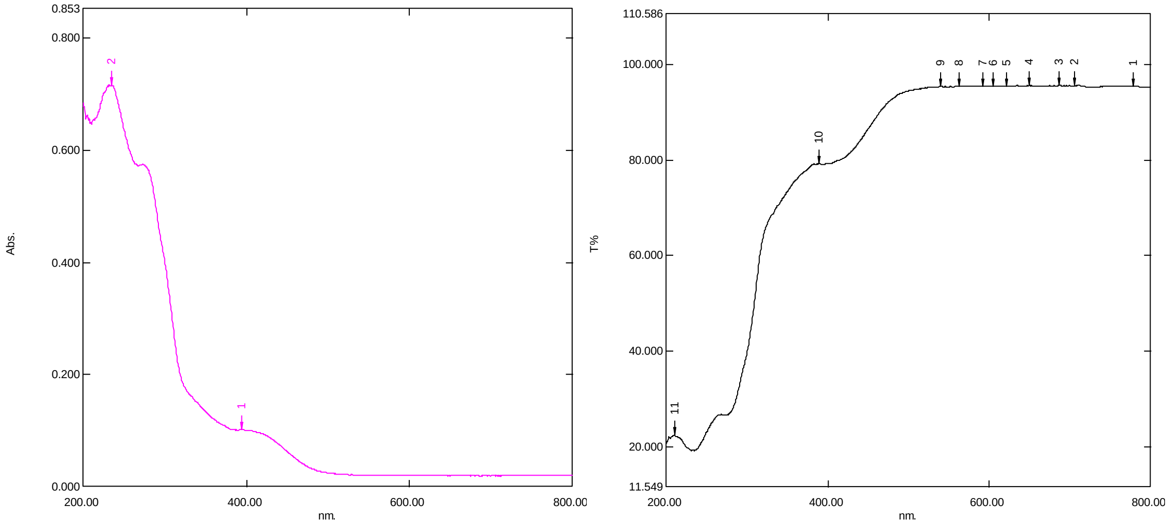


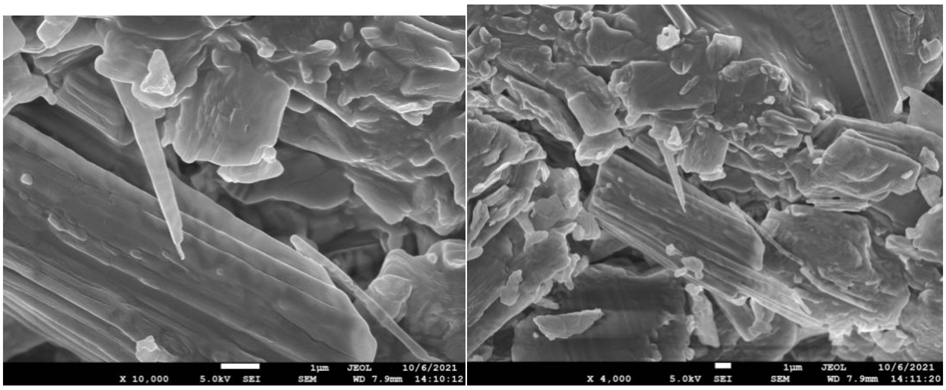
Fig 4. UV absorption and transmittance spectrum;

SEM Analysis

SEM analysis was used to study the morphology of STU that is succinimde thiourea,and the SEM images in different magnification and scales are given in Fig….

The following observations are candid.

1. At a magnifications of 500 and at a scale of 7.9mmKV we observe the crystals have smoothed surfaces.we can also see the significant differences in the following magnification and scales.
2. At a magnifications of 1,000 And at a scale of 7.9mm
3. At amagnifications of 2,000 And at a scale of 7.9mm
4. At a magnifications of 4,000 And at a scale 7.9mm
5. At amagnification of 10,000 and at a scale of 7.9mm



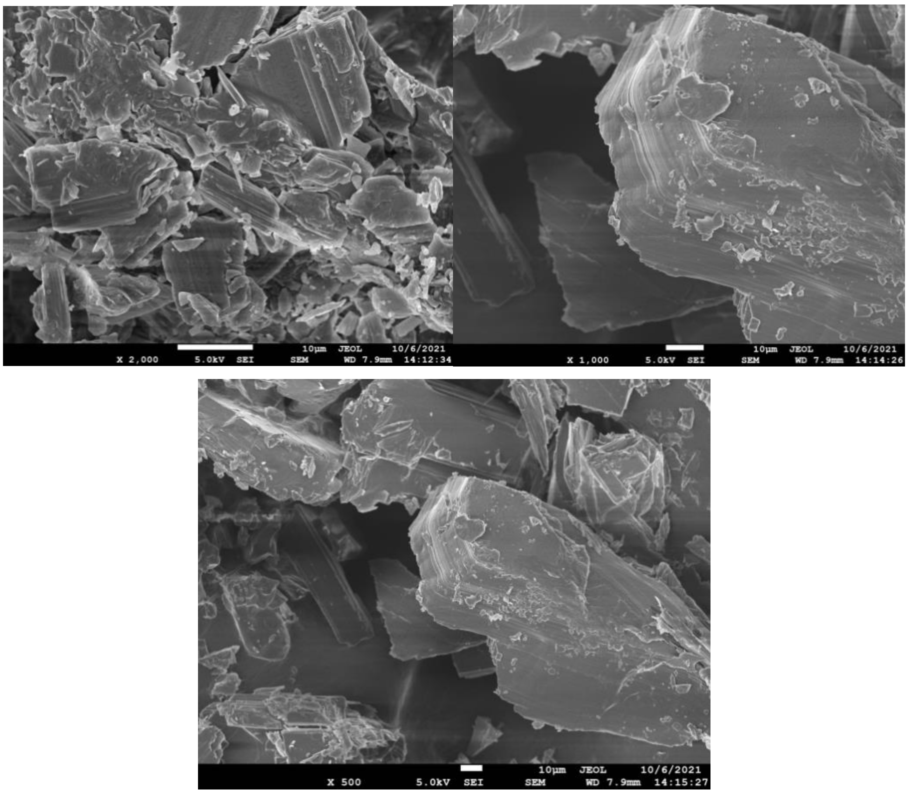


Fig 5. SEM images under various magnification before adsorption

Applications with heavy metal (II)sulphates

Methods

All of the chemicals that were utilised in the tests were of an analytical quality, and the water in which they were carried out was deionized. Various "solutions of heavy metals (Pb(II),Cu(II),Ni(II),Zn(II))sulphates, supplied by qualigens fine chemicals, Mumbai, INDIA (minimum assay 99 percent), were prepared from the solutions containing 200 mg/L as a stock solution, and further dilutions were made as 150 mg/L, 100 mg/L, 75 mg/L, 50 mg/L, and 10 mg/L respectively. The aqueous solution had a pH of 5.0, and this value did not shift much after being diluted. For studies conducted at various pH levels, the acidity of solutions containing heavy metals (Pb(II), Cu(II), Ni(II), and Zn(II))sulphates was altered by the addition of drops of 0.1 M HNO3 and 0.1 M Na OH solution".

"The experiments for the removal of metal were carried out in conical flasks by agitating a pre-weighed quantity of the compound that was then combined with 100 ml of the aqueous heavy metal solution in a constant temperature waterbath shaker (NSW,MUMBAI) for a pre-determined time interval at a constant speed of 200 rpm".

"After this step, the mixture was filtered, and the EDX analysis determined the amount of leftover heavy metal in solution".

"Using the eq-1 equation, we were able to determine the quantity of heavy metal that was absorbed by the combination on a per-unit-mass basis".

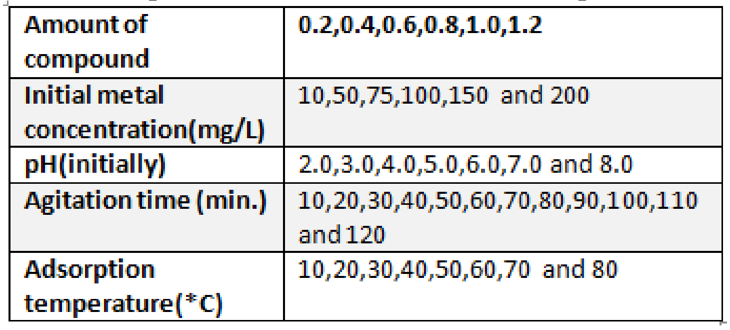
q= Co-Ce/M…………………………………(1)

"where Co and Ce are heavy metal concentrations in mg/L before and after adsorption for time in min,and M is the amount of adsorbent in g takn for 1L of heavy metal solution.teh extent of adsorption in% is found from the eq-2".

Adsorption% = Co _- Ce /Co # 100 ……………..(2)

"All the batch studies were performed in triplicate within error ratio of +_0.5 %.To investigate the effect of various operational parameters like pH, temperature etc, he following experimental conditions were opted for different batch experiments shown in table below".

Table2: Experimental conditions for batch experiments"



Amount of compound	**0.2,0.4,0.6,0.8,1.0,1.2**
Initial metal concentration(mg/L)	10,50,75,100,150 and 200
pH(initially)	2.0,3.0,4.0,5.0,6.0,7.0 and 8.0
Agitation time (min.)	10,20,30,40,50,60,70,80,90,100,110 and 120
Adsorption temperature(*C)	10,20,30,40,50,60,70 and 80

The optimization process involved determining the optimal dosages of HM ions for the adsorption of (Pb(II),Cu(II),Ni(II), and Zn(II)sulphate ions. This process was carried out with six different beginning metal ion concentrations, ranging from 10 to 200 mg/L as indicated in table 1. It has been discovered that the clearance rate is poor at lower concentrations, which indicates that there is insufficient availability of ions for the biomaterial to take up. When given in modest dosages, the binding sites are immediately filled by the metal ions, and as a consequence, there is no additional absorption.

In order to optimise the process of determining the optimal dose of HM ions for the adsorption of Pb(II), Cu(II), Ni(IT), and Zn(II) sulphate ions, six distinct starting metal ion concentrations ranging from 10 to 200 mg/L were used. The results of this process are presented in table 1. There is not enough availability of ions to be uptaken by biomaterial at low dosages, the binding sites are occupied by metals ions fast, and as a consequence, there is no further uptake. This is a general finding that has been made, and it has been discovered that removal is poor at lower concentrations. The next photos, taken with a scanning electron microscope and magnified by a factor of 1000, show the blended compound before it was subjected to adsorption. SEM analysis was then used to investigate the process of surface assimilation of metals at various orientations of the compound. Following the removal of metal through the process of adsorption, the surface morphology of the biomaterial was found to have undergone observable changes, including the formation of discrete aggregates on the compound. Additionally, the biomaterial's particles were discovered to be of varying dimensions, with the external surface featuring steps and kinks. The creation of a glossy deposition on the surface of the compound has been attributed to the interaction of the compound with heavy metals.[60]

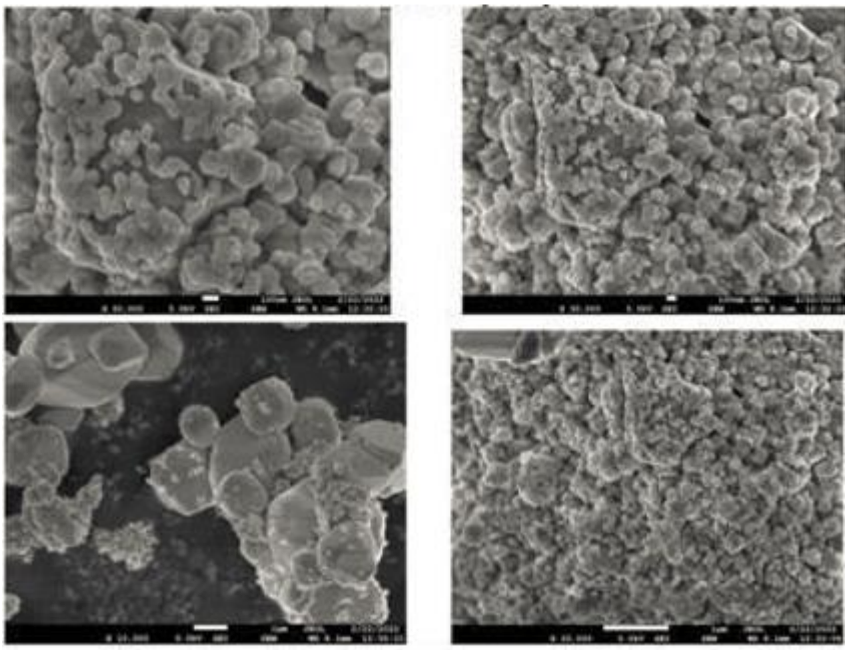
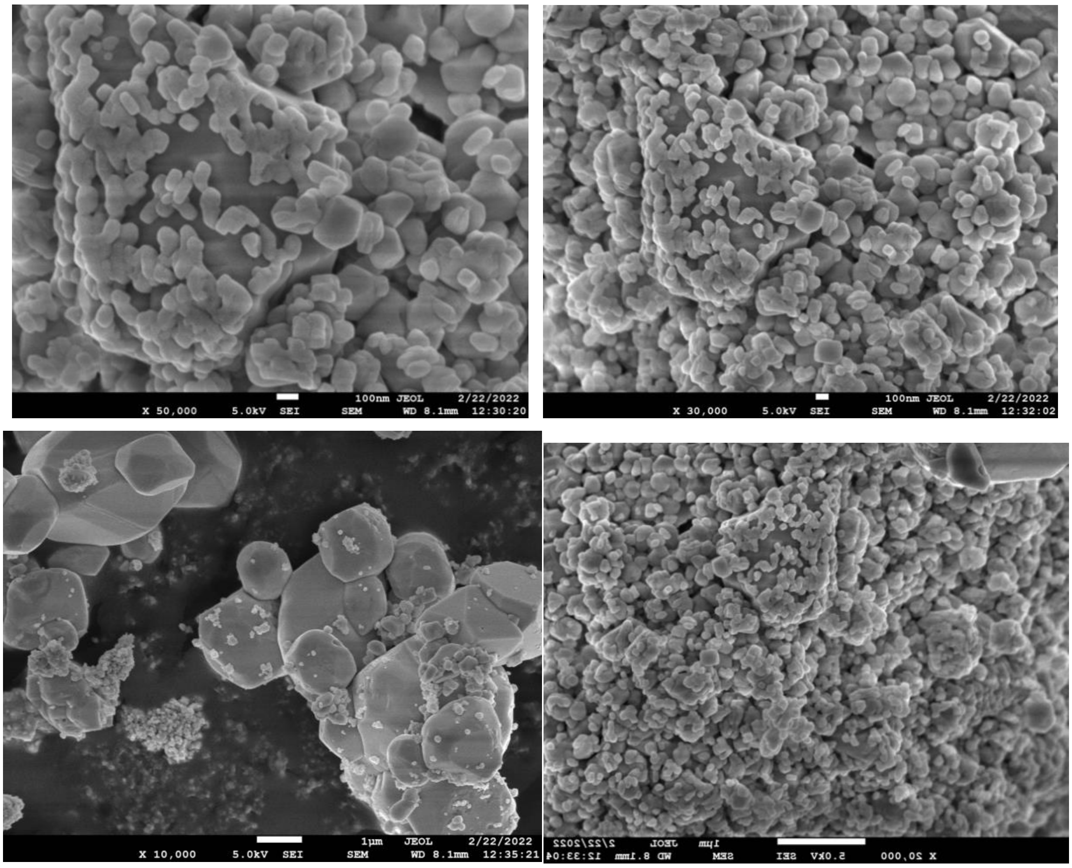


Fig: SEM images under various magnification after adsorption

The next photos, taken with a scanning electron microscope and magnified by a factor of 1000, show the blended compound before it was subjected to adsorption. SEM analysis was then used to investigate the process of surface assimilation of metals at various orientations of the compound. After the metal has been removed from the compound by the process of adsorption, the surface morphology of the biomaterial undergoes observable modifications, and the compound also develops discrete aggregates on its surface. It was discovered that the particles had a variety of dimensions, including kinks and steps on the surface of the particle's exterior. The creation of a glossy deposition on the surface of the compound has been attributed to the interaction of the compound with heavy metals.



Conclusions

STU is the name of the newly synthesised organic substance that may be used in template applications. An examination using powder X-ray diffraction has shown that the doped crystals have the expected structure. The FT-IR spectroscopic study provides independent confirmation that each of the functional groups is present in the crystal lattice. The UV-Vis spectrum determines the transmittance window that is optimal, and it is discovered that the lower cut-off may be set as low as to permit frequency conversion all the way down to the UV area. The fact that the surface of the crystal is so smooth at the microscopic level is evidence that it is possible to add additional molecules and expand into a larger crystal.

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