

GREEN SYNTHESIS OF BENZOTHAZOLE DERIVATIVES AND THEIR *IN VITRO* ANTIMICROBIAL ACTIVITIES

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ABSTRACT

Benzoheterocycles such as benzothiazoles, benzimidazoles and benzoxazoles can serve as unique and versatile scaffolds for experimental drug design. Among the all Benzoheterocycles, benzothiazole has considerable place in research area especially in synthetic as well as in pharmaceutical chemistry because of its potent and significant pharmacological activities. Since, a wide range of methods are available for synthesizing benzothiazole nucleus and its derivatives but a real need exists for new procedures that support many kinds of structural diversity and various substitution. The present review deals with the Various 2-Substituted Benzoxazoles derivatives in moderate to good yield have been prepared in a one-pot reaction by condensation of 2-aminophenol and different aromatic acids in the presence of ammonium chloride as a catalyst and ethanol as solvent 80^o-90^oC. The reaction is green and economically viable. The advantage of this method is extremely mild reaction conditions, short reaction time, high yield, simple experimental technique and compliance with green chemistry protocols.

Keywords: Benzoheterocycles, Benzothiazole, Cyclization and Biological activities.

Introduction

Benzothiazoles are bicyclic ring system with multiple application which have been the subject of great interest because of their biological activities. Literature review revealed the potent in inhibition of human immunodeficiency virus type one (HIV-1) replication by HIV-1 protease inhibition¹, antitumor², analgesic and anti-inflammatory³, antimalarial⁴, antifungal⁵, anticandidous activities⁶ and various CNS activities of benzothiazole⁷. Benzothiazole is a privileged bicyclic ring system. It contains a benzene ring fused to a thiazole ring. The bridge nitrogen and sulphur heterocycles have its own biological importance^{8,9,10}. The small and simple benzothiazole nucleus is present in compounds involved in research aimed at evaluating new products that possess interesting biological activities like-antimicrobial, antitubercular, antitumor, antimalarial, anticonvulsant, anthelmintic, analgesic and anti-inflammatory activity⁸. 2-aminobenzothiazole derivatives were prepared from the substituted aromatic amines, in the presence of ammonium thiocyanate forms substituted 1-phenylthiourea in acidic medium. This substituted 1-phenylthiourea in the presence of oxidizing agent like bromine is cyclised into substituted 2-aminobenzothiazoles. The titled compounds

were evaluated for anti-inflammatory property by λ -Carrageenan-induced paw edema method in rats⁹. Several synthetic methodologies were available for the synthesis of benzothiazole. Generally the condensation of 2-aminobenzene thiol with aldehyde and their nitrile, imide and orthoesters derivatives have been widely used for benzothiazole.

Experimental

The melting points of all synthesized compounds were recorded using hot paraffin bath and are uncorrected. ¹H NMR spectra (CDCl₃) were recorded on Bruker Advance II 400 NMR spectrophotometer using TMS as internal standard. IR spectra were recorded on Perkin-Elmer-1800 FTIR spectrophotometer in the frequency range 4000-450 cm⁻¹ in Nujol mull and as KBr pellets. Mass spectra were recorded on a LC-MS Q-ToF Micro, Mass analyzer (Shimadzu). Chemicals used were of AR grade. The purity of the compound was checked on silica gel-G plates by TLC.

Preparation of 2-(4-methoxyphenyl)-2,3-dihydrobenzo thiazole (3a)

Preparation of 2-(4-methoxyphenyl)-2,3-dihydrobenzo thiazole was carried out by the reaction of 2-aminobenzene thiol (2.5ml) and anisaldehyde in 4 ml of ethanol mixture was added NH₄Cl (0.15g) used as catalyst. The

resulting mixture was stirred for 4 hrs at 90⁰c. The completion of the reaction was confirmed by reaction mixture poured in to ice cold water and product was precipitate out it was crystallized from ethanol to yield of 2-(4-methoxyphenyl)-2,3-dihydrobenzo thiazole (3a), yield 78.18 %, m.p. 100⁰C. The molecular formula was established as C₁₁H₉N₂O (Colour-pale yellow).

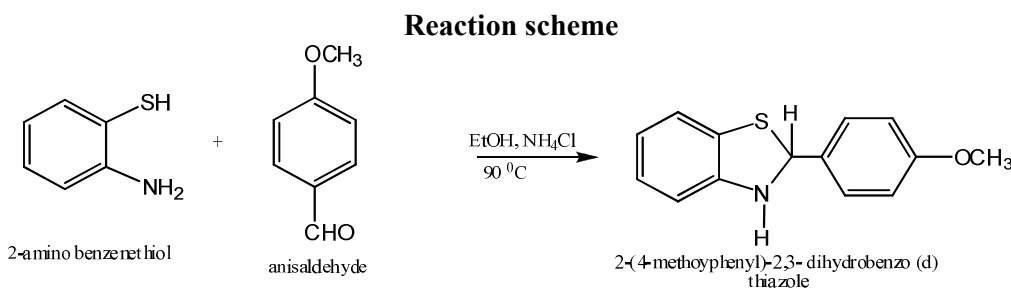
Preparation of 2-(2,3-dihydrobenzo thiazole 2-yl) phenol (3b).

Preparation of 2-(2,3-dihydrobenzo thiazole 2-yl) phenol. Was carried out by reaction of 2-aminobenzene thiol (2.5ml) and Salicylaldehyde in 4 ml ethanol was added NH₄Cl (0.15g) as catalyst. The resulting mixture was stirred for 4 hrs at 90⁰C. After completion of reaction, the reaction mixture was poured in ice-cold water and product was precipitated out. It was crystallized from ethanol to yield 2-(2,3-dihydrobenzo thiazole 2-yl) phenol (3b), yield 90.08 %, m.p. 200⁰C. The molecular formula

was established as C₁₄H₁₂N₂O₂ (Colour-yellow). All other compounds (3c-F) were synthesized in similar manner by treatment of (1) with substituted aromatic aldehyde (2c-F) respectively.

Table No. 1: Reaction of 2-aminophenol (1) (0.01 mole) with different aromatic aldehyde. (2) (0.01 mole) :

Sr. No	Product (3)	-R (2a-e)	Yield (%)	Melting Point ⁰ C	Molecular Formula
1	3a	anisaldehyde	78.18	100	C ₁₁ H ₉ N ₂ O.
2	3b	salicylaldehyde	90.08	200	C ₁₄ H ₁₂ N ₂ O ₂
3	3c	vanillin	88.00	85	C ₁₃ H ₁₀ NO ₂
4	3d	p-chloro benzaldehyde	78.48	94	C ₁₃ H ₉ ClN ₂
5	3e	4-hydroxy benzaldehyde	78.00	140	C ₁₃ H ₁₁ NOS.
6	3f	furfuraldehyde	80.18	185	C ₁₅ H ₁₅ N ₃



Results And Discussion

In order to synthesized substituted Benzothiazole derivatives (3), a relatively more versatile yet simplified procedure was perceived. Our argument have been that an instantaneous condensation of 2-aminophenol and aromatic aldehyde at 80- 90 °C to affords substituted Benzothiazoles with the use of NH₄Cl as catalyst. The strategy worked well affording the desired product in respectable yields. The present reaction have been relatively faster, as anticipated, compared to those in conventional solution phase synthesis. It is necessary to mention that in all cases the conversion was never 100 %. Some amount of starting material recovered after each reaction.

Antimicrobial studies

All the compound have been screened for both antimicrobial and antifungal using cup plate agar diffusion method¹³⁻¹⁴ by measuring the inhibition zone in mm. the compound were taken at a concentration of 1 mg/ml using dimethyl sulphoxide (DMSO) as a solvent. Amikasin (100 µg/ml) was used as standard for antibacterial activity. The compound were screened for antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Proteus vulgaris* and *Pseudomonas aeruginosa* in nutrient agar medium. The compound also screen for antifungal activity against *Aspergillus niger* and *Candida albicans* on potato dextrose agar medium, fliconazole (100 µg/ml) as standard for antifungal activity. Result are presented in Table no. 2

Table no .2 Antimicrobial activities of substituted benzothiazole derivatives.

Compound	Antibacterial**				Antifungal**	
	<i>E. coli</i>	<i>S. aureus</i>	<i>P. vulgaris</i>	<i>P. aeruginosa</i>	<i>C. albicans</i>	<i>A. niger</i>
IIIa	12	13	10	25	20	16
IIIb	15	25	12	22	21	17
IIIc	19	22	14	16	26	19
IIId	15	19	22	20	25	21
IIIe	18	16	13	16	18	22
IIIf	10	17	16	15	19	25
Amikacin	20	23	22	25	-	-
Fluconazole	-	-	-	-	24	25

** zone of inhibitor in mm (15 or less) resistance, (16-20mm) moderate and (more than 20mm)

Sensitive

Aknolegement

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SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE NANOPARTICLES

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ABSTRACT

ZnO nanoparticles were synthesized by chemical route method using zinc acetate dehydrate having different percentage (0.2% & 0.4%) and sodium hydroxide in pellet form as a precursor. ZnO nanopowder were characterized by UV, XRD and Dc electrical conductivity. The thin films of ZnO nanopowder in PVA solution were prepared by solution casting method and conductivity was measured. XRD pattern shows the crystalline nature of ZnO. The grain size decreases with increasing concentration of zinc acetate. From UV spectroscopy the band gap energy is found to be 5.91 eV and 5.3 eV for 0.2% & 0.4% of zinc acetate concentration. Dc electrical conductivity is found to be 2.105×10^{-4} S/cm and 1.22×10^{-4} S/cm for 0.2% & 0.4% of zinc acetate respectively.

Keywords: Zinc acetate, PVA, NaOH, Chemical Route method, XRD, UV, DC electrical conductivity.

Introduction

Nanotechnology involves the study, control and manipulation of materials at the nanoscale, typically having dimensions less than 100 nm (1,2). In recent years, the synthesis of nanomaterials is an important in the various and scientific and industrial fields. The properties of such materials are novel and can be engineered by controlling the dimensions of these building blocks and their assembly via physical, chemical or biological methods (3). Nanostructured materials have unique chemical and physical properties and their physical application in many fields has stimulated the research for new synthetic method for material.

Synthesis and characterization of zinc oxide (ZnO) nanoparticles has found widespread interest during past few years due to their unique electro-optical properties, wide range of applications in various fields. In particular, introduction of ZnO filler into polymeric matrices can modify the optical, electrical and mechanical properties of polymers. Development of new methods of preparation would controls the particle size, size distribution, crystallinity and morphology. ZnO is a wide bandgap semiconductor that displays high optical transparency and luminescent properties in the near ultraviolet and visible region. Here we report the synthesis of ZnO nanoparticles through chemical route method. The structural and optical properties of the prepared ZnO nanoparticles was confirmed using XRD and UV-VIS absorption

spectroscopy and DC electrical conductivity. The effect of molar concentration of ZnO nanostructures was recorded.

Experimental

2.1 Synthesis of Zinc oxide nanopowder : Zinc acetate dehydrate solution having purity 99% and sodium hydroxide in pellet form having purity 99%, supplied by S.D. fine chemicals were used for the synthesis of ZnO nanoparticles. The double distilled water and ethanol are used to remove the impurity. Nanoparticles were synthesized by chemical route method. 0.2M aqueous zinc dehydrate was dissolved in 50 ml distilled water under rigorous stirring. At room temperature, 20M NaOH was added drop by drop into 0.2M zinc acetate dehydrate till the pH reaches to 12. Prepared mixture is stirred continuously for 2 hours with the help of magnetic stirrer. After completion of reaction, the white precipitate was formed. The precipitate was washed thoroughly with distilled water followed by ethanol to remove the impurities. The precipitate was dried in a hot air oven for overnight at 60 °C. Complete conversion of Zn(OH) into ZnO NPs took place during drying. Above procedure was repeated for the synthesis of ZnO NPs only varying the concentration of aqueous Zinc acetate Dehydrates (0.4%).

2.2 Thin film sample Preparation : The composite film of the ZnO / PVA were prepared by dissolving 75 wt% of PVA in 40 ml distilled water under controlled temp of

60⁰ and continuously stirred for 30 min. Then 25 wt% of ZnO powder was added into PVA solution at room temperature and continuously stirred for 1 hr. Then the blend solution was divided into petri-dishes. The free standing casting film was formed and cut into several pieces for use as a substrate for radiation exposure and for further studies such as dielectric conductivity, UV, XRD etc.

2.3 Thickness Measurement : Thickness of the sample is measured by compound microscope with some accessories. This method is used in the present study. The thickness of the sample was measured by the compound microscope in conjunction with a micrometer having a least count of 15.33 μm . The thickness of both the samples is same about 61.33 μm .

2.4 X-ray Diffraction: The X-ray of prepared ZnO nanopowder was recorded by using Hitachi diffractometer. Applying Scherrer's formula, the crystalline size of ZnO sample is calculated.

2.5 UV Spectroscopy: The UV absorption spectroscopy of the ZnO nanopowder was recorded on Perkin-Elmer spectrophotometer.

2.6 Conductivity Measurement: For measuring conductivity thin film of ZnO nanoparticles were prepared in PVA using 1:3 ratio. The films are kept in sample holder. The sample holder assembly was placed in a controlled temperature furnace. The dc electrical conductivity was measured by determining the resistance of a sample within 328-4170 K at the rate of 10/min. The temperature was recorded by a digital thermometer.

Result and Discussion

3.1 X-ray diffraction: Fig.1 and Fig.2 shows X-ray diffraction pattern for samples ZnO-1 and ZnO-2 synthesized by varying the concentration of the zinc acetate dehydrate i.e. 0.2M & 0.4M respectively. Study of standard data confirmed that the synthesized materials have hexagonal ZnO phase. The size of ZnO-1 and ZnO-2 is found to be 63.00 nm and 38.50 nm. The particle size decreases with increase in the concentration of zinc acetate dehydrate. With increasing concentration of zinc acetate

dehydrate crystallinity of the particles decreases causing particles become smaller. Thus, in order to get smaller particles higher concentration of zinc acetate is favorable.

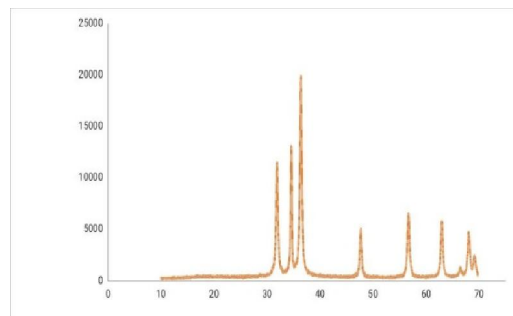


Fig.1: XRD of ZnO-1(0.2)

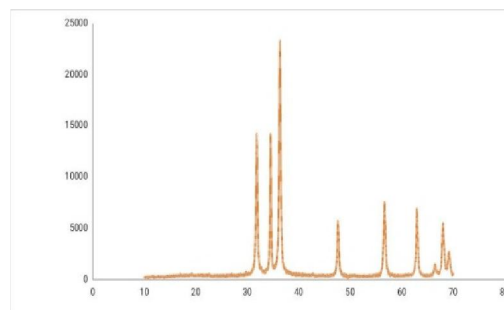


Fig.2: XRD of ZnO-2(0.4)

3.2 UV Absorption Spectroscopy: The band gap energy of the ZnO-1 and ZnO-2 were calculated by the tangent drawn from the graph curve drawn between $\alpha h\nu$ vs $h\nu$. It is found that the band gap energy for ZnO-1 is greater than that of ZnO-2. The band gap energy of ZnO-1 and ZnO-2 is 5.91 eV and 5.36 eV respectively as shown in Fig 3 and Fig 4.

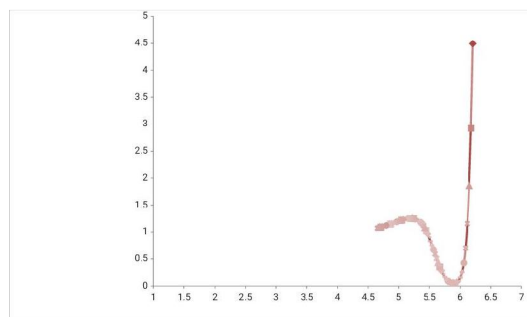


Fig.3: UV-VIS absorption spectra of ZnO-1(0.2)

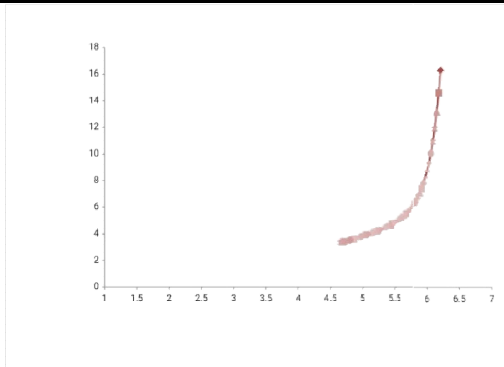


Fig.4: UV-VIS Absorption spectra of ZnO-2(0.4)

3.3.DC Electrical conductivity : Fig 5 & 7 represents the V/I characteristic of ZnO filled PVANanocomposites thin film. The current increases with increasing the voltage drop. Fig 6 & 8 represent the thermogram. $\log \sigma$ VS $1/T$ for ZnO filled PVA nanocomposite thin film. The activation energy calculated from the graph of Fig.6 and Fig.8 and is found to be $E_a = 2.105 \times 10^{-4} \text{ eV}$ and $E_a = 1.22 \times 10^{-4} \text{ eV}$ for 0.2M and 0.4M concentration respectively. The conductivity increases with increasing zinc acetate dehydrate concentration

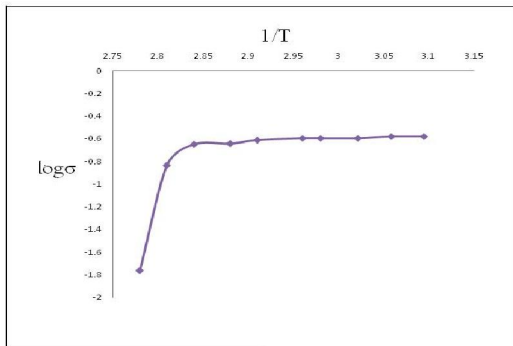


Fig.5: V-I characteristic of ZnO-1(0.2)

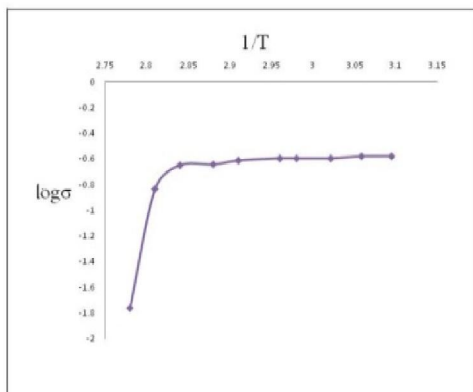


Fig.6 : Conductivity of ZnO-1(0.2)

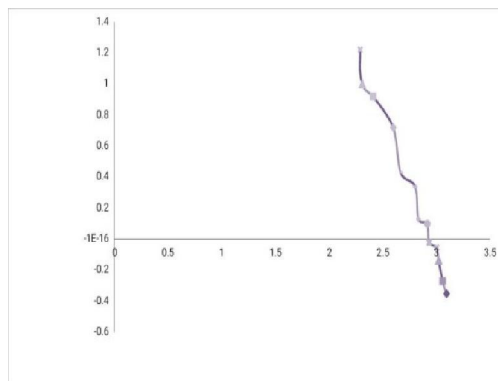


Fig.7 : V-I characteristic of ZnO-2(0.4)

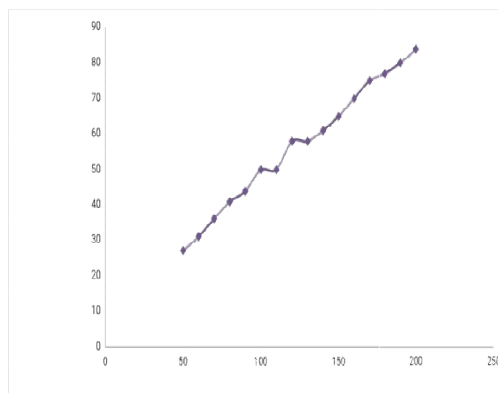


Fig.8 : Conductivity of ZnO-2(0.4)

Conclusion

Zinc oxide nanoparticles were synthesized successfully by chemical route method. XRD confirms the crystalline nature of ZnO nanoparticles. The particle size of ZnO nanoparticles decreases with increasing concentration of zinc acetate dehydrate. The band gap energy decreases with increasing zinc acetate dehydrate concentration. Activation energy decreases with increasing concentration of zinc acetate dehydrate and found the conductivity increases.

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STUDY THE ANTIBACTERIAL ACTIVITY OF SILVER NANO PARTICLES SYNTHESIS BY GREEN CHEMISTRY

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ABSTRACT

The silver nano-particles were synthesized by green route using leaf extract of *Mentha piperita* and *Allium cepa* (Onion). The samples showed change in colour from almost pale yellow to brown, which indicate the formation of silver nanoparticles in the reaction mixture. These nanoparticles at concentration 20ul/ml, 40ul/ml and 50ul/ml were studied for antibacterial activity. The antibacterial activity against *E. coli* and *S. aureus* was found maximum in 50ul/ml concentration after 12 hrs.

Keywords: Silver nanoparticles, antibacterial /biocidal of silver nano particles

Introduction

Silver nanoparticles are the metal of choice as they hold the promise to kill microbe's effectively (Sondi *et al.*, 2004). Chemical methods are the most popular approaches but they are often too expensive and can be toxic (Ittiyavirah S P and Paul A S 2016). Nanoparticles can be formed in several different ways, while bio synthesis of nanoparticles provides advancement over chemical and physical methods as it is a cost effective and environmental friendly. Sarvanan M *et al.*, (2009) reported focuses on the synthesis of metallic bio-nanoparticles of silver using a reduction of aqueous Ag⁺ ions with the culture supernatants of *Staphylococcus aureus* while Shivshankar S *et al.*, (2008) reported the use of Geranium leaf extract in the extracellular synthesis of silver nanoparticles. Safaepour M *et al.*, (2009) synthesized uniformly dispersed silver nanoparticles with a uniform size and shape and investigated the cytotoxicity using a cancer cell line. The cytotoxicity analysis of the sample shows a direct dose- response relationship; cytotoxicity increased at higher concentrations. At concentration of 1ug/ml, silver nanoparticles was able to inhibit the cell line's growth by less than 30%. Conversely, the presence of 5ug/ml of silver nanoparticle significantly inhibited the cell line's less than 60%. Therefore the objective of this study was to find the antibacterial properties of silver nanoparticle synthesized by an eco-friendly process.

Materials & Methods

***Allium cepa* (Onion) extract:** *Allium cepa* extract was prepared by taking 25 gm of thoroughly washed and finely crused onion mixed with 100 ml deionized water in flask and then boiling the mixture for 10 min before finally decanting it.

***Mentha piperita* leaves extract:** 25gm of *Mentha piperita* leaves were washed thoroughly with sterile distilled water and air dried. Leaves were finely cut and were boiled for 2min with 100 ml of sterile distilled water.

Silver Nitrate solution (AgNO₃): For the reduction of Ag⁺ ions, 50 ml of 0.1 mM aqueous of AgNO₃ solution was prepared.

Synthesis of silver nano-particles: Silver nitrate and *Allium cepa* extract was taken for the reduction of Ag⁺ ions, 5 ml of *Allium cepa* extract was mixed to 50 ml of 0.1 mM aqueous of AgNO₃ solution drop wise with constant stirring at 50-60 °C and observe the colour change. Same procedure was carried out for the synthesis of silver nano particles from *Mentha piperita* leaves extract. Shivshankar S *et al.*, (2008) reported on treating aqueous silver nitrate solution with geranium leaf extract, rapid reduction of the silver ions is observed leading to the formation of highly stable, crystalline silver nanoparticles.

Characterization of silver nanoparticles by UV- visible spectrophotometer: The absorption in the visible range directly affects the perceived colour of the chemicals involved,

absorption UV- Visible light spectroscopy is used to follow up with the reaction process (Vahabi K et al., 2005). The reduction of Ag⁺ ions was observed by measuring the UV-Vis spectra of the solution and all the observation were recorded (Table No. 1)

Antibacterial activities of Silver nanoparticles: The antibacterial activity of silver nanoparticles against *E. coli* and *S. aureus* was analyzed by their growth curve. Firstly inoculate fresh media into 10ml of broth (Luria Bertani). The media is supplemented with 20-50 ul/ml silver nanoparticles and bacterial cultures were incubated at 37 °C with continuous shaking at 150rpm, whereas control does not contain any exposure of silver nanoparticles. The growth of *E. coli* and *S. aureus* in broth media was indexed by measuring the optical density (600nm) at regular intervals using UV-Vis spectrometer. The observation was recorded in regular intervals.

Result & Discussion: The formation of silver nanoparticles by reduction of silver ions present in the aqueous solution and observed the colour change during exposure of *Allium cepa* extract and *Mentha piperita* extract was followed by UV –Vis spectroscopy analysis. The absorption spectrum of silver nanoparticles in the presence of *Allium cepa* extract and *Mentha piperita* was shown in Table No. 1. When the *Allium cepa* extract was mixed in the aqueous solution of the silver nitrate, it started to change colour from watery colour to yellowish brown and when *Mentha piperita* extract was mixed it started to change from pale yellow to yellowish brown, the change in colour clear indication of the formation of silver nanoparticles in the reaction mixture.

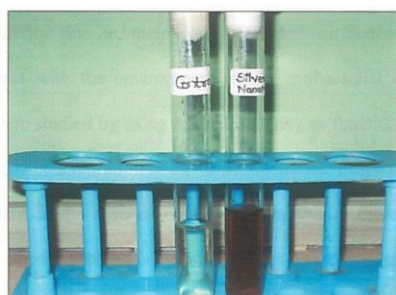


Photo plate 1 : Synthesis of Silver nanoparticles by *Allium cepa* extract

The colour change observed was due to excitation of surface Plasmon vibrations in the silver nanoparticles (Mulvaney *et al.*, 1996). It was reported successful synthesis of silver nanoparticles reducing silver ions present in aqueous solution of silver nitrate complex by the extract of *Mentha piperita* leaves and *Allium cepa* extract comparatively faster and ecofriendly. These nanoparticles at concentration 20ul/ml, 40ul/ml and 50ul/ml were inoculated into fresh LB broth of 10ml each and studied for antibacterial activity, whereas control does not contain any exposure of silver nanoparticles. The observation was recorded (Table No.2) in regular intervals for antibacterial activity against *E. coli* and *S. aureus*, it was found maximum in 50ul/ml concentration after 12 hrs.

Table No. 1

Sr. no	Wavelength (nm)	Absorbance	
		<i>Allium cepa</i> (onion)	<i>Mentha piperita</i>
1	300	0.75	0.78
2	350	0.77	0.92
3	400	1.62	1.74
4	413	1.70	1.84
5	450	1.25	1.34

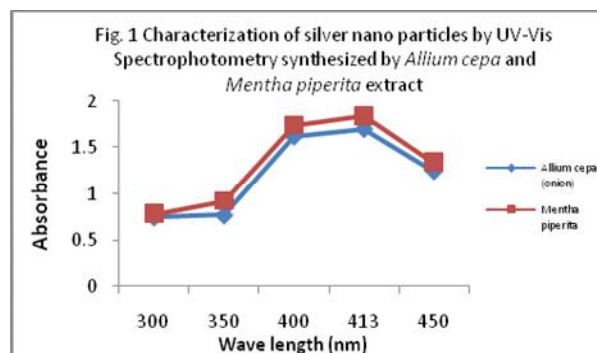


Photo plate 2 : Synthesis of Silver nanoparticles by *Mentha piperita* extract

Table No. 2

Different concentration of Silver nano particles in LB	Optical density at the specific time interval					
	After 4 hrs.		After 8 hrs.		After 12 hrs.	
	<i>E. coli</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>S. aureus</i>
Control	0.15	0.13	0.26	0.22	0.45	0.41
20 μ l	0.12	0.06	0.15	0.10	0.17	0.22
40 μ l	0.07	0.05	0.09	0.07	0.11	0.11
50 μ l	0.05	0.03	0.08	0.06	0.09	0.08

Photo plate 3: Antibacterial activity of silver nanoparticles against *E.coli* at different concentration

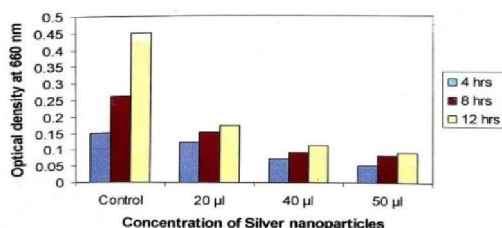
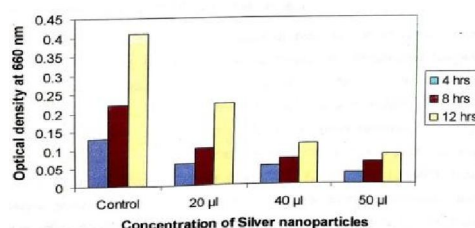


Photo plate 4: Antibacterial activity of silver nanoparticles against *S. aureus* at different concentration



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TO STUDY THE OPTICAL BAND GAP ENERGY OF SrO NANOSTRUCTURED THIN FILM.

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ABSTRACT

The thickness of SrO nanostructured thin film 139nm which was deposited by the method of chemical bath deposition onto glass substrate by using precursors SrCl₂ 6H₂O, NaOH as cationic and anionic without taking complexing agents. The X-ray diffraction studies revealed that, SrO thin film is nanocrystalline in nature with cubic structure. The surface morphology of the SrO film was investigated by means of field emission scanning electron microscopy. The optical studies showed that SrO film exhibits direct as well as indirect optical band gap energy. The electrical resistivity and activation energy of SrO thin film is found to be of the order of $10^6 \Omega \text{ cm}$ and 0.58eV respectively.

Keywords: Thin film; Nanostructures; X-ray diffraction; Electrical and Optical properties

Introduction

In the modern world, nanoscience and nanotechnology plays very important role for the sustainable development of society in view of its variety of applications in many fields. The word “nanotechnology” was introduced first time into a scientific world by N.Taniguchi at the international conference on the industrial production in Tokyo in 1974 in order to describe the super thin processing of materials with nanometer accuracy and the creation of nanosized mechanism and the ideas of nanotechnological strategy which were put forward by Feynman [1]. According to a recent definition suggested by British standards institution “nanoparticles are the particles with one or more dimensions at the nanoscale.” They have defined the nanoscale as dimensions of the order of 100 nm or less [2]. In modern technology, nanostructured metal oxides exhibits novel and enhanced functionalities due to its unusual physical and chemical properties originated by controlling their size during the growth process. In addition, metal oxides such as MgO, CaO, BaO and SrO plays important role in view of its scientific and technological applications. amongst them, strontium oxide (SrO) has been extensively studied by several researchers due to its interesting optical, electrical, thermal and magnetic properties. strontium oxide (SrO) is a fine ceramic material popularly known as strontia. It exhibits many characteristics such as structural phase transition [3, 4], elastic constants [5, 6] and electronic structure [7, 8] which are

adequate for modern applications. the strontium oxide has been commonly used as an environmentally benign catalyst [9], liquid crystal displays [10] and coating materials for thermionic cathodes such as metal cathodes and carbon nanotubes [11, 12].

Recently, nanostructured thin film exhibits novel and technologically interesting physical, chemical and functional properties than those of bulk materials owing to its high surface to volume ratio and quantum confinement effect. A very few attempts have been cited for the growth of strontium oxide thin films by chemical methods such as atomic layer deposition [13], metal organic chemical vapor deposition [14], molecular beam epitaxy [15], etc. In the present work, simple, low cost, non-hazardous and ecofriendly chemical bath deposition method has been employed for the synthesis of nanostructured strontium oxide (SrO) thin film at room temperature. The structural, optical and electrical properties of the as grown strontium oxide thin film was investigated using XRD, FESEM, EDAX, FTIR, UV- Visible spectroscopy and two probe electrical resistivity measurement.

Experimental Methods

In the present work, a chemical bath deposition method is employed to deposit nanocrystalline strontium oxide thin film onto glass substrate at room temperature using 0.1 M SrCl₂ and 0.1 M NaOH as cationic and anionic precursors respectively. Since the well clean glass substrate provide good platform to deposit the

thin film. Before the deposition, glass substrates were boiled in chromic acid for 1h and then clean thoroughly by using soap solution, hydrochloric acid and deionized water respectively, so as to remove any dusty and oily contamination from the substrate surface. For the preparation of strontium oxide thin film, initially 50 ml solution of 0.1 M strontium chloride is kept in 100ml beaker without complexing agents. Further the 0.1M NaOH solution was added drop wise to it till the faint white colored solution with pH 8 is achieved at room temperature. Afterward, previously cleaned glass substrate was rinsed in it for 3h and the solution is stirred using magnetic stirrer, so that the uniform deposition of strontium oxide is achieved with terminal thickness 139 nm. After 3h, the substrate was removed from the solution and dried in air at room temperature. Further grown film was annealed at 723 K for 1h to obtain the pure phase SrO.

The structural characterization of strontium oxide film was carried out by analyzing the X-ray diffraction pattern obtained with Rigaku Table Top X-ray diffractometer with monochromatized Cu K α radiation of wavelength 0.154 nm. The FTIR spectrum of the sample was studied by using a Shimadzu IR Affinity-I make FTIR unit. The film morphology was observed by field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy(EDX) (Model: MERLIN). The optical absorption studies were carried out within the wavelength range 350 – 750 nm using ELICO ® Double Beam SL 210 UV-Visible Spectrophotometer. The variation of electrical resistivity of SrO with temperature was studied by using two probe method.

Results and discussion

The phase and crystal structure of the strontium oxide thin films prepared by chemical bath deposition onto glass substrate was studied by means of x-ray diffraction carried out at 2 θ degree in the range 20 - 80 degree at room temperature. The x-ray diffraction pattern of strontium oxide thin films is shown in figure.1. the (1 1 1) peak observed in the x-ray diffraction pattern at 30.30 degree is due to

cubic structure of strontium oxide [sro] in comparison with the standard x-ray diffraction data card [jcpds: 74-1227]. The average crystallite size of the strontium oxide thin film was determined from the peak (1 1 1) by using debye - scherrer formula [14], $= 0.9 \lambda / \beta \cos \theta$

; where ' λ ' is the wavelength used (0.154 nm); ' β ' is the angular line width at half maximum intensity in radians and ' θ ' is the bragg's angle. The average crystallite size of the strontium oxide thin film was found to be 29 nm indicating the nanocrystalline nature of the materials.

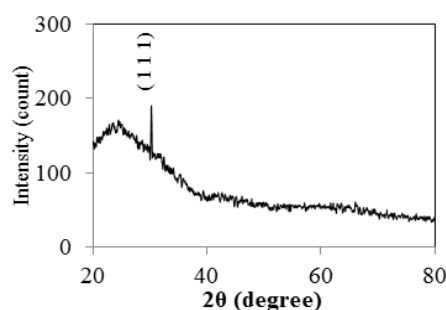


FIGURE. 1. X-ray diffraction pattern of strontium oxide thin film.

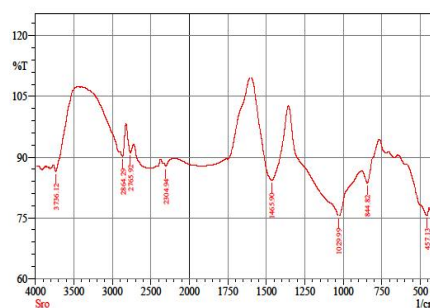


FIGURE. 2. FTIR spectra of strontium oxide thin film.

An FTIR spectrum of strontium oxide thin film was carried out in the middle IR region between 400 - 4000 cm⁻¹. FTIR spectrum of the strontium oxide thin film deposited onto glass substrate is shown in FIGURE.2. The peak observed at 457.13, 844.82 and 1029.99 cm⁻¹ corresponds to the asymmetric and symmetric vibration frequencies of Sr - O bond [15]. However, the peaks observed at 1465.90, 2304.94, 2765.92, 2864.29 and 3736.12 cm⁻¹ may originate due to absorption of moisture from

atmosphere and impurity from KBr during sample preparation.

The surface morphology of the strontium oxide thin film deposited by chemical bath deposition method onto glass substrate was examined by using field emission scanning electron micrographs shown in FIGURE.3A. From the FESEM micrograph it is observed that the nanocrystals of strontium oxide are uniformly distributed all over the substrate. The grain size of the strontium oxide is varies from 29 to 200 nm. This is due to the fact that smaller primary particles have large surface free energy and would therefore tend to agglomerate faster and grow into larger grain. The elemental analysis of the strontium oxide thin film was carried out using energy dispersive X-ray (EDX) analysis (FIGURE.3B). The elemental analysis carried out only for Sr and O elements. The elemental peaks present in the EDAX spectra reveal the formation of strontium oxide (SrO).

The optical absorption measurement of the strontium oxide thin film deposited by chemical bath deposition method onto glass substrate was carried out in the wavelength range 350 to 750 nm at room temperature (Inset of FIGURE.4. The maximum absorption in the visible region is observed shows that the strontium oxide thin film can be used as absorber in the visible region for the optoelectronic devices. The optical band gap energies (E_g) of strontium oxide was calculated by using the equation [16], $h\nu = A(h\nu - E_g)^n$; where, ' α ' is absorption coefficient, ' E_g ' is band gap energy, ' A ' is a constant and ' n ' is equal to 1/2 for direct and 2 for indirect transition. FIGURE.4 illustrates the plots of $(\alpha h\nu)^2$ versus $h\nu$ for strontium oxide. The direct band gap energy ' E_g ' of strontium oxide thin film was estimated by extrapolating the linear portion of the plot to the energy axis and is found to be of the order of 3.7 eV which is smaller than the earlier reports [17]. This decrease in optical band energy may due to quantum confinement effect.

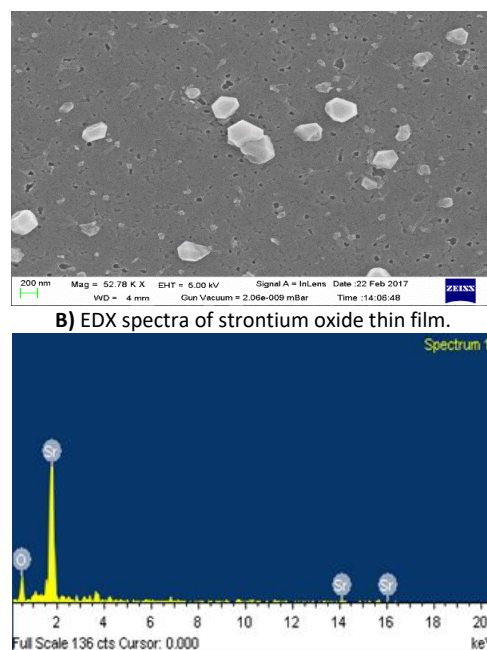


FIGURE. 3. A) FESEM and

The variation of electrical resistivity of strontium oxide thin films with temperature was studied using a dc two point probe method. FIGURE.5. shows the variation of $\log(\rho)$ with reciprocal of temperature. The electrical resistivity of strontium oxide thin films decreases with increase in temperature indicating its semiconducting nature. The electrical resistivity of the strontium oxide thin film at 333 K temperature is of the order of $0.61 \times 10^6 \Omega \text{ cm}$. The activation energy of strontium oxide thin film was calculated using the relation, $\rho = \rho_0 (E_a/KT)$; where ' ρ ' is the resistivity at temperature T, ' ρ_0 ' is a constant; ' K ' is the Boltzmann constant and ' E_a ' is the activation energy. The activation energy of strontium oxide thin films deposited onto glass substrate is found to be 0.58 eV.

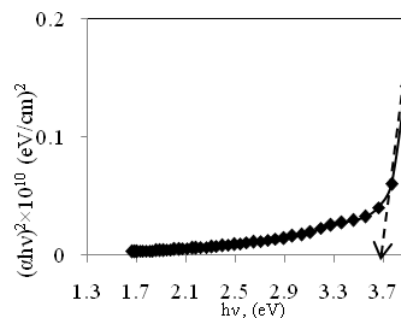
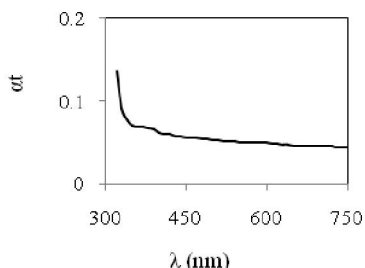


FIGURE.4. The plot of $(\alpha h\nu)^2$ versus $h\nu$ (Inset shows optical absorption spectra) of SrO thin film.



Conclusions

Nanostructured strontium oxide thin film was successfully grown by chemical bath deposition method onto glass substrate. The X-ray diffraction study reveals the nanocrystalline nature of cubic (SrO) strontium oxide. The FESEM image shows the uniform distribution of strontium oxide all over the substrate surface. However, optical band gap and

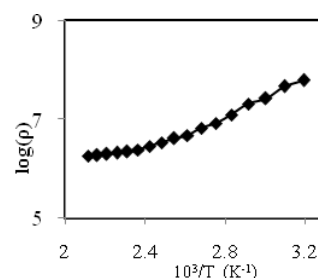


FIGURE.5. The plot of $\log \rho$ versus $10^3/T$ of SrO thin film.

ide thin film is found to be 3.7 and 0.58 eV respectively.

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STUDY OF SOME DECISION TREES CLASSIFICATION ALGORITHM ON HOSPITALS DEFAULT RISK

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ABSTRACT

Mining of data and its analysis have become a comprehensive session in contemporary, applicable precinct. Data mining is a methodology that is based on statistical applications. This method extracts previously undetermined data items from large quantities of data. By using its concept on dataset gathered about COVID-19 in India to make an attempt with some tree classification and analysis to detect medical facility, hospitality to patients, and better understand about the beds availability. This study aims to identify data mining classification algorithms and use them to predict default risks, avoid possible difficulties, and reduce cumulative challenges. The data for this study, which contains individual statewise total health facilities were obtained from the Kaggle.com in COVID19 survey. Three Decision Tree classification algorithms Random tree, random forest and Decision stump were applied to the dataset using WEKA 3.8.4 data mining software. These algorithms were compared considering the root mean error squares, receiver operating characteristic area, accuracy, precision, F-measure, and recall statistical criteria. The best algorithm—Random forest—was obtained and applied to the real dataset to determine the attributes causing the default risk by using odds ratios. The decision trees characteristics of the individuals were examined, and based on the odds ratio values, the results of which individuals and characteristics were more likely to default, were reached. These results are not only beneficial to the literature but also have a significant influence in the medical facilities in terms of the ability to predict patients' default risk.

Keywords: WEKA, Random tree, Random Forest, Decision Stump, Classifiers

Introduction

The vigorous and vast growth in data storage for performing studies by researchers, these machine learning tools like WEKA is very effective in this competitive world. Data mining is the use of automated data analysis technique to discover previously undetected relationships among data items. Data mining often involves the analysis of data stored in a data warehouse. There are many data mining techniques are available like classification, clustering, pattern recognition, and association [2]. Data mining is a topic that involves learning in a practical, non-theoretical sense. We are interested in techniques for finding and describing structural patterns in data, as a tool for helping to explain that data and make predictions from it. Experience shows that in many applications of machine learning to data mining, the explicit knowledge structures that are acquired, and the structural descriptions, are at least as important as the ability to perform well on new examples. People frequently use data mining to gain knowledge, not just predictions [3].

Problem Statement

In this mega war of COVID19 no one country has left from its bad effects. But then also by taking it as challenge we have collected dataset on it and try to get results for the facilities available in India on state wise.

Proposed Methodology

The proposed project was implemented in 3 stages.

- A. *Procuring Data Set* : The dataset of COVID19 for the current research work was downloaded from the website www.Kaggle.com.
- B. *Cleaning Data Set* : A set of data items, the dataset, is a very basic concept for Data Mining. A dataset is roughly equivalent to a two-dimensional spreadsheet or database table. The dataset for Hospital facility contained 12 attributes which were reduced to only 5 attributes by using pre-processor All attribute Filters in WEKA tool namely State/UT, no of rural hospitals, no of rural beds, no of urban hospitals and no of beds available in urban areas. This structure of 5 attributes and 37 instances of states in India

became the final cleaned dataset for the data mining procedures.

C. *Processing Data Set* : Each and every organization is accession vast and amplifying amounts of data in different formats and different databases at different platforms. This data provides any meaningful information that can be used to know anything about any object. Information is nothing just data with some meaning or processed data.

Proposed System

The data pre-processing and data mining was performed using the world famous Weka Data Mining tool. Weka is a collection of machine learning algorithms for data mining tasks. Weka is open source software for data mining under the GNU General public license. This system is developed at the University of Waikato in New Zealand. "Weka" stands for the Waikato Environment for Knowledge Analysis. Weka is freely available <http://www.cs.waikato.ac.nz/ml/weka>. The system is written using object oriented language Java. Weka provides implementation of state-of-the-art data mining and machine learning algorithm. User can perform association, filtering, classification, clustering, visualization, regression etc. by using Wekatool[4].



Fig. 1 WEKA Tool

Performing Decision Tree Classification In Weka

There are number of Decision Trees in Data mining, but here these three decision trees are explained with their characteristics:

1.1 Random Forest Classifier

Random forest, like its name implies, consists of a large number of individual decision trees that operate as an ensemble. Each individual tree in the random forest spits out a class prediction and the class with the most votes becomes our model's prediction.

In statistics and machine learning, ensemble methods use multiple learning algorithms to obtain better predictive performance than could be obtained from any of the constituent learning algorithms alone.[5][6][7] Unlike a statistical ensemble in statistical mechanics, which is usually infinite, a machine learning ensemble consists of only a concrete finite set of alternative models, but typically allows for much more flexible structure to exist among those alternatives.

The fundamental concept behind random forest is a simple but powerful one — the wisdom of crowds. In data science speak, the reason that the random forest model works so well is:

A large number of relatively uncorrelated models (trees) operating as a committee will outperform any of the individual constituent models.

The low correlation between models is the key. Just like how investments with low correlations (like stocks and bonds) come together to form a portfolio that is greater than the sum of its parts, uncorrelated models can produce ensemble predictions that are more accurate than any of the individual predictions. The reason for this wonderful effect is that the trees protect each other from their individual errors (as long as they don't constantly all err in the same direction). While some trees may be wrong, many other trees will be right, so as a group the trees are able to move in the correct direction. So the prerequisites for random forest to perform well are:

- There needs to be some actual signal in our features so that models built using those features do better than random guessing.
- The predictions (and therefore the errors) made by the individual trees need to have low correlations with each other.

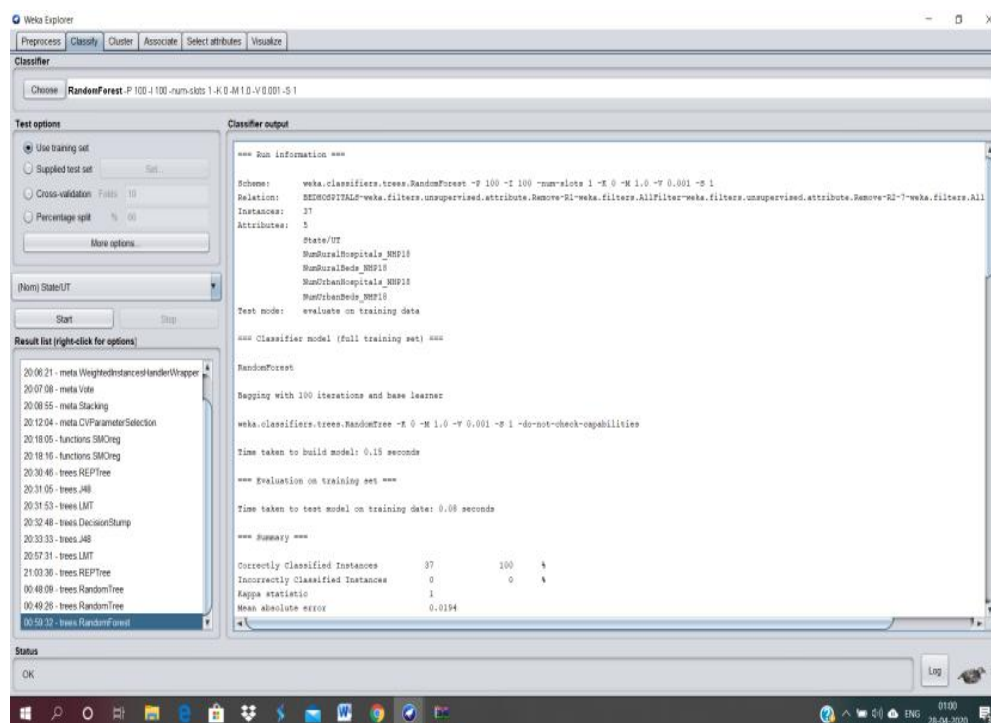


Fig. 2:-Random Forest Classify used with WEKA Tool

5.2 RandomTree Classifier

Random Tree is a supervised Classifier; it is an ensemble learning algorithm that generates many individual learners. It employs a bagging idea to produce a random set of data for constructing a decision tree. In standard tree each node is split using the best split among all variables. In a random forest, each node is split using the best among the subset of predictors randomly chosen at that node.

Random trees have been introduced by Leo Breiman and Adele Cutler. The algorithm can deal with both classification and regression problems. Random trees is a collection (ensemble) of tree predictors that is called forest. The classification works as follows: the random trees classifier takes the input feature vector, classifies it with every tree in the forest, and outputs the class label that received the majority of "votes". In case of a regression, the classifier response is the average of the responses over all the trees in the forest.

Random Trees are essentially the combination of two existing algorithms in Machine

Learning: single model trees are combined with Random Forest ideas. Model trees are decision trees where every single leaf holds a linear model which is optimised for the local subspace described by this leaf. Random Forests have shown to improve the performance of single decision trees considerably: tree diversity is generated by two ways of randomization. First the training data is sampled with replacement for each single tree like in Bagging. Secondly, when growing a tree, instead of always computing the best possible split for each node only a random subset of all attributes is considered at every node, and the best split for that subset is computed. Such trees have been for classification Random model trees for the first time combine model trees and random forests. Random trees employ this produce for split selection and thus induce reasonably balanced trees where one global setting for the ridge value works across all leaves, thus simplifying the optimization procedure. [1] [8] [9] [10]

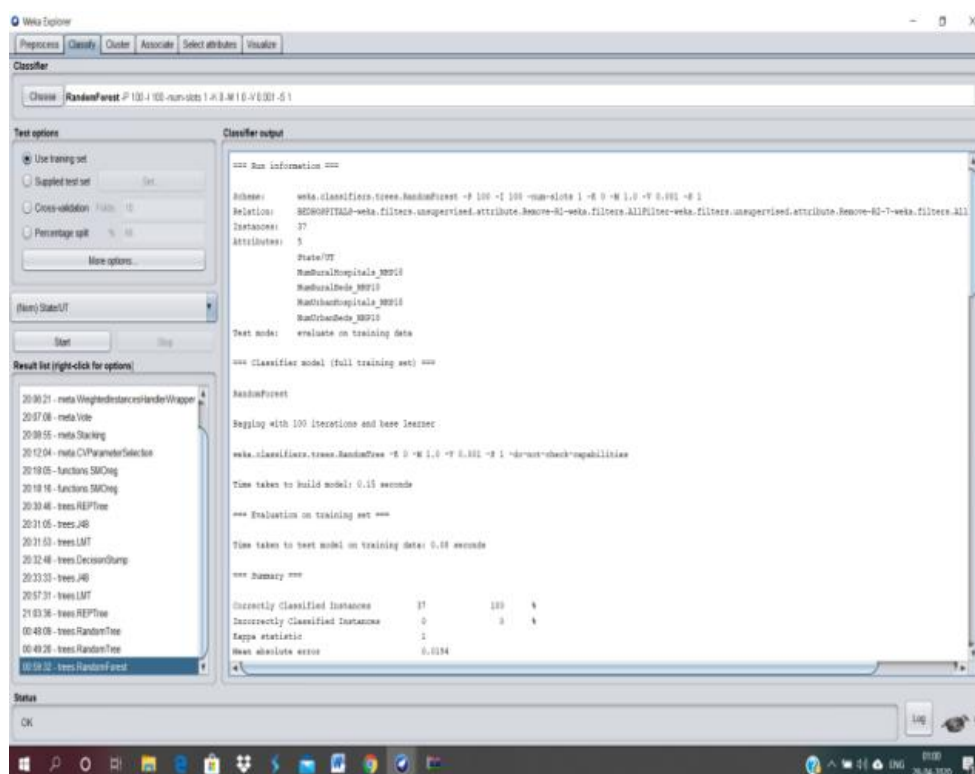


Fig. 3:- Random Forest Classify using WEKA tool

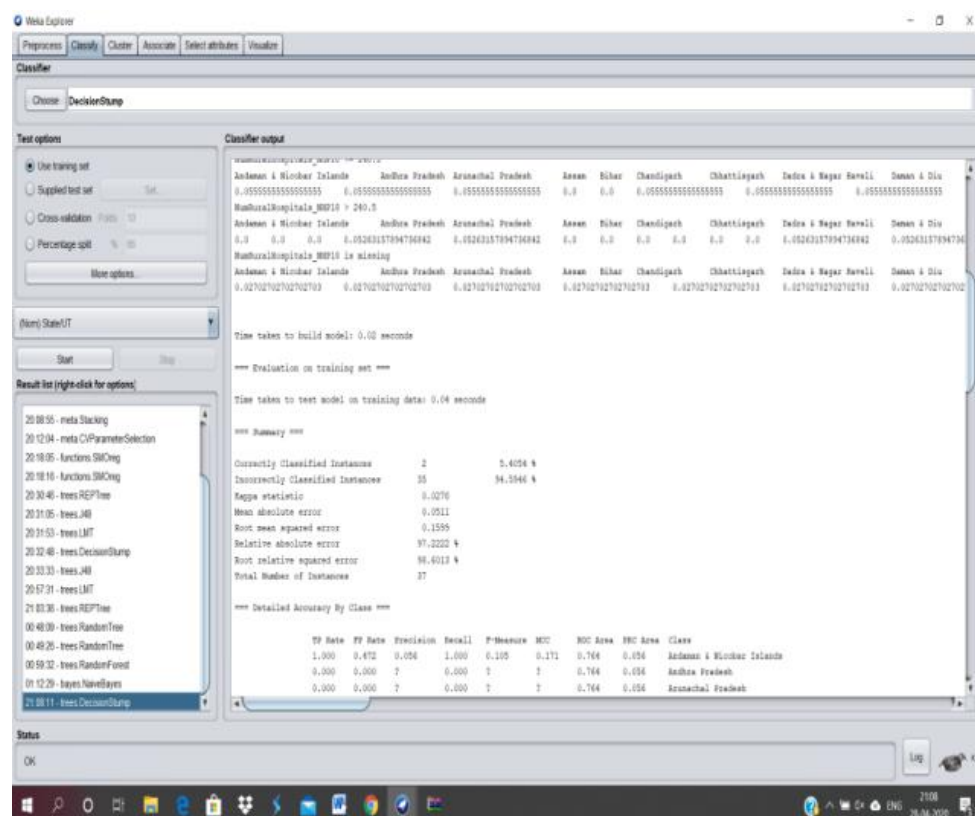


Fig. 4:-Decision Stump Classify by using WEKA tool

5.3 Decision Stump Classifier

The Decision Stump operator is used for generating a decision tree with only one single split. The resulting tree can be used for classifying unseen examples. This operator can be very efficient when boosted with operators like the AdaBoost operator. The examples of the given ExampleSet have several attributes and every example belongs to a class (like yes or no). The leaf nodes of a decision tree contain the class name whereas a non-leaf node is a decision node. The decision node is an attribute test with each branch (to another decision tree) being a possible value of the attribute. For more information about decision trees, please study the Decision Tree operator.

The Decision Stump operator is applied on Set. The criterion parameter is set to 'information gain' and the minimal leaf size parameter is set to 1. The resultant decision tree model is connected to the result port of the process and it can be seen in the Results Workspace. We can see that, this decision tree has just a single split[11].

Comparison

By the comparing the results of RandomForest, RandomTree, Decision Stump Classifiers are supervised trees classifiers of Data Mining machine learning tool like WEKA. By using its amazing techniques available in WEKA which are more convenient to perform these results at here in table fig. 5 below

Classifier Name	RandomForest	RandomTree	DecisionStump
Instances:	37	37	37
Attributes:	5	5	5
Size of the tree :	85	73	-
Time taken to build model:	0.15 seconds	0 seconds	0 seconds
Time taken to test model on training data:	0.08 seconds	0 seconds	0 seconds
=== Summary ===			
Correctly Classified Instances	37 100%	37 100%	2 5.4054 %
Incorrectly Classified Instances	0 0%	0 0%	35 94.5946 %

Kappa statistic	1	1	0.0278
Mean absolute error	0.0194	0	0.0511
Root mean squared error	0.0676	0	0.1599
Relative absolute error	36.8056 %	0%	97.2222 %
Root relative squared error	41.6867 %	0%	98.6013 %

Table Fig. 5:- Comparative table of Classifiers

Conclusion

After analyzing the results of testing the algorithms we can obtain the following conclusions:

- The random forest is a classification algorithm consisting of many decisions trees.
- It uses bagging and feature randomness when building each individual tree to try to create an uncorrelated forest of trees whose prediction by committee is more accurate than that of any individual tree.
- Random forests are a personal favorite of mine.
- The trees of the random forest are more by which we can predict that the hospitals and beds are some ware required to reduce its adjudge default risk in this corona19 era. So that, state wise manipulations will be performed according to it.
- Hence, RandomForest is one of the best classifier in RandomTree and Decision Stumps classifiers in Data minig.

More importantly their predictions need to be uncorrelated (or at least have low correlations with each other). While the algorithm itself via feature randomness tries to manage these low correlations for us, the features we select and the hyper-parameters we choose will impact the ultimate correlations as well.

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ANALYSIS OF HEAVY METALS IN CORIANDER LEAVES LOCALLY COLLECTED FROM AKOLA REGION

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ABSTRACT

In day to day life, pollution due to heavy metals increases due to various factors which show adverse effect on human life. In the present study we have collected coriander samples from local market of Akola region and were analysed for heavy metals cadmium and lead and by nitric acid and perchloric acid decomposition method with the help of atomic absorption spectrometry.

Keywords: Heavy metals, AAS, coriander.

Introduction

Coriander is an annual herb, cultivated throughout the country. It is used for digestion problems including upset stomach, loss of appetite, hernia, nausea, diarrhoea, bowel spasms, and intestinal gas. It is also used to treat measles, haemorrhoids, toothaches, worms, and joint pain, as well as infections caused by bacteria and fungus. Cadmium and lead are the heavy metals due to which various effects on health are observed. Surface waters containing in excess of a few micrograms of cadmium per litre have probably been contaminated by industrial wastes from metallurgical plants, plating works, plants manufacturing cadmium pigments, textile operations, cadmium-stabilized plastics, or nickel-cadmium batteries, or by effluents from sewage treatment plants. Chronic cadmium poisoning produces proteinuria and causes the formation of kidney stones. Solid and liquid (sludge) wastes account for more than 50% of the lead discharged into the environment, usually into landfills, but lead has been dispersed more widely in the general environment through atmospheric emissions-particularly from car exhausts. With the introduction of unleaded fuel, lead emissions from this source declined. Lead pollution may cause brain and kidney damage. It may damage to nervous system. So In the present study we have collected coriander samples from local market of Akola region and were analysed for heavy metals cadmium and lead and by nitric acid and perchloric acid decomposition method

with the help of atomic absorption spectrometry.

Materials and Methods

The coriander plants were collected from the three local markets of Akola region. These three plant samples were shade dried at room temperature and grind in a manual mill to get coarse powders. These powders were kept in the air tight polythene bags and stored at a dry place for further study.

Sample Treatment

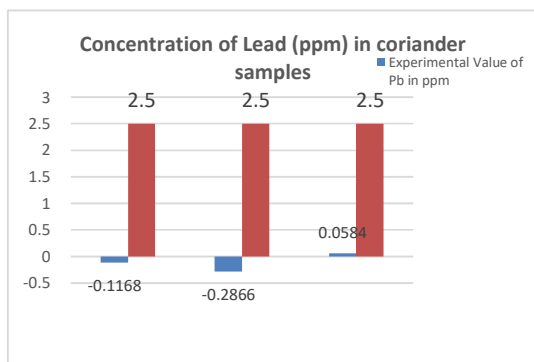
The coarse powdered materials were treated by nitric acid, perchloric acid decomposition method. 2 – 5 gm of the coriander powder were taken in a conical flask. Add some water and 25 ml nitric acid with stirring. Keep the mixture aside for 30 minutes. Now gently heat the mixture for 15 minutes, cool the mixture and then add 10 ml of perchloric acid and again gently heat to concentrate. If the material becomes dark then add 2-3 ml of nitric acid and heat for few minutes. Then the material becomes yellowish or colourless. Then decomposition is completed. Cool the mixture and add 2 ml of HCl & then add water and maintain the pH upto 7. Finally keep the samples in the bottle for analysing heavy metal by using atomic absorption spectroscopy.

Chemicals

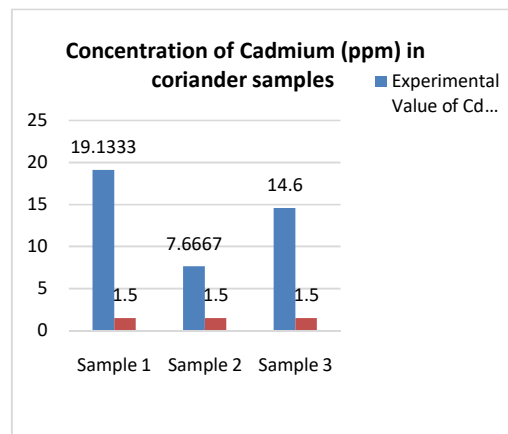
All the chemicals used in the study were obtained commercially & of analytical grade.

Pb – Lead**Table No. 1: Concentration of Lead (ppm) in coriander samples:**

Sr. No.	Samples	Experimental Value of Pb in ppm	Standard value of Pb in ppm
1	Sample 1	-0.1168	2.5
2	Sample 2	-0.2866	2.5
3	Sample 3	0.0584	2.5

**Fig No. 1: Concentration of pb present in coriander sample.****Cd – Cadmium****Table No. 2: Concentration of Cadmium (ppm) in coriander samples:**

Sr. No.	Samples	Experimental Value of Cd in ppm	Standard value of Cd in ppm
1	Sample 1	19.1333	1.5
2	Sample 2	7.6667	1.5
3	Sample 3	14.6000	1.5

**Fig No. 2- concentration of Cd present in coriander sample.****Conclusion**

We have collected the threenumbers of samples of coriander and analysed it. After analysing it, we conclude that the concentration of Pb is very low in all three samples of coriander as compared to standard value. Again the analysis shows that the concentration of Cd is very high in all the three samples of Coriander as compared to standard value.

However, further detailed study in the light of controlling the pollution of heavy metals is advised to get correct insight of the treatment.

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SYNTHESIS AND EVALUATION OF ANTIBACTERIAL ACTIVITIES OF BIOGENIC SILVER NANOPARTICLES FROM BACTERIAL ISOLATES OF LONAR LAKE

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ABSTARCT

Lonar lake is a unique ecosystem formed by meteorite impact, which is located at Deccan Plateau of West-central of India. In the present study, water and sediment sample were collected from different sites of Lonar Lake. All these samples were streak on Horikoshi media B, cultures were maintained as stocks. The pure bacterial isolates were grown in nutrient medium containing AgNO_3 substrate for the biosynthesis of silver nanoparticles. The antibacterial activity of these crude silver nanoparticles produced by alkaliphilic bacteria were studied against pathogenic bacteria such as *Staphylococcus aureus* and *Escherichia coli*. The zone of inhibition shown by isolates code no. W1A, W1B, W1C, and W2B against *S. aureus* was found to be 28 mm, 28 mm, 25 mm and 25 mm, and against *E. coli* all 4 isolates shown 20 mm of zone each. The zone of inhibition shown by silver nanoparticles is significant in comparison with traditional antibacterial agents. The 16S rRNA sequencing of these bacterial isolates were carried out. After the 16S rRNA sequencing the studied isolate code W2B, W2C, W1B, W1C were confirmed as *Bacillus cohnii* strain D7048, *Bacillus cohnii* strain GUFBS253-2, *Bacillus polygoni*, *Bacillus siralis*, respectively.

Key words : Biogenic silver nanoparticles, antibacterial activity, Lonar lake.

Introduction

Lonar lake is a unique ecosystem formed by meteorite impact, which is located at Deccan Plateau of West-central of India. Lonar Crater is filled with saline water and the uniqueness of water is its salinity and high alkalinity Fredriksson et.al.(1973). Lonar lake harbors diverse microorganisms having potential to produce various biologically active compounds which have potential of pharmaceutical and biotechnological application Tambekar et.al.(2004)

Metal nanoparticles produced by nanotechnology have received global attention due to their extensive applications in the biomedical and physiochemical fields Devaraj et.al.(2013). Metals shows antimicrobial potential against the pathogenic microorganisms. The ability of microorganisms to reduce the inorganic metal has opened up an exciting eco-friendly approach towards development of green nanotechnology. The microbial recovery of precious metals with the formation of their nanoparticles is a green alternative to the conventional method Gandhi et.al.(2013). Although silver nanoparticles are widely used in a variety of commercial products. There have been several studies that describe the in vitro toxicity of silver nanoparticles to a variety of different organs,

including the lung, liver, skin, brain, and reproductive organs Ahamed (2010). Antibiotic resistance is a burning problem all over the globe and these bacterial AgNPs shows strong antibacterial activity against pathogenic bacteria Priyragini et.al.(2013)

Lonar lake is a wonder jewel of the earth. We are blessed to have Lonar crater in our country especially in Maharashtra. Microbiologists have found a variety of microorganisms like silver nanoparticles producing bacteria, magnetic bacteria in the lake. The biosynthesis of silver nanoparticles from bacteria which is used as an antibacterial agent is a cost effective and environmentally friendly process.

Materials and methods

A) Enrichment, Isolation and identification of bacterial isolates – Two water and 1 sediment were collected from different sites of Lonar lake. Horikoshi medium A, B & C were used for enrichment of the cultures. Horikoshi(1999). Isolated *Bacillus* species were identified by cultural, morphological, biochemical tests. From these three sample morphologically different bacterial isolates were isolated. The bacteria isolated from water were designated as water sample 1 and water sample 2, for water sample 1 - W1A, W1B, W1C, for water sample 2 - W2A, W2B, W2C

and bacteria isolated from sediment designated as SA and SB.

B) Synthesis, Characterization and Antibacterial activity of crude silver nanoparticles (AgNPs) - Total 8 isolates collected from Lonar lake were sub-cultured in test tube containing 10 mL of nutrient broth containing 3.5 mM AgNO₃. The inoculated broth incubated at dark condition at room temperature for 15 days. After incubation period upon visual observation, the culture incubated in presence of silver nitrate. Along with these the control experiment was also run without AgNO₃. The biosynthesized silver nanoparticles from bacteria isolated from Lonar lake were screened against one Gram – positive and one Gram - negative bacteria such as *S. aureus* and *E. coli* respectively. The method used for antibacterial potential was well diffusion method on nutrient agar. Zone of inhibition showed by silver nanoparticles against pathogenic bacteria were measured.

C) Identification of bacterial cultures –

Table 1 - Zone of inhibition against *S.aureus* & *E. coli*

Culture code	Zone of inhibition showed by Bacterial Ag NPs (mm) against studied bacteria	
	<i>S.aureus</i>	<i>E. coli</i>
W1A	28 mm	20 mm
W1B	28 mm	20 mm
W1C	25 mm	20 mm
W2B	25 mm	20 mm

Silver nanoparticles producing bacterial cultures were identified by using 16S rRNA of bacterial small subunit rRNA genes were

amplified by PCR using primers. The rRNA gene insets were sequenced on ABI sequencer which could be viewed by using softwares like Finch TV, BioEdit, ChromasLite, SeqScanner, etc. Quality of obtained sequence observed through Electropherogram peaks. Sequence analysis was done using BLAST server or server related to specific database at Chromgene pvt Ltd. Bangalore.

Result

In the present study, total three samples comprising of two water and one sediment were collected from different sites of alkaline Lonar Lake, India. In the winter season December 2018. From these samples 8 morphologically different colonies were isolated. The isolates coded as W1A, W1B, W1C, W2A, W2B, W2C and SA, SB. Out of 8 isolates only 4 isolates were found to be efficient for production of silver nanoparticles were isolated from water and it was found that the isolates which were isolated from soil not able to produce silver nanoparticles. The isolate code W1A, W1B, W1C, W2B were biosynthesized the silver nanoparticles by reducing silver nitrate. The preliminary identification of biosynthesized silver nanoparticles was carried out by visual detection of color change from yellow to brown, which indicates the formation of silver nanoparticles.

The supernatant collected after centrifugation was used further for antibacterial activity against *E.coli* and *S.aureus* by Well Diffusion Method. All four isolates shows the zone of inhibition against *E.coli* and *S.aureus*.

For comparison, along with these control experiment also carried out by using only bacterial suspension & only silver nitrate but no zone of inhibition was observed against *S.aureus* & *E. coli*.

16S rRNA sequencing and phylogenetic analysis of Identified species (BLASTn comparison):

1) W1B

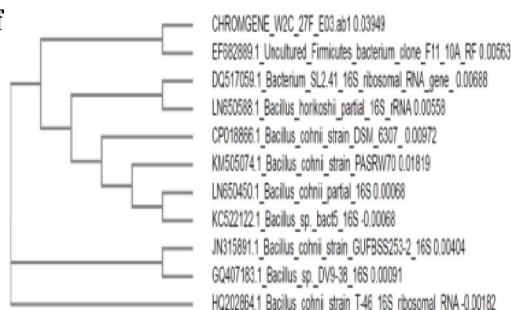
Hit 1: *Bacillus polygoni* gene for 16S rRNA, partial sequence, strain: U0305

Identity: 90.95%

Coverage: 82%

E-value: 5e-68

Accession No: AB734898.1



2) W1C

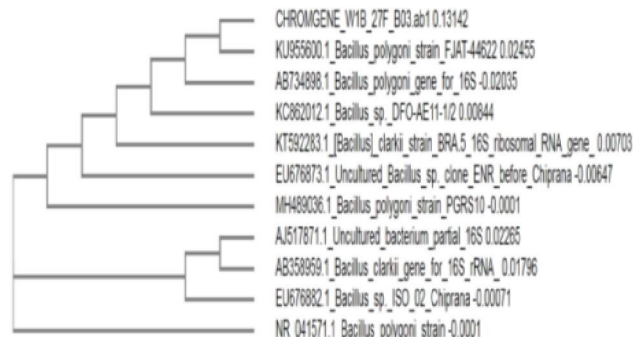
Hit 1: *Bacillus soralis* strain FJAT-45146 16S ribosomal RNA, partial sequence

Identity: 97.61%

Coverage: 92%

E-value: 1e-159

Accession No: KR514577.1



3) W2B

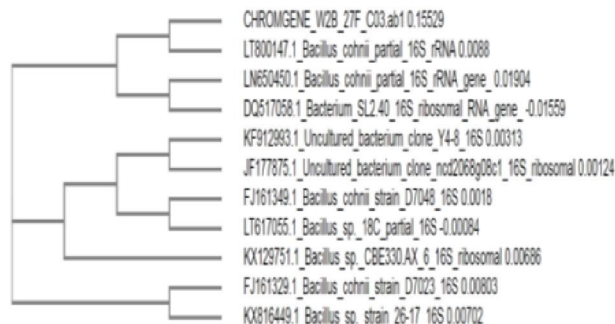
Hit 1: *Bacillus cohnii* strain D7048 16S ribosomal RNA gene, partial sequence

Identity: 89.54%

Coverage: 94%

E-value: 0.0

Accession No: FJ161349.1



4) W2C

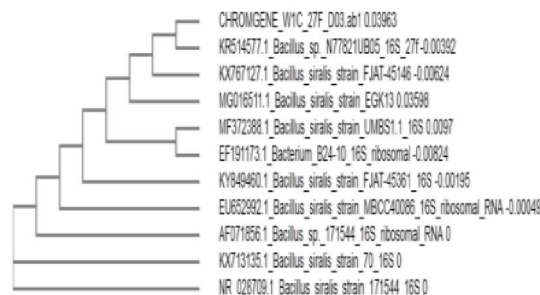
Hit 1: *Bacillus cohnii* strain GUFBS253-2 16S ribosomal RNA gene, partial sequence

Identity: 97.04%

Coverage: 92%

E-value: 0.0

Accession No: JN315891.1



Discussion

Yanhe et.al.(2004) worked on Baer Soda Lake located in the Hulunbeir area of inner Mangolia, Region of China number of diverse bacteria of Baer Soda Lake was characterized using culture and molecular methods. In present study isolation of bacteria was done from alkaline Lonar Lake. 16S rRNA sequencing and phylogenetic analysis isolates were done. Kanekar et.al.(2008) worked on the Lonar Lake, India to identified the bacterial

diversity present in the lake. They collected water and sediment sample from the various sites of lake. Isolation of bacteria from samples was done. 16S rRNA sequencing and phylogenetic analysis were carried out. *Alkalibacillus haloalkaliphilus* was the first report of obligately alkaliphilic organism from Lonar lake. In the present study, 3 samples were collected and from this samples total 8 isolates were isolated Isolation of bacteria were carried out by using different alkaline medium. 16S rRNA sequencing phylogenetic analysis

were also carried out. Shivakrishna et.al.(2013) worked on synthesis of silver nanoparticles from Marine Bacteria *P. aerogenosa*, the marine sample was collected from Nellore Coast, Andhra Pradesh, India. Bacterial strain was grown in Zobell Marine broth for biosynthesis of silver nanoparticles with various concentration of AgNO_3 . The synthesized silver nanoparticles was observed through UV- visible spectroscopy analysis. In present study samples were collected from alkaline Lonar Lake and subjected for synthesis of silver nanoparticles. The production of silver nanoparticles were detected by visual detection. In the work of Tayde(2012) Antibacterial Potential of silver nanoparticles produced from Lonar Lake *Bacilli*, *Bacilli* collected from Lonar Lake were studied. The isolates were grown on nutrient agar containing 3.5 mM AgNO_3 under dark condition. For the preparation of silver nanoparticles isolated *Bacilli* were grown on nutrient broth containing AgNO_3 and incubated for 7 days at 37°C. After 7 days upon visual observation, the culture incubated in the presence of silver nitrate showed a color changes from yellow to Brown. After the synthesis of silver nanoparticles the supernatant of *Bacilli* were used further for the antibacterial activity. In the present study, four silver nanoparticles synthesizing bacteria were isolated. The bacterial isolated were incubated in the presence of AgNO_3 for 15 days after 15 days the colour of broth were changed yellow to brown. The broth were centrifuged at 3000 rpm for 20 minutes. The supernatant was used further for antibacterial activity against pathogenic bacteria. Rathod et.al.(2016) the

actinobacterium *Nocardiopsis valliformis* OT 1 strain isolated from soil collected from the rim of Lonar Lake. In present study silver nanoparticles producing bacterium were isolated from water sample of Lonar crater. The four isolates were showed efficient production of AgNPs. 16S rRNA sequencing and phylogenetic analysis of isolates were carried out.

Conclusion

From above results, it was concluded that the bacterium were present in alkaline Lonar Lake has great potential. These isolates were capable for production of silver nanoparticles.. Out of 8 isolates 4 were gives very predominant antimicrobial activity in which W1A, W1B, W1C, W2B showed strong antimicrobial activity. Our study provides primary verification that Lonar Lake isolates were promising source for silver nanoparticles as antimicrobial substance. Alkaline bacteria producers of potent metabolic compounds used commercially as antibiotics and other novel drugs. Lonar Lake has the capacity to provide active and high amount silver nanoparticles which have potential in medicinal and pharmaceutical industry. The biosynthesis of silver nanoparticles from Lonar Lake bacteria is eco- friendly and commercially easy process and it can potentially recovers the severe problems caused by chemical antimicrobial agents. It is need to be further studied for its potency and broad spectrum activity for improvement in the antimicrobial activity and production of new drugs.

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STUDY OF LOCAL AND GLOBAL THRESHOLDING ON LADAKHI NUMERALS

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ABSTRACT

Image segmentation is a basic step of Image processing. It is used to separate foreground from background. It is done by thresholding methods such as local and global thresholding are used on grayscale image to convert it into binary image. This paper is a study of otsu's and adaptive thresholding and result and correlation on ladakhi numerals.

Keyword: Local thresholding, Global thresholding, Otsu thresholding, Adaptive thresholding

I Introduction

Image segmentation is a initial step of image processing. It is essential for achieving better shape connectivity and separates the foreground from background color of image through which image can be more accurately identify recognition process. Various Image segmentation Methods are used and they are classified into following groups[1]

- Edge detection
- Thresholding
- Region based
- Feature based Clustering

This paper discuss the segmentation by Thresholding

A . Thresholding: A simplest way to segment an image is based on intensity level of an image and is called threshold based. This method is based on a clip-level or threshold values to turn a gray scale image to binary image. The key of this method is to select the threshold valued (T). The thresholding technique can be expressed as

$$T = T[x, y, p(x, y), f(x, y)] \quad (1)$$

Where: T is the threshold value. x, y are the coordinates of the threshold value point. f(x,y) is points the gray level image pixels and p(x,y) is some local property[2][3].

There are two types of thresholding Local thresholding, Global thresholding.

1 Local Thresholding: Local thresholding is also called Adaptive thresholding. In this technique the threshold value is varies over the image depending upon the local characteristic of the image region. In local adaptive thresholding first the image converted into

gray scale image. This method is based on maximum and minimum of mean method and it is used to set threshold values. First find the image size i.e. find number of rows and columns than calculate the mean of maximum pixel size of image and minimum pixel size of the image from that initial threshold values can obtain. Using this threshold value image is segmented by basic threshold technique .the pixels within the follow one segment and other follows another segment. This process is repeated until the threshold value not matched with the pixel value[1].

From (1) if T depends on both f(x,y) and p(x,y) then it will referred to as local thresholding.

2.Global Thresholding: This is simplest of all thresholding. The histogram of complete image is partitioned by a single threshold value T. The single threshold value is used in the whole image[4]. The threshold image g(x,y) can be defined as :

$$g(x,y) = \begin{cases} 1, & \text{if } f(x, y) > T, \\ 0, & \text{if } f(x, y) \leq T \end{cases}$$

The Global thresholding algorithm works as[4][5]:

- Step 1. Select an initial estimate for T.
- Step 2. Segment the image using T. This will produce two groups of pixels. G1 consisting of all pixels with gray level values >T and G2 consisting of pixels values <=T.
- Step 3. Compute the average gray level values mean1 and mean2 for the pixels in

region G1 and G2.

$$w_2(t) = \sum_{i=t+1}^L p_i$$

Step4. Compute a new threshold value
 $T = (1/2)(\text{mean1} + \text{mean2})$

mean of two classes are

$$\mu_1 = \sum_{i=1}^t ip_i / w_1(t)$$

Step 5.Repeat steps 2 through 4 until difference in T in successive iterations is smaller than a predefined parameter T.

$$\mu_2 = \sum_{i=t+1}^L ip_i / w_2(t)$$

Here we discuss the Otsu method which is one of the global thresholding. It stores the intensity values of the pixels in an array. By finding the total mean and variance the threshold value is calculated. From this threshold value each pixel is set to either 0 or 1. i.e. background or foreground, thus the image can change only at once.

using discriminant Analysis, Otsu defined the variance of thresholded image as(between two classes)

$$\sigma_B^2 = w_1(\mu_1 - \mu_2)^2 + w_2(\mu_2 - \mu_1)^2$$

The following formulas are used for calculating total mean and variance. First the pixels are divided into two classes, C1 and C2. Where C1 shows the gray levels[1,...,t] and C2 shows the gray levels[t+1,...,L] [6].

Result

Here we took the 10 ladakhi numerals for experiment. First the resized the original rgb image than converted the image into grayscale image. After that we applied the local adaptive and global otsu's thresholding method on image. The result of these thresholding methods are shown in the table. Than we calculate the correlation between the images. It is observed from result that the correlation between two images obtained from local and global thresholding is between 0 and 0.32 rang.

The probability distribution for the two classes is

C₁: $p_1/w_1(t), \dots, p_t/w_1(t)$ and C₂ : $p_{t+1}/w_2(t), \dots, p_L/w_2(t)$

Where $w_1(t) = \sum_{i=1}^t p_i$

Sr.No.	Original Image	Local Adaptive Thresholding	Gocal Otsu's Thresholding	Correlation between Local thresholding image and Global thresholding image
1				0.0890
2				0.1725
3				0.1860
4				0.1858
5				0.3294
6				0.2604
7				0.2900
8				0.1934
9				0.1783

Table 1. Result of Local Adaptive and Global Otsu's thresholding method

Conclusion	method is better than local adaptive thresholding .
This paper describes Local Adaptive Thresholding and Global Thresholding using Otsu's method. Here compared those two thresholding techniques. From the results as shown in above table we reached on conclusion that result of Global Threshold using Otsu's	Acknowledgement
	Author thankful to Dr D N Besekar sir Associate Professor Department of Computer Science, Shri Shivaji Science College Akola, for their cooperation and guidance
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MODIFICATION OF SOY BASED ADHESIVE WITH CROSSLINKER & CHARACTERISATION BY FTIR, TGA & DSC

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ABSTRACT

Formaldehyde-based adhesives such as urea-formaldehyde (UF) and phenol-formaldehyde (PF) adhesives dominate the current wood adhesive market. However, these adhesives are derived from petrochemicals and carcinogenic formaldehyde. Soy based adhesive have many advantages such as low cost, easy handling and low press temperature. In addition to this, most important property is, it is eco- friendly and depends on renewable sources and is abundant, inexpensive and readily available. However, the bonding characteristic of the adhesive is not as good as synthetic adhesives. In this study, we prepared adhesive by using very less quantity of formaldehyde. An attempt is being made to improve the adhesion properties of soy flour adhesive by chemical modification. They were characterized by their various physical properties and by instrumental techniques such as FT-IR, TGA and DSC. Their performance property was tested by bonding of wood samples in shear mode.

Indtroduction & Literature Survey

Soybean is an important crop cultivated widely throughout the world. Not only an oil seed crop, feed for livestock and aquaculture, but also a good source of protein for the human diet [1-3]. The solubility of soy protein in water is highly dependent upon the pH. In a neutral or alkaline medium, around 80% of the protein can be dissolved [3]. To be used as an adhesive, the globular structure of polypeptide chains in soy protein has to be broken because any good adhesive must consist of relatively large, flexible and inter woven polymer chains. More polar and apolar groups should be exposed for contact. Therefore, it is necessary for soy protein to be disrupted before application [4-5]. Soy-based adhesives are widely used in the production of wood composition elsewhere in the world. Adhesive are polymers that can bind two surfaces through adhesive and cohesive interaction. Adhesives are made of natural and synthetic material. Soy based adhesive have many advantages such as low cost, easy handling and low press temperature. In addition to this, most important property is, it is eco- friendly and depends on renewable sources and is abundant, inexpensive and readily available.

Wood adhesives can be roughly classified into two categories: adhesives from natural materials and adhesives from petrochemicals. Petroleum-based adhesives have many advantages, such as strength and higher water

resistance, but most of them contain phenol formaldehyde, and cross linking agent that causes environmental problem and even toxicity in both processing and product distribution [6]. Petroleum reserve are limited, and politically controlled. In addition to this, these adhesives may not be completely biodegradable. Therefore a need exists to develop a natural adhesive.

In soybean, there is compact structure of protein. Some chemical or enzymatic modifications are required. After the modification, the protein chains are held together by disulphide bonds, hydrogen bond, electrostatic attraction between oppositely charged groups, and hydrophobic interaction and shows better physical properties. Alkali, organic solvents, surfactants, urea, and protease enzymes were used to unfold/modify soy protein. The main component of soy-based protein adhesive is soy flour or soy protein isolate (SPI). The former contains 40-60% protein, while the latter contains more than 90% protein. Both of them can't be used as adhesive directly. Before application, cross-linker or other chemicals should be added. Soy protein was one of the most important adhesives in wood panel industry. When the compact protein structure is unfolded, the protein chains can spread well onto wood surfaces and can easily penetrate wood. All those functional groups such as amino groups, carboxylic acid groups and hydroxyl groups in the unfolded protein can well interact with

wood components, thus forming strong bonding with wood. The use of curing agents for cross linking soy protein is another effective method for improving the strength and water-resistance of the soy-based adhesives. Generally, cross linking agent are sulfur-containing compounds, epoxy compounds, aldehydes etc[10-13].

The objective of this study is to

- prepare soy based adhesive,
- modify soy based adhesive with cross linker
- study performance property of adhesive using wood substrate.

Materials & Methods

Soy flour in the form of flakes was obtained from Saguna Foods Industry, Vani, Hinganghat. It was grounded and filtered with 70 mesh cloth. Protein content of the soy flour was 58.31% and moisture content was 9.31 %. Commercial grade of formaldehyde (37 %) was obtained by the local supplier, Urea and NaOH was obtained from Loba Chemie, Mumbai and are of laboratory reagent grade.

Preparation of soy based adhesive

Water (640 g) and soy flour (160g) were added to a three necked round bottom flask, equipped with a mechanical stirrer, thermometer and condenser. The reactor was put into the water bath [Fig. 1]. With continuously stirring, the mixture was heated to 45°C. Then 30 % NaOH solution(42.6g) was added into the flask. After 30 minutes, 40 % urea (40g) was added. After 20 minutes, heating was stopped and the mass was cooled to 30 °C and filtered through 70 mesh filter cloth [14]. (Sample A-1).

Preparation of cross linker

Phenol (94g) and 37 % formaldehyde (1464g) were put into a 500 mL flat-bottom flask, which was equipped with a condenser, thermometer and mechanical stirrer [Fig. 2]. pH was adjusted to 9 – 9.5 using 30% NaOH solution. After stirring well for several minutes, the temperature of the mixture was slowly increased to 85–90 °C and kept for 60 minutes at this temperature. Then the resin was cooled to room temperature [14].

Preparation of samples with cross linkers

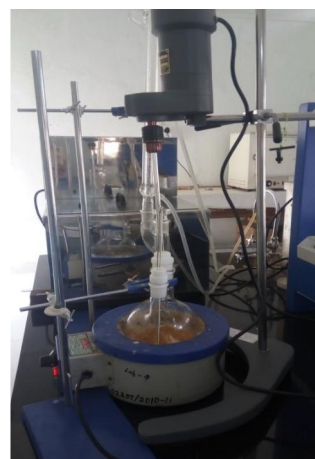
Three samples were prepared using cross linker with base adhesive in different proportion such as 5%, 10 %, 15 % cross linker to study the performance properties of adhesive.

Preparation of wood specimen for testing

Test specimen of wood (*Babbul*) having size 115 mm long, 20 mm wide, 5 mm thickness were prepared. Adhesive (approx. 1.5 g) was applied on one side at one end with area of 20 mm x 20 mm (marked) by brush and another piece of specimen was put on the marked area, then clamped together and stored under ambient condition for at least 24 hrs [Fig. 3]. Five specimen were prepared for each adhesive sample [15].



[Fig 1 : Assembly for making Soya adhesives]



[Fig 2 : Assembly for making Cross linkers]



[Fig. 3 : Bonded samples]

Determination of Protein content (%)

The protein content was determined indirectly by estimation of nitrogen by automated Kjeldahl apparatus of Kjeloplus – CAS VATS.
 $\% \text{ Nitrogen} = (\text{volume of standard acid in ml} - \text{Volume of blank in ml}) \times N \text{ of acid} \times 1.4007 / \text{weight of sample in grams}$
 $\text{Protein} = \% \text{ Nitrogen} \times 6.25$

Determination of moisture content (%)

$\text{Percent moisture} = \text{Mass of Water} \times 100 / \text{Mass of Sample before drying}$

Determination of solid content (%)

Oven-drying method was used to determine the solid content of the adhesive [16].

The content of solid content was calculated from three parallel samples as follows:
 $\text{Solid content (\%)} = (\text{weight of sample after drying}) \times 100 / (\text{weight of sample before drying})$

Determination of pH

pH of the samples were determined using pH-meter VSI 1B model at 25 °C.

Determination of Specific gravity:

$\text{Specific Gravity} = \text{Density of object} / \text{Density of water}$

Determination of Viscosity

The viscosity of adhesive was determined by using Brookfield viscometer RVT model using spindle no. 2 at r. p. m. 20 and at 25 °C.

Determination of tensile strength

Samples were tested by Universal Testing Machine, model STM-1025-M-25N Using load cell of 500 kg, cross head speed 10 mm/min, gage length 20 mm. Five specimen each of the adhesive sample were tested.

FTIR Spectroscopy

FTIR spectrum of given adhesive was determined by using Perkin Elmer spectrum by scanning the sample from 500 to 4000 cm^{-1} and recorded the spectra.

Differential Scanning Calorimetry (DSC)

The soy based adhesive, and their mixture with cross linker was tested by a TA instrument of model DSC Q 20 spectrometer. The specimens were heated from 30 to 230 °C under a heat

rate of 15 °C /min and the thermal changes were recorded.

Thermogravimetry analysis (TGA)

The soy adhesive and cross linker was cured in a oven at 100 ± 2 °C until a constant weight was obtained and then grounded and filleted with 70 mesh cloth . The thermal stability of the cured adhesive and cross linker was tested using a TA Instrument of model (TGA Q 50). About 5 mg of the powdered sample was taken into a pan and scanned from the 30 to 600 °C for adhesive and 30 to 700 °C for cross linker at a heating rate 10 °C /min .The sample weight changes were recorded.

Result And Discussion

The physical properties of adhesive samples prepared are given in Table No. 1

Table No. - 1**Physical properties of adhesive samples**

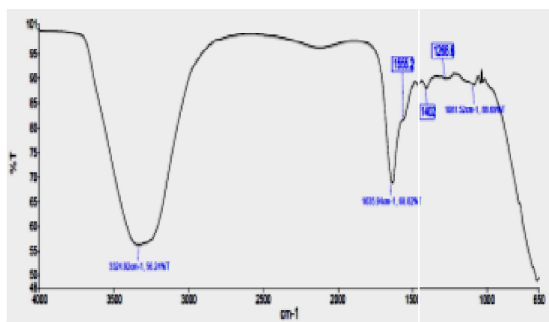
Name of the Sample	Composition (A-1 : C-1)	Appearance	Solids %	Viscosity, centipoises	pH, at 25 °C	Specific gravity
A-1 (base adhesive)	100:0	Brown Viscous Liquid Dispersion	19.59	450	12.52	1.07
C-1 (Cross linker)	0: 100	Pale Brown Liquid	23	-	7.51	-
A-2	95:5	Pale Brown Liquid Dispersion	23.23	-	10.18	-
A-3	90:10	Pale Brown Liquid Dispersion	23.85	-	10.2	-
A-4	85:15	Pale Brown Liquid Dispersion	25.71	-	10.18	-

FT- IR Spectroscopy

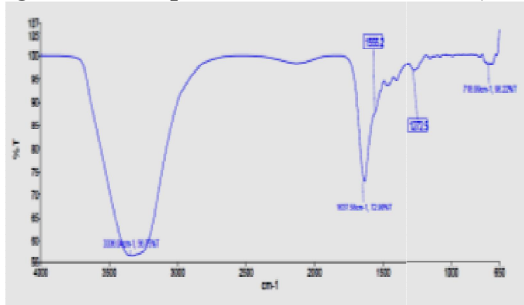
The FTIR spectra of sample A-1, A-2 and C-1 are given in Figure 4, 5, 6 respectively. For SF adhesive (A-1) without addition of PF resin (C-1), the broad band within 3200 to 3500 cm^{-1} was assigned to the free and bound -N-H and O-H group. The protein characteristic absorption band at 1635 cm^{-1} (amide I) 1555 cm^{-1} (amide II) and 1268 cm^{-1} (amide III) , are assigned to C=O stretching , N-H bending , C-N and N-H stretching respectively. After

addition of PF resin of 5% (Sample A-2), some bands are shifted. It indicates that some denser structure was formed. The peak of amide I shifted from 1635 to 1637 cm^{-1} . Second peak of amide III shifted from 1268 to 1272 cm^{-1} .

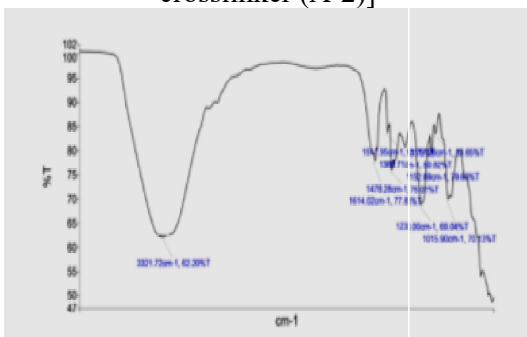
In the spectra of PF resin (Sample C-1), there are various type of band obtained. But after addition of C-1 in A-1, some bands are shifted and some peak are not obtained in spectrum. This also indicates that the resin is properly bound with protein and from a denser structure. [17-25]



[Fig. 4: FT-IR spectrum for SF adhesive,(A-1)]



[Fig. 5 : FTIR Spectrum of sample with crosslinker (A-2)]



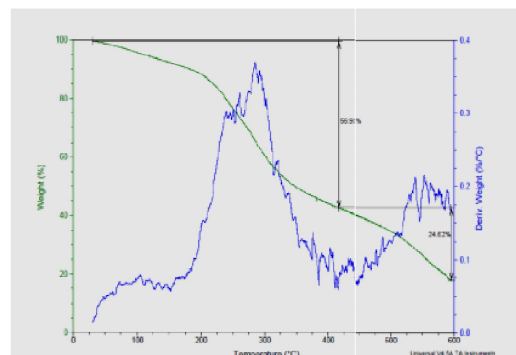
[Fig. 6 : FT-IR spectrum of PF resin (C-1)]

Thermogravimetry analysis (TGA)

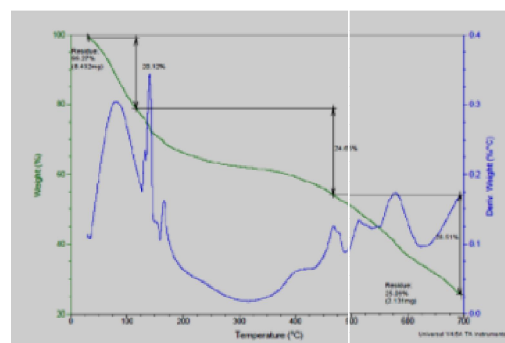
The figure 7 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of SF adhesive (sample A-1). The first stage (I) is a possible post reaction stage, at a temperature region of 50 to 150 $^{\circ}\text{C}$, which is

attributed to the possible subsequent thermal reaction of the material. In these stage small weight loss occurred due to moisture and some highly unstable product. In second stage from 150 to 425 $^{\circ}\text{C}$ almost 60% adhesive degraded. It means our adhesive is stable upto 200 to ~ 250 $^{\circ}\text{C}$. After that the rapid degradation occurred. In third stage, 425 to 600 $^{\circ}\text{C}$ 24% remaining compound degraded. This shows that some highly stable protein structure is present which are degrading at high temperature.

Figure 8 is for PF resin (sampe C-1) shows that for the degradation of resin it required more temperature than adhesive. Thus it is more stable than SF adhesive (sample A-1). Hence after addition of resin, resultant PF/SF adhesive (sample A-2 to A-4) are having better thermal stability [18-25].



[Fig. 7 : TGA spectrum for SF adhesive]

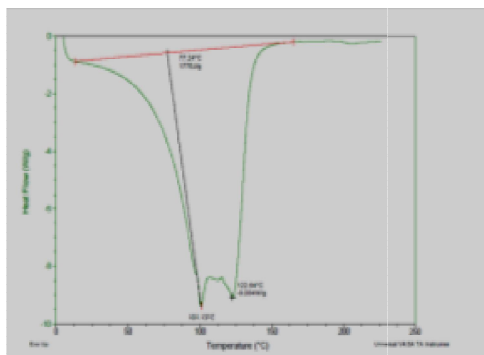


[Fig.8 : TGA spectrum for PF resin]

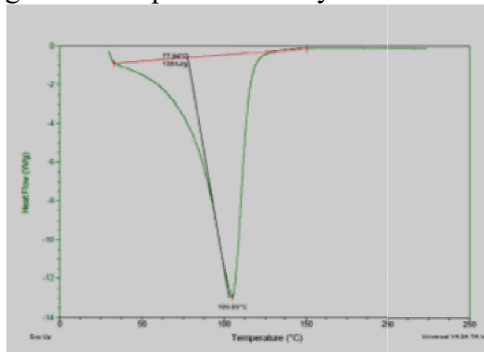
Differential Scanning Calorimetry (DSC)

Fig, 9 and 10 shows the DSC spectra of sample A-1 and C-1 respectively. In Fig. 10, we got some exothermic peak which shows that the given adhesive is not homogeneous or protein part are cross linked by itself. In case of adhesive mixed with cross linker, it gave

exothermic peak at 105 °C. It indicates that reaction is completed between adhesive and cross linker.



[Fig. 9 : DSC spectrum of soy based adhesive



[Fig. 10: DSC spectrum of adhesive with cross linker]

Performance property

Table No. 2 shows the breaking strength of samples.

Table No. 2				
Breaking force (shear strength) of wood sample (in kg)				
Sample designation	A-1	A-2	A-3	A-4
Trial no. 1	59.6	66.1	56.6	50.0
Trial no. 2	52.0	60.0	54.0	44.8
Average	55.81	63.05	55.3	47.4

The dry shear strength of the soy based adhesive with 5% , 10% , and 15% PF cross

linker are given in table no. 2. From these values, we conclude that there are some effect occurs after addition of cross linker in simple adhesive. The breaking force for sample A-1 is ~55.81 kg but after addition of 5% cross linker it increased upto 63.05 kg. But in case of addition of 10% cross linker, there is no such remarkable effect are observed although after addition of 15% cross linker value are slightly decreased. Hence mixing of cross linker upto 5% shows some increment in shear strength value.

Conclusion

A study was conducted on adhesive property of soy based protein which is modified by using 30%NaOH and 40%urea solution . After preparation of adhesive, it was mixed with PF resin which is prepared using basic condition. Various proportion of adhesive samples were prepared using neat soy adhesive and 5%, 10% and 15% PF resin. They were characterized by their various physical properties and by instrumental techniques such as FT-IR, TGA and DSC. Their performance property was tested by bonding of wood samples in shear mode.

The result showed that the mechanical property of soy-based adhesive is improved after linkage with PF resin . After addition of 5% PF cross linker with adhesive formulation, dry shear strength of wood samples improved from 55.81kg to 63.05kg. The solid content and viscosity of resultant adhesive was 19.59 % and 450 cps respectively which was acceptable. The differential scanning calorimetry (DSC) and FTIR result confirmed the cross linking reaction between soy based adhesive and phenol formaldehyde (PF) resin. Result of TGA also shows the thermal stability of both adhesive and cross linker.

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DESIGN AND CHARACTERISATION OF SOME 3-ARYLIMINO-6-N-TERT-BUTYLIMINO-1,2,4,5-DITHIADIAZINE AND THEIR DIACETYL DERIVATIVES.**N.A. Rashidi**Department of Chemistry, Mungsaji Maharaj Mahavidyalaya, Darwha,
rashidinazial@gmail.com**ABSTRACT**

3-Arylimino- 6-N-tert-butylimino 1,2,4,5-dithiadiazine (V) have been synthesized by the interaction of 6-aryl-1-N-tert-butyl-2,5-dithiobiurea(III) and iodine in ethanol. The former compounds (III), in turn, have been prepared by the drop wise addition of hydrazine hydrate to aryl isothiocyanate (I) followed by condensation with tert-butyl isothiocyanate in 1:1 ratio in chloroform medium. The synthesized compounds (V) have been acetylated with acetic anhydride and glacial acetic acid in 1:2 ratio afforded 4,5-diacetyl derivatives (VI). The structures of all these synthesized compounds were established on the basis of chemical transformation, elemental analysis, equivalent weight determination and IR, ¹H-NMR and Mass spectral studies.

KEYWORDS: Thiosemicarbazide, 2,5-dithiobiurea, 1,2,4,5-dithiadiazine, acetylation

Introduction

The synthesis of various substituted 1,2,4,5-dithiadiazine have been reported in literature[1]-[3]. Some of them are shown to possess antifungal activity[4]. The N-tert-butyl-N'-aryl dithiobiurea[5] acts as a key intermediate in the synthesis of various heterocyclic compounds. In view of these observation, in the present work an attempt was made to synthesis some new derivatives of 1,2,4,5-dithiadiazine by the oxidative cyclisation of dithiobiurea with iodine in ethanol. These newly synthesized 1,2,4,5-dithiadiazines were transformed into their diacetyl derivatives.

Materials And Method

All the chemicals were purchased from local market and purified according to established method. Melting point was determined by Thiele's tube method using liquid paraffin and was uncorrected. The purity of compounds was established by thin layer chromatography (TLC). Precoated silica gel aluminium plate was used for TLC (E. Merck). Iodine was used to develop the TLC plates. Infrared (IR) spectra were recorded on Perkin Elmer FT-IR spectrophotometer model (v_{max} in cm⁻¹). ¹H-NMR spectra were recorded on Bruker Advance II 400 NMR spectrometer using deuterated dimethyl sulfoxide-containing tetramethyl silane (Me₄Si) as internal standard (chemical shifts in δ ppm). The Mass spectrum

was recorded on TOF MS ES+ Mass spectrometer.

The reagent aryl isothiocyanate[6] and t-butyl isothiocyanate[7] were prepared as described in literature. The parent compound N-aryl thiosemicarbazide (II)[4]-[9] was obtained by the drop wise addition of hydrazine hydrate to aryl isothiocyanate (I)

Preparation of 6-(m-tolyl)-1-N-tert-butyl-2,5-dithiobiurea (IIIa).

The m-tolyl thiosemicarbazide (IIa) (0.01 mole) was refluxed with tert-butyl isothiocyanate (0.01 mole) in chloroform medium for 1.5 h. After completion of reaction, the solvent was distilled off. The solid product obtained was crystallized from ethanol, m.p 125⁰C.

On extending the above reaction to different thiosemicarbazide (IIb-f), and the related products were isolated in good yield. (Table - 1.1)

(IIIa) : IR spectra[10],[11]: (KBr) cm⁻¹: 3272 (N-H), 3219(N-H), 3180-3115(Ar-H), 2955, 2918, 2849(C-H, t-Bu), 1310 (C-N), 1178 (C=S); **¹H-NMR** (DMSO-d₆) ppm: 1.3 (9H, m, t-Bu), 2.2 (3H, s, CH₃), 3.3 (1H, s, t-Bu-N-H), 4.5 (1H, s, Ph-N-H) 7.0-7.6 (4H, m, Ar-H), 8.7 (1H, s, N-H), 9.4(1H, s, N-H) .

Preparation of 3-(m-tolylimino)-6-N-tert-butylimino-1,2,4,5-dithiadiazine (Va)

Table .1 : Formation of 6-Aryl-1-N-tert-butyl-2,5-dithiobiurea (III).
Reagent : Aryl thiosemicarbazide (II) and t-butyl isothiocyanate

Aryl thiosemicarbazide(II)	6-Aryl-1-N-tert-butyl-2,5-dithiobiurea (III).	Yield %	M.P °C	Found (Calculated) %			
				C%	H%	N%	S%
m-Tolyl thiosemicarbazide (IIa)	6-m-Tolyl-1-N-tert-butyl-2,5-dithiobiurea (IIIa).	75	125	52.60 (52.67)	6.71 (6.80)	18.85 (18.90)	21.61 (21.63)
Phenyl thiosemicarbazide (IIb)	6-Phenyl-1-N-tert-butyl-2,5-dithiobiurea (IIIb).	78	140	50.96 (51.03)	6.34 (6.42)	19.63 (19.84)	22.66 (22.71)
o-Tolyl thiosemicarbazide (IIc)	6-o-Tolyl-1-N-tert-butyl-2,5-dithiobiurea (IIIc).	72	123	52.53 (52.67)	6.76 (6.80)	18.79 (18.90)	21.52 (21.63)
p-Tolyl thiosemicarbazide (IId)	6-p-Tolyl-1-N-tert-butyl-2,5-dithiobiurea (IIId).	80	116	52.44 (52.67)	6.69 (6.80)	18.82 (18.90)	21.59 (21.63)
o-Chlorophenyl thiosemicarbazide (IIe)	6-o-Chlorophenyl-1-N-tert-butyl-2,5-dithiobiurea (IIIe).	69	115	45.40 (45.48)	5.37 (5.41)	17.56 (17.68)	20.21 (20.24)
p-Chlorophenyl thiosemicarbazide (IIIf)	6-p-Chlorophenyl-1-N-tert-butyl-2,5-dithiobiurea (IIIIf).	70	128	45.38 (45.48)	5.32 (5.41)	17.61 (17.68)	20.19 (20.24)

The compound (IIIa) (0.01 mol) was made into paste in ethanol. To this ethanolic solution of iodine was added drop wise with stirring. The colour of iodine was initially disappeared. The addition was continued till violet colour of iodine persisted. The mixture was left overnight at room temperature. The solid separated was found to be acidic to litmus and on titrimetric analysis, identified as dihydroiodides of 3-(m-tolylimino)-6-tert-butylimino-1,2,4,5-dithiadiazine (IVa). The compound was washed with water and crystallized with aq. ethanol (70%), m.p 55⁰. On basification with dilute ammonium hydroxide solution afforded free base (Va). The

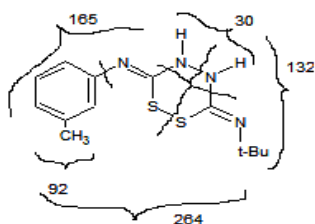
product (Va) was crystallized with aqueous ethanol (70%), m.p 73⁰.

The other substituted 1,2,4,5-dithiadiazines were prepared by extending the above reaction to different dithiobiurea (IIIb-f), and the related products were isolated in good yield. (Table - 1.2)

(Va) : IR spectra: (KBr) cm⁻¹: 3230 (N-H), 2969-2916(C-H, t-Bu), 1492 (C=N), 1316 (C-N), 776 (C-S); **¹H-NMR** (DMSO-d₆) ppm: 1.2 (9H, s, t-Bu), 2.2 (3H, s, CH₃), 6.5 (1H, s, N-H), 6.6 (1H, s, N-H) 6.8-7.9 (4H, m, Ar-H).; **Mass (m/z):** 297[M⁺], 263, 264, 207, 165, & 132.

Table.2: Synthesis of 3-Arylimino-6-N-tert-butylimino-1,2,4,5-dithiadiazine(V) & their 4,5-diacetyl derivatives (VI).**Reagents : 6-Aryl-1-N-tert-butyl-2,5-dithiobiurea (III) and iodine.**

6-Aryl-1-N-tert-butyl-2,5-dithiobiurea (III).	3-Arylimino-6-N-tert-butylimino-1,2,4,5-dithiadiazine(VI)	Yield %	M.P °C	Eq. Wt Found (Calcd)	3-Arylimino-6-N-tert-butylimino-1,2,4,5-dithiadiazine (V).	M.P °C	4,5-diacetyl-3-arylimino-6-N-tert-butylimino-1,2,4,5-dithiadiazine (VI)	Yield %	M.P °C
(IIIa).	(VIa)	82	55	441 (442)	(Va)	73	VIa	75	84
(IIIb).	(VIb)	74	109	436 (438)	(Vb)	118	VIb	70	126
(IIIc).	(VIc)	70	60	439 (442)	(Vc)	69	Vic	64	92
(IIId).	(VId)	69	112	440 (442)	(Vd)	121	VId	62	129
(IIIe).	(VIe)	61	82	470.5 (472.5)	(Ve)	99	VIe	60	104
(IIIIf).	(VIIf)	72	140	469.5 (472.5)	(Vf)	159	VIIf	71	137



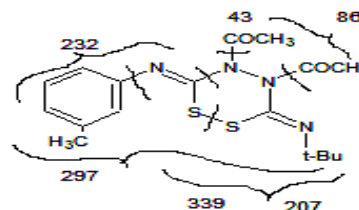
Preparation of 4, 5- diacetyl 1 – 3 - (m-tolylimino) - 6-N- tert- butylimino-1, 2, 4, 5-dithiadiazine (VIa):

A mixture of 3-(m-tolylimino)-6-N-tert-butylimino-1,2,4,5-dithiadiazine (Va) (0.01 mole) and acetic anhydride (0.02 mole) in glacial acetic acid (10.0 ml) was refluxed for 1hr. The reaction mixture was cooled and poured on a little crushed ice, when a cream coloured solid was precipitated (VIa). It was crystallised from ethanol, yield 75%, m.p. 84°C.

On extending the above reaction of acetylation to other 1,2,4,5-dithiadiazines (Vb-f)., related products (VIb-f) were isolated in good yield. (Table -1.3)

(VIa) : IR spectra: (KBr) cm⁻¹: 3265 (N-H), 2967, 2920, 2850(C-H, t-Bu), 1680 (C=O str)

1492 (C=N), 1308 (C-N), 776 (C-S); **Mass (m/z):** 381[M⁺], 339, 297, 307, 207, 132.



Result And Discussion

The synthetic route is outlined in *Scheme. (fig 1)*

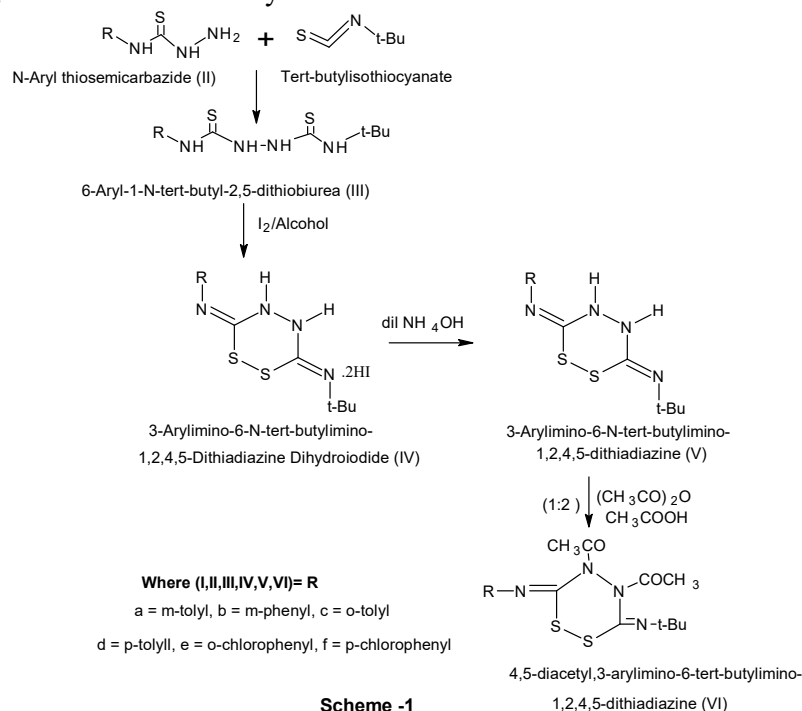
Six substituted aryl isothiocyanate (Ia-f) were synthesized by the reaction of corresponding amines with carbon disulfide and ammonium hydroxide. The N-aryl thiosemicarbazides (IIa-f) were prepared by the treatment of isothiocyanate with hydrazine hydrate in chloroform medium.

The condensation of different thiosemicarbazide (IIa-f) with tert-butyl isothiocyanate afforded a series of 6-aryl-1-N-tert-butyl-2,5-dithiobiurea (IIIb-f).

The compounds (IIIa-f), on treatment with an ethanolic solution of iodine gave the

compounds (IVa-f) which was found to be acidic and identified as dihydroiodides of 3-(arylimino)-6-tert-butylimino-1,2,4,5-dithiadiazine (IVa-f) on titrimetric analysis. On basification afforded free base (Va-f). The compounds 3-(arylimino)-6-N-tert-butylimino-1,2,4,5-dithiadiazine (Va-f) reacted with acetic anhydride in glacial acetic acid and yielded the

diacetyl products as 4,5-diacetyl-3-(arylimino)-6-N-tert-butylimino-1,2,4,5-dithiadiazine (Via-f). The structure of all the synthesized compounds have been elucidated on the basis of their spectral data.



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