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Research articles published by the faculty members in academic year-2018-19

Year-2018-19				
	Title of paper	Name of the author/s	Name of journal	Year of publicati on
1	Electrochemical Study of Galvanostatistically Deposited Cr ₂ O ₃ Thin Film for Supercapacitor	Dhasade S S	Materials Focus	2018
2	Electrodeposited nanoflakes like hydrophilic Co ₃ O ₄ as a supercapacitor electrode	Thombare J. V.	Journal of Physics and Chemistry of Solids	2018
3	Metal-Free One-Pot Chemoselective Thiocyanation of Imidazothiazoles and 2- Aminothiazoles with in situ	Kadam S N	Synlett	2018
	Thiocyanatosuccinimide	Kadeby S.H	Companization	
4	Postmodernism: A New Cultural Process	Mane M T	Literary Endeavour	2018
5	Poetry In Postmodernism	Mane M T	Literary Endeavour	2018



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14	Optical Study of Electrodeposited Vanadium Oxide Thin Films: Effect of Deposition Time	Gaikwad R. S.	International Journal of Scientific Research in Science and Technology	2019
15	Review on Ferrites : Structural Magnetic and Electrical Properties	Dhasade S S	International Journal of Scientific Research in Science and Technology	2019
16	Hydroponics for green fodder production, a need of time	Suryavanshi R.S, Gaikwad S A.	'Research Journey' International Multidisciplinary E- Research Journal	2019

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Electrochemical Study of Galvanostatistically Deposited Cr₂O₃ Thin Film for Supercapacitor



In the present report, we have synthesized chromium oxide (Cr_2O_3) thin films by galvanostatic mode of electrodeposition. The deposited Cr_2O_3 thin films have been studied by various characterization techniques. The structural and surface morphological behavior of deposited Cr_2O_3 thin films have been studied by using X-ray diffraction (XRD) and Scanning electron microscopy (SEM) techniques. The supercapacitive behaviour of the deposited Cr_2O_3 thin films have been analyzed by using cyclic voltammetry (CV), galvanostatic charging-discharging (GCD) and electrochemical impedance spectroscopy (EIS) techniques. The value of specific capacitance was found to be 198 F/g in 0.5 M Na₂SO₄ aqueous solution at scan rate of 5 mV/s.

Keywords: ELECTROCHEMICAL PROPERTIES; ELECTRODEPOSITION; IMPEDANCE; STABILITY; X-RAY TECHNIQUES

Document Type: Research Article

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Electrodeposited nanoflakes like hydrophilic Co₃O₄ as a supercapacitor electrode

P.M. Kharade, J.V. Thombare, A.R. Babar, R.N. Bulakhe, S.B. Kulkarni, D.J. Salunkhe

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Electrodeposited Nanoflakes like hydrophilic Co₃O₄ as a Supercapacitor Electrode

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Abstract:

Hydrophilic cobalt oxide (Co₃O₄) electrode was deposited by galvanostatic electrodeposition method. The Co₃O₄ electrode was characterized by using different characterization techniques such as X-ray diffraction (XRD) shows cubic structure, scanning electron microscopy (SEM) shows nanoflakes like morphology and surface wettability study shows hydrophilic in nature. TEM image of the Co₃O₄ electrode reflects highly crystalline structure. The supercapacitive properties of deposited Co₃O₄ electrode is probed using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques. The Co₃O₄ electrode shows maximum specific capacitance of 315 F.g⁻¹ obtained from CV techniques in 0.5 M Na₂SO₄ solution at scan rate 5 mV.s⁻¹. Hence, the electrodeposited Co₃O₄ electrode is best for supercapacitor application. *Keywords*: Crystal Structure; Deposition; Nanocrystalline Materials; Scanning Electron Microscope; Supercapacitive Properties.

1. Introduction:

In the recent year, increasing globalization and climate changes with decreasing fossil fuels there is great demand for alternative clean energy storage devices. One such device supercapacitor has fascinated much attention due to longer cycle life and higher energy density than conventional capacitor and greater power density than batteries. Supercapacitor exhibits high specific capacitance, fast charging-discharging rate, long cycle stability, lightweight, low cost and environmental friendly. Due to this feature supercapacitor can be used in variety of potential applications such as, hybrid electric vehicles, cellular phones, industry, laser, digital camera, etc[1-3].

The active electrode materials used in supercapacitor are categorized into three main parts: carbon based electrode, Conducting polymer based electrode (CP) and Transition metal oxide based electrode (TMO) etc. Among these transition metal oxides (TMO) based electrodes have possesses great attraction due to multiple oxidation states, high specific capacitance, long cycle life, porosity, low equivalent series resistance etc [4].

The cobalt oxides have been prepared by variety of chemical and physical methods such as: chemical bath deposition[5], spray pyrolysis [6], successive ionic layer adsorption and reaction (SILAR) method[7], electrodeposition [8-10], using anodic aluminum oxide (AAO) template[11], template-free growth[12], hydrothermal process[13-14], pulsed laser deposition [15] and Chemical Vapor Deposition [16]. Also, in the literature few reports are available on electrodeposition of cobalt oxide thin films for supercapacitor application [8,17]. Among the transition metal oxides, cobalt oxide is one of the more versatile oxide materials [18]. It has been extensively studied for its application such as a catalyst [19-20] sensor [21], supercapacitors [8,17], Li-ion batteries [10] and magnetic material [22-23]. In the literature, the thin films are prepared by three different modes of electrodeposition as potentiostatic, galvanostatic and potentiodynamic. Among these modes, galvanostatic mode of electrodeposition is best one. Galvanostatically deposited electrodes have additional

advantage than the others such that it controls film thickness by controlling the charge passing through the electrode-electrolyte interface [24].

In the literature, so many reports are available on the synthesis and characterization of cobalt oxide thin films. Different synthesis method gives different structural as well as morphological properties of cobalt oxide thin films. Surface morphology plays an important role in the supercapacitive study. Pawar et al. have reported hexagonal sheets of Co_3O_4 and Co_3O_4 -Ag for high-performance electrochemical supercapacitors by using one pot hydrothermal method. They have reported maximum specific capacitance of 958 F.g⁻¹ for Co_3O_4 -Ag composite [25]. Patil et al also have reported Core-shell structure of Co_3O_4 @CdS for high performance electrochemical supercapacitor by using economical, scalable and one pot hydrothermal method and a successive ionic layer adsorption and reaction (SILAR) method. The Co_3O_4 @CdS core shell nanostructure-based symmetric supercapacitor displayed excellent capacitive characteristics with a specific capacitance of 360 Fg⁻¹ at scan rate of 10 mVs⁻¹ [26].

In present work, efforts have been taken to study the structural, morphological and supercapacitive properties of electrodeposited nano-structured cobalt oxide thin film.

2. Experimental

The Co_3O_4 electrode was deposited galvanostatic electrodeposition method (GEM) on Stainless steel (SS) substrate with constant current density of 5 mA.cm⁻² for 600 sec and annealed at 300°C for 1 hour.

For the structural clarification of the Co_3O_4 electrode, XRD analysis was employed with copper target in the 2 θ range between 20° to 80°. The surface morphology of the Co_3O_4 electrode was studied by SEM (ZESIS) and the contact angle measurement was made with the help of Rame-Hart contact angle meter .The supercapacitive properties of the Co_3O_4 electrode was carried out using the CV, GCD and EIS techniques by using CH instrument (CHI 660 A) using 0.5 M Na₂SO₄ used as an electrolyte solution.

3. Result and discussion

3.1 X-ray diffraction (XRD) study

In order to identify the crystal structure of the deposited Co_3O_4 electrode, XRD analysis was carried out shown in Fig.1. The XRD spectrum of Co_3O_4 electrode display polycrystalline cubic crystal symmetry and matched with JCPDS data (Card No 42-1467). The peaks indexed by asterisk (*) in the XRD spectrum were the SS substrates only. The Co_3O_4 film shows peaks (220), (311), (422), (511) and (440). The Co_3O_4 film is oriented along (220) plane and rest of peaks shows low relative intensities. Thus, nano-size formed grains are confirmed by small peak width. The absence of any secondary peaks reveals the stoichiometric purity of the sample. Wu et al have reported the spinel cubic crystal structure of electrodeposited Co_3O_4 thin film [8].

3.2 Surface morphological and surface wettability study

Fig. 2(A-B) shows SEM images of Co_3O_4 electrode at two different magnifications (X 10 k and X 300 k). The electrodeposited Co_3O_4 film electrode exhibits a highly porous structure (Fig. 2A) with lots of pores having diameters from 25 to 300 nm (Fig. 2A). The interconnected network is made up of flakes type Co_3O_4 . Furthermore, from magnified image (Fig. 2B) of the Co_3O_4 flakes, it is observed that forming a net-like structure and developing more and more porosity. However, the electrodeposited Co_3O_4 film electrode exhibits a highly homogeneous and compact surface morphology (Fig. 2A). It is believed that porous structure is helpful to improve the electrochemical properties thanks to sufficient contact between active materials and electrolyte, fast ion/electron transfer, and enhanced flexibility. Hence, improved performances of electrodes like capacity, stability etc., can be expected accordingly for porous Co_3O_4 electrodes. Such importance has been explained in the earlier

literature [6, 7, 27]. Supercapacitive properties of film electrodes were tested with the help of aqueous electrolytes hence it's important to study surface wettability study of film electrode with electrolyte. Inset of Fig. 2(A) shows actual photograph of water contact angle with electrolyte. The electrolyte contact angle was found to be 62° . Hence, Co_3O_4 electrode is hydrophilic in nature. In case of supercapacitors, hydrophilicity is one of the important parameter for achieving maximum capacitance [27]. Jagadale et al. [27] have reported the water contact angle for Co_3O_4 electrode is to be 30° . In present work, value of contact angle is relatively high than this one this is may be due to different size and shape of nanostructured Co_3O_4 electrode.

Figure 3(A-B) shows the TEM images of prepared using galvanostatic electrodeposition method. Figure 3(A) shows the corresponding selected area electron diffraction (SAED) pattern, which confirms the crystalline nature of the particles [28]. Figures 3 (B) shows TEM image of the Co_3O_4 electrode 2 nm magnification. The porous part reflects the thick flake like structure as observed in SEM (fig. 2B). It also exhibits planer structure similar to XRD (311) peak,

3.3 Cyclic voltametric (CV) study

Fig. 4(A) illustrates a typical CV of Co_3O_4 electrode within potential range between -1.0 V to +1.0 V/SCE at the scan rate of 5, 10 and 20 mV.s⁻¹ in 0.5 M Na₂SO₄ electrolyte solution. Average specific capacitances are calculated from the CV curves using the following equation:

$$C = \frac{I}{m \left(\frac{dv}{dt} \right)}$$
(1)

Where, I is average current density in ampere, m is deposited mass of electrode in gram and dv/dt is scan rate in volts/s. The specific capacitance Co_3O_4 electrode was found to be 315 F.g⁻¹ at scan rate of 5 mV.s⁻¹. In the present case, the redox process is mainly

governed by the calation and de-calation of Na^+ from the electrolyte into the Co_3O_4 matrix. The electrochemical reaction for Co_3O_4 in Na_2SO_4 neutral aqueous electrolyte is generally believed to be [29].

$$Co_3O_4 + Na^+ + e^- \leftrightarrow Co_3O_4Na$$

(2)

The effect of scan rate on the Co_3O_4 film electrode was examined in 0.5 M Na₂SO₄ electrolyte. In CV curves the redox peaks are visible, which implies that the electrochemical capacitance mainly arises due to pseudocapacitance. In CV curves, not only the calculated current densities increased but also the oxidation and reduction peaks shifted toward higher and lower potentials, respectively. This is may be due to the scan rate dependent calation and decalation of Na⁺ ions into Co₃O₄ matrix. At lower scan rate, both the outer and inner surfaces of Co₃O₄ electrodes are entirely utilized, while at higher scan rates, mostly outer surface is accessed by the conducting ions. The specific capacitance obtained in present case is better than reported value due to porous and nanoflakes like morphology of the Co₃O₄ electrode [7].

3.4 Galvanostatistic charging-discharging (GCD) study:

Fig. 4(B) demonstrates that a typical GCD curve of Co_3O_4 electrode at constant current density of 5 mA.cm⁻² in 0.5 M Na₂SO₄ electrolyte solution. Inset of Fig. 4(B) shows a single cycle of GCD. The charging curve shows exponential increment in the potential of the electrode which confirms the charge storage in the Co_3O_4 electrode. The discharge curve composed of two parts, IR drop indicated by a sudden potential drop due to internal resistance and capacitive feature indicated by a slow potential decay. The values of specific energy, power and coulombic efficiency are calculated from the following equations [30-31]:

Specific energy
$$SE = \frac{V \times I_d \times T_d}{M}$$
 ------(3)

Specific power
$$SP = \frac{V \times I_d}{M}$$
 ------(4)

Coulombic efficiency
$$n(\%) = \frac{T_d}{T_c} X \ 100$$
 (5)

The specific energy and specific power of the Co_3O_4 electrode were found to be 88.4 Wh.kg⁻¹ and 17.4 kW.kg⁻¹, while the coulombic efficiency was found to be 98.30 %.

3.5 Electrochemical Impedance Spectroscopy (EIS) study:

Fig.5 shows Nyquist plots of Co₃O₄ electrode within the frequency range of 10 Hz to 1 MHz in 0.5 M Na₂SO₄ electrolyte solution with two different potentials such as 1.2 V and 1.4V. The corresponding equivalent circuit model used for fitting of EIS data is shown in inset of Fig.5. It was observed that both EIS curve shows the semicircle in the higher frequency region and straight line in lower frequency region [32-33]. The Co₃O₄ electrode and Na₂SO₄ electrolyte solution have difference in conductivity i.e. Co₃O₄ electrode have electronic conductivity and Na₂SO₄ electrolyte have ionic conductivity. Hence, interface has discontinuity in charge transfer process. Thus, impedance behavior at the high frequency region is resistive. The complete resistive bahaviour may be contributed from Faradaic redox process also. The SO_4^{2-} ions may insert into pores of Co_3O_4 electrode which gives rise to the Warburg impedance W, and hence at lower frequencies, a linear part occurs in the impedance plots. The value of solution resistance, Rs and charge transfer resistance, Rct were calculated from Nyquist plot. The value of R_s and R_{ct} was found to be 0.67 Ω and 2.68 Ω , respectively for 1.2 V and that of 0.47 Ω and 2.40 Ω , respectively for 1.4 V. As applied potential increases, straight line deviates towards the Z" axis indicating pseudocapacitive bahaviour due to reversible faradaic redox reactions [14].

Conclusions:

Galvanostatic mode of electrodeposition is best method for synthesis of Co_3O_4 electrode because which provide well defined porous with nanoflakes like surface morphology and hence improves the supercapacitive properties of Co_3O_4 electrode. A nanoflake gives more active sites than the ordinary morphology so the charge carriers easily do calation and decalation. Such improved properties are beneficial for supercapacitors. In supercapacitors, the important aspect is to provide maximum active sites and to provide a channel for fast transfer of charge carriers from electrode to electrolyte and vice a versa; which is fulfilled by galvanostatically deposited Co_3O_4 electrode. Recently, such basic improved properties are a key requirement for the fabrication of supercapacitive devices because supercapacitors have numerous myriad applications in the field of technology.

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Figure Captions:

Fig.1(a) XRD spectrum of Co₃O₄ electrode;

Fig.2(A-B) SEM image of Co_3O_4 electrode at magnifications of 10kX and 300kX, respectively.

Fig.3 :(a) SAED pattern of Co₃O₄ electrode and (b) TEM image of Co₃O₄ electrode.

Fig.4:(A) CV of Co₃O₄ electrode at scan rate of 5, 10 and 20 mV.s⁻¹; (B) GCD study of Co₃O₄

electrode at 5 mA.cm⁻².

Fig.5. EIS study of Co₃O₄ electrode.

Figure:



Fig. 1. XRD spectrum of Co₃O₄ electrode



Fig.2(A-B) SEM image of Co₃O₄ electrode at magnifications of 10kX and 300kX,

respectively.



Fig: 3 SAED pattern and TEM image of Co₃O₄ electrode.



Fig. 4. (A) CV of Co_3O_4 electrode at scan rate of 5, 10 and 20 mV.s⁻¹; (B) GCD study of Co_3O_4 electrode at 5 mA.cm⁻².



Fig. 5. EIS study of Co₃O₄ electrode.

Nanoflakes like hydrophilic Co₃O₄ as a Supercapacitor Electrode

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Graphical abstract:



Research highlights:

- Galvanostatic mode of electrodeposition is one of the best techniques to deposit
 Co₃O₄ electrode.
- Porous nanostructure with nanoflakes.
- \blacktriangleright Hydrophilic Co₃O₄ electrode feasible for supercapacitor.
- \succ Good reversibility of Co₃O₄ electrode.

CERTIN MARK

S. N. Kadam et al.

Letter

Metal-Free One-Pot Chemoselective Thiocyanation of Imidazothiazoles and 2-Aminothiazoles with in situ Generated *N*-Thiocyanatosuccinimide

Α

Shuddhodan N. Kadam Ajay N. Ambhore Madhav J. Hebade Rahul D. Kamble Shrikant V. Hese Milind V. Gaikwad Priya D. Gavhane Bhaskar S. Dawane*

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Abstract A chemoselective thiocyanation of imidazothiazoles and 2aminothiazoles with use of in situ generated *N*-thiocyanatosuccinimide (NTS) at room temperature is described. The protocol offers mild reaction conditions and high chemoselectivity for electrophilic substitution in imidazothiazoles over nucleophilic substitution. This method provides metal-free and easy conversion of imidazothiazoles and 2-aminothiazoles into their corresponding C-3 and C-5 thiocyanates, respectively, in good to excellent yield. The present protocol also offers the effective thiocyanation of bifunctional imidazothiazoles containing aliphatic –OH and C(sp²)–H bond functionalities.

Keywords *N*-thiocyanatosuccinimide, thiocyanation, imidazothiazoles, 2-aminothiazoles, PEG-400

Thiocyanates are considered as one of the most versatile synthons in the field of organic chemistry. They have proved their potency as crucial synthetic intermediates in the synthesis of various sulfur-containing heterocycles such as sulfides,¹ thiocarbamates,² sulfanyl pyridines,³ and thiotetrazoles.⁴ The intriguing properties of thiocyanate have been utilized for the synthetic transformation of useful functionalities such as aryl nitriles,⁵ sulfonyl cyanides,⁶ thiazoles,7 thioesters,8 imidazoles,9 and so on. The thiocyanation reaction is one of the most significant protocols for direct C-S bond formation.¹⁰ Consequently, enormous efforts have been made in order to achieve thiocyanation of various heterocyclic compounds.¹¹ In the midst of various proceedings for thiocyanation of aryl and heteroaryl compounds, incorporating thiocyanate (SCN) particularly into C-H functionalities has always been a center of interest because of its own advantages.¹² For accomplishing this goal several approaches have been encountered (i.e. use of iodinated reagents,¹³ oxidants,¹⁴ and brominating agents¹⁵) in combination with readily available, low-cost thiocyanate salts as thiocyanating agents. But these strategies are mainly focused on imidazopyridines and indoles.¹⁶ Furthermore, the selectivity of direct electrophilic thiocyanation of $C(sp^2)$ –H bonds over nucleophilic substitution by alcoholic –OH, when both groups are present in same compound, by using *N*-thiocyanatosuccinimide (NTS) as a reagent, has not been studied previously.

Imidazothiazoles are considered a significant class of heterocyclic compounds. For example, levamisol and tetramisole, known for their antihelminthic and immunomodulatory properties, respectively, display an imidazothiazole core (Figure 1). The majority of imidazothiazoles exhibit a wide range of biological activities.¹⁷ Thiazoles are structurally very close to imidazoles, with the only difference of sulfur replaced by nitrogen. Vitamin B (thiamin) (Figure 1) is an important naturally occurring vitamin which contains the thiazole ring as an active center involved in various biological processes. Thiazoles are considered to be one of the most compelling heterocyclic compounds because of their broad spectrum of biological activities.¹⁸ Considering these consequential advantages, immense efforts have been made for the synthesis of imidazothiazoles and thiazoles.¹⁹ Introduction of new functional groups into these moieties may modify their biological profile or may imbed new biological activities. For this purpose, direct C-3 and C-5 functionalization of imidazothiazoles and thiazoles, respectively, provides an acceptable strategy.

Conversion of alcohols to their corresponding alkyl thiocyanates or alkyl isothiocyanates has been extensively studied.²⁰ Recently, Mokhtari et al. reported one-pot thio-

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cvanation or isothiocvanation of alcohols by using in situ generated NTS. Thus, existing methods were focused on either thiocyanation of C(sp²)-H bonds or thiocyanation of alcohols to alkyl thiocyanates or alkyl isothiocyanates. However, chemoselectivity for C-3 electrophilic thiocyanation over nucleophilic substitution at the alcoholic -OH group in imidazothiazoles, when both the possibilities are present in one motif, would be an important synthetic route for medicinal chemistry research. Encouraged by our previous work on the thiocyanation of 2-aminothiazoles,²¹ we herein report an efficient, practical, and metal-free approach for the one-pot conversion of functionalized imidazothiazoles and 2-aminothiazoles into their corresponding C-3 and C-5 thiocyanates, respectively. Use of easily accessible NH₄SCN, in situ generated NTS as the reagent. and PEG-400 as the solvent makes the protocol more accessible and efficient (Scheme 1).

We initiated our study on the synthesis of the target compounds by taking 1-(6-(4-chlorophenyl)-3-methylimidazo[2,1-b]thiazol-2-yl)ethanol 1a (Table 1) as the model substrate. In order to investigate the ideal reaction conditions (Table 1), initially, NBS (1.0 mmol) and NH₄SCN (2.0 mmol) were stirred at room temperature (r.t.) in CH₃CN (3 mL) for 15 minutes to induce in situ generation of NTS. Deliberate addition of reactant 1a (1 mmol) to this reagent led to formation of product 2a in 80% yield after three hours (Table 1, entry 1). Remarkably, thiocyanation or isothiocyanation of the alcoholic -OH group was not obtained for any derivative X, Z (Scheme 1) by the nucleophilic substitution route. Enthused by these results, the effect of other solvents such as DMSO, DMF, H₂O, CH₂Cl₂, THF, CH₃OH, and CHCl₃ was tested (Table 1, entries 3-9). In search of a "green" solvent for the reaction²² we preferred to test PEG-400 as a solvent. Interestingly, the best results (93%) were obtained in PEG-400 (Table 1 entry 2). When NCS was employed for the in situ generation of NTS, the formation of the product resulted in a slight decrease in yield with increasing reac-



Figure 1 Some important compounds containing imidazothiazole and thiazole as a core structure

tion time (Table 1, entry 3). This observation may be related with the fact that Br is a better leaving group than Cl. Thus, formation of NTS may take place faster with NBS rather than with NCS. Other reagent and solvents, such as HIO_3 in methanol and HIO_3 in PEG-400 as solvent were also examined (Table 1, entries 17 and 18); both of these combinations resulted in poor yields. Product formation of was not observed without the use of reagent (Table 1, entry 11). When NBS was used as a reagent for bromination at the C-3 position of imidazothiazole followed by thiocyanation with NH₄SCN, this approach was shown to take more time (24



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hours) with decreased yield of product (75%) (see below Scheme 5, c and Table 1, entry 12). Furthermore, the yield of the reaction decreased when (4.0 mmol) of NH₄SCN was used (Table 1, entry 13). The decrease in the quantity of NH₄SCN also decreased the yield of the product (Table 1, entry 14). We also tested $K_2S_2O_8$ for the same reaction with PEG-400 as the solvent; the reaction took a longer time of 20 hours and resulted in a nonseparable trace amount of product (Table 1, entry 19). The formation of product also decreased when NH₄SCN was replaced by KSCN or NaSCN (Table 1, entries 15 and 16). Finally, the optimized reaction conditions were achieved when NBS (1.0 mmol) and NH₄SCN (2.0 mmol) were stirred at room temperature in PEG-400 (3 mL) for 15 minutes to initiate the in situ generation of *N*-thiocyanatosuccinimide. Following slow addition





Entry	Reagent	Solvent	Yield (%)	
1	NTS	CH ₃ CN	80	
2	NTS	PEG-400	93	
3 ^b	NTS	PEG-400	80	
4	NTS	DMSO	78	
5	NTS	DMF	50	
6	NTS	H ₂ O	trace	
7	NTS	CH ₂ Cl ₂	75	
8	NTS	THF	50	
9	NTS	MeOH	70	
10	NTS	CHCl ₃	80	
11	-	CH ₃ CN	n.r.	
12	NBS	PEG-400	75	
13 ^c	NTS	PEG-400	70	
14 ^d	NTS	PEG-400	69	
15 ^e	NTS	PEG-400	60	
16 ^f	NTS	PEG-400	60	
17	HIO ₃	MeOH	50	
18	HIO ₃	PEG-400	40	
19	$K_2S_2O_8$	PEG-400	trace	

^a *Reaction conditions* (unless otherwise specified): **1a** (1.0 mmol), NH₄SCN (2.0 mmol), solvent (3mL), 3 h, r.t.; n.r. = no reaction.

^b NCS was employed for in situ generation of NTS. ^c NH₄SCN (4.0 mmol) was used.

^d NH₄SCN (4.0 mmol) was used.

^e KSCN (2.0 mmol) was used.

^f NaSCN (2.0 mmol) was used.

of 1a (1.0 mmol) (Table 1, entry 2) led to formation of the product in optimal yield of (93%) by stirring at room temperature for three hours. The product could be obtained in analytically pure form upon washing with cold aqueous ethanol, thus avoiding the use of tedious purification by column chromatography. A gram-scale reaction was also performed by using NBS (0.01 mol), NH₄SCN (0.02 mol), and reactant 1a (0.01 mol). In this case, the product yield observed was 75%. Having the optimized reaction conditions in our hand, we further investigated the scope of substrates (Scheme 2). The method was compatible with the tested substrates, and most of the substrates afforded the product in good yields. It is clear from Scheme 2 that halogen substituents at R¹ lead to good yields. Compound 2a (Scheme 2) with a chloro substituent was obtained in excellent (93%) yield, the highest amongst all derivatives. Product **2d** (Scheme 2) with an electron-donating group at R^1 was isolated in moderate vield.

It is notable that no derivative gave alkyl thiocyanate or alkyl isothiocyanate by nucleophilic attack of the alcohol on in situ generated NTS^{20a} (Scheme 1). Furthermore, derivatives with hydroxy and methoxy substituents at R¹ were not able to provide the desired product. The probable reason for the deleterious behavior of these derivatives may be positive mesomeric effect of the electron-donating substituents, due to which they were unable to furnish the product.



Scheme 2 Scope of substrates: Variation of substituents on imidazothiazole. *Reaction conditions*: NBS (1.0 mmol) NH₄SCN (2.0 mmol), substituted imidazothiazole **1a–g** (1 mmol), PEG-400 (3 mL), 3 h. Isolated yields are given.



D

A similar type of thiocvanation reaction was also tried on 2-aminothiazole and, in accordance to other methods reported in literature (Scheme 3),²⁴ the obtained product vield was poor (30%) (Scheme 4, compound **4h**). When we tried the present protocol with aryl-substituted thiazoles, the yield of the corresponding products was satisfactory. This indicates that the arvl group present on the 2-aminothiazole ring is activating the substrate for the electrophilic substitution. To prove the generality of the present methodology, we tried C-5 thiocyanation of 2-aminothiazoles (Scheme 3). Electron-withdrawing substituents such as halogens, proved to facilitate the reaction leading to formation of the products in good yield, amongst which compound 4a (Scheme 4) was obtained with a maximum yield of 92%. Derivatives with electron-donating groups (Scheme 4) furnished the products (such as 4f) with moderate yield. Furthermore, methyl substitution at R^1 (product **4f**) (Scheme 4) did not lead to nuclear thiocyanation in *ortho* position to the donating group (**4x**) (Scheme 3)²¹. Substitution at *meta* position, R², (Scheme 4) delivered the product in poor yield (product **4e**). Reactions for substrates with hydroxy and methoxy substituents were unable to provide the products; this behavior may be justified by the presence of a strong positive mesomeric effect, which may result in inability to form product. The method was further explored for its generality on a new substrate containing an alcoholic group, which led to moderate yield (product **4i**) (Scheme 4).

A probable mechanistic path was further studied by taking few other methods into account for control experiments by using the reactions depicted in Scheme 5. It comes to our notice that the reaction did not proceed in the absence of any reagent even after 28 hours (Scheme 5, a). We also tried to use $K_2S_2O_8$ for thiocyanation of these sub-



Scheme 4 Scope of substrates for 2-aminothiazoles. *Reaction conditions*: NBS (1.0 mmol) NH₄SCN (2.0 mmol), substituted 2-aminothiazole **3a-i** (1 mmol), PEG-400 (3 mL), 3 h. Isolated yields are given.

strates using PEG-400 as the solvent: however, only a nonseparable trace amount of product was formed after a prolonged period of 20 hours (Scheme 5, b). When the reaction was performed with use of NBS as a reagent it required a prolonged period of 24 hours for the formation of product in 75% of yield indicating that bromination was followed by the thiocyanation approach (Scheme 5, c). It was also observed that some amount of reactant was converted into the corresponding ketone as NBS was supposed to act as an oxidant. The time for completion of the reaction was dramatically reduced to three hours when the present approach with in situ generated (NTS) was employed, and the product was obtained in higher yield of 93% (Scheme 5, d). When NTS was employed as a reagent in the reaction we tested (Scheme 5, d) the progress of reaction by mixing it with the radical quencher butylated hydroxytoluene (BHT) in 1:1 molar ratio of reactant which revealed that the reaction progress was not altered. This indicates that the mechanism does not follow a free-radical pathway.

On the basis of these observations made in control experiments and the previous literature,^{14,20a,23} it may be possible that the reaction for C-3 thiocyanation of imidazothiazole proceeds through the mechanism shown in Scheme 6.



First, ammonium thiocyanate reacts with NBS to initiate the formation of electrophilic NTS. Afterwards, substituted imidazothiazole reacts with NTS at the C-3 position. The formed intermediate finally releases the proton for aromatization to furnish the final product (Scheme 6). This protocol ruled out the possibility of nucleophilic attack of alcoholic –OH on the sulfur atom of NTS to produce alkyloxygenyl thiocyanate (ROSCN), which can further react with NH₄SCN to furnish alkyl thiocyanate **X** (Scheme 1) or isothiocyanate **Z** (Scheme 1). In spite of all these possibilities, the reaction has been observed to promote C-3 thiocyanation in imidazothiazole compounds 2a-e (Scheme 1).



Scheme 6 Plausible reaction mechanism for imidazothiazole and 2-aminothiazole

The reaction for C-5 thiocyanation of 2-aminothiazole may proceed through the plausible mechanism shown in Scheme 6. Ammonium thiocyanate reacts with NBS to produce electrophilic *N*-thiocyanatosuccinimide, followed by reaction at C-5 position of 2-aminothiazole. Finally, the formed intermediate releases the proton for aromatization, which results in the final product.

In summary, we have developed a one-pot chemoselective synthetic route for C-3 and C-5 thiocyanation of imidazothiazole and 2-aminothiazole at room temperature.²⁵ The present protocol provides useful information regarding

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the reactivity of in situ generated NTS for thiocyanation of imidazothiazoles comprising an alcoholic hydroxy group. The method provides easy and metal-free chemoselective access for thiocyanation at C-3 position in imidazothiazole through electrophilic substitution, ruling out the possibility of forming alkyl thiocyanate or alkyl isothiocyanate through nucleophilic substitution by alcoholic -OH in the same substrate. This method provides high yields of C-3 and C-5 thiocyanates of imidazothiozole and 2-aminothiazole, respectively, under very mild conditions. The transformation provides a new opportunity for the synthesis of bioactive imidazothiazoles and 2-aminothiazoles, which may gain much attention in the field of synthetic and medicinal chemistry.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1609553.

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(25) Procedure for the Synthesis of 1-(6-(4-Chlorophenyl)-3-methyl-5-thiocyanatoimidazo[2,1-b]thiazol-2-yl)ethanol (2a) (Table 1)

A dried 50 mL round-bottomed flask was charged with NBS (177.98 mg, 1 mmol), NH₄SCN (152.24 mg, 2.0 mmol) in PEG-400 (3 mL) and the reaction mixture was stirred at r.t. for 15 min. The reaction mixture turned milky indicating generation of NTS (shown by TLC). Next, reactant **1a** (292.78 mg, 1 mmol) was added slowly, and the reaction mixture was further stirred for 3 h. After completion of the reaction as indicated by TLC, cold water (20 mL) was added to separate the solid product. The white solid was filtered, dried, and washed with cold aqueous ethanol (0.93 mmol, 93% yield).

Compound **2a**: Mp 111–113 °C. FT-IR: 3195, 2966, 2154, 1893, 1644 cm⁻¹. ¹H NMR (400 MHz, DMSO- d_6): δ = 7.94 (d, 2 H, *J* = 8.0 Hz), 7.62 (s, 2 H), 5.96 (s, 1 H), 5.17 (s, 1 H), 2.73 (s, 3 H), 1.41 (s, 3 H) ppm. ¹³C{¹H} NMR (100 MHZ, DMSO- d_6): δ = 152.62, 152.11, 134.68, 134.20, 131.36, 129.84, 128.87, 124.27, 111.02, 97.97, 62.25, 25.24, 12.39 ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for C₁cH₁₂ClN₃OS₂: 349.0110; found: 350.0174.

Procedure for the Synthesis of 5-thiocyanato-4-(*p*-tolyl)thiazol-2-amine (4f) (Scheme 4)

A dried round-bottomed flask was charged with NBS (177.98 mg, 1.0 mmol) and NH₄SCN (152.24 mg, 2.0 mmol). PEG-400 (3 mL) was added and reaction mixture was stirred at r.t. for 15 min. Formation of a milky color indicated the generation of NTS (shown by TLC). Then, 4-(p-tolyl)thiazol-2-amine (190.26 mg, 1 mmol) was added slowly, and the reaction mixture was further stirred for 3 h. When completion of the reaction was indicated by TLC, the product was separated by addition of cold water (20 mL). The white solid product was filtered, dried, and washed with cold aqueous ethanol (0.78 mmol, 78% yield).

Compound **4f**: Mp 134–136 °C. FT-IR: 3372, 3269, 3045, 2100, 1612 cm⁻¹. ¹H NMR (400 MHz, DMSO- d_6): δ = 7.88 (s, 2 H), 7.69–7.31 (m, 4 H), 2.52 (s, 3 H) ppm. ¹³C{¹H} NMR (100 MHZ, DMSO- d_6): δ = 171.25, 259.25, 139.14, 130.64, 129.39, 129.18, 129.01, 112.57, 21.39 ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for C₁₁H₉N₃S₂: 247.0238; found: 248.0305.

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POSTMODERNISM: A NEW CULTURAL PROCESS

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Abstract:

The paper scrutinizes postmodernism's new cultural process. The shift from modernity to postmodernity brought profound transition in our cultural life. Postmodernism plays crucial role in the process imbedded in the formation of our culture. In fact it is the ingredient of our contemporary culture. Postmodernism celebrates pluralism over centeredness of modern philosophy. Such celebration turns as postmodern hallmark of cultural expression beyond communal, racial, regional and national boundaries. It leads us towards a new culture belong to not any community, race, region, religion or country but universal mankind. The transition brought by postmodernism in art, architecture, fiction, theatre and philosophy is caused for the formation of new culture. In the world of art postmodern art made processed new culture on the basis of the rejection of stylistic integrity of modern art. It presented stylistic diversity. Following univalence impulse, it goes for impurity against purity of modern art. In architecture, postmodernists reject modern ideal of univalence and their views of architecture as visible expression of absolute unity of art, science and industry. Rather they celebrate multivalence and see architecture is inherently symbolic. The tactic of juxtaposing the real and the fictitious distinguishes postmodern fiction from modern. Postmodern authors juxtapose two autonomous worlds as the fictitious and the real world. The characters in the postmodern fiction face the close encounter of their world they belong to and always get confused on what world they are from. In theatrical expression of culture postmodernism replaced aesthetics of presence with aesthetics of absence.

Keywords: postmodernism, cultural process, philosophy, art, architecture, fiction, multivalence, univalence, modernism, stylistic diversity, juxtaposition, fictitious world, real world, realm of appearance, transience, performance, temporality, aesthetic of absence etc.

It is the transition what we see in today's art, architecture, fiction, theatre and philosophy as an interference of postmodernism on the basis of continuation, extension or rather departure from modernism. The transition is integral part of the culture beyond race, path, region, country, language, community of human belong to all the corners of the world. It is known as a New Culture, Anything Goes Culture, Techno-Culture, World Culture or Universal Human Culture. in fact it is a processed culture by the postmodernism known with all these diverse terms. Since it is difficult to define postmodernism, it is also difficult to measure and locate the consequences of postmodernism. Culture is one of them. Today's culture is the outcome of the process in the form of postmodernism. Postmodernism has been contributing in the process of the formation of this culture universal human live in today. It is been in effect since the rejection of enlightenment of modernism came in effect as a consequence of application of postmodernism in all those factors and fields related directly and indirectly to human culture. Culture is identical aspect of particular community, region, race or a country. When we think at universal level we come across various cultures belong to human communities based on region, race, language and country. So the diversity in the cultures is natural feature. In such diversified phenomenon postmodernism advocates a culture beyond the diversity in the cultures. It offers a culture beyond all the factors those are caused for the diversity of the cultures. It has leaded the world and worldly cultures towards universal globalized single culture based on

the multicultural coalition. The move from modernism to postmodernism is the pathway in all the fields and factors those are directly involved in the formation of human culture. As per the requirements and the limitation of this research article lets us observe some of the factors active in the postmodern process of culture play as ingredients: art, architecture, fiction, theatre and philosophy.

Art

In the world of art it is remarkable to know that stylistic integrity is the great virtue of modernist artists. The base to render their art is 'pure'. Purity is one of the characteristics of modernist art. Modernism follows the univalence impulse. In contrast postmodernist art highlights stylistic diversity. It follows multivalence. It prefers not purity of modernism rather it chooses impurity. It embraces diversification on the way of departure from modernism. It is the transition brought by postmodernism. It celebrates plurality rather singularity experienced in modernist art. Postmodern artist apply diversity with very remarkable postmodern technique of Juxtaposition. As we study one of the crucial elements of composition i.e. collage. It is also focused by Jacques Derrida as the prime from of postmodern discourse. It takes the viewer into the process of the production of its meaning. Collage ensures viewer that the meaning it elicits is neither univocal nor fixed or stable. In fact it is inherent heterogeneity of collage that ensures the aspect of meaning. It makes reader or viewer to run for new meaning in the juxtaposition of images. One of the features of postmodernism i.e. pastiche plays very crucial role in such juxtaposing activity. In fact it is necessary to see the statement made by Howard Fox:

"At root postmodern art is neither exclusionary nor reductive but synthetic, freely enlisting the full range of conditions, experiences, and knowledge beyond the object. Far from seeking a single and complete experience, the post-modern object strives toward an encyclopedic condition, allowing a myriad of access points, infinitude of interpretive responses." (H. F., 1987: 29-30)

It is crystal clear that the objective of postmodernism in application of such tactic is to bombard clashing meaning on the viewer to raise questions to lead plural sense of objective meaning. This tactic of postmodernism is being employed in both high and pop-culture context. MTV videos are the best examples of postmodern pastiche. On this attitude of postmodernists Stanley Grenz points out:

"The disjointed, unharmonious design of pastiche with its gaudy color schemes, discordant typography, and the like, has moved beyond the world of avant-garde art into the everyday realm of book jackets, magazine covers, and mass advertising." (G.S., 1996: 26)

Merely Grabbing attraction by applying stylistic diversity is not only the goal of postmodernist artists. They possess an attitude to generate a desire to challenge the established power of modernity available in institution and traditions all over the world. They grab each and every opportunity to challenge the modernist views and its focus on the stylistic integrity of modern artists, what they target as the modernist angle of the individual artist. They reject singularity of works of art through various ways they seek as confiscation, repetition of existed images, accumulation, excerption, quotation. Modern fiction that forms subject remains their target always to attack. The best example of such postmodern critique is the work of Sherrie Levine, a photographic artist. One of her exhibition she exhibited some photographic arts those were rephotographed of well-known artistic photographs of Edward Weston and Walker Evans as her own. Yes, it was an act of plagiarism. It was simply art piracy and it should be charged accordingly. But it was not her motto to fool the viewers by plagiarizing art and earning name out of it rather to catch attention towards the distinction between original arts and its reproduction.

Architecture

Architecture is one of the factors those contribute in the formation of a culture. Up to 1970 architecture was under dominance of modernism. The modernists, special western architects have developed their own style in architecture which is known as International Style. It expresses modern ethos

in architecture. It has initiated a movement in architecture that has faith in human rationality and nurtures the hope to construct a human utopia. The base of their architecture is the principle of unity to follow modern utopianism. According to Frank Lloyd Wright-

"a building should be 'one great thing' instead of a 'quarrelling collection' of many little things" (W.F. L., 1970: 25)

He highlights modern edifice as an organic entity. In fact his views are leading in the establishment process of modern ethos in architecture. Accordingly it was just a criterion that each construction should express one unified meaning to contribute contemporary culture. It was an attempt to generate meaning on the basis of the principle of unity in architecture. There onwards modernists bound to the principle of unity to produce prime architectural characteristic. This principle of unity is known as univalence after its justification given by Charles Jencks. Construction of glass-and- steel boxes became universal pattern of modern architecture. It was widely accepted and even celebrated as one of the essential aspects of enlightenment in modernism. The device of repetition of a theme to rule contemporary world of construction was widely utilized under the way of simplicity of form by architects. In his *A Primer on Postmodernism*, Stanley Grenz exposes this modern attitude and the consequences held in the arena of architecture since it is the ground where postmodernism marked its first footprint.

"As it developed, the central stream of modern architecture became a universalizing movement. It promoted the program of industrialization and demoted the variety characteristic of local expression. As a consequence, the expansion of modern architecture often destroyed the existing urban fabric. It virtually decimated everything that stood in the way of bulldozer, the chief tool of the modern quest for progress" (G. S., 1996: 22)

It was also served that some modern architects were not happy to limit and to subject to modern views and mold accordingly at their level of discipline. They follow their faith that architecture as a visible expression of a new unity of art, science and industry. Here it is necessary to consider the statement made by Walter Gropius as:

"Together let us desire, conceive, and create the new structure of the future, which will embrace architecture and sculpture and painting in one unity and which will one day rise toward heaven from the hands of a million workers like the crystal symbol of a new faith." (G. W., 1919: 25)

It is modern tendency in architecture gave birth to postmodern architecture as a response. Postmodernism replaced 'univalence' by its celebration of 'multivalence'. It goes against of modern views that construction of a building is for the reflection of a perfect unity. Rather postmodernists tried to explore and present incompatibilities of style, form and texture. There are several features of postmodern reaction that present the evident of the rejection of modern architecture. For example postmodern presents ornamentation instead of modernists' contempt of unessential superfluous. Postmodernist architects retain historical and traditional styles and techniques to eradicate modernist architects' rejection of traditionalist past by applying western design that was far from the relic of earlier eras. Postmodern goes on presenting every constructions and buildings including modern express a kind of language that signifies a culture. This angle of architecture which permits a structure to represent an imaginary world to convey a story was missed out by the modernist architects on their way of pure functionality. Postmodern points out that no any architectural wonders as The Taj Mahal, The Great Cathedrals those takes us in another realm of the world would have been possible in the attitude of modernists. Charles Moore rightly states as:

"A Building itself has the power, by having been built right or wrong or mute or noisy, to be what it wants to be, to say what it wants to say, which starts us looking at buildings for what they are saying rather than just accepting their pure existence in the Corbusian manner" (M.C., 1973: 243)

On the basis of repetition and a device what is called an addition of ornamentation post-moderns are trying restore and retain fictional element to architecture. Their pure motto is to reinstitute an attitude to create inventive places rather merely dealing with architecture that runs for pure utility. The claim and assertion of modernists to be universal and to go beyond history, past is challenged by postmodern architecture. Architecture as an articulation of a language of power is the modern view rather expression of reason or logic. According to Paolo Portoghesi

"Modern buildings derive their language from the industrial forms and materials of the modern era and the industrial system they served" (P.P., 1982:3)

It leads us towards a world based on science and technology, since it is a mere expression and exhibition of the experiments o the basis of science and technology. As R. Venturi rightly has rightly stated:

"Modern forms and materials give expression to the brave new world of science and technology" (V.R., 1977:135-36)

In short, we can see the postmodern wish to give up this language of power and explore new hybrid languages that incorporates the postmodern concepts of diversity and pluralism by moving away from dehumanizing uniformity of architecture that advocates a language of standardized mass production. **Fiction**

Fiction is a crucial element in the process of cultural formation of a society. In terms of postmodernism it is very difficult to trace out its influence on literature. Of course there is continuous debate of critics to draw a line between postmodern fiction and its predecessors. The tactic of juxtaposing is a general style of postmodern fiction. As we observe that some have juxtaposed traditional forms and modern one to trace out ironic treatment. And other postmodern authors have juxtaposed real and fictitious. The postmodern literary device of juxtaposition is applied for the characters also. As we read that some of the postmodern authors com narrators highlights on factiousness of the characters along with their actions and their participation in history simultaneously in order to gain moral and emotional response as traditional realistic fiction achieves. Juxtaposition of real and fictitious by interjecting authors is also successful feature of postmodern fiction in order to discuss narrative problems and processes. The simply objective behind is to blur the distinction between real and fictional. It also helps to point out connectivity between author and fictional work. In such treatment is given to the fictional work is as a medium through which author expresses herself or himself and it is also clear that expression of author or his voice is no more separable from fictitious work. It is always noticed as even Stanley Grenz says:

"Postmodern fiction repeatedly juxtaposes two or more pure, autonomous worlds. When this occurs, the characters that inhabit the literature are often confused as to which world they are in and uncertain about how they should act in this close encounter." (G. S., 1996: 29)

The purpose behind applying the tactic of juxtaposition in postmodern fiction is just anti- modernist. Modernist writers tend to handle complexity of meaning but stick to singular reality. Where else, postmodern writers make us to think about the coexistence of diverse realities and their interpenetration. Postmodern literature penetrates on contingency and temporality by rejecting modern views of universal truth. It raises its focus on temporality in order to stop reader to see the world from a vantage point out of the time. In this connection the remark of David lodge is necessary to consider

"And need one sat that the more nakedly the author appears to reveal himself in such texts, the more inescapable it becomes paradoxically, that the author as a voice is only a function of his own fiction, a rhetorical construct, not a privileged authority but an object of interpretation.?" (L. D., 1992:194-95)

We find that even postmodern authors gain kinds of effect of language that breaks closed thought and raise a question or challenges to those entire literary canons those who are not agree with that any discourse is potential to present an account of real.

Spy novel is one of the typical form in postmodern fiction. It juxtaposes two different worlds. Mostly, it is just a domain of appearance, which seems to reflect the real but it is a just an illusion. Working beneath and within such domain of appearance is another realm of appearance which is somewhat illegitimate but still it is authentic than real world. Juxtaposition of these two realms the story catches hold of reader in uncertainty continually. The operation within these two realms raises question such as is really any character appears to be? what is real and true?. such spy stories of postmodern make us to think that are we also living in between such two juxtaposed world?, the events and the people we come across in our life are truly one?

Comparatively science fiction is less postmodern type of fiction. No doubt it rejects modern quest, but it doesn't much interested to uncover timeless truth. It is effective in exploration of other relativities. It leads us towards other world or realities and brings the differences in our notice. It also presents some questions about our world. As: what is truth? What is the energy or force active at work? What are the possibilities in our life? And so on..

Theater

Theater is one more factor to contribute in the cultural process. It is quite active in postmodern scenario. It is very appropriate mode of postmodern expression of the rejection of modernism.

"The modernist movement saw a work of art as transcending time, as expressing timeless ideals. The postmodern ethos, in contrast, celebrates transience and transience is inherent in performance." (B.M., 1977:03)

Post-moderns see our life as transient performance on the stage of the world. Transience and performance are two features as cultural medium to represent real world. Despite of such representation it is not well to say that every theatrical production is an expression of postmodern ethos. According to Steven Connor

"Many scholars date postmodern theater to the upsurge of performance art during the 1960.

its roots lie further back, however, in the work of the French writer Antonin Artaud in the 1930s." (C.S., 1989:134)

In the writing of Antonin Artaud we find invocation for contemporary dramatist about to be protester. In fact he stimulated the entire contemporary dramatist and made them to destroy what he sees as idolatry classical art.

"He advocated replacing the traditional stage and the production of theatrical masterpieces with a 'theater of cruelty'. He called for the abandonment of the older script- centered style and an exploration of the language intrinsic to theater, which includes light, color, movement, gesture and space. He adds transcending the distinctions between actors and observers and draws the audience into the dramatic experience." (C.S., 1989:135)

Artaud dreamed the audience to confront the primal reality of life hidden behind social conventions. His dream came true in 1960s, when theorists went on rethinking on the nature of theatrical expression which was under the influence of the repressive power of traditional authorities they felt to eradicate such influence and make it free to perform. In his 'theater of Cruelty' he criticizes that the script or text itself is utilized to exercise repressive power. He also offers solution as the elimination of the script and treatment to each performance as immediate and unique. Once it is performed it has to disappear forever. Postmodern deals with the theory of performance which replaces 'aesthetics of presence' with 'aesthetic of absence'. It rejects the views that performance holds permanent truth. It only maintain the sense of presence as it evokes what is called an 'empty presence'

Philosophy

Philosophy contributes lot in the formation and in the act of nurturing culture. Postmodern advocates plurality, diversity since it holds the potentiality to hold double-coded meaning on various level of art or object. In postmodern culture Collage, is applied to bring together incompatible source of materials. Along with it another juxtaposing tactic is bricolage which is utilized to reconfigure traditional
objects in order to give ironical treatment through art. The eclecticism of in artists' work drawn from historical eras is prim reflection of postmodern art. Concerning diversity and plurality as key feature of postmodern philosophy are quit crucial to nurture multiple styles in culture. Charles Jencks point out that-

"Post-modernism is fundamentally the eclectic mixture of ay tradition with that of the immediate past; it is both the continuation of modernism and its transcendence. Its best works are characteristically doubly-coded and ironic, making a feature of the wide choice, conflict and discontinuity of traditions, because the heterogeneity most clearly captures our pluralism." (J.C., 1989:07)

It is clear that due to eclecticism in the philosophy, postmodernism celebrates multiculturalism and an 'Anything Goes' attitude or a key ingredient to nurture traditionalism caused for origin to overall human universal culture. It is full of acceptability and adoptability with diversification at all the factors involved in the cultural process. In this context it is accepted to define postmodernism as a cultural process. Since, it has offered a new culture with the feature of plurality against unified singularity of modernism. It replaces integrity of culture with diversity of culture. Original cultural essence is preserved with its quality of multivalence. Mixture, fusion and pastiche are the tools remarkable utilized in the postmodernism in the process of the formation reproduction and reconfiguration of universal culture. May it is with technology, science and all kinds of advancement of enlightenment postmodernism plays its apt role as cultural process beyond community, race, religion, language, region and countries. Its juxtaposition of styles and the emphasis of diversity along with deemphasis of rationality are visible hallmark in postmodern society embedded with contemporary cultural expression.

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63 IMAGES AND MYTHS IN TED HUGHES' RAIN, NOVEMBER AND THEOLOGY

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Abstract:

The present research paper deeply scrutinizes the select poems Rain and November to explore the use of nature and animal imagery in the poems. The poet succeeds in creating vivid picture of the nature by exhibiting exceptional mastery over the phraseology. Use of different literary devices enhances the quality of poem aesthetically. Apt imagery creates mental picture in readers mind. The present research paper also throws light on the use of different types of imagery that ultimately fulfills communicates sensory experiences in powerful way. It also focuses on the use of myths in the poems of Ted Hughes. The poem Theology clearly suggests the shift in attitude where poets are reconstructing old myths in a new way. Such kind of reconstruction is a significant feature of modern literature. Myths having atavistic potential appeals to the human psyche knowingly or unknowingly. The striking quality of Ted Hughes use of mythology is that he is not interpreting myth in a new way rather he is providing alternative version of myth to destabilize the perception which is common in society and theology.

Key Words: imagery, kinaesthetic, visual, olfactory, tactile, auditory, gustatory.

Ted Hughes poetic career started in 1957 with the publication of *The Hawk in the Rain.* The collection marked his rise on the horizons of international poetry. His later collection of poetry entitled as *Crow* (1970) gained much appreciation from the critics. The collection is highly significant for the poems oven around the Crow; a character created by Hughes derived from mythologies particularly taken from the insight from 'Tibetan theology'. The flight of poetic imagination allows Hughes to detect the life of birds and animals from inside which is the major subject of his poetry. Hughes' poetry is the mingling of myths and traditional stories from diverse culture with the careful observation of birds and animals life in their Natural Habitat with all its brutality and violence keeping all human emotion aside. Ted Hughes died on 28 October 1998. He held prestigious post of poet laureate since 1984. He served the *Muse* with several collections of poetry as well as translations but particularly his final collection *Birthday Letters* (1998) is considered as masterpiece in British poetry.

Ted Hughes poetry is also marked with war imagery. The scarcity of bread and butter in his childhood is replaced by the war stories and quenched his intellectual thirst and hunger. He breathed the air polluted by war stories mostly describing the violence, brutality and death. His animal poems are just a kind of projection of human feelings. Ted Hughes stands apart among modern British poets for unique presentation of animal world. His fluid imagination is at its best when he describes animals in their natural habitat. His graphic presentation of nature and animals provides a kind of cinematic visual treat with the help of apt imagery and symbolism. Hughes fascination regarding animals is an inseparable part of his personality. Hughes mind is occupied with animals and he explains his fascination with the words 'interest in animals began when I began'. For him there is no difference between capturing animals and writing poetry.

In a way, I suppose, I think of poems as a sort of animal. They have their own life, like animals, by which I mean that they seem quite separate from any person, even from their author, and nothing can be added to them and taken away without maiming and perhaps even killing them. And they have certain wisdom. They know something

POETRY IN POSTMODERNISM

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Abstract:

It is an attempt to locate the poetics of poetry in the scenario of postmodernism. Since poetry is somehow neglected genre in postmodernism it is breathing to retain in new form and its new thematic as well as semiotics. Even though postmodern poetry is the matter of argument concerning its productivity compare to classical poetry, it is on the move to get establishment as new avant-garde. No issue it faces the criticism as it is heightened form of modern poetry. The radical shift, language experiments and a step ahead of 'existentialism, 'absurdism' and 'ethical relativism', postmodern poetry framing new version of poetics compare to all earlier right from classical to modern. The concept of aesthetics is in dynamic splendid form since instability indeterminacy and cynical playfulness are key features of the postmodern poetry. Going beyond the existence of centre it has established order in disorder, coherency in incoherency and space for meaning in meaninglessness. Typical pluralistic features of postmodernism as polyphonic fragmentation in the poetry provide infinite potentiality in the interpretation causes uplift of the reader and readers' literary competency too. Clichéd style is seemed to be allergic instead it goes for never ending search for fresh semiotics. Along with all these postmodern poetry tried to prove that poet is always immortal along with its ART no matter what age he/she belongs to.

Key Words:

Freud's ID, postmodernism, poetry, polychromatic, polyphonic, postmodern poetics, premeditated meaning, fragmented descriptions, intermittent impulses, commoditization of art, indeterminacy, cynical playfulness, Language Movement

Poetry in postmodernism! An interjection at the beginning of this brief discourse on the genre of poetry in specially social and cultural context is a matter of thinking. At globe poetry is just poetry. It is an exploration of Freud's ID active in everyone. No matter what country you belong, what religion you follow, what colour you are in and what race you come from. Exploration of ID in spoken or written form in terms of disintegrated verse points out disintegration and fragmentation in forms of art in postmodernism. It is quite true that whatever changes takes place in other genres of literature and art reflects in the territory of poetry too. A

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home and at workplace and now in our hand provided through per day GB datas from telecoms in our mobiles. Advance technology and its applications supply miracle working pills, human clones, xdoll industry under the name of sexual independency, robotic lifestyle and eclectic patch work fashion culture lead human towards its exploration of dark wishes. Tantra mantra practices and aggrandizement of tilasmans on electronic media take us in non-existed world, Artificial intelligence and cybernetic competencies are controlling power of human society. The shift of power is taken place since; information is now in form of power. All the grand narratives of the patriarchal, heterosexist and capitalist society are being replaced by micro-narratives. So there is no chance to any grand narrative to console us over the loss of human values and the loss difference between good and bad. Information, as power pervades every aspect of human life leaving no scope for contemplation, individual ontological power. Our old self-satisfactory attitude has no escape from this postmodern scenario which has changed the nature of reality posing the basic question as is there any truth or reality? Poetry in this scenario resembles all the features of postmodernism in its character itself. The freedom of word, theme, issues and the tone presented through fragmented graphic manner became special medium of exploration of all hidden expression in human. The exposure through high-tech world is being exposed going beyond modernist perfection rather it prefer imperfection in meaning destroying all moral and ethics of poetics of poetry itself. Language is experimenting lab for poets in postmodernism. Disorder in structure in terms of syntax and even semantic is quite similar to the disorder in postmodern society and its system. Search of truth and reality is much similar to postmodern poetry's search of its own meaning and coherence which is fluctuating in nature as the nature of reality in human life. Here is an apt example of a poem in postmodernism.

They are clearly difficult

in every sense machined, metallic to the tongue the g listening eye dispersed throughout (the body of a poem) openly ly ing about itself the feel full of folk the truth

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stimulate poetry to come out into new form quite contrastive to the form of poetry of early time. Poetry occupies great space in postmodernism; since, postmodernism is not just living in concrete jungles surrounded by heavy industrialization under the name of development "it is our material and spiritual condition that is a consequence of the tension created by the incompatibility of our organic evolution with the sudden and overwhelming technological revolution that rendered all political and ideological frontiers meaningless. This condition of living does not comprise people's material possessions; it comprises their attitude and behavior determined by the material condition created by the forces of technology."(Shafi Shauq, 2008:44) The condition of human life is quite submissive to inescapable absurdities inherent in our materialistic fragmented world in search of premeditated meaning as it is tried by modernists. Now in postmodernism there is no way for lamenting the loss of values, for deep sadness and rejection, as it was faced by romantics with their allegiance to an utopian alternative; on the contrary it is better to focus individual's position amongst the givens that surround us. It is materialistic way of life in postmodernism may cause humanity and its values. In romanticism it was imaginative world in human warped and found it tiresome. It payed the way towards realistic way of the life. But the excessive utility and dependency on the world of high-tech may results in the same what faced by romantics with the world of imagination. We are living in high-tech materialistic digitalized world. Every one of us is under constant watch. Our every child is with android gadget, with internet excess in his /her hand and is constantly allured by child-devouring monster try to get in its clutch of radiation, long term harmful to human species. Grad narratives are replaced by mini narrative. Invisible tentacles in form of whatsapp, facebook, tweeter, instagram and online chat are now family member in everyone's home to destroy family communication under same roof which result in no sense of exit Societies and accordingly nations are under the clouds of destroying violence, unaccounted killings by automatic deadly weapons, grenade attacks, landmines, tyranny, torture, cyber bug, human body as experimenting lab, loss of faith in each other and solitary confinement in crowed. We are in our land waiting for good, seeking refuge from the clutch of digitization and commoditization at our every move in our own society. Uncertainty in terms of security of life today we are being made to believe extravaganza of the virtual world presented us as Hyperreality fabricated by screens of cell phone, Television, computer and the screen of Hollywood- Bollywood films, animated graphics, soap-operas, DVD libido, cyber-sex sites in

poet has to undergo the influence of his / her time and the political, cultural and over all social activities. No poet of today can find any originality unless he / she is representative in character of his / her time and all the critical notions he / she underlines for his / her every creative act. The notions of creativity available in form of postmodernism are discussed almost every platform of art as: fiction, drama, visual arts, architecture, music, and the poetics of all these arts; but postmodern poetics in poetry is still seen with distrust to support the perspective norms of poetry as absolute and there is no any requirement of change in it. The poetics of poetry up to 20^h century went on exist and it has to be in the scenario of death in theory, myth, history, author, criticism, ad text itself too. Poetry cannot be exceptional for it. Even though, poetry is continued to be written in massive scale. Now creative poets are coming out just after having adequate schooling and they try to catch publishers for their poetry. Cyber industry too works for poetry contents and there are coveted prizes. Numbers of magazines are purely devoted in the work of propagation of poetry. Today poetry which is in post-poetry era finds good spirit. Many of the poems of this period are found as good as the poems of the times when poetry was considered as life and when it is said that poetry is really lived. In fact, the span of poetry is increased. Its domain is widening day by day. It involves feminists, gays, ecologists, sociologists, lesbians, devoted mystics, human-rights activists, social reformists, anti-AIDS agitators, Dalits, subalterns and many more those who find poetry as medium to raise voice and to find propagation for their survive. Poetry in postmodernism became polyphonic. It does not discard the cannons of poetry but it goes on making addition in the list. In thematic terms poetry behaves with wide open nature. It has followed Anything Goes phenomenon of postmodernism. It is now polychromatic to encompass all neglected themes in the genre of poetry of early time. It sounds postmodern in nature and even in structure of its presentation. It is quite flexible to cover coveted issues in human so it's in true sense an exploration of Freud's ID. It is in postmodern in the manner of postmodern and in the sense of postmodern. Postmodernism itself characterized for its exploration of the world found in ID and subconscious domain of society and accordingly world. Plurality, flexibility, uncertainty, indetermination and fluctuating in its interpretation are now the base of poetry known as postmodern. The poetics of poetry in present time is broad enough to wrap all those stuff hidden in dark and in subconscious mind of human. It explores those were reluctant to explore in the time of poetry. In this point of view the poetry in postmodernism is new avant-garde was rare even in modernism. Yes it is to be proper to say that modernism

snared caught and taken in

(the body of falsehood) (the house of life) Jon Mack, from *Scientific Animals* (Jerome Mcgann, 1990: 06)

This is just one way of putting on paper there are many others. It is more narrative rather than language of poetry which is emerged in past twenty years with intellectual and stylistic focus of postmodern poetries. The present poem of Jon Mack is not the part of language movement, as it catches our attention on relation specially inorganic and nonlinear. The aim here is to give a more catholic view of the radical change which poetry has undergone since the Vietnam War. The poets emerged thereafter are being categorized as the L-A-N-G-U-A-G-E Poets. In fact, language has no key objective to seek center in literature, still it tried, rather to mark out a space in which it could work. It is necessary to see if we understand the silent features of postmodern poetries. The key feature here is the de-centering of the "I". The "I" is engulfed in the writing not as an authority but as a witness for and against. The styles of difficulty one can face in the work are also equally important. The footnotes may not help since the difficulties are simpler and more fundamental located at the primary level of grammatical (dis)orders. Here is one more example from Alan Davies' collection:

THE NEW SENTIENCE

You should enjoy your suffering. Realizations come in the form of words if not before. Arguments weaken the facts which in any event never mattered, or existed . You die as what you are. Write bread lines. You don't test the limits of what is by asking the impossible of it. Bunny haunches. And it should go on from there as if everything had happened. The culture made a decision. Mmmrnm. I am a mortal verb. I am asking you, quietly, for you. It's nice to see a face. Maybe something happens that mutes the speechless. There's no way to recall a clarity. Leached passions only overmake the heart. Don't go looking for it. The language. This sex could be our quiet lullaby.

All we ever do is fulfill our fantasies..... (ibid: 13)

It is at the technical level we find derangement of the sentences. In The New Sentence we do see another feature of postmodern poetries: their commitment to ideas and critical thinking as postmodern poetry cannot be separated from the philosophical, critical, and political prose with which they regularly orbit. Sometimes it is not possible to decide whether a particular work is "prose" or 'verse', 'criticism' or 'poetry', Davies himself is a distinctly philosophical poet, exhibiting his own special intellectual commitment. "Postmodern poets are seem to be difficult, 'They are clearly difficult' because they put a high premium on clarity of mind and vision. Such clarity is not easy to achieve, particularly in our time, when the media of human intercourse is a feeding trough of propaganda and feeling and soap. 'They are clearly difficult' because their work demands attention, attentiveness. And they are postmodern because the light they cast falls equally upon the just and the unjust, the trivial and the consequential."(ibid: 8) It is being constant attempt of the world to distinguish such things, but the distinction always results I the humanness of the lucid consciousness. The output is not just illusion of Disney land, a common subject in postmodernism, but the views from those places, the political judgment and the way we live in the world now. Postmodern poetry took us out of fantasy what romantics called 'imagination' and projected the realistic philosophy and the way of human life. Along with all these the world of uncertainty, indeterminacy, pluralistic and mixture of deconstructive culture

home and at workplace and now in our hand provided through per day GB datas from telecoms in our mobiles. Advance technology and its applications supply miracle working pills, human clones, xdoll industry under the name of sexual independency, robotic lifestyle and eclectic patch work fashion culture lead human towards its exploration of dark wishes. Tantra mantra practices and aggrandizement of tilasmans on electronic media take us in non-existed world. Artificial intelligence and cybernetic competencies are controlling power of human society. The shift of power is taken place since; information is now in form of power. All the grand narratives of the patriarchal, heterosexist and capitalist society are being replaced by micro-narratives. So there is no chance to any grand narrative to console us over the loss of human values and the loss difference between good and bad. Information, as power pervades every aspect of human life leaving no scope for contemplation, individual ontological power. Our old self-satisfactory attitude has no escape from this postmodern scenario which has changed the nature of reality posing the basic question as is there any truth or reality? Poetry in this scenario resembles all the features of postmodernism in its character itself. The freedom of word, theme, issues and the tone presented through fragmented graphic manner became special medium of exploration of all hidden expression in human. The exposure through high-tech world is being exposed going beyond modernist perfection rather it prefer imperfection in meaning destroying all moral and ethics of poetics of poetry itself. Language is experimenting lab for poets in postmodernism, Disorder in structure in terms of syntax and even semantic is quite similar to the disorder in postmodern society and its system. Search of truth and reality is much similar to postmodern poetry's search of its own meaning and coherence which is fluctuating in nature as the nature of reality in human life. Here is an apt example of a poem in postmodernism.

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we are landed in. Stability has departed for self-conscious skepticism and indeterminacy. "Postmodern writer is surface-bound and receives absurdity and meaninglessness with cynical playfulness and farcical unconcern. Grand narratives, as Lyotard tells us, are suspect and illusory because they undermine a pluralist view. 'The cultural logic of the late capitalism' has ramified in many directions one of which is the explosion of information which like an irresistible deluge has swept away stability eroded the basic infrastructure of many a concept. As Baudrillard argues in his book, *Simulations* (1983) the onslaught of the media has led to the 'loss of the real' as the distinction between the real and the imaginary stands totally blurred."(G. R. Malik, 2008:03) The poets in postmodernism regularly seek to foreground their artifices in order to dispel that aura of genius and consequence for which poetry too often has sold itself on those market where no one to buy. It seems a hub of anarchy postmodernist landed in. W. B. Yeats might have predicted this:

"Turning and turning in the widening gyre

The falcon cannot hear the falconer;

Things fall apart; the centre cannot hold;

Mere anarchy is loosed upon the world."

(W. B. Yeats 1933:210)

Absurdist criticism is the alternative for postmodern critical method. In fact postmodern critical method is a step ahead of absurdity which at least attempts to get meaning in meaninglessness. It is mere wilderness provide us no criterion to judge and evaluate literature. The poetry in postmodernism is just self-legitimating which requires no metanarative to subsist on and is non-utilitarian; it is purposed only to be. It seems that postmodern literature especially poetry endeavors to mark the distinction between the universal and the timeless literature on one hand and to trash on the other hand, E. M. Foster's nihilistic way of thinking exhibited in Marabar Caves in A Passage to India aptly describes poetry in postmodern even it was written before:

Whatever is said, the same monotonous noise replies, and quivers up and down the walls until it are absorbed into the roof. 'Boum' is the sound as far as the human alphabet can express it, or 'bou-oum' or 'ou-boum'- utterly dull. Hope, politeness,

the blowing of a nose, the squeak of a boot, all produce 'boum'. (Foster 1936:145) In case of search of meaning if we compare postmodern poetry with modern poetry we find modern poetry forced language to meaning erected scaffolding of legend and through illusion

available in every poetry with arbitrary meaning. While postmodern poetry enjoyed freedom for words from the author's intended meanings ad in terms of metaphoric expression it is dominating since its effect in world literature. The purpose of postmodern poetry seems an approximation to on-verbal communication by letting words free from the tyranny of the text and conversing through incoherent images likely in unlimited in numbers and in forms. It is mere urge of postmodern poets to liberate poetry from domineering principles and forms of time and set free the inherent generative and creative powers of language so that the poems, to be just expression free from imposed phonic and visual beauty. Every bits of involved milieu have to assume significance by human virtue of the immediacy of perception. The world of literature expects poets as free from the imposed mystic poses; the poetry has to size hard realities with an equal stark verbal medium by shaking off all sophistication to be ready to accept life in its ugly as well as beautiful rainbow. Postmodern poetry attempts to meet the expectation going away from tradition established by the poetics since ages. The polyphonic expression in the poetry for the reflection its intensity is its key aspects. The poetry has replaced linear narrative and the logical sequence by its fragmented descriptions and intermittent impulses. In the process of composition it is completely free from all aspects of poetics followed up to modernism. This manner as Robert Lowell calls it 'breakthrough' as it is freed expression from the tyranny of rules and regulation so called customs of rhetoric. In historical and social point of view postmodern poetry aims to show certain features of the contemporary avant-garde as we observe in for example, Bernstein's two sets of 'Language Writing' selections in Paris Review, 1983, and in boundary 2, 1984; or in Douglas Messerli's Language Poetries, An Anthology (1987). But still this poetry does not present any sense of how postmodern writing distinctively entered into new generation. The Language Movement well tried to create new compartment for postmodern poetry. The movement began (in the early 70s) as a relatively unnoticed event in the larger postmodern scene - at once localized (even atomized), and scarcely visible beyond itself; and it remained at the periphery of the larger scene throughout its years of development in the 70s and 80s. Only now can we see the comprehensive understanding which this movement acquired, both practically and theoretically, of the larger poetical field in which it had emerged, and where it has always occupied only one relatively small area. Moreover the poetry those were associated with the Movement was always imagined as an event of the USA as the association wasn't fruitful. In The Yellow Book Havelock Ellis wrote an essay in 1889 to describe the style of contemporary poetry

as he points out that contemporary poetry as "one in which the unity of the book is decomposed to give place to the independence of the page, in which the page is decomposed to give place to the independence of the phrase, and the phrase to give place to the independence of the word." (Jerome Mcgann, 1990: 10) Postmodern poetry is influenced by the factors wrapped Western history mostly after II World War. It is characterized by anxiety, helplessness, irrationalism and deconstruction. On the basis of these only Arnold Toynbee in 1947 used the term postmodern for the first time to denote final phase of Western History. Denial of centre, non-coherency are prime move as we notice in the postmodern poetry, which pave the way to raise some question as : if centre and essence are refused only chaos and confusion you are left with- chaos that cannot produce a cosmos which is order. So the disorder and panic are there in postmodern scene. As it is described by Croker and Cook "panic book, panic sex, panic art, panic ideology, panic bodies, panic noise, and panic theory."(Ahmed 1993:10)

There is radical shift observed in the poetry. In spite of all these postmodern poetry is not much different from old and modern poetry. Even it is not accused as non-sense or non-poetry. Many treat it as an extension to modern poetry. In fact it tries to assume itself what modern poetry dreamed to be. At initial stage the poetry is viewed as heightened form of the modern poetry on the basis of its denial of the essence, the center, absence of meaning and relativism as all these ingredients with the terms as 'existentialism, 'absurdism' and 'ethical relativism' were there in modern poetry too. Poetry is always determined by the ethos and philosophical of its age. But the postmodern poetry cannot be bound to its period and the condition of human in the common trouble. Clichéd style is seemed to be allergic instead it goes for never ending search for fresh semiotics as we observe in one of the best postmodern poems, Semiotics (1948) of Pamela Alexander. Individual reader and his/her likes, dislikes, beliefs, education, attitude and most important is life style all are in the consideration of postmodern poetry. It tries to uplift literary competency of today's common person. It is true that without the myth and classical literature it is difficult to retain for the today's poetry. No doubt it is in form and thematic concern it may be far from tradition of classical poetics but it produces famous names as it does not tend to gain name out of the work of poetry. The work of poetry and composing poetry has to be a matter pleasure but the commoditization of art may lead towards morbid and may cause a disease. Poet is always immortal along with its ART no matter what age he/she belongs to,

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Transformation of Subaltern, Marginalized and Dalit in the Postmodern Scenario

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Abstract

The research endeavors to present the defining criteria of Subaltern, Marginalized and Dalit. Itattempts to record the studies subaltern along with defining postmodernism and its exposition to subalterns, marginalized and dalits. The concepts of subaltern, marginalized and dalit are based on social status caste colour rank and numbers as it was the result of grand narrative of socialization since ancient time. It is the postmodernism which has destroyed the boundaries by freely choose culture and Anything Goes lifestyle. The postmodern techno - culture, digitization, mechanized employment, the change of knowledge sources have brought radical transformation. The process of transformation of subaltern marginalized and dalits is coexisted easily in terms of money and buying power. the power of travel and the ability of freely choose culture. Money and buying power is the defining base for subalterns, marginalized and dalits rather than caste region colour and numbers. The distance between center and margin is vanished due to postmodern patchwork of fashion and freely choose lifestyle from around the world. Simultaneously another kinds of postmodernism is coexisted to locate subaltern, marginalized and dalits in terms of economical and political social status. The deprived, oppressed, asylum seekers, unemployed and all those excluding wealthy elitists are labeled as subaltern, marginalized and dalits in the postmodern scenario. The communal culture, traditions are continually crushed on the platform of multi-culture and plurality of postmodernism.

Keywords:

Subalterns, marginalized and dalits who have been omitted from the human discourses within western intellectual life are now established as groups who deserve some kinds of historical and philosophical attention. This transformation is held in postmodernism. Socially politically and economically outcast stood polar opposites (wealthy, white). History as a power game is mere facts constructed by the dominant to keep out marginalized. The transformation dare to rewrite the history and the subalterns, marginalized and dalits are being engaged. As they realized that it's not the time to keep quite but to fight, write / right back to get into the main flow of society. Since postmodern pined up them by vanishing social communal boundaries in freely choose culture. "Postmodernism is marked by the emergence of the post-industrial information economy, replacing the previous classes of aristocracy, middle-class and working class with the information elite, middle-class and underclass.It also implies a nation-state challenged by new worldviews, feminism, multiculturalism and environmentalism. It is anti-capitalist, rejects orthodox morality and is committed to pluralism. The transforming process offered by postmodernism to subalterns, marginalized and dalits advocates that just not to be rag pickers to catch whatever is thrown in the dustbin of the west but to march towards new identity by creating their own plural, refashioned Eastern postmodernism. It is the result in contemporary time we find American universities offer new disciplines like women studies, black studies, subaltern studies dalit studies etc. to be aware with working understanding of reality of human life and value the personal narrative in the world. In postmodernism the transformational politics is the key to change empower the subaltern groups in Indian societies and also worldwide. Michel Foucault rightly points out that:

"Truth is a thing of this world: it is produced only by virtue of multiple forms of constraints. And it induces regular effects of power. Each society has its regime of truth, its "general politics" of truth that is the type of discourse which it accepts."(Foucault, 1980, P. 31)

It's the essence filled in the transformation of subaltern, marginalized and dalits and some other subaltern groups by the postmodern scenario. The process itself produced coexisted postmodernism which has given transformed identity of subaltern, marginalized and dalits leading beyond social, political, cultural and national boundaries. from macrostructures such as economy towards daily life, ideology, social interaction and culture. Foucault presents his views about the state power:

"It is always aggressive and his identification of resistance with the marginalized and suppressed made sense at a time when radical struggles were being led by groups peripheral o mainstream culture and power relations, such as, disaffected youth, women, blacks, dalits and other subaltern groups, gays and lesbians" (A. H. Tak, 2008, p. 55)

Postmodern knowledge theories ensured that the contradictory worldviews are equivalent. All knowledge systems are mare arbitrary and none of them is objective. Due to postmodern scenario all knowledge systems are mixed in one another under interdisciplinary approaches of studies. They all are mixed in one another and produced 'hybridism' across traditions and cultures. English language got mixed with Hindi and turned as Hinglish. For example, *chicken tikka*. Cultural mixer observed with sari and gown, white women wear nosepins as Indian women do. National culture turned as global culture and presented mis-mash of hybridity. Meera Nanda in her *postmodernism*, *Hindu nationalism and vedic science*argues as:

"The reinterpretation of "Western" science to fit into the tradition-sanctioned, local knowledge of "the people" has been advocated by theories of "critical traditionalism" propounded by AshisNandy and Bikhu Parekh in India and the numerous admirers of HomiBhabha's obscure writing on "hybridity" abroad (Nanda 2004, p. 30)

In his book madness and civilization Michel Foucault clears that the process of great confinement has created 'bourgeois civilization' in opposition of to 'madness'. He points out that by locking up the unemployed, the poor, and the criminals in workhouses, asylums, charitable institutions, prisons the individual freedom is suppressed by a morally authoritarian 'work ethic', which enforced on the west. The subalterns, dalits are swarming in the bourgeois work ethic of utilitarianism and are being rich and making their societies poor. "The human subject has been colonized by a wholly libidinalized capitalist economy which keeps us in pursuit of the latest commodity" (Kantaria, 1997)

Postmodern scenario presented new platform for disposed and subaltern groups. It has shifted the focus on marginalized, dalits and oppressed groups those are thrown out away from main stream of human society and dominated politically and economically since centuries. "In contrast to the international travelers, the world is also filled with refugees and asylum seekers striving to cross the more and more tightly patrolled borders of the richer nations as they struggled from poverty, danger and oppression of their homelands to those countries that seem to hold out the promise of freedom and prosperity." (Malpas, 2005 p. 3)

It is cleared that the lifestyles and consumer choice of postmodernism has produced another kinds of postmodernism which is featured with deregulation, dispersal and disruption. It causes the crush of tradition, civilization and communal essence continually. The refugees and asylum seekers, oppressed those are striving to cross tight borders are counted as subaltern, marginalized and dalit to distinguish them from wealthy and elitists. The stability of postmodernism is danger since there is a conflict between two contemporary extremes. The exploration of contemporary situation to gain the opportunities and their challenges offered by the conflict of postmodernism while transforming identity of subaltern, marginalized and dalit is being grate task in front of postmodern thinker or artist. Since postmodernism explores the fragmentation and undermines the rigid boundaries between the center and the margin. Postmodernism made us to believe that there is no fixed reality we mould the reality as per our cultural purpose, interest and traditional needs. In Indian context, we observe that the reality concerned the division of region into two nations to maintain peace in the region which is prescribed by the western colonizers is being continually believed even after seventy years after independence. It is postmodernism to make us realize that reality is the part of culture. In the course of time it gets changed as culture gets changed and it varies community to community. In postmodern scenario multiculturalism or pluralism ensured mix culture as a way life in terms of fashioning dimension in western continents. "Multiculturalism calls attention to the experiences of marginalized groups whose stories were unheard. Postmodernism has allowed subaltern societies to argue that white male culture has achieved domination over other cultures through values such as rationality, humanism and universality- values those multiculturalists claimare not objective but only tools for oppressing other people by making them face their own inferiority." (A. H. Tak, 2008, p. 54)

Postmodernism deals with the question of universal which known as unified self. Due to multiculturalism and fragmented way of life the self is strongly influenced freely choose culture. Michel Foucault justified it on the basis of theory by shifting the focus of radical analysis away

Postmodernism has been transforming the world in bothners. It vanishes the boundaries between centers and margin and simultaneously it strengthens the borders between rich and poor. In terms of privileges and money poor and deprived are being marginalized and dalits. Those are under privileged in terms of facilities and buying power is now defined as subalterns, marginalized and dalits. In Indian wealthy and western elitists those are having money and buying power traveling around the world and are being beneficial the essence of Anything Goes of postmodernism. So the contemporary culture is rested on money and buying power. It became base and criteria to enter in the Anything Goes postmodern world. Hence borderless postmodern world is open only wealthy and elite from all corner of the world, rest of all are subalterns, marginalized and dalits. They are thrown away from the center of postmodern world. They are deprived from the power to travel, ability to consume and freely choose their lifestyle. The essence of postmodernism has changed defining base of subalterns, marginalized and dalits. It cleared that the dispossessed people from around the world for which the globalization seems a loss of security and self - determination rather than an expansion of opportunity. Such dispossessed are now dalit and marginalized. On the basis of money power the customized employment turned techno employment and information and skill turned as knowledge. Customized employment became mechanized and techno-digitalized employment, which resulted in the lost of skill based, manual, employment right from the raise of modernism and continued up to contemporary time. Simon Malpas argues for the mater as:

"In the West, many customary form of employment have vanished as companies move abroad to areas where labour is less expensive or less regulated, often leaving behind them communities bereft of occupation, wealth and self-worth. In the developing world local resources have been bought up by international corporations and whole peoples have become subject to the violent fluctuations of world markets without the safeguard of western systems of welfare support that might protect them from destitution or even starvation during an economic downturn" (Malpas, 2005 p. 3)

The groups are borne by the techno - culture and buying power are in category of subaltern and marginalized. The consumer lifestyles of the wealthy are quite more than fantasies or hopeless aspirations. Simon Malpas continues:

Postmodernism, subaltern, marginalized, dalit, elitists, asylum seekers, center, transformation boundaries, multi-culture, Anything Goes way of life, freely choose culture Full paper

The term postmodernism refers to the phenomenon in literature, philosophy, architecture, culture, art, eclectic lifestyle and anything goes culture. It also points towards the coexisted postmodernism which is simply rest on the money and buying power. This coexisted postmodernism is concerned to the transformation the concepts of subaltern, marginalized and dalits. In early time there was limited response to the studies of subaltern, marginalized and dalit in the academic world. Since 1988 it entered into global academic it was accepted in worldwide. Specially, in U. S. A. it is highlighted by Edward Said. Gavatri Chakravarty Spivak initiated it in the academic with her publication Selected Subaltern Studies which was edited by Ranajit Guhu and Spivak, with a foreword by Edward Said. In her project with the touch of some original criticism Gavatri Spivak raised the question: 'Can Subaltern Speak?' and she argues that 'if the subaltern can speak, then he is no longer subaltern. The fact is that every time he protests, he fails - that is the inevitable mark of his subalternity.' (Spivak, p. 289-291) Ranjit Guha, Edward Said and Spivak tried to rescue the subaltern from the assault of foreign elites (theoretical implication of imperialism), the native elites (nationalism) and economistic (Marxism). Postmodernism through genealogy of Foucault, Deconstruction of Derrida and Marxism suggested by Lyotard gave new phase to the studies of subaltern, marginalized and dalit. The transformation of subaltern into new identity is on the ground of economy. Culture and lifestyle are the defining factors for the identity of subaltern, marginalized and dalit.

Contemporary world's culture is assisted by technology so it is known as techno culture which does not belong to any particular community or nation. It is being moved on in its incomprehensible growth on the basis of scientific development. As it is the part of commodity it has created commoditized culture. Western technology and fashion presented multiple opportunities and lifestyles open to the people of every corner of the world. In postmodern world every person becomes internationalized consumer. The borders those distinguishes civilization, tradition, communities and social interactions fluid. The way of life, social conversation, mass communications are just matter of choice. Cultural implications, communal customs have been transformed or even annihilated as boundaries. The patchwork of eclectically collected images and signs can produce our identity. The world is at our fingertips. We can buy any kinds of lifestyle from anywhere we please. The applications of television, mobile, internet, social sits, Facebook, twitter, blogs and whatsapp presented shrinking world in terms of space and time. It resulted in 'always in touch' culture for mobile users; the flow of stories from every corner of the world is at click of remote instantly of television viewers; the information in varieties from any corner of the world is at the press of keys of internet surfers. We have been habitual of international multimedia and we have interdependent world market. We are in globalised techno cultured lifestyle. As Jean-Francois Lyotard, French postmodern theorist says that we are living in the world where

"Eclecticism is the degree zero of contemporary general culture: you listen to reggae; you watch a western; you eat McDonald's at midday and local cuisine at night; you wear Paris perfume in Tokyo and dress retro in Hong Kong; knowledge is the stuff of TV game show.... Together, artist, gallery owner, critic, and public indulge one another in the Anything Goes- it is time to relax." (Lyotard, 1992, p. 8)

Postmodernism believes the idea of anything goes since; there is no absolute fixed lifestyle no fixed truth, no particular way of thinking the knowledge is with interdependent perspective. The communal boundaries are just subject to countries and regions but in terms of social, cultural, political economical and educational perspective they are almost destroyed. The distance between center and margin is vanished. Subalterns marginalized and dalits are now fragmented parts of grand narratives of world literature. The phenomenon of postmodernism has transformed the scenario of subalterns marginalized and dalitswith anything goes lifestyle and freely choose culture. Postmodernism offered the liberty to everyone from all the corners of the world to choose and mix the ideas, fashions and way of life from around the world as it is the essence of postmodernism. It made us relax to enjoy the fulfillment of rare wish in the multicultural postmodern world. It is the one side effect of postmodernism since it presents another side of it which is coexisted reluctantly and functions as overturned unseen process that transformed the images of subalterns, marginalized and dalits in terms of money and buying power ofelitists. Lyotard states that:

"This realism of Anything Goes is the realism of money....This realism accommodates every tendency just as capitalism accommodates every 'need' – as long as these tendencies and needs have buying power." (Lyotard, 1992 p. 8)



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हिंदी उपन्यासों में किन्नर विमर्श

प्रा.डॉ. दिलीप कोंडीबा कसबे हिंदी विभाग, विज्ञान महाविद्यालय, सांगोला.

प्रस्तावना :-

यह एक यथार्थ है कि किन्नर विमर्श विचार - विमर्श है, संवेदना का विमर्श है, अपमानित,उपेक्षित, वंचित एवं शोषित किन्नर का जीवन्त एवं कारुणिक दस्तावेज है। किन्नर आर्थिक, सामाजिक दृष्टि से शोषित रहे है। वे या तो निरक्षर होते है या केवल साक्षर, अल्पशिक्षित। अतएव नौकरी न होने के कारण, उन्हें कोई काम न देने के कारण वे आर्थिक अभाव में रहते है | उनके लिए शिक्षा, चिकित्सा की कोई सुविधाएँ उपलब्ध नहीं होती । ऐसी स्थिति में सार्वजनिक स्थलों, बसों, ट्रेन, स्टेशन पर तालियाँ बजाकर भीख माँगना ही विकल्प शोष रहता है। किसी के यहाँ बच्चे का जन्म हुआ हो, विवाह आदि अवसर हो, ये नेग माँगने जाते है । परंतु नगर - महानगरों में सुरक्षा से घिरे फ्लेटों में एवं शादी के मण्डपों आदि में



सुरक्षा कर्मचारी इन्हें घुसने ही नहीं देते। सार्वजनिक स्थानों में इन्हें हिकारत से देखा जाता है | विषम आर्थिक स्थिति के कारण भूख शमन हेतु ये सेक्स वर्कर बन जाते है।

• हिंदी उपन्यासों में किन्नर विमर्श :

२१ वी शताब्दी में किन्नर समाज के लिए कई संभावनाएँ दृष्टिगत होने लगी | साहित्य की सबसे लोकप्रिय विधा उपन्यासों में किन्नर विमर्श पर विचार किया गया | इसी दृष्टि से प्रमुख उपन्यास है - यमदीप, मैं भी औरत हूँ, किन्नर तथा - तिसरी ताली - गुलाम मंडी, पोस्ट बॉक्स नं. २०३-नाला सोपारा, मैं पायल, जिंदगी ५०-५० |

१) यमदीप :

नीरजा माधव का उपन्यास 'यमदीप' का शीर्षक प्रतिकात्मक है | यमदीप को दीपावली की पूर्व संध्या को घर के बाहर घूरे पर जलाया जाता है | इसलिए वह उपेक्षितही रहता है | यह उपन्यास किन्नर जीवन का यथार्थ आख्यान है, कथा में रंजन नहीं व्यथा है | लेखिका ने यहाँ उनकी पुत्री के जन्म पर बाधावा गाने एवं नेग लेने आये किन्नरों को देखकर उनके संवेदनशील मन में इनके जीवन को लेकर कई प्रश्न उपस्थित हुए | नागफनी के कॅटीले- से ये प्रश्नन मन- मस्तिष्क को चुभते रहे, सालते रहे और उन्हीं के उत्तर के रु प में उपन्यास का सजन हआ है |

यमदीप अभिशप्त होता है जैसा कि किन्नरों का जीवन भी अभिशाप होता है | लेखिका का के अनुसार पूरक है, एक दूसरे के अर्धांश है | यही स्त्री- पुरु ष मानवर्निर्मिती के कारण है | परंतु जहाँ स्त्री एवं पुरु ष दोनों के अतिरिक्त तीसरा लिंग उत्पन्न हो वहाँ यमदीप जैसी कृतियाँ सृजित होती है | उपन्यास का प्रारंभ ही किन्नरों के संवेदनशील एवं मानवतावादी गुणों से होता है | एक पागल स्त्री प्रसव वेदना से तडपती हुई एक बच्ची को जन्म देकर मर जाती है | तब शिष्ट समाज केवल दर्शक बनता है | तब किन्नर नाजबीबी का समाज पर व्यंग्य प्रहार अत्यंत तीक्ष्ण है | "अब कोई पूछनहार नहीं इसका तो क्या हम भी छोड जायेंगे ?अरे ! हम हिंजडे है, हिंजडे, इनसान है क्या जो मुँह फेर ले |"



DABCO entrapped in agar-agar : A heterogeneous gelly catalyst for multi-component synthesis of 2-Amino-4*H*-Chromenes

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ABSTRACT

An efficient method for the multi-component synthesis of 2-amino-4H-chromenesby reaction of malanonitrile with various aldehydes and phenols in the presence of gel entrapped DABCO as catalyst is reported. **Keywords :** Multi-component reactions, Gel Entrapped Base Catalysts, Recyclability.

I. INTRODUCTION

The rapid assembly of molecular diversity utilizing multi-component reactions (MCRs) has received a great deal of attention, most notably for the speedy synthesis of novel molecular libraries¹. These methodologies are of particularly great utility when they lead to the formation of privileged medicinal and industrial scaffolds. 2-Amino-4*H*-chromene scaffolds are of significant medical relevance since theyhave widespread applications includingantiviral², antimicrobial³, antiproliferative⁴, mutagenicity⁵, antitumor⁶, sex pheromone⁷ and central nervoussystem activity⁸.Looking at their importance from pharmacological and industrial point of view, several methods for the multi-component synthesis of2-amino-4*H*-chromeneshave been reported. These method include both homogeneous as well as heterogeneous conditions, catalyzed by piperidine⁹, aqueous K₂CO₃¹⁰, triethyl amine¹¹, basic ionic liquid¹², CATBr¹³, ammonium salt¹⁴, NaOH¹⁵, I₂/K₂CO₃¹⁶, TiCl⁴¹⁷, InCl³¹⁸ and heteropolyacid¹⁹ have been also employed. Although the literature on synthesis of2-amino-4*H*-chromene enjoys a rich array of versatile methodologies, new efficient approaches can be valuable additions to the contemporary arsenal of synthetic strategies.

The concept of gel entrapped base catalysts (GEBCs) combines the advantages of alkali and organic bases with those of heterogeneous supports²⁰. These catalysts are prepared by immobilization of alkali or organic bases by entrapping them in an aqueous gel matrix of agar-agar which is a polymer composed of repeating agarobiose units alternating between 3-linked β -D-galactopyranosyl (G) and 4-linked 3, 6-anhydro- α -L-galactopyranosyl (LA) units (Fig.1). This method reduces the amount of bases used and affords easy and efficient separation of products from the catalyst. Besides this, bases like alkalis when exposed to air, absorb moisture and are spoiled. On the contrary, the GEBCs do not absorb moisture on exposure to air and remain intact. The use of GEBCs in organic synthesis also provides excellent opportunity of recyclability and reusability which is seldom possible using bases alone as catalysts. However, despite their well recognized advantages, there have been only limited and sporadic

reports dealing with use of GEBCs in synthetic chemistry^{21, 22.} The interesting properties of GEBCs spurred us to tap their barely exploited potential in organic synthesis.

In our continued interest in the applications of novel catalysts in organic synthesis²³, we report herein the synthesis of 2-amino-4*H*chromenes of phenols, aldehydes and malanonitrile in the presence of gel entrapped DABCO as a catalyst.

Results and Discussion

Initially, we focused our attention towards the synthesis of gel entrapped DABCO. A series of experiments were under taken in which different concentrations of DABCO (5-25 %) were dissolved in a varying amount of agaragar in water. After a considerable experimentation, we found that 20 % w/w of agar-agar aqua gel containing 10 % DABCO resulted in the formation of soft gel that served as GEBC in the present work.gel entrapped DABCOwas white jelly like substance that could be cut into pieces. The changes in of physical nature of gel entrapped DABCO was studied in various solvents. The gel remained intact in ethanol, methanol, acetone, dichloromethane, toluene, 2-propanol and water.

Thermal behaviour of gel entrapped DABCO was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (**Fig. 2**). The TGA/DSC curverevealed that the loss of water occurs initially upto \sim 150 °Cand is accompanied with endothermic peak in DSC curve. The thermal decomposition of DABCO embedded polymer matrix occurs in two distinct steps giving approximately weight loss 11 % in each step. It is also revealed from the DSC curve that these processes are exothermic. The decomposition iscompleted at the temperature 510 °C.

Our next task was to demonstrate the catalytic activity of gel entrapped DABCO in thesynthesis of 2-amino-4Hchromenes (Scheme 1). As a trial case, equimolar mixture of phenol, benzaldehyde and malanonitrile (5 mmol each) was stirred in the presence of 1 gm of various GEBCs in ethanol at ambient temperature till the completion of reaction as monitored by thin layer chromatography. The reaction proceeded efficiently yielding the corresponding of 2-amino-4H-chromene 10 minutes. In order to check the generality of this methodology, a series of2-amino-4*H*-chromeneswere prepared by reaction of malanonitrile with various phenols and aryl aldehydes. The results are summarized in (Table 1). With both electron-poor and electron-rich benzaldehydes, the corresponding products were obtained in good to excellent yields. The reaction of the sterically hindered 2substitued benzaldehydes even gave higher yields highlightening the general applicability of the protocol. Further, we have also studied the reaction in absence of catalyst. It is worthy of note that in blank experiment no reaction was observed under similar conditions in the absence of gel entrapped DABCO. The striking feature of all the reactions was the isolation of products. It was interesting to observe that after specified time, the product precipitates out of the reaction mixture that can be isolated simply by filtration. The product obtained after sufficient washing with water was found to be practically pure. The identity of all the compounds was ascertained on the basis of IR, ¹H NMR, ¹³C NMR and mass spectroscopy data. The physical and spectroscopic data are in harmony with the proposed structures.

In the GEBCs, the reagent entrapped in the gel may leach into the solvent. To study the leaching of DABCO in solvent, 1 gm gel entrapped DABCOwas stirred in 5 mL of ethanol at room temperature. The catalyst was filtered and water (3 mL) was added to the filtrate. The DABCO leached out was then determined by titrating against 0.1 N hydrochloric acid solution using methyl red as an indicator. It was observed that only 5 % DABCO leached out

from gel into ethanol. Using the amount of DABCO same as that leached out, the reaction between phenol, benzaldehyde and malanonitrile did not gave quantitative yield of the corresponding product. This clearly demonstrated that catalysis was solely due to intact gel entrapped DABCOrather than leached DABCO.

The plausible mechanism for the formation of 2-amino-4*H*-chromenesusing gel entrapped DABCO is shown in (**Fig 3**) Initially, the catalyst facilitates the formation of dicyanoolefin (**5**) by Knoevenagel condensation between aryl aldehyde and malanonitrile as well as generation of phenolate anion (**6**) from phenol. The addition of phenolate anion to dicyanoolefin results in the formation (**7**) which on cyclization furnishes imine (**8**) that results in the formation of 2-amino-4*H*-chromene (**4 a-1**).

The recovery and reuse of catalysts is highly preferable for the large scale operations and industrial point of view. To check the possibility of GEC recycling, the reaction of phenol, benzaldehyde and malanonitrile using gel entrapped DABCOin ethanol was studied. After completion of the reaction, the catalyst was separated from reaction mixture, washed with ethanol and reused in another reaction with identical substrates. The catalyst showed a remarkable recyclability as the corresponding yields started at 96 % and reached 90 % at fifth run(Fig. 3).

Experimental

Melting points were determined in an open capillary and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer. The samples were examined as KBr discs ~5% w/w. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avon 300 MHz spectrometer using DMSO/CDCl₃ as solvent and TMS as internal reference. Mass spectra were recorded on a Shimadzu QP2010 GCMS with an ion source temperature of 280 °C. The thermal gravimetric analysis (TGA) curves were obtained by using the instrument STA 1500 in the presence of static air at a linear heating rate of 10 °C/min from 25 ° to 1000 °C. All chemicals were obtained from local suppliers and used without further purification.

Preparation of gel entrapped DABCO

To a boiling mixture of agar-agar (5 gm) in water (35 mL) was added a mixture of base (2.5 gm) in water (2.5 mL). The resultant solution was boiled with stirring for five minutes and cooled in ice bath to yield the desired gel entrapped DABCOcatalyst.

General procedure for the multi-component synthesis of 2-amino-4H-chromenes

A mixture of phenol (5 mmol), aldehyde (5 mmol) and malanonitrile (5 mmol) was stirred in the presence of gel entrapped DABCO(1 gm) in 5 mL of ethanol at ambient temperature till the completion of the reaction as monitored by TLC. The resulting crude product was filtered off, washed with water and recrystallized from ethanol to afford pure products.

Spectral data of representative compounds

2-Amino-4-aryl-3-cyno-7-hydroxy-4*H*-chromene(**4a**):IR (KBr): υ 3429, 3211, 2193, 1651, 1505, 1447 cm⁻¹; ¹H NMR (300 MHz, DMSO): δ 4.50 (s, 1H), 6.40 (s, 1H, ArH), 6.48 (d, 1H, J=8.3 Hz, ArH), 6.80 (d, 1H, J=9.2 Hz, ArH), 6.85 (s, 2H, NH₂), 7.15-7.21 (m, 3H, ArH), 7.30 (t, 2H, J=7.1 Hz, ArH), 9.68 (s, 1H, ArOH); ¹³C NMR (75 MHz, DMSO): 57.74, 102.80, 112.69, 113.52, 121.00, 126.75, 127.75, 128.58, 129.84, 146.18, 149.24, 157.37, 160.30; MS (EI): m/z = 264 (M⁺).

2-Amino-3-cyno-4(phenyl)-4*H*-benzochromene(**4b**):IR (KBr): υ 3448, 3304, 3010, 2910,2204, 1649, 1633, 1550, 1450, 1375, 1267, 1100, 1022 cm⁻¹; ¹H NMR (300 MHz, DMSO): δ 4.79 (s, 1H), 6.88 (brs, 2H, NH₂), 7.14 (d, 1H, J=8.3 Hz, ArH), 7.21-7.28(m, 5H, ArH), 7.45-7.56(m, 3H, ArH), 7.77 (d, 1H, J=8.3 Hz, ArH), 8.21(d, 1H, J=8.3 Hz, ArH) ; ¹³C NMR (75 MHz, DMSO): 57.06, 78.61, 79.05, 79.49, 117.90, 121.36, 123.38, 124.08, 126.39, 126.65, 126.81, 127.14, 127.76, 128.04, 128.85, 133.14, 145.85, 160.45; MS (EI): m/z = 298 (M⁺).

Conclusion

In conclusion, a novel and highly efficient methodology for the multi-component synthesis of 2-amino-4Hchromene by reaction of malanonitrile with various aldehydes and phenols in the presence of gel entrapped DABCO. The method offers several significant advantages, such as high conversions, easy handling, clean reaction profile and short reaction time, which make it a useful and an attractive addition to the existing methodologies.

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Entry	Aldehyde	Phenol	Product	Time (Min)	Yield⁵ (%)	M. P. (°C)°
1	СНО	ОН		10	96	235 (234-236) ²⁴
	2a	3a	4a			
2	CHO	OH	CN	10	92	209 (210-211) ²⁵
	2b	ЗЪ	4b			
3	СНО	СССС ^{ОН} Зс	CN NH ₂ O	10	93	280 (278-280) ²⁵





ОН

3e

OH

OH

3g

3h

ОН





112 (112-114)24 92



СНО

ÓМе

СНО

ÓМе 2f



191 (190-192)25













СНО

Ċl

2h

СНО

| Cl 2i















9

10





CI CN



248 (248-250)24 89 10

86

ОΗ

ÓН

205 (206-208)25



^aAll products were characterized by IR, ¹H NMR, ¹³C NMR and mass spectrometry. ^bIsolated yields.

^cLiterature values in parenthesis.

Table 1. Gel entrapped DABCOcatalyzed synthesis of 2-amino-4H-chromenes^a



Scheme 1: Multi-component synthesis of 2-amino-4H-chromenes using gel entrapped DABCO



Fig. 3: Recyclic use of gel entrapped DABCO in of2-amino-4H-chromene synthesis



Eco-friendly Synthesis of benzopyran Derivatives by Using Greener Catalysts

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ABSTRACT

A protocol has been developed for the efficient synthesis of structurally diverse terahydrobenzo[b]pyran via three-componentreactions of dimedone, malanonitrile with various aldehydes and in the presence of gel entrapped NaOH as a catalyst.

Keywords : Gel Entrapped Base Catalyst, terahydrobenzo[b] pyran, recyclability

I. INTRODUCTION

Multicomponent reactions (MCRs) have attracted considerable attention owing to high synthetic efficiency, and, in many cases, the facile construction of novel molecular libraries. These methodologies are of particularly great utility when they lead to the formation of privileged medicinal scaffolds.Tetrahydrobenzo[b]pyransare an important class of heterocyclic scaffolds in the field of drugs and These compounds widely used anti-coagulant, pharmaceuticals. are anti-cancer and antiancaphylactiaspasmolytic agents.¹⁻⁴ In addition, they have been shown to act as cognitive enhancers, for the treatment of neurodegenerative disease, including Huntington's disease, amyotrophic lateral Sclerosis, Alzheimer's disease, AIDS associated dementia and Down's syndrome as well as for the treatment of Schizophrenia and myoclonus.^{5, 6} The polyfunctionalizedbenzopyrans are used as cosmetics, pigments and biodegradable agrochemicals.⁷ Other than their biological importance, some tetrahydrobenzo[b]pyrans have been widely used as photoactive materials.8Looking at their importance from pharmacological and industrial point of view, several methods for the multi-component synthesis of tetrahydrobenzo[b]pyrans have been reported. These include both homogeneous as well as heterogeneous conditions, catalyzed by Na₂SeO₄, hexadecyldimethylbenzyl ammonium bromide,9 NaBr,10 tetra-methyl ammonium hydroxide (CH3)4 N+OH-,11 TEBA,¹² KF-montmorillonite,¹³ KF-alumina,¹⁴organocatalysts,¹⁵ acetic acid,¹⁶ diammonium hydrogen phosphate¹⁷and hexadecyltrimethylammonium bromide.¹⁸Microwaves¹⁹and ultrasonic irradiation²⁰have also been used to promote the reaction. Although the literature on synthesis of tetrahydrobenzo[b]pyrans enjoys a rich array of versatile methodologies, new efficient approaches can be valuable additions to the contemporary arsenal of synthetic strategies.

The concept of gel entrapped base catalysts(GEBCs) combines the advantages of alkali and organic bases with those of heterogeneous supports.²¹These catalysts are prepared by immobilization of alkali or organic bases by entrapping them in an aqueous gel matrix of agar-agar which is a polymer composed of repeating agarobiose units

alternating between 3-linked β -D-galactopyranosyl (G) and 4-linked 3, 6-anhydro- α -L-galactopyranosyl (LA) units. The use of GEBCs in organic transformationsabates the amount of bases used and affords easy and efficient separation of products from the catalyst simply by filtration. Often, bases like alkalis absorb moisture when exposed to airand get spoiled. On the contrary, the GEBCs do not absorb moisture on exposure to air and remain intact. They also provide excellent opportunity of recyclability and reusability which is rarely possible using bases alone as catalyst. Further advantages of GEBCs include their ease of handling and being less corrosive. However, despite of their well recognized advantages, there have been only limited and sporadic reports dealing with the use of GEBCs in organic synthesis.²²

In continuation to our research work devoted to the development of green methodologies for MCRs.²³ we report herein an efficient synthesis oftetrahydrobenzo[b]pyransfrom dimedone, malanonitrileand aryl aldehydes in the presence of Gel entrapped NaOH as a catalyst.

Results and Discussion

We focused our initial studies on synthesis of Gel entrapped NaOH (acronymed as GENaOH). A series of experiments were under taken in which different concentrations of NaOH (5-25 %) were dissolved in a varying amount of agar-agar in water. After a considerable experimentation, we found that 20 % *w/w* of agar-agar aqua gel containing 10 % NaOH resulted in the formation of soft gel that served as GEBC in the present work. The GENaOH was light yellow jelly like substance that could be cut into pieces .The changes in physical nature of GENaOH were studied in different solvents. The GENaOH swelled in water and become soft. The nature of gel remained intactin organic solvents like ethanol, acetone, dichloromethane, toluene and isopropanol.

The TGA analysis of agar-agar and GENaOHare displayed in fig. The TGA profiles shows three different weight losses at different temperatures. The forth weight loss which occure below 150 °C for GENaOH as well as agar could be due to removal of physisorbed or occluded water. The second step of decomposition which is initial above 240 °C in both agar-agar as well as GENaOH differed in their amount of respective weight losses (GENaOH ~8%, agar- agar 63.5% could be assigned to thermal decomposition of agar polymer was agar-agar. The decomposition of remaining polymer matrix is accompanied with ~21 % weight loss. Third step in the temperature range of 440-480°C. On the other hand the additional exothermic weight loss centered at 710 °C is observed and could be assigned the decomposition of carbonates frame if any. The entrappment of NaOH in gel matrix is evidenced by the comparatively large residual weight observed in the TGA profile of GENaOH than that of agar-agar.

In order to assess the catalytic activity of GENaOH inthesynthesis of tetrahydrobenzo[b]pyrans(Scheme 1), an equimolar mixture of dimedone, malanonitrile and benzaldehyde (5 mmol each) was stirred in the presence of 1 gm of GENaOH in ethanol at ambient temperature till the completion of reaction as monitored by thin layer chromatography. The reaction proceeded efficiently vielding the corresponding tetrahydrobenzo[b]pyran in 91% yield in just 5-15minutes. In order to check the generality of this methodology, a series of tetrahydrobenzo[b]pyrans were prepared by reaction of dimedone, malanonitrile with various aryl aldehydes. We were gratified to find that with both electron-poor and electron-rich benzaldehydes, the corresponding products were obtained in excellent yields. The reaction of the sterically hindered onitrobenzaldehydeeven gave higher yields high lightening the general applicability of the protocol. The striking feature of all the reactions was the isolation of products. During the course of the reaction the product precipitates out and can be isolated simply by filtration. The product obtained after sufficient washing with water was found to be practically pure. The identity of all the compounds was ascertained on the basis of IR, ¹H NMR,

¹³C NMR and mass spectroscopy data. The physical and spectroscopic data are in consistent with the proposed structures.

It has been well established that in case of the GEBCs, the reagent trapped in the gel may leach into the solvent. To study the leaching of NaOH in solvent, 1 gmGENaOH was stirred in 5 mL of ethanol at room temperature. The GENaOH was filtered and water (3 mL) was added to the filtrate. The NaOH leached out was determined by titration with 0.1 N succinic acid solution using phenolphthalein as an indicator. The study revealed that only 3.91 % NaOH leached out from gel into ethanol. Using the amount of NaOH same as that leached out, the reaction between dimedone, malanonitrile and benzaldehyde did not gave quantitative yield of the corresponding product. This clearly demonstrated that catalysis was solely due to intact GENaOH rather than leached NaOH.

A proposed mechanism for the formation oftetrahydrobenzo[*b*]pyrans using GENaOH. The mechanism suggests that in step-1 Knoevenagel condensation takes place to form the α -cynocinnamonitrile derivative. In step-2 the active methylene of dimedone react with the electrophilic C=C double of α -cynocinnamonitrile giving the intermediate 6, which tautomerizes into 7. The latter is then cyclized by nucleophilic attack of the OH group on the cyano (CN) moiety, giving intermediate 8. Finally, the expected product 4 is afforded by tautomerizeation (8-4).

The use of catalyst is especially interesting when it can be used several times. To investigate the possibility of catalyst recycling, the reaction of dimedone, malanonitrile with benzaldehyde using GENaOH in ethanol was carried out. After completion of the reaction, the GENaOH was recovered by simple filtration, washed with ethanol and reused in another reaction with identical substrates. The catalyst could be reused for five runs without noticeable drop in the yield of product.

Experimental

Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer. The samples were examined as KBr discs ~5% w/w. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avon 300 MHz spectrometer using DMSO/CDCl₃ as solvent and TMS as internal reference. Mass spectra were recorded on a Shimadzu QP2010 GCMS with an ion source temperature of 280 °C. The thermal gravimetric analysis (TGA) curves were obtained by using the instrument STA 1500 in the presence of static air at a linear heating rate of 10 °C/min from 25 ° to 1000 °C.Melting points were determined in an open capillary and are uncorrected. All chemicals were obtained from local suppliers and used without further purification.

Preparation of gel entrapped NaOH

To a boiling mixture of agar-agar (20 Mg) in water (60 mL) wasadded a solution of NaOH (10 gm) in water (100 mL). The resultant solution was boiled with stirring for five minutes and cooled in ice bath to yield the desired GENaOH.

General procedure for the multi-component synthesis of tetrahydrobenzo[b]pyrans

A mixture of dimedone (5 mmol), malanonirile (5 mmol) and aryl aldehyde (5 mmol) was stirred in the presence of GENaOH (1 gm) in 5 mL of ethanol at ambient temperature till the completion of the reaction as monitored by TLC. The resulting crude product was filtered off, washed with water and recrystallized from ethanol to afford the desired product.

Spectral data of representative compounds

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4H-benzopyra: IR (KBr): υ 3396, 3323, 3213, 2961, 2199, 1976, 1660, 1371 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆): δ 1.05 (s, 3H), 1.12 (s, 3H), 2.21 (d, 1H), 2.22

(d, 1H), 2.44 (s, 2H), 4.39 (s, 1H), 4.50 (s, 2H), 7.17-7.31 (m, 5H); ¹³C NMR (75 MHz, DMSO-d₆): 27.39, 28.92, 32.13, 35.88, 50.52, 59.03, 113.36, 120.03, 126.92, 127.50, 128.57, 144.78, 158.91, 162.73, 196.05; MS (EI): m/z = 294 (M⁺).

Conclusion

We have described a general and highly efficient procedure for the preparation of multi-component synthesis of tetrahydrobenzo[*b*]pyransfromdimedone, malanonitrileand aryl aldehydes in the presence of gel entrappedNaOH. The method offers several significant advantages, such as high conversions, easy handling, clean reaction profile, no energy consumption, high conversions, cost effective short reaction timeandgreen methodology which make it a useful and an attractive addition to the existing methodologies.

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Scheme 1: GENaOH catalyzed multicomponent synthesis of tetrahydrobenzo[b]pyrans

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Review on Ferrites : Ferrite properties and its Applications

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ABSTRACT

Magnetic nanoparticles display awesome new phenomena which include superparamagnetism, excessive-field irreversibility, high saturation field, more anisotropy contributions, or shifted loops after field cooling, these phenomena rise up from finite size and ground results that dominate the magnetic behavior of character. Each ability software requires the magnetic nanoparticles to have extraordinary properties, as an example, in information storage applications, and other applications such as in electronics and medical fields Keywords : Superparamagnetism, Excessive-Field Irreversibility, High Saturation Field, More Anisotropy Contributions, Shifted Loops, Field Cooling

Graphical Abstract:



I. INTRODUCTION

Inductive components for energy electronics are regularly exposed to symmetrical and asymmetrical square wave voltages. The usual method for predicting magnetic losses under such operating conditions is based entirely on a good generalization of the Steinmetz equation. [1] Electrical resistivity of ferrite nanofibres enhances by reinforced soft magnetic composite and also used for applications [2] Structural and electrical properties of bismuth ferrite thin films enhances by annealing thin films with atmosphere [3] At10 kHz, 1200 A/m, 25°C and 550 mT at 100°C saturation flux density and the power losses of a MnZn ferrite polycrystalline material is reported [4] The properties of Mn–Zn ferrites by the dopping of yetrium enhances the lattice constants and grain sizes to its maximum value and electromagnetic properties [5] The evaluation of things chargeable for the excessive-frequency shift of the complex ermeability(mn) dispersion place in polymer composites of manganese-zinc(MnZn) ferrite, as well as to the growth in their thermo magnetic stability [6] As a function of frequency dielectric properties of Mn0.4Zn0.6Fe2O4 ferrites prepared by co-precipitation technique have been investigated [7]Inversion degree of spinels of solgel synthesized cobalt ferrites is achieved by adding excessive cations [8] coprecipitated Co-Zn and Mn-Zn ferrite particles in substituted by zinc improves structural and magnetic properties[9] Phase-pure metastable Mn-Zn ferrites were obtained as a result of low-temperature combustion synthesis from different fuels these Ferrite does not contain an extraneous non-magnetic phase (such as hematite), as evidenced by the absence of the characteristic peak for such a phase in XRD samples[10]

II. Result and Discussion

Atul Thakur et. al reported, Compressive stress due to changes in A-site and B-site Fe³⁺ ions due to grain size reduction. The migration of iron from the A-site to the B-site generates compressive stress in the nanoparticles due to the smaller distance between the B-site ions (0.292 nm) compared to the A-site ions (0.357 nm), the increased degree of inversion in nanometer ferrite may also contribute to compressive stress[11]. It can be reported by Bamzai that the material consists of several irregular cubic grains within the pure Mg ferrite and the aggregation of these grains increases with increasing Dy3+ ion concentration, It is also seen that it increases with further increase in $Dy^{3+}[12]$. It was observed that the dense particles of pure, Dy3+ ion-substituted were well crystallized into irregular shapes with large pores, it is

observed that the average particle size of these particles decreases with Dy³⁺ ion substitution, with the average size ranging from 1 to 4 mm, The value of magnetization increases with increasing value of applied magnetic field and saturates to a value of about 1000 Oer [12]. The atomic coordinate x(=y=z) of oxygen atom is called the u parameter and the u parameter for sample L is 0.2608(2), which matches the parameter for sample H within experimental errors. If the oxygen atoms are arranged in ideal cubic close-packing and one-eighth of the tetrahedral and half of the octahedral interstices are occupied by transition metal atoms, then the u parameter is 0.25, denoted as A and B sites which affects in the projection is tilted slightly from [110] and when the u parameter exceeds 0.25, the oxygen atom moves away from the nearest A site in the [111] direction, increasing the size of the A site and decreasing the size of the B site[13].

A.V.Raut et al.reported that the value of dx increases with increasing zinc substitution and is attributed to the increase in mass overcoming the decrease in volume. H (dB less than dx) is attributed to pore formation during the synthesis process. the bulk density increases with increasing zinc substitution. This is due to the higher atomic weight of zinc (65.39 Ω) than the cobalt ion (58.93 Ω). The porosity (P%) of the zinc-substituted cobalt ferrite was estimated from the dx and dB values. it is also reported, that the (P%) decrease in within the increase in Zn substitution in is due to the increase in X-ray density of, with porosity values ranging from 22% to 19% [14]. The saturation magnetization (Ms¹/₄65,628-5,316emu/g) exhibits sizedependent behavior. The presence of Zn at the octahedral site in the spinel lattice of cobalt ferrite causes spin canting, which causes the reduction of Ms. The correlation between decrease in crystal size and increase in tilt angle shows that Ms decreases by due to tilt rotation due to decrease in grain size[14]. Tulu Wegayehu Mammoa reported, that Co-ferrite materials synthesized using sol-gel auto combustion method by the substitution of manganese enhances

the structural, amgnetic and electrical properties of ferrites, It was also observed that, the lattice parameters and the unit cell volume of the samples were almost reduced; and crystal size increased by and then decreased with increasing Mg content ,while Xray and apparent density decreased as Mg content increased, therefore, porosity increases with Mg concentration increases [15]. The results presented F. Ameen Ramiza et al indicate that the lattice parameter increases with increasing Mn ion content. The increase in lattice parameter can be attributed to the ionic radius of the ions. The lattice constant value of ZnFe₂O₄ was found to be 8.42 A°, which is very consistent with the value obtained from the JCPDS map where a = 8.44A°, while the lattice constant value of MnFe₂O₄ a was found to be 8.48A°[16]. The measured network parameters for all samples increased from 8.40 to 8.48A°. he also explained that, The X-ray density decreased linearly with the Mn concentration. The particle size of the samples was also affected by the manganese concentration. The smallest particle size (6,198) was obtained at X=0.27 when irradiated for 6 hours[16]. Radu George Ciocarlana et al. reported that, a new series of ferrite nanoparticles has been obtained, with different metals $(M_{0.25}Cu_{0.25}Mg_{0.5}Fe_2O_4, where M = Mn, Zn, Co, Ni).$ The XRD diffraction patterns confirmed the phase purity and were used to determine the crystal size (3-16 nm). The activated surface of nanoparticles with OH and C-O groups was observed by by FTIR spectroscopy and confirmed by XPS analysis. The magnetic properties show that the Co and Ni ferritic nanoparticles are superparamagnetic while the Zn and Mn ferrite nanoparticles are ferromagnetic[17]. Mamata Maisnam et al. explined that during the exchange, a local shift of the electrons is obtained in the direction of the applied field and this determines the polarization. At sufficiently low frequencies, since the interface polarization plays a dominant role, electrons jump to the grain boundary, and if the grain boundary resistance is high enough, the electrons accumulate at the boundary and generate a large capacitance at high values of ε' at low frequencies. As the frequency increases, the superposition of electrons at the grain boundary decreases due to the reversal of direction thereby reducing the motion the polarization and thus leading to a lower value of ε' . In addition, ɛ' becomes very weak and almost constant beyond a certain frequency (50 kHz) indicating that in addition to this frequency of the external field, electron exchange between iron ions cannot follow the alternate field[18]. Ionic polarization and electron polarization contribute to the generation of at the very high frequency (1012–1015 Hz), which is beyond the scope of the present study[18]. The change of saturation magnetization as a function of Zn²⁺ ion concentration is explained by Mathur et al. The initial increase in the value of 4Π Ms is attributed to the fact that at low concentrations, Zn2+ ions tend to flow preferentially to site A, resulting in an increased and only slight decrease in the magnetic moment of site B.magnetic field. the torque of position A, so the net magnetic torque increases. When the concentration of nonmagnetic Zn^{2+} ions exceeds x = 0.3, these ions also go to site B. He also reported Increasing the size of the particles results in a higher magnetic moment per unit volume. Figure 5 shows the change of Curie temperature of ferrite (both normal and hot pressed) with increasing Zn^{2+} ion concentration. The substitution of the opposite ions from Zn²⁺ leads to a change in the spin order from Yafet-Kittel (Y-K) type to Neel type. The energy required to compensate for rotational alignment in the Neel spinning order is greater than the energy required in the Y-K type spinning order, causing an increase in the Curie temperature.hot pressed ferrite has a higher Curie temperature than samples of the same composition normally prepared [19]. This is attributed to the higher density of magnetic ions in the low porosity hotpressed samples, which requires higher energy for to compensate for spin alignment[19]. The decrease in loss and increase in permeability upon addition of cobalt could be explained by the effect of cobalt on anisotropy. The power loss, at constant frequency and

magnetic field strength, is determined by the temperature characteristic of the crystal isotropy (K₁) which governs the temperature characteristic of the magnetization at saturation[20]. K₁ represents the resistance of the energy barriers that the magnetic dipoles must overcome in order for them to leave their original orientation and align themselves in the direction of the external applied field. The anisotropy constant (K₁) depends on the crystal symmetry and interactions between ions occupying different sites of the lattice. When K₁ is small, it is easier to orient the magnetic dipoles in the favorable direction of the external magnetic field and then the magnetic permeability (μ i) becomes higher and the power loss (Pv) decreases[20].

III. CONCLUSION

Ferrite has been researched and applied for more than years and is considered a technologies ranging from hard magnets to magnetic recordings and microwave devices. However, the advances in applications and manufacturing technologies over the past years of are impressive. Bulk ferrites remain a major group of magnetic materials, while nanostructured ferrites show impressive promise for applications in broader fields.

This examination showed that the neural network's preparation time is decreased drastically by utilizing a fuzzy rationale controller to adaptively fluctuate the learning parameters. At the point when this strategy is applied for the letter acknowledgment task, it yields a 92% exactness, which is a superior exhibition than the initially proposed approach, a Holland-style classifier. Also, this method can decrease the chance of overshooting and in some cases help the system escape a nearby least. The system's capacity to join during preparing and the last execution are reliant on the learning parameters. Our examination strengthens this reality, as our reproductions have shown that an "off-base" benefit of learning rate can prompt poor

letter acknowledgment precision. Besides, the approach is convenient, and can be practiced on other neural networks applications.

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समकालीन हिंदी कथा-साहित्य में विविध विमर्श

खण्ड - एक (मुस्लिम, आदिवासी, बाल तथा दिव्यांग विमर्श)

> समकालीन हिंदी कथा साहित्य में विविध विमर्श

विशेषांक संपादक : डॉ.सी. सुरेटया इसुफ अल्ली शेख असोसिएट प्रोफेसर तथा शोध निर्देशक अध्यक्षा, हिंदी विभाग, मा.ह. महाडीक कला एवं वाणिज्य महाविद्यालय, मोडनिंब, तह. माढा, जि. सोलापुर, महाराष्ट्र-भारत. अध्यक्षा, हिंदी अध्ययन मंडल, सोलापुर विश्वविद्यालय, सोलापुर



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आदिवासी विमर्श

डाँ. दिलीप कोंडिबा कसबे एम. ए. एम. फील, पीएच.डी. विज्ञान महाविद्यालय, सांगोला (सोलापुर)

काहित्य समाज का दर्पण है तो शिक्षा परिवर्तन की ताकद है। इसलिए ही अविकसित, अधुत, उपेक्षित, करणनों में रहने वाले आदिवासी विमर्श के स्थिती एवं गति का मर्माकन अनेक साहित्यकारों ने किया है, के बाने मही अर्थों में हम कह सकते है कि जहाँ सुरज की किरण नही पहुंची, जहाँ जाना अमुमकिन था, 🗰 बादिवासी जनजीवन की वैभिन्यता चित्रित कर साहित्यकारों ने महनीय कार्य किया है, कर रहे है| का वा 'आदिवासी' का अर्थ-

जादि' याने पहला आरंभ तो 'आदम' का अरबी अर्थ मनुष्य का आदि प्रजापति, मनु के समांतर संक्षेप में वाने किसी प्रदेश या राज्य के मुल निवासी" प्रोफेसर गिलानी के मतानुसार- "एक विशिष्ठ भूप्रदेश में न्यत्र. ममान बोली बोलने वाला, अक्षरों की पहचान न होनेवाला, समुह, गट 'आदिवासी समाज' जिला है।" साथ ही डॉ. रिव्हर्स, डब्लू.जे.पेरी तथा श्री. मुजुमदार आदियों की भी यही मान्यता है। इसके 📲 विवेकीराय के मतानुसार- "पिछडे अंचलों, पहाडों वनों के निवासियों को आदिम-आदिवासी माना है| 🛲 🖅 न्दप्ट है, अविकसित, अंधश्रध्दा, रुढि-प्रथा तथा संस्कृति के साथ चिपककर रहनेवाला दुर्गम स्थानों में म्बापन करनेवाला भारतीय सुपत्र आदिवासी है।"

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बहाँ यह वास्तव है कि मनुष्य अपने परिवेश की उपज है, ऐसे ही अपने परिवेश को बदलना होगा। इभाग्य की स्थिती है कि काफी बरस हुए जंगलो में रहनेवाला, अर्धनग्न व्यक्ति जिसे हम आदिवासी 🚔 वे आज भी विकास से काफी दूर रहा है| शायद इसके कारण अज्ञान, अंधश्रध्दा, शोषण, अर्थाभाव, क्राप्टन धर्म प्रभाव और अप्रगत आंचल उनके चिरसाथी है।

नक्षेप में आजादी के आंदोलन में योगदान देनेवाले आदिवासी समाज के लिए संबंधित सरकार विकास किन्द्र योजनाएँ सुरु करके उनका विकास कर रही है। जैसा कि उन्हे संवैधानिक आरक्षण देकर उनका म्बन्दर पनपित करने का प्रयास चल रहा है।

करिणामत: आज आदिवासी समाज में राजनिति नेता मौलिक योगदान दे रहे है। इसमें वनांचल किंग्स् जोन्यद, भारत सेवक संघ, वनवासी विका मंडल, गिरीजन सेवा जैसे संघटन द्वारा भी इनकी स्थिति कि में परिवर्तन हो रहा है। आजादी का आंदोलन, ईसाईयों का बढता संपर्क, यातायात की सुविधा, न्वनों का विकास, शिक्षा प्रसार, विभिन्न संचार माध्यमों का प्रसार, सेवाभावी संस्था का कार्य तथा क्वोधन कार्यक्रम आदि के कारण आदिवासी के स्थिति में धिरे-धिरे परिवर्तन दिखाई दे रहा है।

किंग सियों कीगरीबी हटाओं-

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बान्तवतः गरीबी का अर्थ है- 'मनुष्य को आधारभूत आवश्यकताओं जैसे रोटी, कपडा और मकान के न्ताव म्वाम्थ एवं शिक्षा प्राप्ति के लिए पर्याप्त आय का न होना है। गरीबी से मुक्ति दिलाने के लिए १ र १९३५ को दिवंगत श्रीमती इंदिरा गांधी ने "गरीबी हटाओ" कार्यक्रम के अंतर्गत बीस सूत्रीय कार्यक्रम



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सौंदर्यशास्त्र में मानवीय जीवन-मूल्य

प्रा.डॉ. दिलीप कोंडीबा कसबे हिंदी विभाग, विज्ञान महाविद्यालय, सांगोला.

मनुष्य जीवन मूल्यवान है | अतः मनुष्य ने विशिष्ट मूल्यों के अनुरु प ही जीवन जिता है | 'मूल्य' शब्द 'मूल ' धातू में 'यत' प्रत्यय के आगमन से निष्पन्न हुआ है, जिसका अर्थ - किसी वस्तु के विनिमय में दिये जानेवाली राशी, दाम अथवा किमत है | परंतु आज 'मूल्य' शब्द का प्रयोग 'वैल्य' गुण के अर्थ में लिया जा रहा है | साथ ही 'मूल' शब्द प्रेरणा, आदर्श, अनुशासन, प्रतिमान आदि अनेक अर्थों में प्रयुक्त हो रहा है | सी.ए. मूर ने भारतीय 'जीवन मूल्य' की चर्चा करते हुए कहाँ है - "पुरुषार्थ, अर्थ, काम, धर्म ही 'मूल्य' है|"² इससे यह स्पष्ट होता है कि, 'मूल्य' वे है जो मानव - जीवन व्यवहार में हित संवर्धक होते है | इसी के आधार पर जीवन - मूल्यों के अनेक रुप आदि सामने आते है -



१) वैयक्तिक जीवन मूल्य - इसमें किसी एक व्यक्ति की विशेष की आकांक्षा, संवेदनाओं अभिवृत्तियों से संबंधित 'मूल्य' को वैयक्तिक मूल्य कहते है | किंतु आज वैयक्तिक जीवन मूल्यों में भी किसी दूसरे व्यक्ति विशेष की ओर से संकोचितता निर्माण की जा रही है, ऐसा मेरा मानना है |

२) समष्टिगत जीवन मूल्य - समष्टिगत मूल्यों में मानव जीवन की अभिवृत्तियों से संबंधित विश्वजन, राष्ट्र, संस्कृति आदि आते है | जैसे मानव प्रेम, राष्ट्र प्रेम, समाज प्रेम, संस्कृति प्रेम, त्याग, दया, विरता, अर्थ, अहिंसा, सहायता, क्रांति, परिवर्तन, समन्वय, एकता की अभिवृत्ति से उत्पन्न मुल्य स्वीकृत है |

३) दार्शनिक जीवन मूल्य - मूल्य को दार्शनिकता में काफी महत्व है | वास्तवतः दार्शनिक मूल्यों से मध्ययुगीन संतो-भक्तों में सूर, कबीर, तुलसी के आधुनिक चिंत को में अरविंद , रविंद्रनाथ ठाकुर आदि प्रभावित हुए नजर आते है | साथ ही वेद, उपनिषद, प्राकृत- अपभ्रंश आदि दर्शन ग्रंथो, जैन, बौधो और नाथों के सिध्दांत मूल्यवर्धित है | पाश्चात्य दार्शनिकों में कांट, हेगले, अरस्तु तथा सुकरात आदियों ने भी दार्शनिक मूल्यों को जीवन तत्व का संबंध जोडा है | डॉ. दीवान चंद ने कहा है - "पृथ्वी पर कोई वस्तु इतनी महान नहीं , जितना मनुष्य है और मनुष्य में कोई अंश इतना महान नहीं जितना उसका मन |"³ यहाँ यह स्पष्ट है कि, दार्शनिक मूल्य उत्पत्तिका केंद्र मन के साथ चिंतन और विचार भी है जो मानव जीवन को सही दिशा देते है |

8) आध्यात्मिक जीवन मूल्य - आध्यात्मिक मूल्यों में मन, आत्मा और परत्मा आता है | इसका कारण हम यह मान सकते है कि, कबीर, सुर, तुलसी, जायसी, निरा आदि के अराध्यदेव गुणों मूल्यों से संपन्न है, जैसे सत्य, शिव, सुंदर | क्योंकि सभीयों की इच्छा मोक्षप्राप्ती (ब्रम्ह) है |

भ) नैतिक जीवन मूल्य - नैतिक का संबंध आचरण से है | और नैतिक मूल्य का संबंध व्यवहार, नीति, आचार-विचार, रुढि-परंपरा से है | यह नैतिक मूल्य शुभ-अशुभ, श्रेयस-प्रेयस, स्थापना, निर्माण, उपलब्धि, अन्वेषण एवं शुभ की ओर अग्रसर है |

६) सौंदर्य जीवन मूल्य - सौंदर्य चरम मूल्य है | क्योंकि सौंदर्य में वैयक्तिकता होने के कारण प्रकृति सौंदर्य, मानवीय सौंदर्य, सांस्कृतिक सौंदर्य आदि मर्मांकन इसमें आता है | जैसे - "उस मूल्य मर्यादा को गृहण करने का पथ उच्छृखल नही, वरन स्वतंत्रता और दायित्व से संबंधित स्वधर्म का पथ है |"³ इस प्रकार आर्थिक मूल्य, भौतिक मूल्य,कल्याणकारी मूल्य,आनंदवादी मूल्य आदि मूल्यों को अनन्य साधारण महत्व है |

(9) भौतिक जीवन मूल्य - भौतिक जीवन मूल्यों की अभिवृध्दी मानव के भितरी अभिवृत्तियों से है जो भौतिक अभ्युदय में सहायक होती है | साधन सामग्री के मूल्य इसके अंतर्गत आते है | जैसे - कला-कौशल, भौतिक सामग्री, संस्थाएँ जो सभ्यता का निर्माण करती है जिसके कारण वह स्वतंत्रता तथा सुरक्षा का कारण बनती है | इस दृष्टि से संपन्न सभ्यता भी साधनात्मक मूल्य है | Contents lists available at ScienceDirect



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Research Article

Design, synthesis and in silico study of pyridine based 1,3,4-oxadiazole embedded hydrazinecarbothioamide derivatives as potent anti-tubercular agent



Ajay N. Ambhore^a, Sonali S. Kamble^b, Shuddhodan N. Kadam^a, Rahul D. Kamble^a, Madhav J. Hebade^a, Shrikant V. Hese^a, Milind V. Gaikwad^a, Rohan J. Meshram^{c,*}, Rajesh N. Gacche^{d,*}, Bhaskar S. Dawane^{a,*}

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Keywords: Hydrazinecarbothioamide 1,3,4-oxadiazole Antitubercular Antioxidant Hemolytic activity Molecular docking

ABSTRACT

Development of novel, safe and effective drug candidates combating the emerging drug resistance has remained a major focus in the mainstream of anti-tuberculosis research. Here, we inspired to design and synthesize series of new pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene-hydrazinecarbothioamide derivatives as potential antitubercular agents. The anti-tubercular bioactive assay demonstrated that the synthesized compounds exhibit potent anti-tubercular activity (MIC = $3.9-7.81 \mu g/mL$) in comparison with reference drugs Rifampicin and Isoniazid.We employed pharmacophore probing approach for the identification of CYP51 as a possible drug target for the synthesized compounds. To understand the preferable binding mode, the synthesized molecules were docked onto the active site of Sterol 14α -demethylases (CYP51) target. From the binding free energy of the docking results it was revealed that the compounds were effective CYP51 inhibitors and acts as antitubercular agent.

1. Introduction

In the current state-of-the-art, rapidly emerging multidrug resistant (MDR) pathogeneic microorganisms has exerted crisis on the human health (Yuan et al., 2017). It is the leading cause of death in the world and a huge burden on the developing countries. Tuberculosis (TB) is one of the peril disease. It is caused by a pathogenic bacteria Mycobacterium tuberculosis (Mtb) (China Raju et al., 2011). Dreadfulness of this disease is clarified by the Global Tuberculosis report of WHO which predicted that near about 1.8 million deaths occur due to TB and 10.4 million new TB infected cases were notified in 2015 (WHO, 2016). Experimental settings have demonstrated that TB forms granulomatous lesions, consisting of clusters of infected macrophages and fibroblasts with T lymphocytes and B lymphocytes which are utilized by Mtb to evade annihilation by the immune system of the host (Clark et al., 2017). Such behavior of Mtb leads to adverse effect on the host's immune system that increase the chances of acquiring a HIV co-infection (Mekonnen et al., 2015). This was also explained by WHO (2016) that near about 55% TB patient were documented HIV positive (Karabanovich et al., 2014). The management of this disease is again complicated due to emergence of the multi drug resistance (MDR) and extensively drug-resistant (XDR) strain of *Mtb* (Kamal et al., 2013). The convenient treatment of TB necessarily required long-term regimen due to the non-replicating persistence tuberculosis phenotype (Krishna et al., 2014). It is found that inappropriate treatment generates a harmful effect and makes a significant contribution to the emergence of drug resistant *Mtb* strains (Chauhan et al., 2014). This is apparent and imperative to combat the increasingly frequent drug resistant strain of *Mtb*. To address these needs, it has been a major task for chemists to enlarge their attitude towards the modification of available clinical drugs with new molecular scaffolds possessing potential activities against MDR strain.

Hydrazinecarbothioamides are recognized as one of the most competent biological promoters owing to nitrogen and sulfur donors, which equip them to bear an enormous diversity of coordination modes (Aly et al., 2009). Hydrazinecarbothioamides are embedded in manifold

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Received 1 December 2018; Received in revised form 5 March 2019; Accepted 10 March 2019 Available online 13 March 2019 1476-9271/ © 2019 Published by Elsevier Ltd. compounds acquiring the wide range of biological activity and their possible beneficial bio-property depends upon their parent aldehyde or ketone (Aly et al., 2010). They are endowed with antitumor and antiprotozoal properties as well as antiviral potential (Beraldo and Gambinob, 2004; Grover and Kini, 2006; Pelosi, 2010). Their parasiticidal action against *Plasmodium falciparum* and *Trypanosoma cruzi*, make it an important pharmaceutical agent in malarial and Chagas's disease (Du et al., 2002; Greenbaum et al., 2004). Also, they are figured out as antibacterial (Wujec et al., 2012), antifungal (Siwek et al., 2012), analgesic, anti-inflammatory (Salgin-Goksen et al., 2007), antiviral (Pelosi, 2010) and anticonvulsant (Botros et al., 2013) therapeutic agents. Furthermore, it is realized that complexation of hydrazinecarbothioamide with transition elements, especially iron and copper boost their bioactive properties as compared to the uncomplexed state (Easmon et al., 2001).

Along with this diversified biological activities, derivatives of hydrazinecarbothioamides are peculiar towards the antitubercular property. As a mycolic acid biosynthesis inhibitor, Thioacetazone and pacetamidobenzaldehyde thiosemicarbazone reported as one of the second line oldest anti TB drug (Zafer et al., 2016). Beyond this, a huge number of compounds ingrained with thiosemicarbazides scaffold were assessed against *Mtb* and proclaimed as potent antitubercular agent (Fernando et al., 2010).

Furthermore, Oxadiazoles are a very well inevitable class of heterocyclic compounds with assorted pharmaceutical applications. In the field of medicinal chemistry and synthetic study, 1,3,4-oxadiazole endorse an imperative scaffold. It embraces a broad spectrum as it carries diverse biological potentials like antibacterial (Patel et al., 2012), anticancer (Bondock et al., 2012), anticonvulsant (Almasirad et al., 2007), anti-HIV (El-Sayed et al., 2009), antioxidant (Kotaiah et al., 2012), antiinflammatory (Gilani et al., 2010) and hypoglycemic (Gudipati et al., 2011) activities. Thus, the synthesis of oxadiazole offers a great impulsion to research in the development of bioactive compounds.

On the basis of aforementioned litrature and from our previous work (Mogle et al., 2016; Kamble et al., 2014a,b; Hebade et al., 2016; Ambhore et al., 2017; Hese et al., 2017), herein we inspired to design and synthesize a new series of anti-tubercular agents by embedding 1,3,4-oxadiazole in hydrazinecarbothioamide scaffold. This framework anticipates that hydrazinecarbothioamide could provide anti-tubercular activity, whereas 1,3,4-oxadiazole scaffold could increase the compound's adhesive effect. Our intention is to describe the beneficial synthesis of novel pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene-hydrazinecarbothioamide derivatives (**5a-k**) and to communicate data of *in vitro* evaluation of anti-tubercular activity against *Mtb* (MTCC 300). Also, the synthesized compounds were screened for their antioxidant and hemolytic property. We also present the data of molecular docking used to interpret the blueprint of synthesized molecular skeleton binding with the identified receptor.

By and large, wide-ranging proteomics approaches are implemented in the identification of putative binding proteins for compounds; once they are synthesized and their initial antibacterial activities are known. With this approach, the protein expression profiles of cell or tissue are compared in the presence or absence of the newly synthesized molecule. However, considering the time intense and the painstaking nature of this method, it is not very popular in drug target discovery procedures (Liu et al., 2010a,bLiu et al., 2010c; Huang et al., 2004). Instead, we have applied *in silico* target profiling method for effective recognition of probable drug targets employing online software PharmMapper (Liu et al., 2010a,bLiu et al., 2010c). This server identified Sterol 14 α demethylases (CYP51) as a potential tubercular drug target for the proposed compounds in this report. (Figs. 1 and 2)

CYP51 is a member of sterol 14 α -demethylases family and it contributes to sterol biosynthesis by removing 14 α -methyl group from sterol nucleus. It has been reported that *Mtb* is susceptible to therapeutic agents that target CYP51, thereby suggesting it's imperative role in tubercular physiology and may act as an effective drug target Computational Biology and Chemistry 80 (2019) 54-65



Fig. 1. Molecular structure of bioactive thiosemicarbazide moiety.



Fig. 2. Molecular structure of thiosmicarbazide derivatives used in present study.

(McLean et al., 2007). We have utilized virtual screening for predicting binding free energies of the newly synthesized pyridin-4-yl-1,3,4-ox-adiazol-2-yl-thio-ethylidene-hydrazinecarbothioamide derivatives in the active site of CYP51 using the computational method based on a Lamarckian genetic algorithm for molecular docking.

2. Results and discussion

2.1. Chemistry

The synthetic route of the title compound pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene-hydrazinecarbothioamide derivatives (**5ak**) is depicted in the Scheme 1. According to the scheme, compound 2 was prepared from the reported methodology (Gilani et al., 2011). Furthermore, compound1-(substitutedphenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio) ethanone (**4a-k**) was prepared by the reported methodology (Zhang et al., 2012) with slight modification. Structure of synthesized compounds **2** and (**4a-k**) was confirmed by spectral data.

Finally, the target compound pyridin-4-yl-1,3,4-oxadiazol-2-yl-thioethylidene-hydrazinecarbothioamide derivatives (**5a-k**) were



Scheme 1. Synthesis of pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene hydrazinecarbothioamide derivatives (5a-k).

synthesized by the clean condensation of 1-(substituted-phenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)ethanone (**4a-k**) with thiosemicarbazide by using catalytic amount of acetic acid in PEG-400 at 70–80 °C in 2–3 hrs. All newly synthesized compounds were purified by recrystallization and characterized by IR, ¹H NMR, ¹³C NMR and HR-MS spectral analysis (Table 1, Fig. 3).

2.2. Biology

2.2.1. Anti-tubercular activity

Susceptibility of newly synthesized compounds 2-(1-(substitutedphenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)ethylidene)hydrazinecarbothioamide derivatives (5a-k) against multidrug resistance Mtb (MTCC 300) was endorsed by Resazurin microtiter assay (REMA). The results of the assay are depicted graphically in Fig. 4, which conceded the susceptibility of the synthesized compounds against the given strain of Mtb. Compound 5b, 5d, 5e, and 5f were found to be competent growth inhibitors (MIC = $3.90\,\mu\text{g/mL})$ of the selected mycobacterium strain when compared with the standard anti-TB drugs like Rifampicin (0.24 µg/mL) and Isoniazid (0.48 µg/mL). Compound 5c also demonstrated good anti-mycobacterium activity (MIC = $7.81 \,\mu\text{g/mL}$), while the compounds like 5a, 5 h, and 5i showed moderate anti-mycobaterial profile (MIC = $15.62 \mu g/mL$) against MTCC 300 starin. The remaining compounds like 5 g, 5 j, and 5k displayed an average growth inhibition (MIC = $125 \,\mu\text{g/mL}$) of the selected mycobacterium strain.

The synthesized panel of compounds consist of free thiourea moiety. Litreture accumulated in the recent past describes the 'thiourea nucleus' as a basic prerequisite and pharmacophore for the manifestation of anti-TB activity. More precisely thiourea drug thiocarbanilide isoxyl (ISO) and its series of derivatives strongly inhibits the synthesis of mycolic acids and inhibit shorter chain fatty acid (Phetsuksiri et al., 2003; de Souza et al., 2009). The structure activity relationship revealed that the presence of two or more than two pharmacaophore collectively showed synergyc effect on antituberculosis activity of target compounds. Ahsan et al. (2012) reported that the presence of oxadiazole scaffold in the compounds act as pharmacophore against the *Mtb* strains. The antituberculosis screening of the compounds revealed that the compounds exhibiting the anti-tuberculosis activity, since it contains the oxadiazole nucleus. Furthermore, it was confirmed that the presence of substituted sulfanyl moiety enhance anti-tuberculosis activity of the oxadoazoles (Karabanovich et al., 2014). The presence of hydrazinocarbothiamides (Sens et al., 2012) group in association with pharmacophores such as oxadiazoles (Martinez-Grau et al., 2018; Roh et al., 2017; Jain et al., 2016) and substituted sulfanyl enhance the antituberculosis activity of target compounds (Karabanovich et al., 2014). A curtosy look at the activity of compounds 5b, 5c, 5d, 5e and 5h reveals that there is asignificant effect of incorporation of electron withdrawing substituent on the benzyl ring (Karabanovich et al., 2014). Whereas the incorporation of electron donating substitutent on benzene ring (5 g, 5 j, and 5k) decreases the antituberculosis activity.

2.2.2. Antioxidant activity

Antioxidants play a vital role in tuberculosis. It reduces the tissue inflammation and oxidative stress formed during active infection by resisting the effect of reactive oxygen species (ROS). As the newly synthesized compounds displayed promising antitubercular activity, it is essential to evaluate its antioxidant property. Antioxidant activity was carried out by using 2,2-diphenyl-1-picrylhydrazyl (DPPH), Hydroxyl radical (OH) and Superoxide anion radical (SOR) scavenging method (Melagraki et al., 2009) taking ascorbic acid as standard. Results of DPPH, OH and SOR radical scavenging assay for compounds (**5a-k**) were expressed as % antioxidant activity (Table 2).

The DPPH scavenging assay has been used for exploring the antioxidant activity of pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidenehydrazinecarbothioamide derivatives (**5a-k**). The found result clearly illustrates that all synthesized derivatives are interacting with stable free radical DPPH. Compound **5b** (78.33 \pm 0.10), **5d** (72.52 \pm 0.10), **5e** (79.22 \pm 0.22), and **5f** (77.92 \pm 0.10) exhibited significant activity in comparison with ascorbic acid (85.42 \pm 0.78). Remaining derivatives possess moderate activity. DPPH radical scavenging results are in accordance with Prabhudeva et al. (2017), wherein, the compounds with nitro groups are found to possess less antioxidant effect. This observation was further known to be associated with strong

Table 1

Physiochemical data of synthesized compounds (5a-k).

Sr. No.	Comp code	Structure	Yield (%)	M.P. (°C)
1	5a		84	155-157
2	5b	H ₂ N S Br N-N O S N N	87	163-165
3	5c		89	157-159
4	5d		89	160-162
5	5е		83	188-190
6	5f		86	177-179
7	5 g	N HN HANNES	85	172-174
8	5 h		82	160-162
9	5i		81	183-185
10	5 j	H ₂ N S H ₂ N S OCH ₃	82	181-183
11	5k		84	182-184
		HN H ₂ N S		

electron withdrawing potential of nitro group. In the present study **5d** which posses nitro group, scored less antioxidant effect as compared to bromo (**5b**) and di chloro (in **5e**) substitutions.

In case of hydroxyl (OH) radical scavenging activities it was observed that compounds **5b** (74.14 \pm 0.17), **5d** (75.40 \pm 1.02), **5e** (78.11 \pm 0.34), and **5f** (74.20 \pm 0.50) demonstrated highest scavenging activity when compared with standard ascorbic acid (84.12 \pm 0.11) while other derivatives showed the significant activity. Electron withdrawing groups like chloro- are classically known to favour the release of hydrogen, therefore the presence of two chlorogroups in compound 5e can be considered as determining factor for achieving highest hydroxyl (OH) radical scavenging activities. Of note, the compound 5f which do not possess any electron withdrawing group has scored lowest scavenging activities (Dhiman et al., 2018).

Superoxide anion radical (SOR) radical scavenging activities indicated that the compound **5b** (74.50 \pm 1.10), **5d** (74.02 \pm 1.10), **5e** (76.50 \pm 0.30), and **5f** (76.40 \pm 1.10) exhibited strong activity as compared to standard ascorbic acid (85.63 \pm 0.52), whereas the rest compounds displayed moderate SOR radical scavenging activities. The overall range of SOR scavenging activity of all the tested compounds was 55.38–76.50%. The variation exhibited in the radical scavenging result could be attributed to the effect of different substituent in the synthesized derivatives. For example, it has been demonstrated that presence of halogenated (chloro-, bromo-) and nitro- substitutions influence the superoxide anion radical (SOR) scavenging activities (Kamble et al., 2015).

The synthesized panel of compounds (5a-5k) possess free thiourea moiety, having N-H as an ionisable proton. The concerned literature describes that, the molecules containing thiourea functional group having N-H ionizable proton is strongly associated with free radical scavenging activity (Yehye et al., 2015; Lucarini et al., 1994). As summarized in the Table 2, the compounds 5b, 5d, 5e, and 5f demonstrated impressive free radical scavenging potential, while remaining compounds showed moderate to good antioxidant profile. The variety of substituent like electron donating (EDG) and electron withdrawing groups (EWD) on the aryl ring of the test compounds are also associated with increase or decrease in the antioxidant profile (Ariffin et al., 2014). For example, the compounds like 5b, 5e, 5h, 5i which possess halogens at meta or para position on aryl ring have demonstrated considerable DPPH, OH and SOR radical scavenging activity (Table 2). It is well established fact that the halogens have non-bonding electrons and they can donate electron density through pi bonding, the mechanism called as resonance donation. The compound 5d has also demonstrated considerable free radical scavenging profile. The molecule 5d possess electron withdrawing -NO2 group on the aryl ring of hydrazine derivatives, the -NO2 group may be helping for delocalization of electron and might contribute towards enhancing antioxidant activity (Kareem et al., 2016).

Another possible mechanism that can be proposed for the effective antioxidant effects of the test compounds can be either hydrogen atom transfer (HAT) and single electron transfer (SET) mechanism. The presence of an -NH group in the thiourea (Fig. 2) belong to hydrazine of thiosemicarbazides, which can undergo homolytic bond fission and donate a hydrogen atom *via* a HAT mechanism leading to neutralization of the free radicals (Bondet et al., 1997; Al-Amiery et al., 2012; Satheshkumar et al., 2014). Although the compounds **5** g, **5** j, **5**k possess an electron donating groups on aryl ring, however they have exhibited low to moderate antioxidant activity. Perhaps, the lower resonance effect associated with these compounds might be a possible cause for the low to moderate antioxidant effects (Djukic et al., 2018).

2.2.3. Hemolytic assay

The *in vitro* hemolytic assay of pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene-hydrazinecarbothioamide derivatives **(5a-k)** was carried out towards the RBCs. The result was displayed in Fig. 5 which clearly revealed that all the screened compounds have insignificant



Fig. 3. Tautomeric form of hydrazine carbothioamides (5a-k).



Fig. 4. Anti-tubercular screening of pyridin-4-yl-1,3,4-oxadiazol-2-yl-thioethylidene-hydrazinecarbothioamide derivatives (5a-k).

 Table 2

 DPPH, OH and SOR radical scavenging assay of compound (5a-k).

Compound Code	DPPH (%)	OH (%)	SOR (%)
5a	62.45 ± 1.09	60.25 ± 0.20	64.50 ± 0.20
5b	78.33 ± 0.10	74.14 ± 0.17	74.50 ± 1.10
5c	64.63 ± 1.03	57.52 ± 0.40	61.85 ± 0.20
5d	72.52 ± 0.10	75.40 ± 1.02	74.02 ± 1.10
5e	79.22 ± 0.22	78.11 ± 0.34	76.50 ± 0.30
5f	77.92 ± 0.10	74.20 ± 0.50	76.40 ± 1.10
5 g	58.10 ± 0.05	60.20 ± 0.20	55.80 ± 0.20
5 h	70.40 ± 0.10	73.80 ± 0.30	68.86 ± 0.44
5i	71.01 ± 0.16	70.15 ± 0.40	67.75 ± 0.22
5 j	62.50 ± 0.3	60.70 ± 0.10	57.45 ± 0.12
5k	57.80 ± 0.15	60.20 ± 0.15	55.38 ± 0.10
Ascorbic acid	85.42 ± 0.78	84.12 ± 0.11	85.63 ± 0.52

The results are expressed as the mean values from three independent experiments \pm standard deviation.

hemolytic activity as compare to the positive control (Triton X-100) and all were within the permissible limit of 5% for hemolysis.

2.2.4. Molecular modeling and docking study

2.2.4.1. Target identification. Pharmacophore is defined as the 3D arrangement of the essential features of a molecule to interact with a precise drug target receptor (Liu et al., 2010a,b,c). PharmMapper server is based on ligand-protein reverse docking strategy and functions by 'probing' the ligand into a database of already created pharmacophore models of binding sites (Li et al., 2006; Gao et al., 2008). Thus, the software checks for the compatibility between the pharmacophore model of compound and that of proteins active site/ binding site. A 'Fit score' is assigned that reflects compatibility of ligand to the binding site of protein on the basis of pharmacophore features that are shared between them. Thus, higher fit score shall correspond better



Fig. 5. Hemolytic activity of synthesized compounds (5a-k). Results are expressed as the mean values from three independent experiments \pm Standard deviation (SD).

compatibility of ligand towards the binding site of the protein. Fit scores are needed to be normalized within unity in order to be compared with each other. Thus, the valve of normalized fit score near 1 would correspond best results among identified targets. The software also outputs z'-score that represents a measure of statistical confidence while comparing results. Large positive z'-score of identified target indicates the high significance of the target to a query compound, on the contrary, large negative z'-score indicates that the target identified is not significant. Table 3 describes top ranked targets obtained from the server along with their normalized fit score and z'score. Pharmmapper identified Sterol 14 α -demethylases (CYP51) as a potential drug target for pyridin-4-yl-1,3,4-oxadiazol-2-yl-thioethylidene-hydrazinecarbothioamide derivatives (5a-k) with a normalized fit score of 0.8744. This value indicates the best fitting of the pharmacophore model of compounds at the binding site of CYP51 in comparison with other identified targets. Furthermore, it possesses highly positive z'-score indicating high statistical significance. Comparison of normalized fit score (signifying appropriate compatibility of ligand to protein in terms of pharmacophore model) and z'-score obtained from the pharmacophore mapping analysis indicate that human CYP51 with PDB ID 2VKU might act as potential target. Pharmmapper detected five featured pharmacophore model for pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene-

hydrazinecarbothioamide derivatives (5a-k) that comprise of two hydrophobic patches around the terminal pyridine ring and phenyl ring (Fig. 6). Two hydrogen bond donors were detected in the pharmacophore model, first located at the nitrogen from the pyridine ring (PYR) and the second oneis placed on the nitrogen of the oxidazole ring (OXD). The sulfur atom from the Thiosemicarbazide (TSC) moiety is expected to act as an acceptor. Considering the structure of substrate of this enzyme that contains a multiple fused ring in steroid nucleus; the pharmacophore model identified in current study seems to be in accordance with experimental observations that CYP51 prefers ligands with hydrophobic regions. Moreover, the active site of this enzyme is lined with lipophilic residues that may effectively form hydrophobic or van der Waals contacts with the two hydrophobic patches pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidenein hydrazinecarbothioamide derivatives (5a-k). Thus, the pharmacophore model obtained in current study brings focus on the fact that hydrophobic features in consort with two hydrogen bond

Table 3

-			1	1	1	1	•	•	DI 3.0			1 1	• .	3.7 1. 1	C* .
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101	ιαu		oplancu	υv	Difarmaco	DIIOIC	mapping	i usini	i marmiyia		, anang	cu accore		INDIMANZCU	III SCOIC.
									,						

Name	PDB ID	No of features	Fit score	Normalized fit Score	Z'Score	Swissprot ID
Cytochrome P450 51	2VKU	5	4.372	0.8744 ^a	2.744	P9WPP9
Ribonuclease pancreatic	1EOS	8	4.776	0.597	2.745	P61823
Mitogen-activated Protein kinase 14	2ZB0	8	4.64	0.580	2.598	Q16539
Heat shock protein HSP 90 alpha	2BSM	8	4.637	0.5796	4.061	P07900

^a Target showing comparatively Normalized fit score.

donors and one hydrogen bond acceptor may act as determining chemical factors that governs the ligand's potential in recognition as CYP51 inhibitor. Furthermore, the pharmacophore model presented in this report can act as a springboard for enhancing further chemical synthesis of synthetic derivatives intended to inhibit CYP51 using pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene-

hydrazinecarbothioamide derivatives (**5a-k**) as a basic chemical scaffold.

2.2.4.2. Structural analysis of docked complexes. To further cross validate the outcomes from PharmMapper server and to correlate the observed *in vitro* anti-mycobacterial inhibition results and confirm the suitability of synthesized pyridin-4-yl-1,3,4-oxadiazol-2-yl-thioethylidene-hydrazinecarbothioamide derivatives (**5a-k**) for CYP51, we further initiated molecular docking investigation. Moreover, structural analysis of docking complexes provides valuable information regarding possible interactions that are given compounds might form at the binding site of mycobacterial CYP51. This information, thus confirms suitability of given compounds for identified receptor. Table 4

summarizes the details of ligand- CYP51 interactions of the most promising compounds.

The Heme binding site and active site of this protein are located in close proximity and often contain overlapping residues. This large cavity is located in the central region and extends from surface of protein as a tunnel. Such a voluminous cavity might be effectively utilized to accommodate the heme and sterol substrate simultaneously during catalysis and thus might be used in the same way to hold the newly synthesized pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidenehydrazinecarbothioamide derivatives (5a-k) during inhibition. Crystallographic study of this protein indicates that the majority of the residues in this cavity are lined with hydrophobic side-chains and it also hosts numerous polar residues (Eddine et al., 2008). These facts are exactly complementary to the structure of compounds under current investigation. The newly synthesized compounds contain three aromatic rings that might precisely occupy the hydrophobic pockets, while the polar functional groups might have been engaged by forming hydrogen bonds with the polar side chains in the active site. This structural data, thus confirms that the PharmMapper server has identified an



Fig. 6. Docked complexes of CYP51with compound 5b, 5d, 5e and 5f (yellow sticks) making hydrogen bonds (Magenta lines) with residue at the active site (White sticks) with heme (green sticks). Residues in van der Waal's contact and hydrophobic interaction are depicted in lines.

Table 4

Docking results for synthesized pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene-hydrazinecarbothioamide derivatives in mycobacterial CYP51, by AutoDock 4.2.



Compound code	Binding Free Energy (Kcal/ mol)	Hydrogen bonding pair (HBD in Å)	Residues in hydrophobic interaction or van der Waals contact
5a	-8.07	His259 (NE2) ^{sc} ::Lig(C):S2 ^{TSC} (3.29) Ala256 (O) ^{bb} :: Lig(C):N6 ^{TSC} (2.96) Thr80 (OG1) ^{sc} :: Lig (A):N4 ^{PYR} (2.68)	Gln72, Ala73, Tyr76, Phe78, Met79, Phe83, Thr260, Leu321, Ile323, Hem
5b	8.57	Ser252 (O) ^{bb} ::Lig (C):N6 ^{TSC} (2.81) Hem (O1D):: Lig (C):N5 ^{TSC} (3.04) Ile323 (O) ^{bb} :: Lig(B):N3 ^{OXD} (2.74)	Gln72, Tyr76, Phe78, Met79, Phe83, Phe255, Ala256, Leu321, Ile322, Pro320, Met433, Val435
5c	-7.52	His259 (NE2) ^{sc} ::Lig (C):N1 ^{TSC} (3.22) Gln72 (OE1) ^{sc} ::Lig (B):N4 ^{OXD} (2.93) Ile323 (N) ^{bb} ::Lig (C):N6 ^{TSC} (2.86) Ile322 (N) ^{bb} ::Lig (D):O1 ^{NBZ} (2.96) Met433 (O) ^{bb} ::Lig (D):O2 ^{NBZ} (2.95)	Ala73, Tyr76, Met79, Phe255, Ala256, Leu321, Hem
5d	- 6.89	Gln72 (O) ^{bb} ::Lig(C): N7 ^{TSC} (2.52) Ala73 (O) ^{bb} :: Lig(C): N7 ^{TSC} (2.87) Met433 (O) ^{bb} ::Lig(A):N5 ^{PYR} (3.04)	Tyr76, Phe78, Met79, Phe83, Phe255, Ala256, Leu321, Val434, Hem
5e	-8.14	Gln72 (O) ^{bb} :: Lig (A):N4 ^{PYR} (3.08) Ala73 (O) ^{bb} :: Lig (A):N4 ^{PYR} (2.86) Ile323 (N) ^{bb} ::Lig (D):O1 ^{NBZ} (2.78) Hem (O1D):: Lig(B):N2 ^{OXD} (2.69)	Tyr76, Phe78, Met79, Phe83, Phe255, Ala256, His259, Thr260, Leu321, Met433
5f	-7.74	Ala73 (O) ^{bb} :: Lig (A):N4 ^{PYR} (3.00) Hem (O1D):: Lig(B):N3 ^{OXD} (2.97)	Gln72, Tyr76, Phe78, Met79, Phe83, Arg96, Phe255, His259, Leu321, Met433, Val434
5 g	-7.16	Tyr76 (OH) ^{sc} ::Lig (D):F ^{NBZ} (3.07) Ala256 (O) ^{bb} :: Lig(C):N6 ^{TSC} (2.44) His259 (NE2) ^{sc} ::Lig (C):N5 ^{TSC} (3.25) Ala73 (O) ^{bb} :: Lig (A):N4 ^{PYR} (2.89)	Gln72, Met79, Phe83, Arg96, Phe255, Thr260, Leu321, Ile323, Hem
5 h	-7.82	Gln72 (O) ^{sc} ::Lig(C): N5 ^{TSC} (2.66)	Tyr76, Phe78, Pro93, Arg96, Phe255, Ala256, His259, Leu321, Ile323, Met433, Hem
5i	-7.58	Hem (O1D):: Lig(B):N3 ^{OXD} (2.95)	Gln72, Tyr76, Phe78, Met79, Phe83, Arg96, Phe255, Ala256, Leu321, Met433
5 j	-6.68	His259 (NE2) ^{sc} ::Lig (C):N5 ^{TSC} (3.17) Arg96 (NH1) ^{sc} :: Lig (D):O1 ^{NBZ} (3.34)	Tyr76, Phe78, Met79, Phe83, Leu321, Ile322, Ile323, Met433, Val434, Hem
5k	-4.71	Hem (O2A):: Lig(B):N3 ^{OXD} (2.72)	Gln72, Tyr76, Phe78, Met79, Phe83, Pro93, Arg96, Pro320, Leu321, Ile322, Ile323, Met433, Val435

^{sc}represent side chain, ^{bb} represent backbone. PYR(A), OXD(B), TSC(C), NBZ(D) are Pyridine, Oxadiazole, Thiosemicarbazide, Nitrobenzene substituent; N2 represent Nitrogen at second position and O1 represent Oxygen at first position respectively. Interaction" Pro93 (O)^{bb}:: Lig (A):N4^{PYR} (3.24)" is to be read as" Proline-93 forms hydrogen bond by backbone O atom with fourth nitrogen atom from Pyridine moiety of ligand with distance.3.24"

appropriate target protein with a suitable pharmacophore model.

Compound 5 g is observed to be actively forming polar interaction with Tyr-76 while most of the remaining compounds are found to be either in van der Waal's contact or show hydrophobic interaction with this residue. Crystallographic study of CYP51 in complex with substrate analog estrol indicate that interaction with Tyr-76 is essential for effective catalysis. Moreover, this residue is found to be highly conserved among all the reported CYP51 sequences (Podust et al., 2004). It is also observed that the side chain of Tyr-76 can effectively form stacking interaction with the substituted phenyl ring (ring D from Table 4) from this series. Crystallographic evidences suggest that such stacking contacts are known to play a key role in stabilizing inhibitors like 2-(benzo [d]-2,1,3-thiadiazole-4-sulfonyl)-2-amino-2-phenyl-N-(pyridinyl-4)acetamide (BSPPA), α -ethyl-N-4-pyridinyl-benzeneacetamide (EPBA) (Podust et al., 2007) and 4,4'-Dihydroxybenzophenone (DHBP) (Eddine et al., 2008). Experiment with high throughput screening assay conducted to find out inhibitors of CYP51 revealed active hydrophobic contact of residue Tyr-76 with the identified inhibitor (Chen et al., 2009). Therefore, in view of the above mentioned observations, interaction with Tyr-76 can be considered as an important factor in defining mycobacterial inhibitory effect via present pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene-hydrazinecarbothioamide derivatives (5a-k).

Similarly, all compounds except **5c** and **5h** are found to be supported by residue Phe-83. Compound **5a**, **5c**, **5g** and **5j** are found to be in hydrogen bonding distance of the side chain of reside His-259, while compound **5e**, **5f** and **5h** are stabilized by non-polar contact of the

same residue. This residue is experimentally known to line the binding site and contribute in interaction with substrate (Podust et al., 2001). Sequence analysis conducted on CYP51 from individuals spanning diverse kingdoms, including animals, fungi, higher plants and bacteria, it was observed that residue at these three residues plays an important role in defining the substrate specificity of CYP51 in these diverse species (Podust et al., 2001). Therefore, based on *in vitro* observations demonstrated here, along with in silico docking data, it can be assumed that compound from present series might have been in interaction with Tyr-76, Phe-83 and His-259 that shaped the ant-tubercular effect.

Compound **5b**, **5c** and **5e** is found to be in hydrogen bond contact distance of the backbone atoms of residue Ile-323; while, compound **5a**, **5 g**, **5 h**, **5 j** and **5k** seems to be stabilized *via* van der Waals contacts. Interestingly, this residue is experimentally validated to participate actively not only in the binding of estrol but also regulate the dynamics of secondary structures during the process of catalysis as well as inhibition. Moreover, interaction with the carbonyl group of Ile-323 is characterized to participate in a dual role of defining selectivity of inhibitors like DHBP and recognition of substrates. Therefore, interaction with these residues can be considered as an important factor in the observed CYP51 dependent mycobacterial growth inhibition.

Structural analysis of docking results indicates that compounds **5c**, **5d**, **5e**, and **5 h** are observed to be forming hydrogen bonds with Gln-72 while all remaining compounds are in non-polar carbon contact with this residue. There are crystallographic publications that report contribution of hydrophilic and/or charged groups of Gln-72 in the

stabilization of the complex of CYP51 with inhibitor DHBP (Eddine et al., 2008). Evidences from an experimental screening of numerous compounds identified that interaction with Gln-72 stabilize inhibitor 8 via its sulfonamide moiety (Chen et al., 2009). Compound 5c and 5d seem to be in polar interactions by forming hydrogen bonding interaction with backbone carbonyl of Met-433; whereas numerous other compounds from the series are in non-polar contact with it. Such interaction is crystallographically validated to stabilize CYP51 complexes with inhibitors including Estriol and fluconazole (Podust et al., 2004), BSPPA and EPBA (Podust et al., 2007) along with DHBP (Eddine et al., 2008). Screening data of Chen et al indicated active involvement of the side chain of residue Met-433 in the stabilization of enzyme-inhibitor complex (Chen et al., 2009). In view of the structural data obtained from molecular docking in combination of previous cryatallographic data discussed here, the possibility of the present compound via interaction with Gln-72 and Met-433 in poisoning CYP51 mediated biochemical reaction cannot be wholly dismissed.

3. Conclusion

The study results revealed that the suitability of newly synthesized pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene-hy-

drazinecarbothioamide derivatives (5a-k) as a potential anti-tubercular agent. It was also found that the substituents like bromo, nitro, and methyl present in 5b, 5c, 5d, 5e and 5f shows impressive anti-TB activity as compared to the other tested compounds, while compound 5a, 5 h, and 5i also show significant anti-TB activity. Amongest the tested panel of synthesized molecules, the compounds 5b, 5d, 5e, 5f and 5i demonstrated considerable free radical scavenging potential, whereas, the remaining compounds exhibited moderate antioxidant activity. Overall the structure activity relationship links the requirement of bromo, nitro and methyl substitution as a key substitute for the manifestation of anti-tubercular and antioxidant activity. All the synthesized compounds showed insignificant toxicity. Thus, by in silico investigation, the present investigation demonstrates the successful construction of a ligand based pharmacophore model for the inhibition of CYP51 in mycobacteria. Binding free energy values indicate that compounds from the present study can be potentially used as lead compounds for further developing effective CYP51 inhibitors. Based on in vitro observations and in light of the structural analysis of docked complex, we try to propose the possible mechanism of action of pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene-hydrazinecarbothioamide derivatives in mycobacterial CYP51 inhibition.

4. Experimental

4.1. Chemistry

All the melting points were determined in an open capillary tube and are uncorrected. The chemicals and solvents used were of laboratory grade and purified. Completion of the reaction was monitored by thin layer chromatography on the precoated sheet of silica gel-G (Merck, Germany) using UV lamp for detection. IR spectra were recorded using KBr pellets on an FTIR Schimadzu spectrophotometer. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in (DMSO)-d₆ with an Avance spectrometer (Bruker, Germany) at a 400-MHz frequency using TMS as an internal standard, chemical shifts are reported in parts per million and coupling constant in hertz (Hz). Multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), m (multiplet). Mass spectra were on an EI-Shimadzu QP 2010 PLUS GS-MS system (Shimadzu, Japan). Elemental analysis was performed on a Carlo Erba 106 Perkin-Elmer model 240 analyzer (Perkin-Elmer, USA) 4.1.1. General procedure for the synthesis of 5-(pyridine-4-yl)-1,3,4-oxadiazole-2(3 H)-thione (2)

A mixture of isoniazid (0.005 mol), and carbon disulfide (5 ml) in alcoholic KOH (20 ml, 10%) were refluxed for 12 h. After completion of the reaction (monitored by TLC) the solution was cooled at room temperature and poured into ice cold water and acidified with dil HCl. The solid product separated out was filtered and recrystallized from aqueous acetic acid as white crystals.

IR (KBr) υ cm⁻¹: 3273 (NH), 1610 (C = N), 1375 (C-O-C), 1282 (C = S); ¹H NMR (400 MHz, DMSO-d₆, TMS, δ , ppm):14.66 (s, 1H, NH),8.82 (d, J = 33 Hz, 2H, Ar-H),7.82 (d, J = 43 Hz, 2H,Ar-H).

4.1.2. General procedure for the synthesis of 1-(substituted phenyl)-2((5-(pyridin-4-yl))-1,3,4-oxadiazole-2-yl) thio)ethanone(4a-k)

A mixture of 2(0.015 mol), substituted phenacyl bromide (3a-k) (0.015 mol) and BEC (10 wt %) was stirred in PEG-400 at 70–80 °C for 2–3 hour. After completion of the reaction (monitored by TLC), the catalyst was separated by simple filtration and the reaction mixture was poured into ice cold water. After neutralization with dil. HCl solid separate out which was filtered and recrystallized by aq. acetic acid as pink colored crystals.

4.1.2.1. -(4-chlorophenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio) ethanone (4a). M.P. 131–133 °C; Yield,89%; IR (KBr, cm⁻¹): 3088 (Ar-H), 2959 (CH₂), 1678 (C = O), 1615 (C = N), 1312 (C = S), 1293 (C-O-C oxadiazole), 1185 (C-S-C);¹H NMR (400Mz, DMSO-d₆, TMS, δ , ppm): 8.81 (d, 2H, Ar-H), 8.08 (d, 2H, Ar-H),7.88 (d, 2H, Ar-H),7.67 (d, 2H, Ar-H),5.21 (s, 2H, CH₂); EIMS: 331[M+].

4.1.2.2. -(4-bromophenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio) ethanone (**4b**). M.P. 158–160 °C; Yield, 87%; IR (KBr, cm⁻¹): 3156 (Ar-H), 3092 (CH₂), 1672 (C = O), 1624 (C = N), 1332 (C = S), 1280 (C-O-C oxadiazole), 1192 (C-S-C); ¹H NMR(400 Mz, DMSO-d₆, TMS, δ , ppm): 8.97 (d,2H, Ar-H), 8.16 (d, 2H, Ar-H), 7.94 (d,2H, Ar-H),7.89 (d,2H, Ar-H),5.38 (s, 2H, CH₂); EIMS: 374 [M+].

4.1.2.3. -(4-nitrophenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio) ethanone (4c). M.P.136–138 °C;Yield, 90%;IR (KBr, cm⁻¹): 3148 (Ar-H), 3096(CH₂), 1689 (C = O), 1620 (C = N), 1315 (C = S), 1278 (C-O-C oxadiazole), 1150 (C-S-C); ¹H NMR (400Mz, DMSO-d₆, TMS, δ , ppm): 8.78 (d,2H, Ar-H), 7.96 (d, 2H, Ar-H), 7.72 (d, 2H, Ar-H), 7.56 (d, 2H, Ar-H), 5.12 (s, 2H, CH₂); EIMS: 342 [M+].

4.1.2.4. -(3-nitrophenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio) ethanone(**4d**). M.P. 129–131 °C;Yield, 89%; IR (KBr, cm⁻¹): 3130 (Ar-H), 3054 (CH₂), 1682 (C = O), 1627 (C = N), 1335 (C = S), 1240 (C-O-C oxadiazole), 1178 (C-S-C); ¹H NMR (400Mz, DMSO-d₆, TMS, δ , ppm): 8.92 (d, 2H, Ar-H), 8.12 (d, 2H, Ar-H),7.91 (d, 2H, Ar-H),7.78 (d,2H, Ar-H),5.30 (s, 2H, CH₂);EIMS: 342 [M+].

4.1.2.5. -phenyl-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)ethanone (4f). M.P. 158–160 °C; Yield, 87%; IR (KBr, cm⁻¹): 3040 (Ar-H), 2963 (CH₂), 1684 (C = O), 1636 (C = N), 1290 (C = S), 1194 (C-O-C oxadiazole), 1113 (C-S-C); ¹H NMR(400 Mz, DMSO-d₆, TMS, δ , ppm): 8.82 (d,2H, Ar-H), 8.28 (d, 2H, Ar-H), 7.79-5.08 (m,5H, Ar-H); EIMS: 297 [M+].

4.1.2.6. -(4-fluorophenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio) ethanone(**4** g). M.P. 125–128 °C; Yield, 89%;IR (KBr, cm⁻¹): 3128 (Ar-H), 3012 (CH₂), 1662 (C = O), 1631 (C = N), 1246 (C = S), 1379 (C-O-C oxadiazole), 1163 (C-S-C); ¹H NMR (400Mz, DMSO-d₆, TMS, δ , ppm): 8.92 (d, 2H, Ar-H), 8.54 (d, 2H, Ar-H), 7.58 (d, 2H, Ar-H), 7.32 (d, 2H, Ar-H), 5.28 (s, 2H, CH₂); EIMS: 315 [M+].

4.1.3. General procedure for the synthesis of 2-(1-(substituted phenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)ethylidene) hydrazinecarbothioamide (5a-k)

An equimolar quantity of 1-(substituted phenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)ethanone (**4a-k**) (1.00 mmol) and thiosemicarbazide (1.00 mmol) aredissolved in PEG-400 and stirred at 70–80 °C for 2–3 hrs in presence of catalytic amount of acetic acid (2–3 drops). Progress of the reaction was noticed by TLC technique. After completion of reaction, the reaction mixture was poured in ice-cold water. The separated solid was filtered by simple filtration method, wash with hot water, dried and recrystallized by aq. acetic acid to collect the final product (**5a-k**) in good yields.

4.1.3.1. -(1-(4-chlorophenyl)-2-((5-(pyridine-4-yl)-1,3,4-oxadiazole-2-yl) ethylidine) hydrazinecarbothioamide (5a). M.P.155–157 °C; Yield, 84%; IR (KBr cm⁻¹): 3415 (NH), 2924 (aliphatic C-H), 1618 (C = N), 1327 (C-S-C), 1074 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 11.83 (s, 1H, SH, enolic), 9.69 (s, 1H. NH, tautomeric), 8.76 (s, 1H, NH), 7.99-7.37 (m, 8H, Ar-H), 6.36 (s, 1H, H_a), 6.29 (s, 1H, H_b); ¹³C NMR (100 MHz, DMSO-d₆, δ , ppm): 178.40, 160.40, 155.06, 150.10, 149.57, 137.21, 136.13, 132.92, 132.43, 131.88, 129.79, 129.07, 128.84, 121.28, 33.21; EIMS: 404 [M+]; Elemental Analysis. Calculated (found) for C₁₆H₁₃ClN₆OS₂: % C, 47.46 (47.42); H, 3.24 (3.28); N, 20.76 (20.73); S, 15.84 (15.88).

4.1.3.2. -(1-(4-bromophenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl) thio)ethylidene) hydrazinecarbothioamide (5b). M.P.163–165 °C; Yield, 87%; IR (KBr cm⁻¹): 3475 (NH), 3393 (NH), 2986 (aliphatic C-H), 1600 (C = N), 1294 (C-S-C),1082 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 11.54 (s, 1H, SH, enolic), 10.02 (s, 1H, NH, tautomeric), 8.72 (s, 1H, NH), 8.13-7.39 (m, 8H, Ar-H), 6.52 (s, 1H, H_a), 6.44 (s, 1H, H_b); ¹³C NMR (100 MHz, DMSO-d₆, δ , ppm): 178.61, 159.26, 151.20, 144.14, 136.54, 131.07, 130.24, 129.05, 128.61, 128.06, 127.3, 34.35; EIMS: 447 [M + 2]; Elemental Analysis. Calculated (found) for C₁₆H₁₃BrN₆OS₂: % C, 42.77 (42.74); H, 2.92 (2.95); N, 18.70 (18.73); S, 14.27 (14.25).

4.1.3.3. -(1-(4-nitrophenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl) thio)ethylidene) hydrazinecarbothioamide (5c). M.P.157–159 °C; Yield, 89%; IR (KBr cm⁻¹): 3455 (NH), 3091 (aromatic C-H), 2915 (aliphatic C-H), 1608 (C = N), 1292 (C-S-C), 1119 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 11.70 (s, 1H, SH, enolic), 9.81 (s, 1H. NH,

tautomeric), 8.31 (s, 1H, NH), 7.78-7.24 (m, 8H, Ar-H), 6.39 (s, 1H, H_a), 6.31 (s, 1H, H_b); 13 C NMR (100 MHz, DMSO-d₆, δ , ppm): 171.26, 155.72, 150.46, 141.86, 135.11, 130.92, 130.58, 130.01, 129.48, 128.88, 128.19, 126.97, 126.21, 32.86; EIMS: 415 [M+]; Elemental Analysis. Calculated (found) for C₁₆H₁₃ClN₇O₃S₂: % C, 46.26 (46.23); H, 3.15 (3.17); N, 23.60 (23.64); S, 15.44 (15.48).

4.1.3.4. -(1-(3-nitrophenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)

thio)ethylidene) hydrazinecarbothioamide (5d). M.P.160–162 °C; Yield, 89%; IR (KBr cm⁻¹): 3492 (-NH), 3112 (aromatic C-H), 2980 (aliphatic C-H), 1626 (-C = N), 1287 (C-S-C), 1089 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆, δ, ppm): 11.52 (s, 1H, SH, enolic), 9.92 (s, 1H. NH, tautomeric), 8.73 (s, 1H, NH), 7.89-7.07 (m, 8H, Ar-H), 6.42 (s, 1H, H_a), 6.37 (s, 1H, H_b); ¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): 164.89, 153.24, 149.69, 144.19, 142.47, 130.69, 130.14, 129.72, 128.96, 128.24, 127.35, 126.70, 126.25, 34.11; EIMS: 415 [M+]; Elemental Analysis. Calculated (found) for C₁₆H₁₃ClN₇O₃S₂: % C, 46.26 (46.23); H, 3.15 (3.18); N, 23.60 (23.62); S, 15.44 (15.48).

4.1.3.5. -(1-(3,4-dichlorophenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)ethylidene) hydrazinecarbothioamide (5e). M.P. 188–190 °C; Yield, 83%; IR (KBr cm⁻¹): 3518 (NH), 3087 (aromatic C-H), 2972 (aliphatic C-H), 1598 (C = N), 1322 (C-S-C), 1082 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 11.87 (s, 1H, SH, enolic), 9.88 (s, 1H.

NH, tautomeric), 8.72 (s, 1H, NH), 7.92-7.28 (m, 7H, Ar-H), 6.56 (s, 1H, H_a), 6.38 (s, 1H, H_b); ¹³C NMR (100 MHz, DMSO-d₆, δ , ppm): 167.31, 163.86, 161.19, 156.71, 151.01, 145.55, 138.46, 136.24, 130.76, 130.29, 124.34, 35.17; EIMS: 439 [M+]; Elemental Analysis. Calculated (found) for C₁₆H₁₂Cl₂N₆OS₂: % C, 43.74 (43.77); H, 2.75 (2.78); N, 19.13 (19.17); S, 14.60 (14.57).

4.1.3.6. -(1-phenyl-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-. yl)thio) ethylidene)hydrazinecarbothioamide (5f)

M.P.177–179 °C; Yield, 86%; IR (KBr cm⁻¹): 3469 (NH), 3086 (aromatic C-H), 2967 (aliphatic C-H), 1618 (C = N), 1269 (C-S-C), 1091 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 11.54 (s, 1H, SH, enolic), 9.84 (s, 1H. NH, tautomeric), 8.66 (s, 1H, NH), 8.44-7.22 (m, 9H, Ar-H), 6.64 (s, 1H, H_a), 6.58 (s, 1H, H_b); ¹³C NMR (100 MHz, DMSO-d₆, δ , ppm): 168.12, 155.72, 150.42, 145.87, 136.57, 132.41, 130.69, 129.28, 128.71, 128.02, 126.86, 30.89; EIMS: 370 [M+]; Elemental Analysis. Calculated (found) for C₁₆H₁₄N₆OS₂: % C, 46.26 (46.23); H, 3.15 (3.18); N, 23.60 (23.63); S, 15.44 (15.41).

4.1.3.7. 2-(2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)-1-(p-tolyl) ethylidene)hydrazinecarbothioamide (5 g). M.P.172–174 °C; Yield, 85%; IR (KBr cm⁻¹): 3490 (NH), 3078 (aromatic C-H), 2989 (aliphatic C-H), 1592 (C = N), 1278 (C-S-C), 1086 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 11.68 (s, 1H, SH, enolic), 9.76 (s, 1H. NH, tautomeric), 8.81 (s, 1H, NH), 7.82-7.27 (m, 8H, Ar-H), 6.49 (s, 1H, H_a), 6.43 (s, 1H, H_b), 2.34 (s, 3H, -CH₃); ¹³C NMR (100 MHz, DMSO-d₆, δ , ppm): 170.20, 155.71, 150.39, 142.86, 141.22, 132.19, 130.46, 129.72, 128.96, 128.24, 127.35, 126.70, 126.25, 34.11, 20.51; EIMS: 384 [M+]; Elemental Analysis. Calculated (found) for C₁₇H₁₆N₆OS₂: % C, 53.11 (53.13); H, 4.19 (4.16); N, 21.86 (21.89); S, 16.68 (16.69).

4.1.3.8. 2-(1-(4-fluorophenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl) thio)ethylidene)hydrazinecarbothioamide (5 h). M.P. 160–162 °C; Yield, 82%; IR (KBr cm⁻¹): 3487 (NH), 3055 (aromatic C-H), 2941 (aliphatic C-H), 1605 (C = N), 1290 (C-S-C), 1118 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 11.68 (s, 1H, SH, enolic), 9.92 (s, 1H, NH, tautomeric), 8.79 (s, 1H, NH), 7.7.7.39 (m, 8H, Ar-H), 6.61 (s, 1H, H_a), 6.49 (s, 1H, H_b); ¹³C NMR (100 MHz, DMSO-d₆, δ , ppm): 169.84, 164.54, 161.19, 154.36, 150.18, 147.96, 130.27, 129.75, 126.55, 125.90, 124.93, 122.14, 120.68, 32.26; EIMS: 388 [M+]; Elemental Analysis. Calculated (found) for C₁₆H₁₃FN₆OS₂: % C, 49.47 (49.44); H, 3.37 (3.35); N, 21.64 (21.67); S, 16.51 (16.49).

4.1.3.9. -(1-(3-chlorophenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl) thio)ethylidene) hydrazinecarbothioamide (5i). M.P. 183–185 °C; Yield, 81%; IR (KBr cm⁻¹): 3463 (NH), 3077 (aromatic C-H), 2956 (aliphatic C-H), 1624 (C = N), 1287 (C-S-C), 1091 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 11.69 (s, 1H, SH, enolic), 9.72 (s, 1H. NH, tautomeric), 8.85 (s, 1H, NH), 7.88-7.16 (m, 8H, Ar-H), 6.76 (s, 1H, H_a), 6.51 (s, 1H, H_a); ¹³C NMR (100 MHz, DMSO-d₆, δ , ppm): 164.38, 161.24, 158.46, 150.61, 144.32, 137.87, 136.07, 131.25, 130.68, 129.77, 126.17, 122.42, 31.66; EIMS: 404 [M+]; Elemental Analysis. Calculated (found) for C₁₆H₁₃ClN₆OS₂: % C, 47.46 (47.49); H, 3.24 (3.28); N, 20.76 (20.74); S, 15.84 (15.88).

4.1.3.10. -(1-(4-methoxyphenyl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)ethylidene) hydrazinecarbothioamide (5j). M.P. 181–183 °C; $Yield, 82%; IR (KBr cm⁻¹): 3510 (NH), 3106 (aromatic C-H), 2966 (aliphatic C-H), 1612 (C = N), 1329 (C-S-C), 1118 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆, <math>\delta$, ppm): 11.84 (s, 1H, SH, enolic), 9.91 (s, 1H. NH, tautomeric), 8.79 (s, 1H, NH), 7.99-7.03 (m, 4H, Ar-H), 6.62 (s, 1H, H_a), 6.49 (s, 1H, H_b), 3.46 (s, 3H, -OCH₃); ¹³C NMR (100 MHz, DMSO-d₆, δ , ppm): 167.57, 161.42, 160.38, 158.20, 148.94, 141.64, 130.88, 129.16, 128.72, 122.30, 118.85, 58.60, 32.56; EIMS: 400 [M+]; Elemental Analysis. Calculated (found) for C₁₇H₁₆N₆O₂S₂: % C, 50.98 (50.96); H, 4.03 (4.05); N, 20.98 (20.99); S, 16.01 (16.03). 4.1.3.11. -(1-([1,1'-biphenyl]-4-yl)-2-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)ethylidene) hydrazinecarbothioamide (5k). M.P. 182–184 °C; Yield, 84%; IR (KBr cm⁻¹): 3498 (NH), 3078 (aromatic C-H), 2990 (aliphatic C-H), 1631 (C = N), 1294 (C-S-C), 1121 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 11.82 (s, 1H, SH, enolic), 9.76 (s, 1H. NH, tautomeric), 8.51 (s, 1H, NH), 8.34-7.26 (m, 13H, Ar-H), 6.41 (s, 1H, H_a), 6.36 (s, 1H, H_b); ¹³C NMR (100 MHz, DMSO-d₆, δ , ppm): 165.47, 153.35, 149.89, 146.17, 144.38, 141.76, 134.03, 130.46, 130.11, 129.72, 129.34, 128.23, 128.02, 127.62, 127.19, 126.86, 126.22, 30.89 ; EIMS: 370 [M+]; Elemental Analysis. Calculated (found) for C₂₂H₁₈N₆OS₂: % C, 46.26 (46.23); H, 3.15 (3.18); N, 23.60 (23.57); S, 15.44 (15.42).

4.2. Biology

4.2.1. Evaluation of anti-tubercular activity

The mycobacterium strain Mtb (MTCC 300) was obtained from Microbial Type Culture and Gene Bank, Institute of Microbial Technology, Chandigarh (PB), India, and was sub-cultured and sustained on to Lowenstein Jensen media as illustrated previously (Chaturvedi et al., 2007). The sensitivity of test Mtb (MTCC 300) strain towards the synthesized compounds (5a-k) exhibited by agar diffusion technique (Kamble et al., 2014a,b). Stock solution (0.1, 0.5, and 1.0 mg/mL) of the individual compounds were prepared in dimethyl sulfoxide (DMSO). A sterile borer of 7-mm diameter was used to bore holes into the inoculums-seeded solidified Middlebrook 7H9 agar. A 30µL volume of individual compounds was loaded into the labeled well in the prepared media plate using a sterile pipette. The test was executed in three similar experiments. The plates were put up in the refrigerator for prediffusion of the sample and incubated at 37 °C for 48 h. The growth of the tested organisms was observed after the incubation of 48 h, and the diameter of inhibition of zone was measured. The antimycobacterial activity of Rifampicin (a standard antitubercular drug) was also demonstrated at the same time.

4.2.2. Resazurin microtiter assay (REMA) plate method for determination of MIC

Susceptibility of multidrug resistance Mtb (MTCC 300) was estimated against synthesized compounds by Resazurin microtiter assay (REMA). The REMA plate assay was carried out in an identical fashion as depicted earlier (Taneja and Tyagi, 2007) with slight modification. Prior to the experiment, a stock solution of the resazurin sodium salt powder (Himedia, India) was prepared at 0.02% (w/v) in distilled water, sterilized by filtration, and stored at 4 °C for up to one week. The inoculums were prepared from fresh Middlebrook 7H9 broth supplemented with 0.1% casitone, and 0.5% glycerol and supplemented with oleic acid, albumin, dextrose, and catalase. Briefly, all perimeter wells of the 96-well microtiter plate (Becton Dickinson, Falcon) were filled with the sterile deionized freeze cold water to reduce evaporation of medium in the left-over wells during incubation. Remaining wells are filled with 100 µL Middlebrook 7H9 broth. And serial two-fold dilutions of each drug were prepared directly in the plate. 100 µL of inoculums was added to each well. The plates were sealed with a plastic tape and incubated at 37 °C. After seven days of incubation, 30 µL of resazurin solution was added to each well, and the plate was re-incubated overnight. The bacterial growth results in the reduction of resazurin which indicate the change in colour from blue to pink. The change in the colour from blue to pink indicates the growth of bacteria. The MIC was calculated as the lowest drug concentration which prevents colour change from blue to pink.

4.2.3. Antioxidant activity

In this study, we screened *in vitro* DPPH (1,1-diphenyl-2-picryl-hydrazil), OH (hydroxyl) and SOR (superoxide anion) radical scavenging assay to check the antioxidant potential of the newly synthesized compounds (**5a-k**) by using the spectrophotometric methods. Ascorbic acid was used as standard and the results are summarized in Table 2.

4.2.3.1. DPPH scavenging activity. DPPH free radical scavenging activity was carried out as per the previously reported method (Bandgar et al., 2012). In brief the reaction mixture contains an equal volume of DPPH solution $(10^{-4}$ M, in absolute ethanol) with individual concentrations (100 μ M) of newly synthesized compounds. After incubation (30 min) at room temperature, the absorbance was measured spectrophotometrically at 517 nm.

4.2.3.2. Hydroxyl radical (OH) scavenging activity. OH radicals were generated by using the Fenton reaction system (Aksoy et al., 2013). The reaction cocktail contained $60 \,\mu\text{L}$ of $1 \,\text{mM}$ FeCl₃, $90 \,\mu\text{L}$ of 1, $10 \,\mu\text{m}$ phenanthroline, 2.4 ml 0.2 M phosphate buffer (pH 7.4), $150 \,\mu\text{L}$ of 0.17 M H₂O₂ and 100 μ M of individual synthesized compound solution. Adding H₂O₂ initiated the reaction. After the 5 min incubation at room temperature, the absorbance of the mixture was observed spectrophotometrically at 412 nm.

4.2.3.3. Superoxide anion radical (SOR) scavenging assay. SOR scavenging activity was carried out as per the previously reported method (Liang et al., 2014). The reaction mixture contained 1 mL of NBT (300 μ M), NADH (936 μ M) respectively and the individual concentrations of synthesized compounds (100 μ M) in Tris-HCl buffer (100 mM, pH 7.4). The reaction was started by adding PMS (120 μ M) to the mixture. The reaction cocktail was incubated at 25 °C for 5 min and the absorbance was measured at 560 nm.

The percentage activity of DPPH, OH, SOR radical scavenging activity was calculated using following equation.

Activity(%) =
$$1 - \frac{T}{C} \times 100$$

Where T = Absorbance of the test sample and C = Absorbance of the control sample.

4.2.4. Hemolytic activity

In vitro hemolytic activity of pyridin-4-yl-1,3,4-oxadiazol-2-yl-thioethylidene-hydrazinecarbothioamide derivatives (5a-k) were determined as per the previous reported method (Rajput et al., 2013). Human red blood cells were used for determining hemolytic activity. In brief, fresh human erythrocytes were collected in the tubes containing 2 mg/mL of EDTA. The erythrocytes were harvested by centrifugation (Eppendorf Microcentrifuge 5418) for 10 min at 2000 \times g at 20 °C. Plasma was discarded and washed thrice with phosphate buffer saline (PBS). Afterward, the PBS was added to the pellet to achieve 10% (v/v)erythrocytes/PBS suspension. 10% suspension was diluted 1:10 in PBS. From each suspension, 100 µL was added in triplicate to 100 µL of individual concentrations of compounds (5a-k) derivatives (5 mg/mL) in the same buffer in tubes. The tubes were incubated for 1 h at 37 °C and centrifuged for 10 min at 2000 \times g at 20 °C. The 150 μL supernatant was taken into a microtiter plate and the absorbance was measured at 540 nm by using thermo make automatic ex-microplate reader (M 51118170). Triton X-100 (1%, w/v) was used as a positive control. The percentage of hemolysis was calculated by using the following formula and results are described graphically in Fig. 4.

% Hemolysis =
$$\frac{Testcompound treatedsample-Buffer treated sample}{1\% titronX100 treatedsample - Buffer treatedsample} X 100$$

4.2.5. Molecular modeling/docking study

4.2.5.1. Pharmacophore probing for target identification. Pharmacophore matching approach was utilized to identify targets for novel synthetic derivatives using PharmMapper server. Initially, compounds were obtained in sdf format to upload to PharmMapper server. Multiple conformers, but not more than 300, were allowed to be generated. All available protein targets were utilized for pharmacophore mapping in

this study. Rest of parameters was set to default values.

4.2.5.2. Molecular docking. Already standardized molecular docking protocol was used in this study that is described in detail elsewhere Gacche et al. (2015). AutoDock 4.2 was used via the PyRx interface for molecular docking procedure (Huey et al., 2007). Following section briefly summarizes the procedure.

4.2.5.3. Target preparation. The 3D structural coordinates of enzyme CYP51 (PDBID 2VKU) [Eddine et al., 2008] was downloaded from Protein Data Bank. The model coordinates file from database represents monomer that was co-crystallized with a Heme prosthetic group (HEM) along with numerous molecules of its sterol substrate mimic 4,4'dihydroxybenzophenone (DBE) and various sulfate ions (SO4). As per the requirement of AutoDock, the PDB file was converted to pdbqt format using Make macromolecule command from PyRx.

4.2.5.4. Compounds. 2D structures of all pyridin-4-yl-1,3,4-oxadiazol-2-yl-thio-ethylidene-hydrazinecarbothioamide derivatives (5a-k) were drawn in ChemDraw[®] 8.0 (CambridgeSoft, Cambridge, MA, USA) and their SMILES were obtained. Subsequent to this step, FROG2 server (Miteva et al., 2010) was employed to generate 3D conformers of these compounds in sdf format. Open Babel utility in PyRx environment was employed to import ligand molecules in sdf format for subsequent energy minimization using the UFF force field. Molecules were minimized for over 200 steps applying a conjugate gradient optimization algorithm, updating the molecules at every step.

4.2.5.5. Testing validity of AutoDock 4.2 and virtual screening. The validity of a docking system can be checked by testing the ability of a docking program to reproduce the experimental binding mode of a ligand. Root Mean Square Deviation (RMSD) value of the predicted poses to experimentally verified pose is calculated following docking experiment. As the RMSD value indicates the measure of spatial similarity between two structures, the prediction of a binding mode is considered as successful if the RMSD value is typically found to be less than 2.00 Å (Kamble et al., 2016). To obtain the grid file, Auto-grid program was utilized. In order to cover entire active site, the affinity grid of $50 \times 50 \times 50$ points was set using the spacing of 0.375 Å. The conformational search for obtaining optimal binding pose was carried out using the Lamarckian genetic algorithm. Each Lamarckian job was set to have 10 runs, restricting the initial population to 150 structures. The maximum number of energy evaluation and generation were set to 27,000. The single top individual was allowed to survive the next generation, the rate of gene mutation and crossover was set to 0.02 and 0.8 respectively; the rest of parameters were set to default values. The final structures were clustered according to native autodock scoring function. The top ranked conformations of each ligand were selected. RMSD value of 0.77 Å was obtained from the docking experiment of crystallographic ligand DBE back in the ligand binding site of CYP51. This value indicates that the predicted binding mode is nearly identical to the X-ray crystallography conformer. The same set of parameters was used for virtual screening of synthesized compounds.

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Optical Study of Electrodeposited Vanadium Oxide Thin Films: Effect of Deposition Time

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ABSTRACT

Vanadium oxide thin films were prepared by potentiostatic mode of electrodeposition method. X-ray diffraction study confirms formation of vanadium oxide thin film. Surface morphological study was carried out with the help of Scanning Electron Microscopy. Structural and morphological analyses revealed that the deposited vanadium oxide is polycrystalline in nature with porous nanostructure. The effect of deposition time on optical properties was studied by means of UV-Visible absorption spectroscopy. The UV-Visible absorption spectroscopy reveals that the films deposited at lower deposition times show a relatively low degree of optical absorption, while the spectral absorbance of the films increases with the increase in deposition time. From Tauc's plot, the calculated values of forbidden energy gap E_g vary from 2.33 eV to 2.54 eV.

Keywords: Electrodeposition, Vanadium oxide, thin films, UV-Visible absorption spectroscopy, forbidden energy gap

Introduction:

Vanadium oxides tuning their phase from semiconductor to metal and hence they have flexibility to tune electrical resistivity and optical absorbance. Due to this researchers have taken efforts to use vanadium oxides in variety of applications like optical switching, high capacity lithium batteries, and smart windows for solar cell and optoelectronic devices [1-4]. Vanadium pentoxide (V₂O₅) is the most stable vanadium oxides and because of orthorhombic structure it exhibits anisotropic electric and optical properties [5-6]. The optical properties of vanadium oxide thin films are generally depending upon films crystalline nature, surface morphology and thickness etc. So, basically all these things are connecting to numerous synthesis parameters.

Researcher across globe made efforts to optimize the deposition parameters to receive best quality film with superior phase transition performance, through some physical methods, like magnetron sputtering, molecular beam epitaxy (MBE), sol gel, pulsed laser deposition (PLD) and post annealing [7-10]. But, preparation of vanadium oxide thin film by physical method requires highly sophisticated instruments. Also, maintaining the experimental conditions during the preparation is a hard task. So, the alternative way is to use chemical methods for synthesis of vanadium oxide thin films. Most preferred chemical methods includes electrochemical deposition [11], chemical vapour deposition [12], hydrothermal growth [13] and sol–gel [14] etc. Amongst chemical methods, electrodeposition has some special advantages over others like easy synthesis, not required sophisticated instruments etc.

Bahgat and et al. [15] have reported electrical and optical properties of highly oriented nanocrystalline vanadium pentoxide. They have reported direct and indirect band gap of vanadium oxide thin films as 2.22 eV and 0.27 eV, respectively. Dultsev and et al. [16] have reported structural and optical properties of vanadium pentoxide films prepared by sol-gel method. They have reported that thickness of film affects the optical band

gap energy of vanadium oxide films. The shift of the optical band gap is assigned to change in the stoichiometric composition of the film.

In this paper we present an inexpensive and easy-to-process electrodeposition method to produce vanadium oxide thin film. An effort has been taken to study effect of deposition time on optical properties of electrodeposited Vanadium Oxide thin films.

2. Experimental details:

2.1 Film deposition:

We have deposited vanadium oxide thin films using two electrode systems. In two electrode system of electrodeposition, working electrodes were stainless steel (SS304) and ITO coated glass substrate and counter electrode was graphite. The deposition bath was maintained at constant temperature of 333 K. We have prepared a deposition bath consisting of vanadyl sulphate for the electrodeposition of vanadium oxide thin film electrodes on stainless steel and ITO coated glass substrates. The pH of the bath was adjusted by adding few drops of concentrated HNO3. To obtain good quality of vanadium oxide thin film, we have optimized preparative parameters like precursor concentration, deposition potential and temperature. All other rest of the deposition parameters are kept constant during the experiment, mentioned in Table1. After deposition films were rinsed with distilled water to remove excessive growth of the film and kept for drying in air. The dried film is used for characterizations.

ruble r. optimized parameters					
Details	Optimized values				
Mode	Electrodeposition				
Deposition Potential	1.5 V				
Bath composition	0.05 M VOSO4.H2O + few drops of				
	concentrated HNO3				
рН	~ 3				
Deposition bath	Aqueous				
(medium)					
Deposition time	(a) 2 min; (b) 4 min; (c) 6 min.				
Temperature	333 K				
Substrate	Stainless steel and ITO coated glass				

Table 1: Optimized parameters

2.2 Characterization techniques:

Crystal structure of the electrodeposited vanadium oxide thin films was studied by using XRD in the range of diffraction angle 2θ from 20–80° by using Rigaku D/max 2550Vb+ 18 kw with Cuk_a diffractometer. The SEM images were used to study the surface morphology of the vanadium oxide thin film. UV-Visible absorption study of vanadium oxide thin films was studied by UV-Visible absorption spectrometer.

3. Result and discussion

3.1 X-Ray diffraction study:



Figure 1: XRD pattern of electrodeposited vanadium oxide thin film deposited at 6 min.

Figure 1 illustrates XRD pattern of vanadium oxide thin film deposited at 6 min. The XRD pattern exhibited four broad peaks, which appear at 20 values of 34°, 44°, 50° and 65°. The diffraction peaks matches with the standard data (JCPDS: 41-1426). According to the standard diffraction data (JCPDS: 41-1426), these diffraction peaks correspond respectively to the (022), (114), (062) and (241) planes of an orthorhombic structure of vanadium oxide. From Figure 1, it is observed that the deposited vanadium oxide is in polycrystalline in nature. The electrodeposited vanadium oxide thin film does not show any additional peaks, which indicates no secondary phase was formed. The average crystallite size of the vanadium oxide thin film was estimated from the full width at half maximum (FWHM) according to the (062) plane using Debye- Scherrer equation (1) [17]:

$$D = \frac{0.9\lambda}{\beta.\cos\theta} - \dots - (1)$$

Where, λ is the X-ray wavelength, β is the full width at half maximum of the XRD peak and θ is the Bragg diffraction angle. The calculated value of crystallite size was found to be 10 nm.

3.2 Surface morphological study:



Figure 2: SEM images of electrodeposited vanadium oxide thin films for film deposited at a) 2 min; b) 4 min and c) 6 min.

The surface morphologies of the vanadium oxide thin films obtained with different deposition times at 333 K were determined by using scanning electron microscopy (SEM) and are shown in Fig. 2. When the SEM images of the films were examined, it was observed that as electrodeposition time increased from 2 min to 6 min, the number of coalescence in the film increased and further surface area of substrate covered. At the same time as, it was observed that because of the clusters collections (ion-by-ion mechanism) and clusters growth (cluster-by-cluster mechanism) on the surface of substrate a porous structure formed. These results are in good agreement with the literature. Guneri and et al [18] have reported that effect of deposition time on structural, electrical, and optical properties of SnS thin films deposited by chemical bath deposition. They reported that as deposition time increases the number of aggregations in the film increased and a more homogeneous structure formed.

3.3 UV-Visible absorption spectroscopy:

The spectral absorbance characteristics of electrodeposited vanadium oxide thin films at different deposition times are shown in Figure 3 (A). The curves indicate that the films deposited at lower deposition times show a relatively low degree of optical absorption, while the spectral absorbance of the films increases with the increase in deposition time. The spectral characteristic curves show that the optical absorption decreases with increase in wavelength. The effect of the deposition time on the forbidden energy gap values was calculated by the optical absorbance measurements. The optical absorbance A and the optical absorption coefficient were determined by measuring log (1/T) and using the formula;

Where T is the transmittance and d is the film thickness. Fig. 3 (A) shows the optical absorbance of the films deposited at a) 2 min, b) 4 min and c) 6 min. Fig. 3(B) shows the Tauc's plot of the films deposited at a) 2 min, b) 4 min and c) 6 min. The optical absorption coefficient α as a function of photon energy hv is given as

$$\alpha h \nu = B \left(h \nu - E_g \right)^n \dots (3)$$

where n is an exponent, v is the frequency of the incident photon, h is the Plank's constant, B is a constant, and Eg is the forbidden energy gap of the material. The exponent n can take the values 2, 3, ½ and 3/2 for indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively [19-22]. Plotting of $(\alpha hv)^2$ versus (hv) and extrapolating to $(\alpha hv)^2=0$ gives the value of E_g . The calculated E_g values vary from 2.33 eV to 2.54 eV.





Figure 3: (A) UV-Visible absorption spectra of films deposited at a) 2 min, b) 4 min and c) 6 min; (B) Tauc's plot for films deposited at a) 2 min, b) 6 min and c) 8 min;

Conclusions

In summary, we have successfully deposited vanadium oxide thin film by low cost and simple method i.e. potenetiostatic mode of electrodeposition. By varying deposition time between 2 min to 6 min, may alter the structural, morphological and optical properties of vanadium oxide thin films. XRD study confirmed the polycrystalline nature of vanadium oxide thin film. SEM images showed that a porous structure formed due to two types of mechanism as ion-by-ion mechanism and cluster-by-cluster mechanism on the surface of substrate. From UV-Visible absorption study it is observed that the spectral absorbance of the films increases with the increase in deposition time.

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Review on Ferrites : Structural Magnetic and Electrical Properties

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ABSTRACT

Researchers are taking extraordinary interest in the preparation and characterization of lithium ferrites due to their wide variety of applications in many fields. lithium ferrites are a class of smooth magnetic materials which have excellent electric, magnetic and optical properties. The properties of lithium ferrites include high cost of resistivity, Permeability, permittivity, saturation magnetization, low power losses and coercivity. The above referred to wonderful features of lithium ferrites make them appropriate for the use in various packages. In medical field these ferrites are used for treatment cancer and MRI. Lithium ferrites are also utilized in electronic applications.

Keywords : Treatment Cancer, MRI. Lithium, Permeability, Permittivity, Saturation Magnetization, Low Power Losses

Introduction:

Ho doped Lithium-Zink ferrites and its dielectric behavior at high frequency and magnetic properties are studied[1] sol-gel synthesized CoFe2-xHoxO4 nano ferrites its structural and physical properties were studied [2] The change in magnetic and structural properties of Gadolinium doped cobalt-zinc ferrites governed by spin rotations and domain wall movement were explained [3] Co_{0.5}M_{0.3}7Cu0.13Fe₂O₄ ferrites were studied for its structural, magnetic and electrical behavior, [4] By aloe vera plant-extracted ferrite nanoparticles of MFe₂O₄, M = Ni, Co, Mn, Mg, Zn are prepared [5] zinc ferrite nanoparticles synthesized from Sugarcane juice and its application as degradation of mixed dyes and antibacterial activities are studied[6] Electric and dielectric properties of Neodymium substituted manganese -nikel-zinc are explained[7]

Metal ions substituted cobalt ferrites synthesized by sol–gel auto-combustion route were studied for magnetic properties [8] Nanocrystalline Mn-Zn Ferrites synthesized by microwave assisted method were studied, [9] NiCr_xFe_{2-x}O₄ ferrites were studied for its optical, electric, mechanical, and Magnetic properties, [10]

Graphical Abstract: Study of Ferrites



The remanent magnetization and coercivity of the Nanocomposites of hexaferrite became 2 and a 2.5 instances better, respectively by means of adding BaFe_{11.7}A_{10.15} Zn_{0.15}O₁₉ section. The Cole-Cole plots of the nanocomposite x=0.4 at the chosen temperatures suggests two successive semicircles at all the selected temperatures. The First low frequencies semicircle elucidates the contribution of the grain boundary and the second, at excessive frequencies, offers the contribution of grain to conduction manner. Multilateral applications for change spring magnets can be manufactured the usage of the ones nanocomposites. These hexaferrite was fabricated by using the citrate–nitrate auto combustion method [11]

Nanoparticles of roughly spherical in shape with size in range of 10–15 nm, are estimated from X-ray diffraction and TEM micrographs with increase in crystal size coresivity increase and decreases with decreases in size of the magnetic particles. The variation in valance states Mn and Fe atoms in Zn_xMn_{1-x}Fe₂O₄ is studied. The magnetic properties of Zn_xMn_{1-x}Fe₂O₄ will degrade with loss of Zinc is observed. Due to the combined effects of oxygen partial pressure and temperature in the region of 450°c the phase is not stable for Zn_xMn_{1-x}Fe₂O₄.[12]

Humaira Anwar et al. studied, Structural, Electrical and Dielectric Parameters of Mn-Zn Nano Ferrites prepared by the chemical co-precipitation method, changes due to increase of temperature, while the resistivity of ferrite deceases with increases of temperature. Activation energy of the samples was found to be in the range of 0.70 to 0.77eV. Due to agglomeration in of Mn-Zn ferrites Porosity, crystallite Size, resistivity increases and density decreases with increase in temperature. Maximum weight loss is observed up to temperature of 518 K. The dielectric constant decreases rapidly with increase in frequency [13] It is seen that the coercivity value of the all of nanocomposites are decrease than natural hard Phase and for one-pot synthesized nanocomposites, are greater than pure smooth phase. The coercivity reduction in composites organized by using physical Mixing approach is lots astounding and for smooth phase content material better than 50 %. It is decrease than natural pure phase. For high values of the smooth phase, the exchange Force at the soft grains is weakened and dipolar interaction among pure phase.Moments becomes enormous. So, the opposite domains inside the smooth section with Low nucleation area may be nucleated without problems. This could lower the coercivity Of composite [14]. In addition, whilst the importance of the reverse field is Progressively expanded, the domain partitions of the pure phase flow in the direction of the Interface between the soft and hard phases and could invade into the hard phase Area, which leads to the irreversible magnetization reversal of the hard section. Therefore neighboring grains could purpose additional demagnetizing effect and Bring about the reduction of average coercivity of the composite, as compared to the Pure hard phase [14]. Shuli He et al. explained Maximized precise loss of electricity and intrinsic loss strength drawing near theoretical limits for alternating-current (AC) magnetic-subject heating of nanoparticles are said. That is performed by way of engineering the powerful Magnetic anisotropy barrier of nanoparticles through alloying of hard and soft ferrites. 22 nm Co0.03Mn0.28Fe2.7O4/SiO2 nanoparticles attain a precise loss power price of 3417 W g⁻¹ metallic at a area of 33 kA m⁻¹ and 380 kHz [15]. Biocompatible Zno.3Fe2.7O4/SiO2 nanoparticles gain particular Loss energy of 500 W g-1Steel and intrinsic loss energy of 26.8 nHm² kg⁻¹[15]. At field parameters of 7 kA m⁻¹ and 380 kHz, below the medical safety Limit. Magnetic bone cement achieves heating good enough for bone Tumor hyperthermia, incorporating an ultralow dosage of just 1 wt% of nanoparticles[15]. In cell hyperthermia experiments, these nanoparticles exhibit excessive cellular death price at low field parameters. Zn0.3Fe2.7O4/SiO2 nanoparticles show cellular viabilities above ninety seven% at concentrations up to 500 µg mL⁻¹ inside forty eight h, suggesting toxicity lower than that of magnetite[15]. Cristina Ileana Covaliu et al. reported that, biomedical applications magnetic nanoparticles coated with polysaccharide polymers were studied and these microorganisms of as prepared hybrid materials show the nontoxic properties. The magnetic properties of all ferrite nanoparticles and hybrid materials have Shown the super paramagnetic normal behavior, that the saturation magnetization (Ms) values are much decrease than the ones of the corresponding "bulk" ferrite. The lower of Ms might be because of the decrease of the particle sizes[16]. The weak hysteresis might be assigned to the small length of the nanoparticles having a single magnetic domain. In addition, taking into account that at the maximum Losses (eddy currents losses), these substances being aggressive for some medical fields[16]. All Hybrid materials exhibit a decrease saturation magnetization and a decrease susceptibility than the uncoated ferrite nanoparticles due to the decreased content of the magnetic aspect within the composite material however the values are enough excessive for medical programs [16]. Cristina Ileana Covaliu also reported the cobalt ferrite nanoparticles (CoFe₂O₄) have a different Conduct: its mixture with polyvinylpyrrolidone (PVP) increases now not only the saturation magnetization, but additionally the hysteresis parameters (coercivity and remanence). An rationalization may be the huge agglomeration of the magnetic nanoparticles that allows the multidomain magnetic structure. He also reported the cobalt ferrite nanoparticles with sizes less than 10 nm have low magnetic reaction skills considering the biomedical applications[17]. As zinc concentration increases the microstructure and relaxation frequency of as synthesized Mn–Zn ferrites changes there is tendency to increase the grain size as the Zn concentration increases, the study also reveals that the average grain sizes of microstructures increases with increasing dwell time[18] **References:**

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Hydroponics for green fodder production, a need of time

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Abstract

Now a days there is scarcity of fodder due to unpredictable nature, either drought or wet conditions of environment. Farmers are always worried about agriculture along with agricultural practices, they are also depending on cattle as well as dairy farming to meet day to needs. Green fodders are staple feed for these animals. It is well accepted fact that feeding dairy animals is incomplete without including green fodder in their diet. Some of the farmers are not aware regarding the importance of green fodders and hydroponic technique. Dairy animals producing 12-15 liters milk per day can be maintain by feeding green fodders. Therefore for economical and sustainable dairy farming fodder production round the year is highly essential. In order to meet the increasing demand of fodder the best alternative is hydroponic technique.

Key words: Hydroponics, green fodders, staple food, dairy farming.

Introduction

It is technique of growing terrestrial plants in a nutrient solution. It is subset of hydro culture. It is a method of growing plants without soil by using mineral nutrient solution in a water solvent. Terestrial plants grown with their roots exposed to the mineral solution. Hydroponic fodder systems are usually used to sprout cereal grains, such as corn, barley oats wheat, sorghum corn or legumes, such as alfa affa,,clover .Maize is the most commonly grown forage in India. The word hydroponic comes from Latin word meaning working water. It is art of growing plants without soil. Some hydrosystem are used in technique. Nutrient solution contains all macro and microelements. There are six types of hydroponic system, water culture, wick flow, drip, nutrient film technique, and aeroponic. Drip system is used here.

The earliest record of work on growing terrestrial plants without soil was in the 1627 book "Sylve Sylvrum' by Francis Bacon. (1929), William Fredrick Gericke of California University begin publically promoting that solution culture can be used for agricultural crop production¹. Two other scientists Dennist R. Hoagland and Danial I. Arnon from California university (1938) wrote classic agricultural bulletin, *The water culture method for growing plants without soil.*² There is record of crop plants growing by hydroponic technique (2017) from Canada. Canada had hundreds of acres of large scale commercial hydroponic green houses producing tomatoes, chillies and cucumbers.³

Objectives:

- 1. To know the importance of green fodder production technology to the layman.
- 2. To generate awareness about the need of this technique.
- 3. To train, to motivates, to develop skills in youth, farmers for production of green fodder.

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- 4. To develop entrepreneurship aspects.
- 5. To understand the economical and ecological scope of technology.
- 6. To develop opportunities to develop commercially variable hydroponic shades, supplying green fodder to the local market and implanting the practice in local communities.
- 7. To minimize use of fungicide and pesticide.
- 8. To preserve land and water conservation.

Material and Methodology:

The work is undertaken by creating Shade net (10 mtrs. by 10 mtrs.) hydroponic fodder system consist of a framework of shelves made up of PVC pipes on which plastic trays are stacked. After soaking the seeds overnight, a layer of seeds are kept moist, but not saturated. They are supplied with moisture via drip or spray irrigation. Holes in the trays facillate drainage and the waste water are collected in a tank. The seeds will usually sprout within 24 hours and in 5 to 8 days have produced a 6 to 8 inches high grass mat, after the mat is removed from the tray,



it can grow into feed mixer or be hand feed to livestock. There is minimal waste. These plastic trays are used for green fodder production. Mineral solutions are provided through drip for growing fodder. It contains all essential nutrients in liquid form. Maize a green fodder is developed especially in this project. We can also produce organic vegetables, crop plants. Commercially floriculture can be also achieved by using the technology.

How to Grow Hydroponic Fodder



Conclusion:

Dairy animals producing 12-15 liters milk per day can be maintain by feeding green fodders. Therefore for economical and sustainable dairy farming fodder production round the year is highly essential. In order to meet the increasing demand of fodder the best alternative is hydroponic technique. It is economical, pollution free, requires less water, provide sterile environment to the plants. It provides a best technique for liquid organic farming. It helps in commercial production of fodder. Nutritional value of green fodder is ideal as it provide high quality of protein, enzymes and vitamins, folic acids, antioxidents.It allows digestive system of animals to function with maximum efficiency Farmers, students, layman are aware regarding the

importance of green fodders and hydroponic technique. It is opportunity of self employment to the farmer.

Hydroponics farming can have a great future in India only if its value is known or understood by the Indians. Hydroponics culture has proved an alternative for raising fresh vegetables and impressive floriculture. As competition for land and water increases and feed prices continue to rise, green fodder could become a viable option for more livestock products.

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