

# NATURAL ACID CATALYZED SYNTHESIS OF SCHIFF BASE AND ITS STABILITY STUDIES WITH TRANSITION METAL COMPLEXES OF N'-(2-HYDROXYNAPHTHALENE - 1YL) METHYLENE) ISONICOTINOHYDRAZIDE BY $p^H$ METRICALLY.

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## ABSTRACT

The present article deals with synthesized ligand as Schiff base of N'-((2-hydroxynaphthalene-1yl) methylene) isonicotinohydrazide from 2- hydroxynaphthaldehyde & isonicotinic acid hydrazide by using gallic acid catalyst from green tea leaves. Gallic acid commonly present in different plant and fruit. Extraction method of gallic acid from green tea leaves has been simple heat reflux extraction method. Gallic acid is a polyphenol. Gallic acid possesses neuroprotective effect, anticancer, antioxidant and many medicinal properties. By using Gallic acid reaction completed in minimum time. Synthesize compound characterized by FTIR & <sup>1</sup>H-NMR analysis. the stability constant of proton-ligand and metal ligand have been determined by 10% Ethanol water mixture at 303<sup>0</sup>K by Bjerrum method as accepted by Calvin and Wilson by  $p^H$  metric method titration. To determine metal ligand stability constant (logK) and proton ligand stability constant ( $P^k$ ) value. It is observed that metal ion form 1:1 and 1:2 Schiff base complex of N'-((2-hydroxynaphthalene-1yl) methylene) isonicotinohydrazide. Also indicating the interaction between the transition metal ion and synthesize Schiff base ligand of N'-((2-hydroxynaphthalene-1yl) methylene) isonicotinohydrazide and also investigating the stepwise formation of complexes.

**Keywords:** Green tea leaves, 2- hydroxynaphthaldehyde, isonicotinic acid hydrazide, Schiff base, stability constant and  $p^H$  metric.

## Introduction

Isonicotinic acid hydrazide most important role in medicinal chemistry. Isoniazide derivative showed properties such as anti-analgesic<sup>1</sup>, anti-cancer<sup>2-4</sup>, anti-inflammatory and anti corrosive<sup>5-7</sup>. and also it exhibits the tuberculosis activity<sup>8-9</sup>. the isoniazide functions to prevent the synthesis of mycolic acid in metabolic cell wall<sup>10</sup>. in the reported work of arylhydrazone chelator having better antimalarial agent<sup>11</sup>. the most discovery advances in pharmaceutical chemistry have been made heterocyclic compounds. this compound played important role in controlling biological activity. Some researcher synthesize Schiff base in different manner within 2-3 min. solvent free under microwave irradiation<sup>12</sup>. A series of new coordination complex of CO, NI and Cu naphthaldehyde substituted aroyl hydrazones<sup>13</sup> several methods Schiff bases have been reported by using lewis acid<sup>14</sup>. the some novel synthesize Schiff base ligand shows biological importance large number of uses in organic synthesis<sup>15</sup>. The development of new heterogeneous catalyst as MFA from Fly ash

for the synthesis of azomethine derivatives of Isoniazide.<sup>16</sup>

Now a day more challenges for the development of non hazardous organic synthesis. and to minimize this problems verma and its co-workers develop the ecofriendly synthesize of N-sulfonylimines under microwave irradiation by using less amount of solvent<sup>17</sup>. the new methods Schiff base synthesis by using sonicator, UV chamber and grinding method.<sup>18</sup> many researcher have been reported Schiff bases by different methods as like at high temperature, costly catalyst, different apparatus and more time consuming reactions. So, the minimize this draw backs of different methods. This approaches Patil S. and its co-workers synthesized the Schiff bases using lemon juice catalyst<sup>19</sup> then we have been planned to search the new rout of green approach for the synthesis of Schiff base by using gallic acid. and gallic acid is green compound this extracted from green leaf of green tea plant.<sup>20</sup> The gallic acid is phenolic compound and it is chemically called 3, 4, 5-trihydroxy benzoic acid. It has been implicated cardiovascular disease, cancer and also. Some

chemist have been reported that antimicrobial activity of gallic acid.<sup>21-22</sup> the research explain on various drying treatment for green tea to calculate phenolic groups.<sup>23</sup> Nayeem N. and its co-workers found that gallic acid derivatives played pivotal role in imparting medicinal properties of plant therefore it has been consider as promising lead as molecule for new drug development<sup>24</sup>. After literature review we have been synthesized Schiff base of N'-((2-hydroxynaphthalene-1yl) methylene) isonicotinohydrazide by using gallic acid catalyst.

Deosarkar and its co-workers have been studied the stability constants of 4-amino-3-naphthol-sulphonic acid with Co (II) metal ions and 3-amino, 4-hydroxy, 5-nitro benzene sulphonic acid with Cu (II) metal ions in different percentage of ethanol-water mixtures having varying dielectric constants<sup>25</sup>. The solution have been studied of binary (1:1) complexes of Sm (III) and Tb (III) with 3-(2-hydroxy-5- methylphenyl)-1,5-diphenyl- 2-pyrazoline(HMPPPz)(L1) and 3-(2-hydroxy-5-methylphenyl)-5-diphenyl-2- pyrazoline (HMPPPz) in 70% dioxane-aqueous medium.<sup>26</sup> the method was developed for the aliphatic organic mono-, di-, and tricarboxylic acids and their complexes with basic metal ions such as the alkali(I) and alkaline earth(II) metal ions, the lanthanide(III) ions, the actinide(III and IV) ions and its estimate stability & protonation constant of ligand.<sup>27</sup> Meshram Y K & its co-workers to estimate the values of metal-ligand stability constant of substituted isoxazolines.<sup>28</sup> Narwade & its co-workers have been studied metal ligand stability constants of some lanthanides with some substituted sulphonic acids.<sup>29</sup> After literature review we are going to the interesting study of chelating properties of complex of N'-((2-hydroxynaphthalene-1yl) methylene) isonicotinohydrazide .

### Experimental Section

#### Material & methods:

All chemicals purchased from SD Fine & sigma Aldrich from Mumbai. The all the

chemicals and salt used without further purification. The green tea leaves collected from garden of farm of tade shivar in village area. UV, FTIR & <sup>1</sup>H-NMR were obtained. The <sup>1</sup>H-NMR spectra were measured with Bruker 500MHz Advanced spectrometer.

#### Extraction of known Heat reflux Extraction Method [Jun Xi. & el] of Gallic Acid From green leaves:

The green tea leaves were dried on paper 10 days in the presence of clear sun light .then dried leaves crushing in to the powder by mixer and getting fine powder of green tea leaves. 5g Green tea powder mixed with 100ml 50% methanol and boiled it about 50 min.then filter the solution and collect the extract .this extract was centrifuged for 20 min.and then supernant solution of gallic acid was used as catalyst.

#### Synthesis of Schiff base N'-((2-hydroxynaphthalene-1yl) methylene) isonicotinohydrazide.

Schiff base have been prepared by general procedure: equimolar amounts of isonicotinic acid hydrazide and the corresponding aldehyde as 2- hydroxynaphthaldehyde were vigourly stirring in catalytic solution for 40-50 min.at moderate temperature on hot plate magnetic stirrer and the progress of reaction was by TLC analysis. The faint yellow product was obtained the filter it.

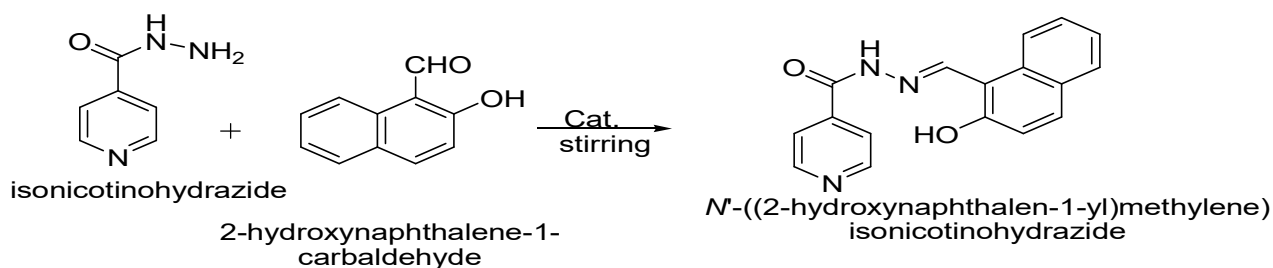
**Analytical data:** Faint yellow solid, M.P. =182-184<sup>0</sup>C & Yield = 68 %

**UV data –λmax:** 332 nm

**IR Spectra cm<sup>-1</sup>(KBR):** 3223 (-OH alcoholic), 3051 (N-H), 1681 (C=O amide), 1562 (C=N), 1300 (C-O).

**<sup>1</sup>HNMR (500MHz) DMSO-D<sup>6</sup> δppm:** 7.251-7.269 (d, J=9.0Hz,1H),7.416-7.446 (t, J=7.5Hz,1H), 7.618-7.651 (t d, J=8.0,1.0Hz, 1H), 7.894-7.923(m, 3H), 7.957-7.975 (d ,J=9.0Hz, 1H), 8.323-8.340 (D, J=8.5Hz, 1H), 8.845-8.857 (d, J=6.0Hz,2H), 9.490 (s ,1H), 12.417 (bs, 1H), 12.536 (s,1H).

**Fig-1. Reaction scheme for synthesis of ligand of N'-((2-hydroxynaphthalene-1-yl)methylene)isonicotinohydrazide.**



### P<sup>H</sup> Metric Section

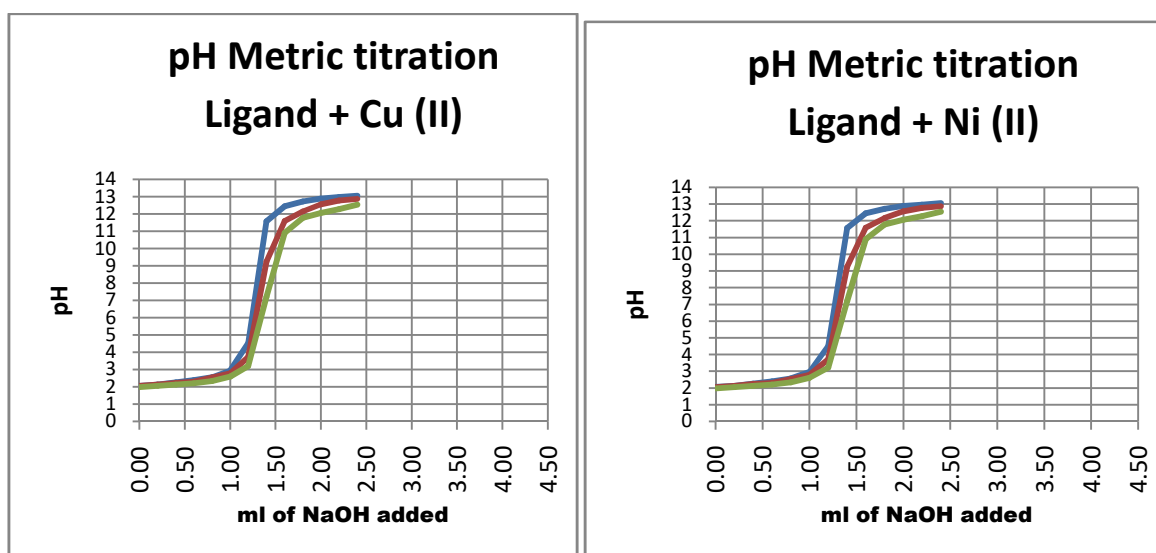
According to literature review, we were used synthesized for P<sup>H</sup> measurement, then we was carried out with equip-tronic EQ-610 pH meter (accuracy  $\pm 0.01$  units) using combine glass electrode at 303<sup>0</sup>K temperature. pH meter was calibrate with buffer solution of pH=7 & 9.2 at 29  $\pm 1$ <sup>0</sup>C. Metal sulphate & nitrate solutions were prepared in distilled water as pH 6.9 and metal ion solution was prepared as Cu(II), Ni(II), Co(II), Fe (II)&Mg (II). The solution of N'-((2-hydroxynaphthalene-1-yl)methylene) isonicotinohydrazide prepared in 10% ethanol solvent. The pH metric readings in 10% ethanol – water mixture were converted to [H<sup>+</sup>] ion solution. All solution solutions were titrating with standard solution of NaoH (0.2N) Calvin Bjerrum method.<sup>30</sup> this was consuming

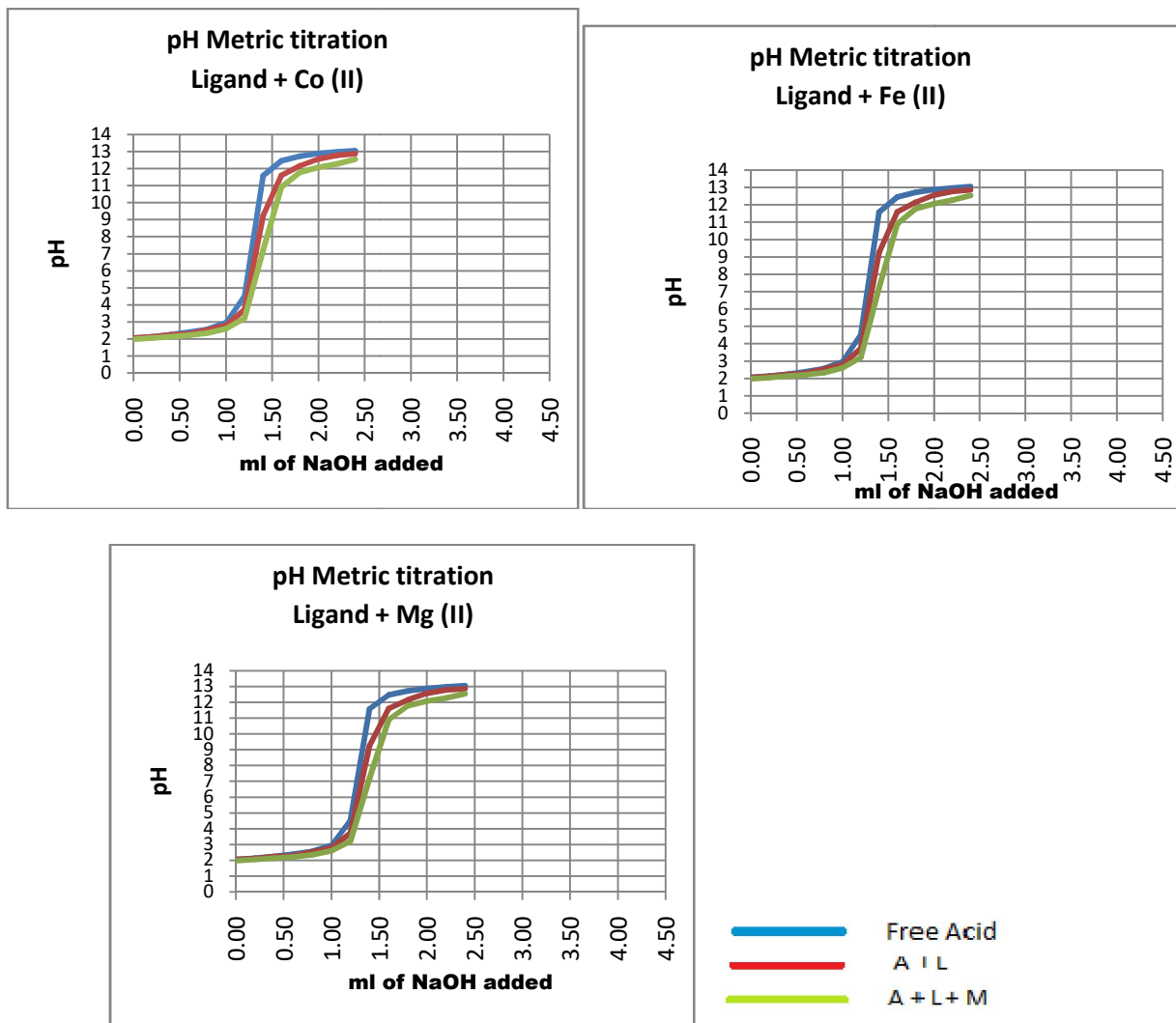
by Irving & Rossotti.<sup>31</sup> The following three solutions were titrated one by one against standard NaoH (total volume 25ml).

1. Free HCL [A]
2. Free HCL + Ligand (A+L)
3. Free HCL + Ligand + Metal ion (A+L+M)

After fixed time of interval P<sup>H</sup> meter were stable then reading obtained from each titration curves were plotted as pH Vs volume of 0.2N NaoH added as shown in (Fig.2). The formation of synthesize ligand between transition metal ion was indicated by the significant separation starting from pH =2.5 up to 13 for transition metal ion with N'-((2-hydroxynaphthalene-1-yl)methylene) isonicotinohydrazide. This may possible due complete dissociation of hydroxyl group present in the synthesized ligand.

**Fig.2-Plot pH Vs Volume of NaoH added**



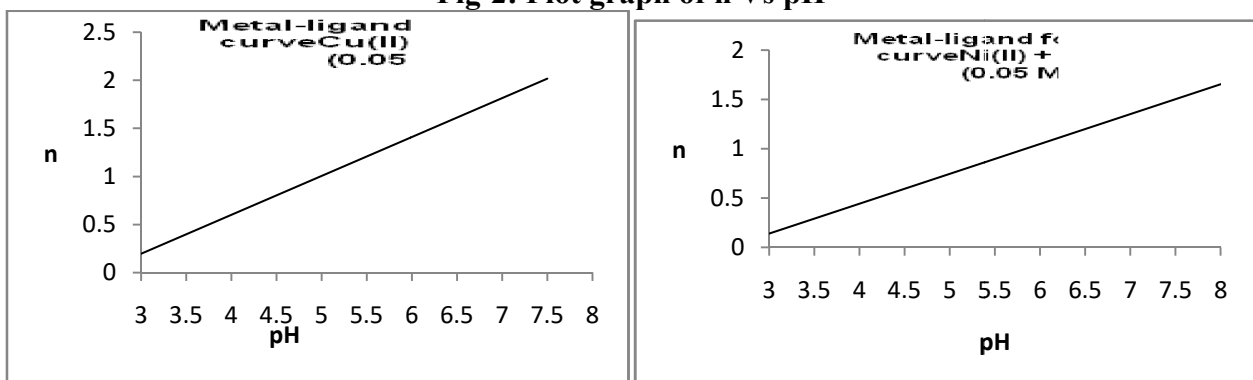


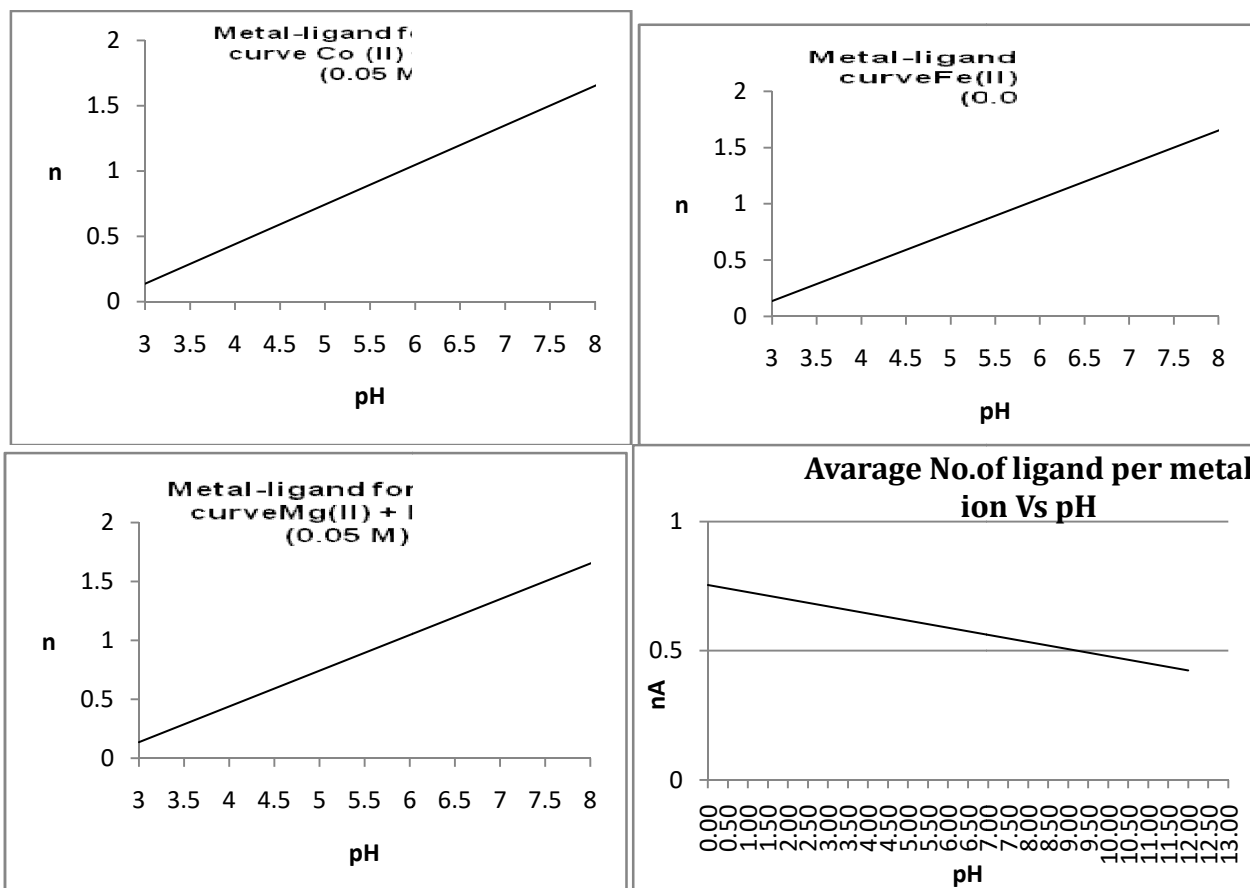
**Result And Discussion**

The titration data used to construct the curves between volume of NaOH and  $P^H$ . They are called acid-ligand titration curves. Synthesized heterocyclic ligand may be ionized as acid having replaceable  $H^+$  ion from -OH group. Therefore it is represented as HL i.e.  $HL \rightleftharpoons H^+ + L^-$ . This determined by two methods first was half integral method and second one point wise calculation method. The  $\bar{n}A$  values at

various B (where B is the corrected pH for non-aqueous solvents) were calculated from the acid and ligand titration curves using the Irving–Rossotti equation. In Fig.2 the proton–ligand formation curves plotted for value of  $\bar{n}A$  Vs pH. It clear that ligand have one ionizable proton (the enolized hydrogen ion of the -OH group).the two method we obtained proton ligand stability constant was most appreciable with each other.

**Fig-2: Plot graph of  $\bar{n}$  Vs pH**





**Metal–ligand stability constants:** we were determined the stepwise formation constants of Cu(0.01M), Ni(0.01M), Co(0.01M),Fe (0.01M)&Mg (0.01M) with synthesized Schiff base ligand in 10% ethanol-water mixture and directly putting the value of  $\log k_1$  and  $\log k_2$  from the formation curves of  $\bar{n}A$  Vs pH using integral half method at  $\bar{n} = 0.5, 1.5$ . And accurately value was calculated by point wise calculation as shown in table–1&2. The maximum value of  $\bar{n}$  was  $\sim 2$  for the formation of 1:1 & 1:2 metal-ligand complexes.

**Table-1: Determination of Schiff base and metals stability constant (logK) of transition Metal ion with at 0.05M ionic strength.**

System	Logk <sub>1</sub>	Logk <sub>2</sub>	Logk <sub>2</sub> / Logk <sub>1</sub>	-Logk <sub>2</sub> / Logk <sub>1</sub>
Cu(II)-Schiff base	6.25	3.75	2.5	1.666666667
Ni(II)-Schiff base	7.55	4.25	3.3	1.776470588
CO(II)-Schiff base	5.75	3.55	2.2	1.61971831
Fe(II)-Schiff base	6.35	3.25	3.1	1.953846154
Mg(II)-Schiff base	6.35	3.65	2.7	1.739726027

**Table-2: Proton ligand stability constant of ligand 0.05M ionic strength: at 303 K Temperature**

System	Constant pK	
	Half integral	Point wise calculation
Schiff base	9.05	8.18

**Conclusion**

In the part of synthesis of Schiff base N'-((2-hydroxynaphthalene-1-yl) methylene) isonicotinohydrazide by using gallic acid from green tea leaves during the reaction no pollution take place and minimum time required to completed the reaction. It was ecofriendly reaction. In the pH metric from the curves of pH Vs ml. of NaoH added we observed that significant starting from pH=2.5 to 13 that solution color changes faint yellow to dark yellow so, it was cleared that formation of complex between metal ion and ligand. From the table-1 cleared that less difference between values of  $\log k_1$  and  $\log k_2$  showed stepwise formation of metal-ligand complex. It also showed that the stability constant  $\log k_2$  metal-ligand complex decreases in the order of Irving Williams series as Ni > Cu > Mg > CO > Fe.

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**SYNTHESIS, SPECTRAL STUDIES AND ANTIBACTERIAL ACTIVITY OF SCHIFF BASE LIGAND DERIVED FROM ISONIAZIDE.****\*P. R. Bhangale<sup>1</sup> and A. N. Sonar<sup>2</sup>**<sup>1</sup>TVE'S Dhanaji Nana Mahavidyalaya, Nehru Vidya Nagar Faizpur.<sup>2</sup>Shri. V. S. Naik College, Raver.

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**ABSTRACT**

The Schiff base ligand *N'*-((5-chloro-3-methyl-1-phenyl-pyrazol-4-yl) methylene) isonicotinohydrazide was obtained by the condensation of Isonicotinic acid hydrazide (isoniazide) with 5-chloro-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde. The synthesized ligand characterized by techniques like Thin Layer Chromatography, Melting Point, Solubility, Spectroscopic techniques like <sup>1</sup>H-NMR (Nuclear magnetic resonance), <sup>13</sup>C-NMR spectroscopy and Mass spectra, FT-IR spectral studies of synthesized compound are also reported. The antibacterial activity of the ligand were tested against some gram positive and gram negative bacteria such as *S. aureus*, *E. coli*, *P. vulgaris*.

**Keywords** Schiff base ligand, isonicotinic acid hydrazide, spectra study, antibacterial activity.

**Introduction**

Isoniazid has enjoyed a lot of interest due to its antituberculosstatic, and antibacterial properties [1]. Isoniazid forms metal chelates with many bivalent ions. These complexes has been used in the structure determination of the isoniazid [2-3]. Several research papers have described the bactericide and fungicide properties of a variety of mixed ligand complexes of metal ions with isoniazid and hydrazones derivatives [4-5].

Hydrazide, an effective class of organic compounds, is known for therapeutic and biological activities [6,7]. Most of the hydrazides have been reported for their anti-fungal, anti-bacterial and antiinflammatory activities [6-9]. Isoniazid (isonicotinic hydrazide; INH) is the primary drugs used in combination with ethambutol, rifampin, streptomycin and pyrazinamide used to treat tuberculosis [10]. Despite the large number of compounds containing the isoniazid moiety which have been already synthesized and tested, Still there is a need for synthesis of new compounds containing isoniazid moiety, due to the increasing resistance of bacterial strains of certain type of antibiotics [11]. The remarkable biological activity of acid hydrazides R-CO-NH-NH<sub>2</sub> a class of Schiff bases or the aroyl hydrazones, R-CO-NH-N=CH-R' and the dependence of their mode of chelation with transition metal ions present in the living system have been of great interest [12-15]. Isoniazid was reacted with number of

substituted aromatic aldehydes to gives Schiff bases [16]. The coordination compounds of aroyl hydrazones R-CO-NH-N=CH-R' have been reported to act as enzyme inhibitors [17] and are very useful due to their pharmacological applications [18,19]. Isoniazid is a drug of proven therapeutic importance and is used against a wide spectrum of bacterial ailments, such as tuberculosis [20].

Heterocyclic compounds are distributed widely in nature and are essential for many biochemical processes. In the past few decades the introduction of a number of pharmaceutical compounds which contain five, six, and seven-membered rings such as piperazines, piperidines, imidazoles, benzodiazepines, and other heterocycles containing nitrogen, sulfur, and oxygen have been seen [21]. This kind of systems plays an important role in many biological processes due to their metal-coordinating ability [22]. Bioinorganic compounds and biomimetics, containing azomethine group C=NH, are widely represented [23]. Schiff base ligand have been investigated intensively for strong coordination capacity with metal ions and their diverse biological activities [24-27]. The tuberculostatic activity of isonicotinic acid hydrazide and its aroylhydrazones containing azomethine nitrogen C=NH is attributed to their ability to form stable metal complexes with d- and f-block metal ions [28-30]. Interest in the study of hydrazones has been growing because of their antimicrobial, antituberculosis,



and antitumour activity [31–34]. It has been found that Isoniazid Schiff bases shows a better anticancer and antitubercular activity than isoniazid [35, 36]. Enzymatic acetylation of the antitubercular isoniazid by N-acetyltransferase shows a metabolic pathway in humans being for isoniazid. The therapeutic activity of the drug is greatly reduces by acetylation resulting in underdosing, decreased bioavailability, and acquired isoniazid resistance. Chemical modification in a functional group of the hydrazine unit of isoniazid that blocks acetylation, while maintaining strong antimycobacterial action, has the potential to improve clinical outcomes and to reduce the emergency in patients of acquired isoniazid resistance. Isoniazid Schiff bases and their metal complexes exhibit better antimicrobial activity than isonicotinic acid hydrazide [37,38].

In inorganic chemistry Schiff bases plays an important role as they easily form stable complexes with most of the transition metal ions in the periodic table [39]. Schiff bases are formed from the condensation of isoniazid, INH with different aldehydes represent an important class of chelating ligands and their metal complexes are of great interest due to their importance in biological, pharmacological and clinical applications [40]. The derivatives of hydrazone are used in the treatment of some diseases such as tuberculosis, leprosy and mental disorders and as fungicides [41].

In present work, we described the synthesis of N'-((5-chloro-3-methyl-1-phenyl-pyrazol-4-yl)methylene)isonicotinohydrazide (Scheme 1). The Schiff base ligand have been characterized by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  spectra,

mass spectra, FT-IR. The antibacterial activities of Schiff base ligand (L) have also been studied against some gram positive and gram negative bacteria such as S-aureus, E-coli, P-vulgarius.

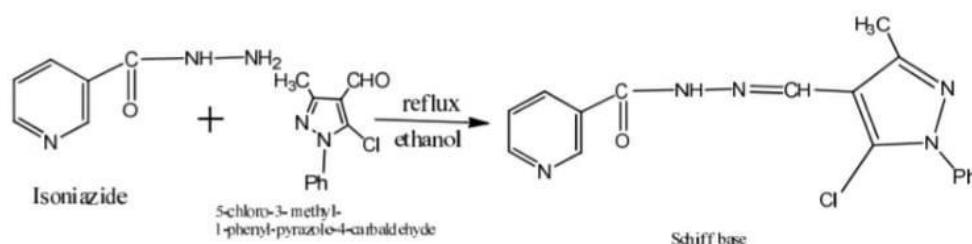
## Experimental Section

### Materials and Methods

All the Chemicals used for the preparation of ligand were purchased from sigma Aldrich, Metal salts from S.D Fine chemicals LTD. and they are of high purity and were used without any further purification. Before using solvents, Drying of solvents were carried out by standard methods. The FT-IR spectra of the free ligand were recorded on a SHIMADZU FT-IR Spectrophotometer in KBr pellets in the region  $4000\text{--}400\text{ cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the free ligand were determined on a Bruker Avance 400MHz and 100 MHz respectively in  $\text{CDCl}_3$  using trimethylsilane (TMS) as an internal reference. MP were recorded using open capillary method.

### Preparation of Ligand

To a solution of isoniazide (0.1mol) and 5-chloro-3-methyl-1-phenyl-pyrazole-4-carbaldehyde (0.1mol) in 20 ml ethanol was added. A few drops of 10% NaOH were added to adjust the pH and the reaction mixture then refluxed with stirring for 2 hrs progress of reaction was monitored by TLC. After the completion of reaction the obtained product was collected by filtration through buchner funnel. Solid obtained was recrystallised from suitable solvent (42–44). Physical characterisation of schiff base ligand are given in Table 1.



Scheme 1- Synthesis of Schiff Base

**Table 1 Physical characterisation of the Schiff base**

Comp	M.F.	Physical State	M.P.	Yield
L	C <sub>17</sub> H <sub>14</sub> N <sub>5</sub> OCl	White	204- 208 <sup>o</sup> C	81.2 %

**Result and Discussion**

The ligand N'-((5-chloro-3-methyl-1-phenyl-pyrazol-4-yl) methylene) isonicotinohydrazide was synthesized by the reaction of 5-chloro-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde and isoniazide in solvent ethanol by known procedure[39-41].

White shiny crystals of ligand (L) are formed, It is soluble in hot ethanol, DMSO, DMF, Acetone, hot methanol. but it is insoluble in water. The ligand was characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectra, mass spectra, FT-IR spectra. Solubility of prepared schiff base ligand L are shown in Table 2.

**Table 2 Solubility of prepared schiff base ligand L**

Ligand	Acetone	Ethanol	Methanol	Hexane	Chloroform
L	S	S	S	S	S

Petroleum ether	Ether	CHCl <sub>3</sub>	Benzene	DMF	DMSO	Water
S	S	S	S	S	S	IN

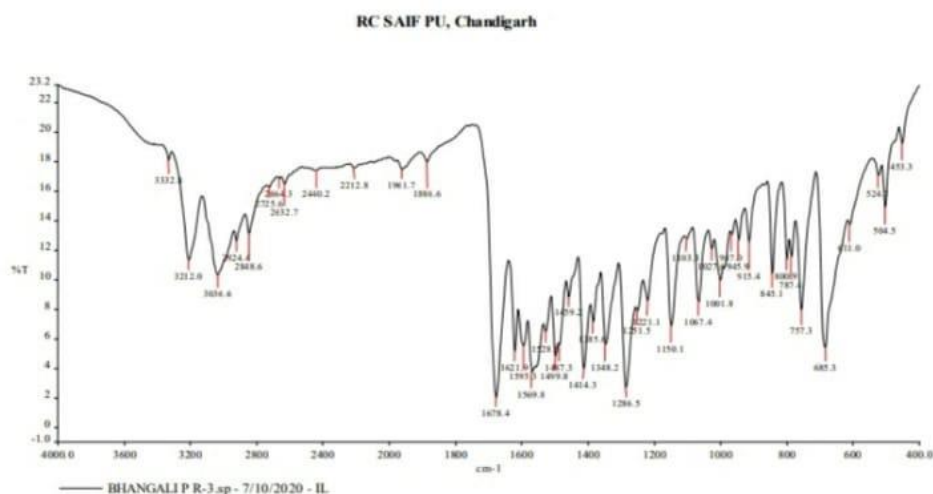
S = Solubility  
IN = Insolubility

**Spectral Characterization****1) FT-IR Spectral Data**

When the infrared light is passed through a sample of organic compound, some of the frequencies absorbed & the absorbed or the transmitted is plotted against frequency, the result is infrared spectrum the excitation of molecular vibration & rotation gives rise to absorption in the infrared region of the spectrum.

The ligand is stable & have sharp MP that indicate the purity of ligand. The free ligand L shows the stretching frequency at 3212 cm<sup>-1</sup> and at 1678 cm<sup>-1</sup> due to  $\nu(\text{NH}_2)$  and  $\nu(\text{C}=\text{O})$  group respectively.

The IR spectra of schiff base ligand shown in figure 1

**Fig.1 IR spectra of the ligand****2) <sup>1</sup>H-NMR Spectra of the ligand:-**

The <sup>1</sup>H-NMR spectra of ligand was recorded in CDCl<sub>3</sub> with TMS as an internal reference using Bruker Avance 400MHzNMR Spectrometer.

The <sup>1</sup>H-NMR spectrum exhibited number of characteristics signals of the ligand L. The <sup>1</sup>H-NMR spectrum of ligand showed a single peak at =11.94 ppm due to presence of -NH. The

signals observed at 8.72 ppm due to doublet of two protons of pyridine ring (d,2H, py) The peak observed at =7.82 ppm ppm due to doublet of two protons of pyridine ring (d,2H, py). The singlet peak at 7.41 ppm was assigned to phenyl protons, The peak at =2.50 ppm was

assigned to -CH<sub>3</sub> proton. signals of the ligand as shown in fig.2. <sup>1</sup>H NMR (δ ppm); 11.94(s,1H,-NH); 8.72(d,2H,Py); 8.46(s,1H,=CH); 7.82 (d,2H,Py); 7.41(s,5H,ph); 2.50(s,3H,-CH)

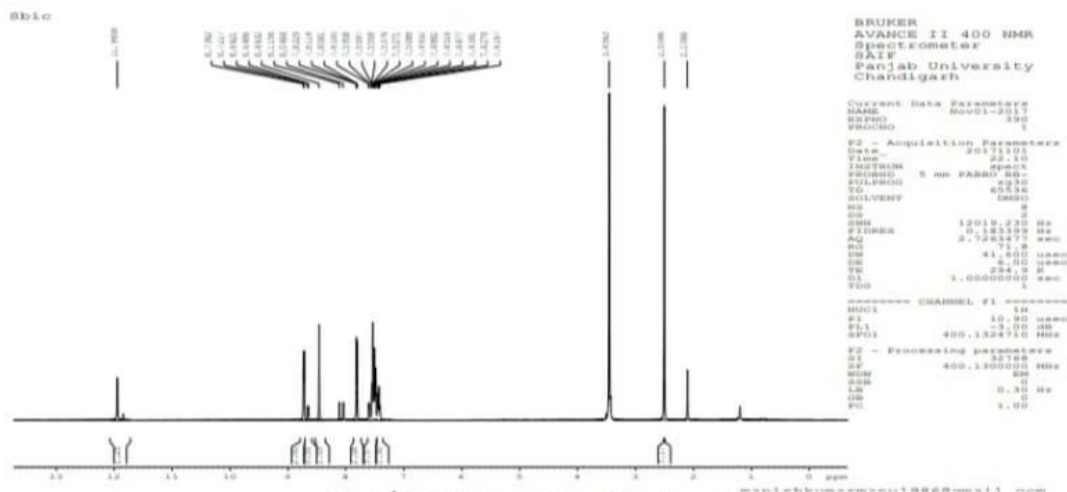


Fig.2. <sup>1</sup>H -NMR spectra of the ligand

3) <sup>13</sup>C-NMR Spectra

<sup>13</sup>C-NMR spectra of the Schiff base ligand L was recorded in DMSO-d<sub>6</sub> and are shown in fig.3. <sup>13</sup>C-NMR (δppm); 161.0; 149.9; 149.1; 148.8; 141.2; 140.3; 137.18; 128.9; 127.40; 124.53; 121.31; 113.0; 14.36;

The <sup>13</sup>C-NMR spectra of the Schiff base ligand showed a peak at 161.0 ppm which was assigned to the carbonyl group. The peak at 149.9 ppm that was assigned to the carbon of the azomethine group

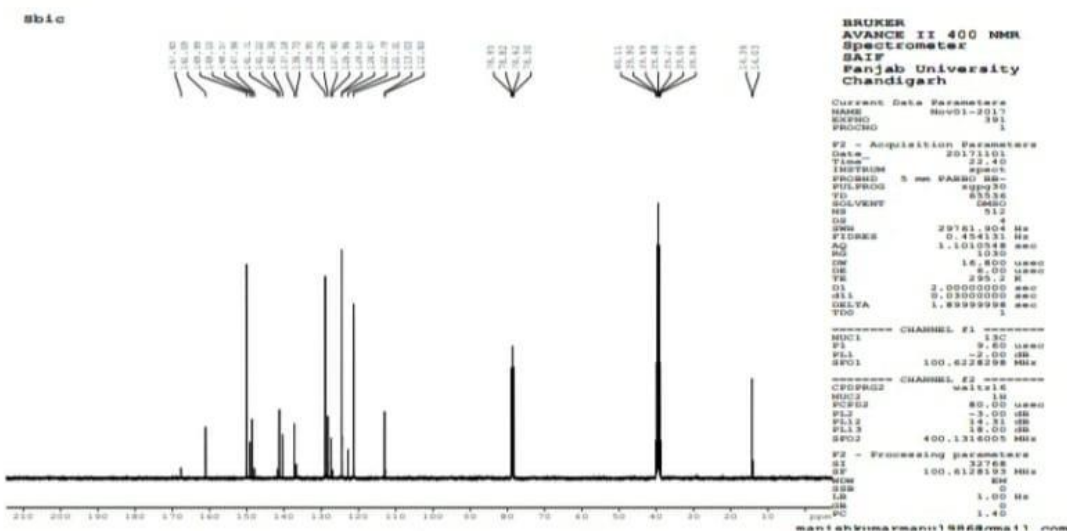


Fig.3 <sup>13</sup>C-NMR spectra of the ligand

#### 4) Mass spectra

The mass spectra mainly applied in analysis of ligand. The formation of ligand was confirmed through MS technique. Fig 4 shows the mass

spectrum of ligand. The molecular ion peak was observed at  $m/z=339(m+1)$  consistent with the molecular weight of ligand confirm the formation of ligand.

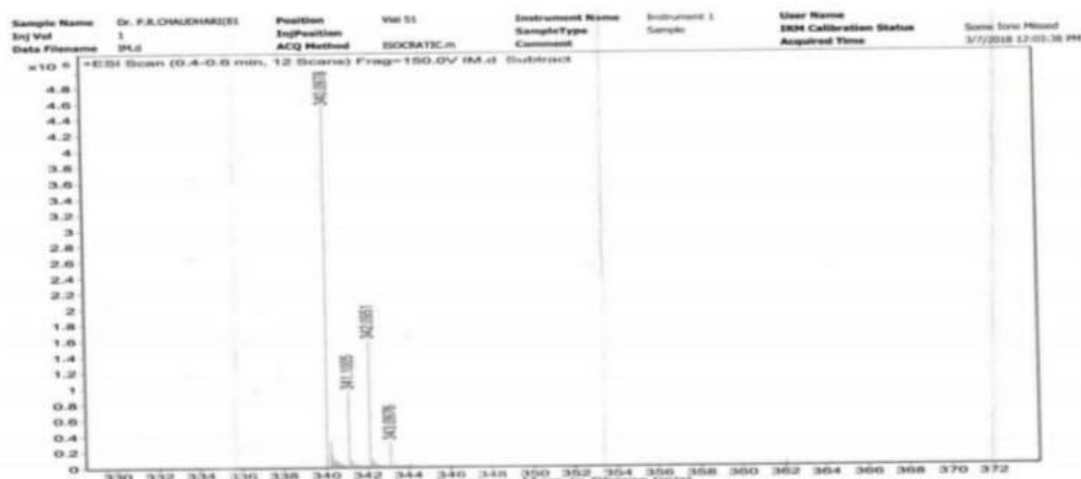


Fig.4 Mass spectrum of ligand

#### Biological activity studies

The synthesised Schiff base ligand was tested against some bacteria *S.aureus*, *E-coli*, *P.vulgaris*. The zone of inhibition based upon size around the disc was measured in mm. The result of the antibacterial inspected of ligand at a concentration 100g/ml against these bacteria are shown in Table 3. The results of antibacterial activity are shown in fig 5. The antibacterial activities of the synthesized ligand were determined using agar well diffusion method. The nutrient agar (HiMedia, 13 g) was suspended in distilled water (1000 mL) and heated to boiling till it dissolved. The medium and petri dishes were autoclaved at 15 psi for 20 min. In each petriplate, 20 ml of sterilized medium was added. After setting the agar, 10 % suspension culture (inoculum) was added in each petridishes and spread thoroughly by rotary motion of the plate. After inoculation, wells were scooped out with 7 mm sterile cork borer and in each cup 100  $\mu$ L of 1 % test solution of ligand were added.

Table 3. Antibacterial activity data of the ligand L

Sr No	Compound	Inhibition zone (mm/mg sample)		
		E-coli	S-aureus	P-vulgaris
1	$C_{17}H_{14}N_5OCl$	08 mm	10 mm	12 mm



Fig 5. Result of antibacterial activity

#### Conclusion

The Schiff base ligand *N*-((5-chloro-3-methyl-1-phenyl-pyrazol-4-yl)methylene)isonicotinohydrazide has been synthesised as given in scheme 1 the structure of above ligand were in good agreement with spectral and analytical data.

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## 'नव्वदोत्तरी कवितेची समीक्षा स्वरूपआणि विशेष'

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### प्रस्तावना

समीक्षा या संकल्पनेत विश्लेषण आणि मूल्यमापन प्रक्रियेला महत्त्व असते. लेखक वाचक आणि समीक्षक या साहित्य व्यवहारातील महत्त्वपूर्ण घटकांना सांधणारा दुवा म्हणजे समीक्षा होय. लेखक वाचक आणि समीक्षक यांना मार्गदर्शक दिशा दिग्दर्शनासाठी समीक्षाव्यवहाराचे उपयोजन होते. लेखकाच्या ठायी असणाऱ्या विशेष क्षमता व न्यूनता प्रकट करण्यासाठी समीक्षा महत्त्वाची ठरते. वाचकाच्या साहित्य आकलनाला व्यापक करण्यासाठी समीक्षा महत्त्वाची असते. समीक्षकाची साहित्याच्या प्रकृतीची आणि स्थिती गतीची जाण अधिक प्रगल्भ करण्यासाठी समीक्षा व्यवहार महत्त्वाचा ठरतो. वा. ला. कुलकर्णी याबद्दल लिहितात 'साहित्य ही समाजाची एक अत्यंत महत्त्वाची सांस्कृतिक गरज आहे. ज्या समाजाला त्याचे स्वतःचे असे साहित्य नाही त्याच्या सांस्कृतिक जीवनात मोठी उणीव निर्माण होते ; म्हणूनच समाजाला त्यांच्या साहित्याबद्दल सोत्साही करणे, त्यात घ्यायला मदत करणे, साहित्य व्यापार हा आपल्या जीवनाचा एक महत्त्वाचा घटक आहे याची योग्य जाण त्याच्या ठिकाणी निर्माण करणे हे साहित्य समीक्षेचे अप्रत्यक्ष प्रयोजन ठरते. श्रमानवी समाजजीवनातील सांस्कृतिक विश्वातील साहित्य व्यवहार व समीक्षा यांच्यातील परस्पर संबंधावर वरील विश्लेषणातून प्रकाश पडतो. कविता या वाङ्मय प्रकाराची समीक्षा विस्तृत व व्यापक स्वरूपात झालेली आहे. नव्वदोत्तरी कवितेची समीक्षा संख्यात्मक दृष्ट्या मोठ्या प्रमाणात झालेली आहे. नव्वदोत्तरी कवितेचे मूल्यमापन करून केवळ न थांबता नव्वदोत्तरी काव्य समीक्षा पूर्वकालीन मराठी कवितेचे पुनर्मूल्यमापन करते. विशेषता नवकविता व साठोत्तरी कवितेचे पुनर्मूल्यमापन नव्वदोत्तरीकाव्य समीक्षेने केले आहे. साठोत्तरी कवितेची चिकित्सा करून साठोत्तरी कवींचे सामर्थ्य व खुजेपणा मांडण्याचा प्रयत्न नव्याने झालेला दिसतो. आजही काव्य समीक्षेच्या प्रांतात मूल्यमापन व पुनर्मूल्यमापनाची प्रक्रिया सुरु आहे.

कवितेच्या समीक्षेचा विचार करताना एक गोष्ट प्रकर्षाने जाणवते ती म्हणजे नव्वदोत्तरी कवींनी केलेली समीक्षा विपुल आहे. कवी स्वतःच्या कवितेची, समकालीन कवी व पूर्वसूरींची तटस्थ समीक्षा करत आहेत.

नव्वदोत्तरीकवितेची समीक्षा विविध पद्धतीने झालेली आहे. आस्वादक, मूल्यमापनात्मक, मानसशास्त्रीय, रूपनिष्ठ शैलीनिष्ठ समीक्षा नव्वदोत्तरी कवितेची झालेली दिसून येते. नव्वदोत्तरी कवितेची समीक्षा अधिक प्रमाणात आस्वादक अंगाने झालेली दिसते. विश्लेषण व मूल्यमापन या प्रक्रियांना नव्वदोत्तरी काव्यसमीक्षेत गौण स्थान मिळालेले दिसते. आस्वादक अंगाने समीक्षा करत असताना मूल्यमापन, विश्लेषण अपूर्ण राहते. नव्वदोत्तरी काव्य समीक्षेत सैद्धांतिक समीक्षा व उपयोजित समीक्षा कमी प्रमाणात झालेली दिसून येते. रूपनिष्ठ व शैलीनिष्ठ समीक्षा अल्प प्रमाणात झालेली आहे.

नव्वदोत्तरी कवितेची समीक्षा स्वरूप आणि विशेष:

१. ग्रंथ रूपातून केली गेलेली नव्वदोत्तरी कवितेची समीक्षा
२. वाङ्मयीन नियतकालिकातील नव्वदोत्तरी कवितेची समीक्षा
३. संपादित ग्रंथातील लेख स्वरूपातील नव्वदोत्तरी कवितेची समीक्षा
४. वृत्तपत्रातून प्रकाशित झालेली नव्वदोत्तरी कवितेची समीक्षा
५. कवितासंग्रहना लिहिलेल्या प्रस्तावना मधील काव्य समीक्षा
६. संस्थात्मक पातळीवरील नव्वदोत्तरी कवितेची समीक्षा
७. वाङ्मयीन प्रवाहांच्या प्रेरणेने झालेली नव्वदोत्तरी कवितेची समीक्षा
८. विद्यापीठीय संशोधन पदवीसाठी प्रबंध रूपातून झालेली नव्वदोत्तरी कवितेची समीक्षा

अशा बहुविध स्वरूपाची समीक्षा नव्वदोत्तरी कवितेची झालेली दिसून येते. संख्यात्मक दृष्ट्या विपुल असली तरी या समीक्षेला मर्यादा आहेत. यातील बहुतांश समीक्षा आस्वादक स्वरूपाचे आहे. ढोबळ विधानात्मक असे या समीक्षेचे स्वरूप आहे. विस्तृतता, सूक्ष्मता, मूल्यमापनात्मकता यांचा अभाव ही नव्वदोत्तरी काव्य समीक्षेची मर्यादा सांगता येते.

३. स्वतंत्र ग्रंथ रूपातून केली गेलेली नव्वदोत्तर कवितेची समीक्षा :

यातील काही ग्रंथ अत्यंत मौलिक स्वरूपाचे आहेत. अक्षयकुमार काळे, किशोर सानप, रवींद्र ठाकूर, वसंत आबाजी इहाके, नागनाथ कोतापल्ले, प्रकाश देशपांडे केजकर, निशिकांत मिरजकर, वसंत पाटणकर, श्रीधर तिळवे, चंद्रकांत पाटील, महेंद्र कदम, किसन पाटील, पी. विठ्ठल, देवानंद सोनटक्के इत्यादी समीक्षकांनी स्वतंत्र ग्रंथरूपाने नव्वदोत्तरी कवितेच्या समीक्षेची साक्षेपी मांडणी करण्याचा प्रयत्न केलेला आहे. वरील अभ्यासकांच्या काव्य समीक्षेचे वर्गीकरण आपणास करता येते. नव्वदोत्तरी कालखंडातील कवी व कवींचे काव्यसंग्रह आस्वादक अंगाने विचारात घेतले आहेत. मूल्यमापन, विश्लेषण, सूक्ष्मता या समीक्षेत आढळून येत नाही.

अक्षयकुमार काळे यांनी ' अर्वाचीन मराठी काव्य दर्शन ' या ग्रंथात नव्वदोत्तरी कवींचा धावता आढावा मांडून या कवितेचे विशेष स्पष्ट केले आहेत. त्यांच्या ग्रंथात विशिष्ट कालखंडाचा अभ्यास समग्रतेने मांडण्याचा प्रयत्न केलेला दिसतो. नव्वदोत्तरी कवितेचे समग्र विश्लेषण येत नाही.

किशोर सानप यांच्या ' युगांतराची कविता ' या ग्रंथातून त्यांनी नव्वदोत्तरी कविता हासमीक्षा विषय केला आहे. नव्वदोत्तरीकवितेतील अजय कांडर,मोहन कुंभार,अशोक कोतवाल, पी. विठ्ठल, सुनील अभिमान अवचार, फेलिक्स डिसोजा,सुखदेव ढाणके, जयराम खेडेकर, श्रीकांत देशमुख, संतोष पद्माकर पवार, शशिकांत शिंदे, राजीव जोशी, सुरेश सावंत, लोकनाथ यशवंत, वीरधवल परब,कल्पना दुधाळ,मनीषा साधू, अजीम नवाज राही,भगवान निळे, वाहरू सोनवणे इत्यादी नव्वदोत्तरीकवींच्याकवितेचे उत्तम विश्लेषण प्रस्तुत ग्रंथात केलेले आहे.या ग्रंथातील समीक्षाही आस्वादकतेबरोबरच नव्वदोत्तरी कवींचे विशेष, वेगळेपण,प्रवृत्ती स्पष्ट करणारी आहे.किशोर सानप यांच्या ग्रंथातील मर्यादा नोंदवताना एक गोष्ट सांगता येते ती म्हणजे नव्वदोत्तरी कवितेतील महानगरीय कवींच्या काव्यसंग्रहाचे विश्लेषण या ग्रंथात येत नाही.हेमंत दिवटे,मंगेश नारायण काळे,श्रीधर तिळवे, खांडेकर संजीव, सलील वाघ,अरुण काळे,सिद्धार्थ तांबे या कवींच्या कवितांचा विचार केलेला नाही. ही मर्यादा मान्य करूनही किशोर सानप यांच्या'युगांतराचीकविता' हा ग्रंथ नव्वदोत्तरी कवितेचे विस्तृत, सूक्ष्मपणे वस्तुनिष्ठ, व्यापक समीक्षा करणारा महत्त्वाचा ग्रंथ ठरतो.

निशिकांत मिरजकर यांनी संपादित केलेल्या 'नव्या वाटा नवी वळणे ' हा काव्यसंग्रह व त्याला निशिकांत मिरजकर यांनी लिहिलेली प्रस्तावना ही नव्वदोत्तरी कवितेचे उत्तम विश्लेषण करणारीआहे.साक्षेपीपणे कवींची केलेली निवड त्यातून नव्वदोत्तरी कवितेतील महत्त्वपूर्ण कवींचा आपल्याला अंदाज बांधता येतो. ही प्रस्तावनात्रोटक स्वरूपातील आहे परंतु या प्रस्तावने मधून नव्वदोत्तरी कवितेची ओळख आपल्याला होते.

प्रकाश देशपांडे केजकर यांचा 'समकालीन मराठी कविता' हा ग्रंथ नव्वदोत्तरी कवितेची समीक्षा करणारा ग्रंथ आहे.मुख्य प्रवाहातील कविता, दलित कविता,आदिवासी कविता, मुस्लिम कविता, ग्रामीण कविता, स्त्रीवादी कविता असे नव्वदोत्तरी कवितेचे वर्गीकरण या ग्रंथात केलेले आहे.

' ौथी नवता: नवनियतकालिके' हा श्रीधर तिळवे यांचा ग्रंथ आहे. श्रीधर तिळवे नव्वदोत्तरी कालखंडातील महत्त्वाचे कवी आहेत. नव्वदोत्तरी कवितेची समीक्षा करण्यासाठी कोणते तत्व प्रधान मानले पाहिजे याचे विश्लेषण प्रस्तुत ग्रंथात येते.नव्वदोत्तरी कवितेच्या समीक्षेची सैद्धांतिक मांडणी करण्याचा प्रयत्न श्रीधर तिळवे यांनी केलेल्या समीक्षेत दिसतो.

वसंत पाटणकर यांचा 'कवितेचा शोध' हा ग्रंथ कवितेचे सैद्धांतिक विश्लेषण करणारा महत्त्वाचा ग्रंथ आहे. नव्वदोत्तरीकाव्य समीक्षेचा विचार करत असताना वसंत पाटणकर

यांची सैद्धांतिक मांडणी समग्रलक्षी स्वरूपाची ठरते.याबरोबरच सुधीर रसाळ यांचा कविता आणि प्रतिमा 'हा ग्रंथही काव्य वाङ्मयप्रकाराचे स्वरूप स्पष्ट करणार हा सैद्धांतिक ग्रंथ आहे.

वसंत आबाजी इहाके यांचा 'कवितेविषयी' हा ग्रंथ समीक्षेतील महत्त्वाचा ग्रंथ आहे. नव्वदोत्तरी कालखंडातील कवितेचे अशय सूत्र स्पष्ट करण्याचा प्रयत्न इहाके यांनी केलेला आहे. एकूणच या ग्रंथातील काव्य वाङ्मय प्रकाराची सैद्धांतिक मांडणी महत्त्वपूर्ण अशी आहे.

चंद्रकांत पाटील यांचा 'कवितेसमक्ष' हा ग्रंथही नव्वदोत्तरी कवितेचे विश्लेषण करणारा आहे. सद्यकालीन मराठी कवितेचे स्वरूप स्पष्ट करणारा असा हा ग्रंथ आहे.

डॉ. किसन पाटील यांचा 'नव्वदोत्तरी कविता : नवी रूपे' हा ग्रंथही नव्वदोत्तरी कवितेतील काही कवींच्या काव्यसंग्रहाचा आस्वादक अंगाने घेतलेला शोध असे याचे स्वरूप आहे. डॉ. महेंद्र कदम यांचा 'कवितेची शैली' हा ग्रंथही नव्वदोत्तरी कवितेचा शैलीच्या अंगांनी विश्लेषण करणारा ग्रंथ आहे. ग्रामीण काव्य प्रवाहातील कवींची शैली विशेष डॉ. महेंद्र कदम यांनी मांडले आहेत.

नागनाथ कोतापल्ले यांचा 'मराठी कविता आकलन आणि आस्वाद' या ग्रंथातही नव्वदोत्तरी कालखंडातील काही काव्यसंग्रहाच्या वैशिष्ट्येवर प्रकाश टाकलेला दिसतो.

याबरोबरच डॉ. रवींद्र ठाकूर यांचा 'प्रवाह आणि प्रतिक्रिया' हा ग्रंथही इ. स. 1975 नंतरच्या मराठी कवितेचे विश्लेषण करणारा आहे. नव्वदोत्तरी कवितेतील काही कवींवर इ.स. 1975 नंतरचा कवींचा प्रभाव कसा आहे हे स्पष्ट करणारा हा ग्रंथ आहे.

'मराठी कविता समकालीन परिदृश्य' या ग्रंथात पी. विठ्ठल यांनी नव्वदोत्तरी कवितेची सैद्धांतिक मांडणी केलेली आहे. जागतिकीकरणाचे सूत्र केंद्रवर्ती ठेवून नव्वदोत्तरी कवितेच्या मूल्यमापनाचा प्रयत्न प्रस्तुत ग्रंथात केला आहे. नव्वदोत्तरी कवितेतील श्रीकांत देशमुख, कविता महाजन, संतोष पद्माकर पवार, श्रीधर नांदेडकर, अजीम नवाज राही, वीरधवल परब, ऐश्वर्य पाटेकर, कल्पना दुधाळ, अभय दाणी, रवी पवार, महेश लीला पंडित, वीरा राठोड, केशव देशमुख, बालिका जानदेव, महेश लोंढे, मोहन शिरसाट यांच्या कवितेचे आस्वादक मूल्यमापन असे या ग्रंथाचे स्वरूप आहे.

देवानंद सोनटक्के यांचा 'कवितेचा अंतः स्वर' हा ग्रंथही आस्वादक स्वरूपात नव्वदोत्तरी कवितेची चिकित्सा करणारा आहे. सुरुवातीच्या तीन लेखांमध्ये कविता प्रकाराची सैद्धांतिक मांडणी केलेली आहे. नव्वदोत्तरी कवितेतील महत्त्वाच्या कवींच्या कवितेचे स्वरूप, विशेष विस्तृतपणे या ग्रंथातून विशद केलेले आहेत. अशा प्रकारे आपल्याला स्वतंत्र ग्रंथ रूपातून केल्या गेलेल्या नव्वदोत्तरी कवितेच्या समीक्षेचा थोडक्यात विचार करता येतो.

४. संपादित ग्रंथातील लेख स्वरूपातील नव्वदोत्तरी कवितेची समीक्षा:

आज गौरव ग्रंथ मोठ्या प्रमाणात निघत आहेत. अभ्यासकांनी लेख स्वरूपात नव्वदोत्तरी कवितेचा आढावा घेतलेला आहे.

'साहित्य आणि समाज' संपादक - नागनाथ कोतापल्ले, गो.म.पवार गौरव ग्रंथ, 'वाङ्मयीन प्रवृत्ती तत्त्वशोध', संपादक -केशव मेश्राम, डॉ. दादा गोरे गौरव ग्रंथ, 'मराठी कविता: परंपरा आणि दर्शन' संपादक -रवींद्र शोभणे, प्राचार्य राम शेवाळकर गौरव ग्रंथ, 'समकालीन साहित्यचर्चा' संपादक - मनोहर जाधव, डॉ.नागनाथ कोतापल्ले, गौरव ग्रंथ इत्यादी संपादित ग्रंथांमधून नव्वदोत्तरी कवितेचे समीक्षापर लेख प्रकाशित झालेले दिसतात. वसंत पाटणकर व हरिश्चंद्र थोरात यांचे नव्वदोत्तरी कवितेवरील सैद्धांतिक लेख महत्त्वपूर्ण असे आहेत.

५. वाङ्मयीन नियतकालिकातील नव्वदोत्तरी कवितेची समीक्षा :

अक्षर चळवळ (1985), कवितारती (1985), शब्दवेध (1988) अभिधा (1992 ते 1998), अभिधानंतर (1998 ते 2008), नवाक्षर दर्शन (2004), खेळ (2004), उर्मी (2005), ऐवजी (2006) सौष्ठव, साक्षात अशी काही कविताकेंद्री नियतकालिके सुरु झाली. या नियतकालिकांनी नव्वदोत्तरी कवितेच्या समीक्षेला गंभीरपणे अभिव्यक्त करण्याचा प्रयत्न केला. वाङ्मयीन नियतकालिके आणि कविता यांच्यातील संबंधाविषयी डॉ. आशुतोष पाटील लिहितात " वाङ्मयीन नियतकालिकांची, विशेषता कविताकेंद्री नियतकालिकांची भूमिका काव्य संस्कृतीला आकार देण्यात सर्वाधिक महत्त्वाची ठरत असते. कारण लिहिली जाणारी कविता ही संग्रहरूपाने कालांतराने पण प्राधान्याने वाङ्मयीन नियतकालिकातून प्रथम वाचावयास मिळते. कविता हा एक स्फुटरचना प्रकार असल्याने त्याच्या चलनवलनासाठी अन्य वाङ्मय प्रकारांच्या तुलनेत अधिक निकडीने नियतकालिकांची आवश्यकता असते. त्यामुळे जुन्या कवीबरोबरच नव्या कवींच्या अभिव्यक्तीला एक मंच उपलब्ध करून देण्याची आणि काव्याभिरुचीची पत व प्रत दोन्हीही उंचावण्याची ऐतिहासिक जबाबदारी नियतकालिकांवर सर्वार्थाने असते."२

वरील विश्लेषणातून नियतकालिकांचे वाङ्मयीन पर्यावरणातील स्थान स्पष्ट होते.

वाङ्मयीन नियतकालिके वाङ्मयीन अभिरुचीला वळण देत असतात. कविताकेंद्री वाङ्मयीन नियतकालिकांमुळे नव्वदोत्तरी काव्य समीक्षेला अभिव्यक्तीचे एक साधन उपलब्ध झाले. या नियतकालिकांमुळे कविता हा वाङ्मय प्रकार वाङ्मय विश्वाच्या केंद्रस्थानी आला. या वेगवेगळ्या नियतकालिकांनी नव्वदोत्तरी कवितेविषयी सैद्धांतिक मांडणी उभी करण्याचा प्रयत्न केला. यातील काही नियतकालिकांनी नव्वदोत्तरी मराठी कविता विशेषांक प्रकाशित केले. यामध्ये

१. अभिधानंतर, दिवाळी, 2003

२. नवाक्षर दर्शन, वर्ष तीन, अंक दोन, जानेवारी मार्च 2007

३. खेळ, एप्रिल, मे, जून, 2010 सतरावा

४. सर्वधारा, जानेवारी मार्च 2017 ५. अतिरिक्त मार्च 2013

६. अतिरिक्त ऑगस्ट 2014

नव्वदोत्तरी मराठी कविता विशेषाकांमध्ये नव्वदोत्तरी कवितेचे विस्तृत व व्यापक मांडणी अभ्यासकांनी करण्याचा प्रयत्न केलेला दिसून येतो. या नियतकालिकातील समीक्षा मांडणीमध्ये जाणीपूर्वकता, आग्रहीपणा अधिक दिसून येतो. या नियतकालिकातील काही लेखांची मांडणी एकांगी स्वरूपाची आहे. नव्वदोत्तरी काव्य समीक्षेच्या प्रवाहामध्ये या नियतकालिकांच्या कामगिरीला विशेष महत्त्व आहे. वाङ्मयीन नियतकालिकातील नव्वदोत्तर कवितेची समीक्षा करणाऱ्या समीक्षकांनी मध्ये द.गो.काळे,मंगेश काळे, दिनकर मनवर, नितीन रिंटे, प्रविण बांदेकर,उदय रोटे, रणधीर शिंदे, हेमंत दिवटे,आशुतोष पाटील, महेंद्र भवरे,एकनाथ पगार, गोविंद काजरेकर,श्रीधर तिळवे, देवानंद सोनटक्के, पी.विठ्ठल,महेंद्र भवरे, मनोहर जाधव या नव्या समीक्षकांचा समावेश करावा लागतो. या नव्या दमाच्या समीक्षकांसोबतच वसंत पाटणकर, हरिश्चंद्र थोरात, वसंत आबाजी डहाके, राजन गवस डॉ. नागनाथ कोत्तापल्ले या जुन्या पिढीतील समीक्षकांचा ही आपल्याला समावेश करता येतो.एकूणच या विविध नियतकालिकातील काव्य समीक्षेमध्ये आजच्या काळातील साहित्यविचारांचे प्रतिबिंब आढळते. साहित्याच्या विविध दृष्टिकोनबरोबरच नव्या पिढीचे नवी संवेदनशीलता या नियतकालिकांनी जपलेली दिसते. वाङ्मयीन नियतकालिकांनी काव्य या वाङ्मय प्रकाराला व काव्य समीक्षेला समकाळाशी जोडणारी समग्र विचारदृष्टी दिली.

६. वृत्तपत्रातून प्रकाशित झालेली नव्वदोत्तरी कवितेची समीक्षा:

सकाळ, लोकमत, लोकसत्ता, महाराष्ट्र टाईम्स या सारख्या वृत्तपत्रांमधून रविवार पुरवणीतनव्वदोत्तरी कवींच्या काव्यसंग्रहाचा परिचय, परीक्षणप्रकाशित झाले आहेत. सर्वसामान्य वाचकाला परिचय व्हावा म्हणून लिहिलेली ही परीक्षणे लेख काव्य समीक्षेत महत्त्वाचे आहेत. विशेष लेखांमध्ये आजच्या कवितेत काय घडत आहे याचा परिचयात्मक मांडणी या समीक्षेत केलेली दिसून येते. सर्वसामान्य वाचकांसाठी हे समीक्षापर लेखन महत्त्वाचे ठरते.

७. कवितासंग्रहांना लिहिलेल्या प्रस्तावनामधील काव्यसमीक्षा :

मराठी वाङ्मय व्यवहारात काव्यसंग्रह प्रस्तावना लिहिण्याची प्रदीर्घ परंपरा आहे.कवी स्वतःच्या काव्यसंग्रहालाप्रस्तावना लिहितात या प्रस्तावने मधून कवी आपली काव्यनिर्मिती प्रक्रिया उलगडून सांगण्याचा प्रयत्न करतात. आपली भूमिका, दृष्टिकोण अभिव्यक्त करण्यासाठी कवी प्रस्तावना लिहितात. ज्येष्ठ अभ्यासक,कवींची प्रस्तावना काव्यसंग्रहासाठी घेतली जाते. या प्रस्तावनेत प्रस्तुत कवितेची बलस्थाने मांडली जातात.कवितेची पाठराखण केली जाते. कवितेचे स्वरूप आणि प्रेरणा सांगितल्या जातात. प्रस्तावनेमध्ये लेखनात मूल्यमापनाचा अभाव असतो. मर्यादा, दोष न सांगण्याचा प्रघात असतो. त्यामुळे उणिवा दोष कळत नाहीत.त्यांची पुनरावृत्ती होत राहते. एकूण कवितेचे वेगळेपण शोधत असताना

परंपरेतील कविते स्थानही निश्चित केले जाते. नागनाथ कोतापल्ले, वसंत आबाजी डहाके, द. ता भोसले, मनोहर जाधव, यशवंत मनोहर, किसन पाटील यांसारख्या अभ्यासकांनी नव्वदोत्तरी कवींच्या कविता संग्रह प्रस्तावना लिहिल्या आहेत. या प्रस्तावनांचे स्वरूप मुख्यतः आस्वादक स्वरूपाचे असते. मूल्यमापनाच्या दृष्टीचा अभाव या प्रस्तावनेतील समीक्षेत दिसतो.

८. संस्था पातळीवरील नव्वदोत्तरी कवितेची समीक्षा :

संस्थात्मक पातळीवर वाङ्मयाचा अभ्यास करण्याची मराठी वाङ्मय विश्वात प्रदीर्घ परंपरा आहे. विशिष्ट लेखकाचा अभ्यास, विशिष्ट कालखंडाचा अभ्यास, विशिष्ट वाङ्मय प्रकारचा अभ्यास, विशिष्ट वाङ्मयीन प्रवाहांचा अभ्यास करण्याची परंपरा मराठीत आहे. सार्वजनिक वाचनालय नाशिक या संस्थेच्यावतीने मराठी साहित्यिकांची समीक्षा करणाऱ्या ग्रंथ प्रकाशित करण्यात आला. प्रदक्षिणा खंड -दुसरे प्रकाशित करण्यात आला. या ग्रंथातील 'स्वातंत्र्योत्तर कविता' हा रवींद्र घवी यांचा लेख मराठी कवितेचा आढावा घेणार आहे. स्वातंत्र्योत्तर मराठी कवितेचा मागोवा या लेखात घेतलेला आहे. तो मुख्यतः काव्यनिर्मितीच्या अंगाने घेतलेला व नव्या प्रवृत्ती दर्शवणारा आहे. नव्वदोत्तरी कवितेचा अंधुक उल्लेख या लेखात आहे.

ललित मासिकाच्या सुवर्णमहोत्सवी वर्षानिमित्त कविता विशेषांक प्रकाशित करण्यात आला. 'बदलती मराठी कविता व काव्यसंस्कृती: काही परिमाणे' असे या अंकाचे शीर्षक होते. या अंकात अतिशय गंभीरपणे मराठी कवितेच्या स्थितीगतीचा आलेख मांडण्यात आला आहे. वसंत आबाजी डहाके, उदय रोटे, रणधीर शिंदे, वैजंतीमाला जाधव -भोसले, निशिकांत मिरजकर, प्रवीण दशरथ बांदेकर, आशुतोष पाटील, निशिकांत ठकार या सर्व मान्यवर समीक्षकांचे लेख नव्वदोत्तरी काव्य समीक्षेला समृद्ध करणारे आहेत. महाराष्ट्र साहित्य परिषद पुणे यांनी मराठी वाङ्मयाचा इतिहासाचे खंड प्रकाशित केले आहेत. यामध्ये खंड सातवा इ.स. 1950 ते 2000 -भाग दुसरा हा अतिशय महत्त्वाचा आहे. यामध्ये 1950 ते 1975 डॉ. प्रभा गणोरकर आणि इसवी सन 1975 ते 2000 हा डॉ. नीलिमा गुंडी यांचे प्रदीर्घ लेख महत्त्वाचा आहे. या लेखात मराठी कवितेचा इतिहास मांडला गेला आहे. या लेखात डॉ. नीलिमा गुंडी लिहितात, "1975 ते 2000 हा कालखंड म्हणजे मराठी कवींसाठी एक गुंतागुंतीचा वास्तव होते. या वास्तवाचा अनुभव घेणे त्याचे संवेदन जाणून घेणे आकलन व चिंतन या पातळीवर ते संवेदन नेणे आणि त्याला कलात्मक रूप देणे ही प्रक्रिया सोपी नाही " ३वरील विश्लेषणातून नव्वदोत्तरी कवितेच्या वास्तवाचे भान आपल्याला येते. नव्वदोत्तरी काव्यची अत्यंत पायाभूत माहिती देणारे असे लेखन प्रस्तुत खंडात डॉक्टर नीलिमा गुंडी यांनी केलेले आहे. अभ्यासकांना उपयुक्त माहिती देणारे लेखन असे या लेखाचे स्वरूप आहे. अशा प्रकारे आपल्याला संस्थात्मक पातळीवरील नव्वदोत्तरी कवितेच्या समीक्षेची वाटचाल मांडता येते.

९ वाङ्मयीन प्रवाहांच्या प्रेरणेने झालेली नव्वदोत्तरी कवितेची समीक्षा :

नव्वदोत्तरी कवितेचे वर्गीकरण करण्यासाठी कवितेतील वाङ्मयीन प्रवाहांचा आधार घेतला जातो.दलित, आदिवासी, महानगरी, ग्रामिण, स्त्रीवादी, मुस्लिम,जनवादी अशा स्वरूपात वाङ्मय प्रवाहांचे वर्गीकरण केले जाते. यातील दलित, वाङ्मय प्रवाहातील नव्वदोत्तरी कवितेची समीक्षा संख्यात्मकदृष्ट्या अधिक प्रमाणात झाल्याचे दिसून येते. नव्वदोत्तरी दलित कवितेची समीक्षा ग्रंथ रूपातून प्रकाशित झालेली आहे. नव्वदोत्तरी एकूणच मराठी कवितेची सैद्धांतिक व आस्वादक समीक्षा दलित साहित्याच्या अभ्यासकांनी केलेली आहे. नव्वदोत्तरी दलित कवितेची सैद्धांतिक,मूल्यमापनात्मक, विस्तृत समीक्षा महेंद्र भवरे यांनी तीन ग्रंथांमधून केली आहे. 'दलित कवितेतील नवे प्रवाह, मराठी कवितेच्या नव्या दिशा' ;

'दलित कविता आणि प्रतिमा' या तीन ग्रंथातून एकूणच दलित कवितेची साक्षेपी समीक्षा महेंद्र भवरे यांनी केलेली आहे.दलित कवितेतील नवे प्रवाह आणि मराठी कवितेच्या नव्या दिशा या ग्रंथांमधून नव्वदोत्तरी दलित कवींच्या काव्यसंग्रहाचे आस्वादक अंगाने समीक्षा केली गेली आहे. आस्वादप्रक्रिया बरोबरच नव्वदोत्तरी दलित कवितेच्या विशेषांवर या समीक्षेतून प्रकाशझोत टाकला आहे. नव्वदोत्तरी दलित कवितेचे स्वरूप, विशेष,प्रेरणा महेंद्र भवरे यांनी स्पष्ट केले आहेत. नव्वदोत्तरी दलित कवितेचे वेगळेपण त्यातील वृत्ती-प्रवृत्तींचे विश्लेषण महेंद्र भवरे यांच्या समीक्षेतून येते. नव्वदोत्तरी दलित कवितेचा युगधर्म महेंद्र भवरे यांनी स्पष्ट केला आहे.

महेंद्र भवरे यांचा 'दलित कविता आणि प्रतिमा' हा ग्रंथ नव्वदोत्तरी दलित कवितेच्या समीक्षेतील महत्त्वाचा ग्रंथ ठरतो.दलित कविता ही चळवळीची कविता आहे.या जाणिवेने सामाजिक अभिनिवेश बाळगत या कवितेची आस्वादक अंगाने समीक्षा केली गेली. परंतु या कवितेतील सामाजिक बांधिलकी बरोबरच कवितेतील कलातत्व, सैद्धांतिक वाङ्मयीन मूल्यांचा शोध महेंद्र भवरे यांनी 'दलित कविता आणि प्रतिमा'या ग्रंथातून घेतला आहे. हा ग्रंथ एकूणच नव्वदोत्तरी मराठी काव्य समीक्षा क्षेत्रातील महत्त्वाचा ग्रंथ आहे. नव्वदोत्तरी दलित कवितेच्या समीक्षाचा विचार करत असताना अनेक अभ्यासकांनी 'अस्मितादर्श' या नियतकालिकातून नव्वदोत्तरी दलित कवितेची चिकित्सा केलेली दिसून येते. नव्याने कविता लिहिणाऱ्यांसाठी दिशा दिग्दर्शनाचे कार्य अस्मितादर्शने केले. नव्वदोत्तरीदलित कवींच्या काव्यसंग्रहाला अनेक अभ्यासकांनी प्रस्तावना लिहिल्या आहेत.त्यांचे स्वरूप आस्वादक स्वरूपाचे आहे. मूल्यमापन न करता कवींच्या चांगल्या बाजू ठळकपणे मांडण्याचा प्रयत्न झालेला दिसतो. उणीवा,मर्यादा यांचा ओझरता उल्लेख या प्रस्तावनावजा समीक्षेतकेलेला दिसतो.

गंगाधर पानतावणे, यशवंत मनोहर, प्रा.केशव मेश्राम,अर्जुन डांगळे,सदा कऱ्हाडे,भालचंद्र फडके,रा.ग.जाधव, दत्ता भगत, डॉ.मनोहर जाधव या अभ्यासकांनी नव्वदोत्तरी दलित कवितेचे विश्लेषण निमित्तपरतत्वे केलेले आहे.प्रस्तावना, नियतकालिकातील काव्यसंग्रहाची



समीक्षा,पुस्तक परिचय या स्वरूपात हे लेखन आहे. यात सैद्धांतिक, विस्तृत,मूल्यमापनात्मक असे या लेखनचे स्वरूप नाही. केवळ आस्वादकपर,पाठराखण करणारे असे हे लेखन आहे.एकूण दलित साहित्याची सैद्धांतिक मांडणी अनेक ग्रंथातून केली गेलेली आहे.वरील काही अभ्यासकांनी वेगवेगळ्या काव्यसंग्रहांना लिहिलेल्या प्रस्तावनाची पुस्तके प्रसिद्ध केली आहेत.या ग्रंथांमध्ये सुसूत्रता दिसून येत नाही. ते लेखन शेवटी नौमत्कीक ठरते.केशव मेश्राम यांनी संपादित केलेल्या 'विद्रोही कविता ' या पुस्तकाची प्रस्तावना समीक्षात्मक स्वरूपाचे आहे.यशवंत मनोहर यांनी लिहिलेल्या 'काही कविता संग्रहाच्या निमित्ताने या ग्रंथात नव्वदोत्तरी कालखंडातील काही कवींचे काव्यसंग्रह डोळ्यासमोर ठेवून केलेले लेखन समाविष्ट आहे. या लेखनाचे स्वरूप कसे आहे. याविषयी या पुस्तकाच्या मलपृष्ठावरील मजकूरात लिहिलेले आहे कीया ठिकाणी कवींना प्रोत्साहन देणे हे प्रस्तावनेचे प्रयोजन असले.तरी ते एकमेव प्रयोजन नाही दव्या संग्रहाकडे पाहण्याची एक निश्चित दृष्टी निर्माण व्हावी व त्यांच्या कवितेतील काव्य आणि विचार यांचा वाचकाला आस्वाद घेता यावा हा या प्रस्तावनेच्या उद्देश आहे.यशवंत मनोहर यांच्याकडे स्वागतशील,साक्षेपी व कलात्मकतेने कवीला व वाचकाला बरोबर घेऊन जाण्याचे सामर्थ्य आहे.याचा प्रत्यय प्रस्तुत प्रस्तावनेतून येतो.

एकूणच प्रस्तावनापर लेखनातील सकारात्मक बाजू या विचारातून स्पष्ट होते.प्रस्तावनापर लेखनाचे मर्म सांगताना यशवंत मनोहर लिहितात "प्रस्तावना म्हणजे शास्त्रकाट्याची कसोटी लावून केलेली समीक्षा नव्हे. कवितासंग्रहाच्या प्रस्तावनेतून कवितेच्या आकलनाची एक दिशा साकार होते.कविता म्हणून अभिप्रेत असलेल्या मर्माचे प्रकाशन मात्र प्रस्तावना करते.प्रस्तावनेत दोषदिग्दर्शन नसतात असे नाही पण हे दोष दिग्दर्शन अत्यंत सूचक पद्धतीने आपुलकीच्या ओलाव्याने केलेले असते " ४ वरील विवेचनातून काव्यसंग्रहाच्या प्रस्तावनापर समीक्षेचे स्वरूप आपल्या लक्षात येते.

डॉक्टर मनोज जाधव यांच्या 'परीवर्तनाचे प्रवाह' या पुस्तकाचे स्वरूपही वरील यशवंत मनोहर यांच्या विश्लेषणाला लागू ठरणारे आहे. या ग्रंथातील सैद्धांतिक चर्चा महत्त्वाची अशी आहे.वेगवेगळ्या निमित्तांनी लिहिलेले नव्वदोत्तरी कवितेवरील समीक्षा लेख महत्त्वपूर्ण असे आहेत.

नव्वदोत्तरी दलित कवितेचा विचार करत असताना काही अभ्यासकांचे स्वतंत्र ग्रंथ महत्त्वाचे आहेत. यात 'मराठी दलित कविता: एक चिकित्सक अभ्यास ' डॉ. सुनील कुमार चंदनशिवे, 'दलित कवितेतील अस्मिता ' डॉ. बिरा पारसे या दोन ग्रंथांचा समावेश करावा लागेल. हे दोन्ही पुस्तके प्रबंधातून ग्रंथरूपात झालेली रूपांतर अशी आहेत.याबरोबरच 'आंबेडकरी कवितेच्या अंतरंग ' हे हरीश खंडेराव यांचाग्रंथही नव्वदोत्तरी दलित कवितेचे

विश्लेषण करणारा आहे. अशा प्रकारे आपल्याला नव्वदोत्तरी दलित कवितेच्या समीक्षेचे स्वरूप सांगता येते.

नव्वदोत्तरी दलित कवितेबरोबरच विकसित झालेला आदिवासी कवितेचा प्रवाह होय. नव्वदोत्तरी आदिवासी कवींचा काही दलित अभ्यासकांनी दलित कवितेचा समावेश केला आहे. डॉ. विनायक तुमराम यांचे 'शतकातील आदिवासी कविता' हा संपादित काव्यसंग्रह महत्त्वाचा असा आहे. या ग्रंथाला असलेली डॉ.विनायक तुमराम यांची जवळपास शंभर पानांची प्रस्तावना ही अत्यंत विस्तृतपणे आदिवासी कवितेचे सैद्धांतिक मांडणी करणारी आहे. डॉ. तुकाराम रोंगटे यांचे 'आदिवासी कवितेचा उषःकाल आणि सद्यस्थिती' हा ग्रंथही नव्वदोत्तरी आदिवासी कवितेचे स्वरूप विशद करणारा आहे.

नव्वदोत्तरी स्त्रियांची कविता या प्रवाहाचे सखोल विश्लेषण करणारा विस्तृत असा ग्रंथ उपलब्ध नाही. नियतकालिकांतील लेख हाच काय तो या प्रवाहाचे विश्लेषण करणारा ऐवज ठरतो. आधुनिक मराठी कवयित्रींची कविता 'हा रा.ग.जाधव यांचा ग्रंथ स्त्रियांच्या कवितेची चिकित्सा करणारा ग्रंथ आहे. या ग्रंथात इसवी सन 1980 ते 1995 या कालखंडातील स्त्रियांच्या कवितेचे विशेष स्पष्ट करण्याचा प्रयत्न केलेला आहे.

नव्वदोत्तरी ग्रामीण कविता या प्रवाहाचे समीक्षा : लेख स्वरूपात, संपादित पुस्तकातून, नियतकालिकातून झालेली दिसून येते. 'ठी ग्रामीण कवितेचा इतिहास - कैलास सार्वेकर यांच्या ग्रंथात 1990 पर्यंतच्या ग्रामीण कवितेचा इतिहास मांडला आहे. याबरोबरच आनंद यादव, नागनाथ कोतापल्ले, द. ता.भोसले, वासुदेव मुलाटे, राजन गवस, माधव पुटवाड, चंद्रकुमार नलगे, भास्कर चंदनशिव, रवींद्र ठाकूर, गणेश देशमुख यासारख्या समीक्षकांनी मराठी ग्रामीण कवितेची समीक्षा विविध वाङ्मयीन नियतकालिकातून, प्रस्तावना मधून, संपादित ग्रंथातील लेखांमधून, केलेली दिसते. वसंत पाटणकर यांनी कवितारती मध्ये 'इंद्रजीत भालेराव यांची कविता' या विषयी लिहिलेला लेख नव्वदोत्तरी ग्रामीण कवितेची सकस मूल्यमापनात्मक समीक्षा करणारा आहे.

महानगरी संवेदनेच्या नव्वदोत्तरी कवितेवर ग्रंथ रूपातून समीक्षा झालेली दिसून येत नाही. त्रोटक स्वरूपात महानगरी कवितेवर समीक्षा झालेली दिसून येते. जनवादी, मुस्लिम, ख्रिस्ती अशा प्रवाहांच्या स्वरूपात मूल्यमापनात्मक साक्षेपी समीक्षा नव्वदोत्तरी कवितेची झालेली दिसून येत नाही.

१०. विद्यापीठीय संशोधन पदवीसाठी प्रबंध रूपातून झालेली नव्वदोत्तरी कवितेची समीक्षा :

महाराष्ट्रातील विविध विद्यापीठांमध्ये एम.फिल, पीएच्.डी पदवीसाठी प्रबंध रूपातून नव्वदोत्तरी कवितेची समीक्षा झालेली दिसून येते. नव्वदोत्तरी कालखंडातील मराठी कविता, कवितेला केंद्र ठेवणारी नव्वदोत्तरी वाङ्मयीन नियतकालिके, नव्वदोत्तरी कालखंडातील कवी, नव्वदोत्तरी कालखंडातील कवितेतील प्रवाह, नव्वदोत्तरी कवितांची शैली, नव्वदोत्तरी

कवितेतील मिथके,प्रतिमा यांची समीक्षणात्मक समीक्षात्मक मांडणी या प्रबंधातून झालेली दिसते. मुख्यतः नव्वदोत्तरी कवितेतील आशयसूत्रे वाङ्मयीन मूल्ये यांचे विश्लेषण या समीक्षेतून झालेली दिसते.

११.नव्वदोत्तरी काव्य समीक्षेचे विशेष :

१. नव्वदोत्तरी कवितेची समीक्षा विस्तृतपणे मूल्यमापनात्मक स्वरूपात अल्प प्रमाणात झालेली आहे.

विस्तृता, सूक्ष्मता,मूल्यमापनात्मकता यांचा अभाव ही नव्वदोत्तरी काव्य समीक्षेची मर्यादा सांगता येते.

२. नव्वदोत्तरी कवितेविषयी तात्विक, सैद्धांतिक मांडणी करणारी समीक्षा कमी प्रमाणात झाली आहे.

३. नव्वदोत्तरी कवितेचे मूल्यमापन करून केवळ न थांबता नव्वदोत्तरी काव्य समीक्षा पूर्वकालीन मराठी कवितेचे पुनर्मूल्यमापन करते. विशेषता नवकविता व साठोत्तरी कवितेचे पुनर्मूल्यमापन नव्वदोत्तरी काव्य समीक्षा करते.

४. नव्वदोत्तरी कवितेची समीक्षा विविध पद्धतीने झालेले आहे. आस्वादक समीक्षा विपुल प्रमाणात झालेली आहे. मानसशास्त्रीयरूपनिष्ठ, शैलीनिष्ठ,स्त्रीवादी मूल्यमापनात्मक समीक्षेचा अभाव नव्वदोत्तरी कवितेत दिसतो.

५. कविताकेंद्री वाङ्मयीन नियतकालिकांमुळे नव्वदोत्तरी काव्य समीक्षेला एक अभिव्यक्तीचे साधन उपलब्ध झाले.वाङ्मयीन नियतकालिकांमधून नव्वदोत्तरी काव्य समीक्षा गंभीरपणे प्रकट होताना दिसते. वाङ्मयीन नियतकालिकांनी नव्वदोत्तरी कवितेविषयी सैद्धांतिक मांडणी केली. विविध वाङ्मयीन नियतकालिकांनी नव्वदोत्तरी मराठी कविता विशेषांक प्रकाशित केले. ते अंक नव्वदोत्तरी कवितेची चिकित्सा करणारे आहेत.नव्वदोत्तरी काव्य समीक्षेत या विशेषांकाचे स्थान महत्त्वपूर्ण असेआहे.

६. नव्वदोत्तरी काव्यसंग्रहांना लिहिलेल्या प्रस्तावनांमध्ये मूल्यमापनाचा अभाव दिसून येतो. मर्यादा, दोष न सांगण्याचा प्रघात प्रस्तावना लेखनात दिसतो.केवळ कवितेची बलस्थाने मांडली जातात. त्यामुळे काव्यसंग्रहाच्या प्रस्तावनेतील समीक्षा ही परिपूर्ण ठरत नाही.

**समारोप :**

थोडक्यात कवितेविषयी प्रत्यक्ष समीक्षणात्मक ऐतिहासिक किंवा सैद्धांतिक समीक्षा अल्प प्रमाणात झालेली दिसते. नव्वदोत्तरी काव्य समीक्षा विपुल प्रमाणात झालेलीआहे. या समीक्षेने कवितेविषयीची जाण विविधांगी व समृद्ध केले आहे. नव्वदोत्तरी काव्य समीक्षाही वाङ्मयीन अभिरुचीला वृद्धीगंत करणारी आहे. समकालीन काव्याभिरुचीला नव्वदोत्तरी काव्यसमीक्षेनेआकार दिला आहे.नव्वदोत्तरी काव्यसमीक्षेत काही जेष्ठ समीक्षकां बरोबरच नवोदित समीक्षकांची मांडणीही लक्षवेधी स्वरूपाचे आहे. नव्वदोत्तरी काव्य समीक्षे विविध

स्वरूपात अविष्कृत होते.नव्वदोत्तरी काव्य समीक्षा ही नव्वदोत्तरी कवितेचे स्वरूप, विशेष,प्रेरणा यांना प्रकट करते.नव्वदोत्तरी कवितेतील प्रतिमासृष्टी,प्रतीके,मिथके, रचनाबंध यांना नव्वदोत्तरी काव्य समीक्षेने स्पष्ट केले आहे.

नव्वदोत्तरी काव्यातील भाषाशैली, संवादात्मक, लयबद्धता, उपरोधिकता,उपहास,सूचकता,संवादात्मकता प्राक्कथा यांना नव्वदोत्तरी काव्य समीक्षेने सैद्धांतिक स्वरूप दिलेले दिसत नाही. नव्वदोत्तरी काव्य समीक्षा आस्वादक स्वरूपात मोठ्या प्रमाणात लिहिली गेली आहे.

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## Preparation and sensing performance of tin oxide thin films

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### Abstract:

Tin oxide thin films have been prepared by air assisted spray pyrolysis method. XRD was used to know crystal structure. The gas sensing behavior was investigated at different operating temperatures. CO gas detection was also investigated and stability of thin films were studied and discussed.

**Keywords:** Spray Pyrolysis, Tin oxide, response and recovery time.

### Introduction:

Tin oxide is a versatile material having applications in the areas like transparent electrodes in photoelectric conversion devices namely amorphous silicon solar cells, liquid crystal display, gas sensor and many more [1], mainly due to their outstanding features. Gas sensors have a great influence in many areas, such as environmental monitoring, domestic safety.

In order to improve the gas sensing properties of the sensors, nature of the grains plays an important role in addition. Spray Pyrolysis opens up the possibility to control the film morphology and particle size in the nanometer range. Spray pyrolysis is a versatile technique for deposition of metal oxides [2].

In the present investigations, nanocubes SnO<sub>2</sub> thin films were prepared by spray pyrolysis technique. Phase purity was studied using XRD techniques. These nanocubes SnO<sub>2</sub> were tested for detection of different gases and were observed to be most sensitive to CO at 350<sup>o</sup> C.

### Experimental details:

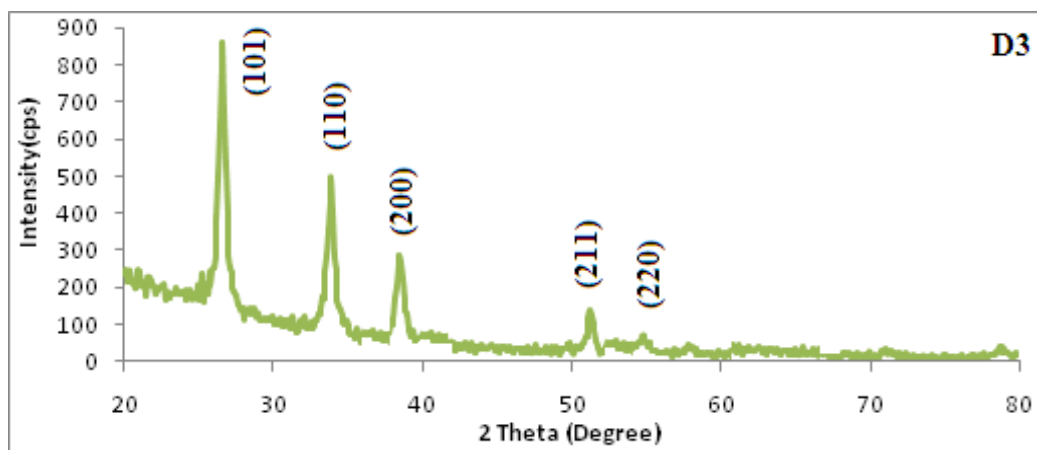
Tin oxide thin films were prepared from aqueous solution of tin (II) dichloride dehydrate (SnCl<sub>2</sub>.2H<sub>2</sub>O), Purified Merck) dissolved in deionized water to a concentration of 0.05 M for the preparation of thin films. The spray produced by nozzle was sprayed onto the ultrasonically cleaned glass substrates heated at 300 ± 5<sup>o</sup> C. The deposition parameters like

spray rate 5 ml/min. was adjusted using air as a carrier gas, nozzle to substrate distance (25 cm) were kept constant, and to and fro frequency of the nozzle ( $18 \text{ cycles min}^{-1}$ ) were kept constant at the optimized values indicated in brackets.

Various parameters such as nozzle-to-substrate distance, deposition time and flow rate of solution, deposition temperature and concentration were optimized to get good quality films and as prepared Tin oxide thin film samples D1 (= 5 ml/min), D2 (= 10 ml/min), D3 (= 20 ml/min) and D4 (= 30 ml/min) were annealed in air at  $500^\circ \text{C}$  for 1 hour.

## Results and discussion:

### *Phase studies using X-ray diffraction:*



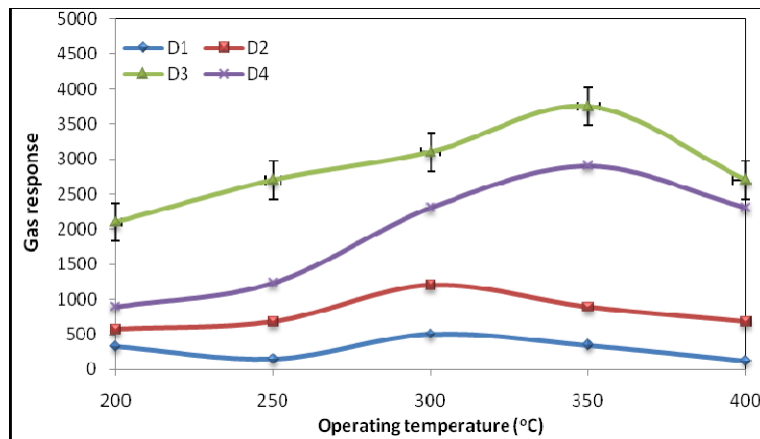
**Fig. 1.** X-ray diffractogram of Tin oxide most sensitive thin films samples: D3

Figure 1 shows the X-ray diffractogram of most sensitive thin films samples D3. The peaks in the XRD pattern are match well with the reported ASTM data of pure  $\text{SnO}_2$ . The crystallite size was found to be 15 nm.

### **Gas sensing performance of the thin films:**

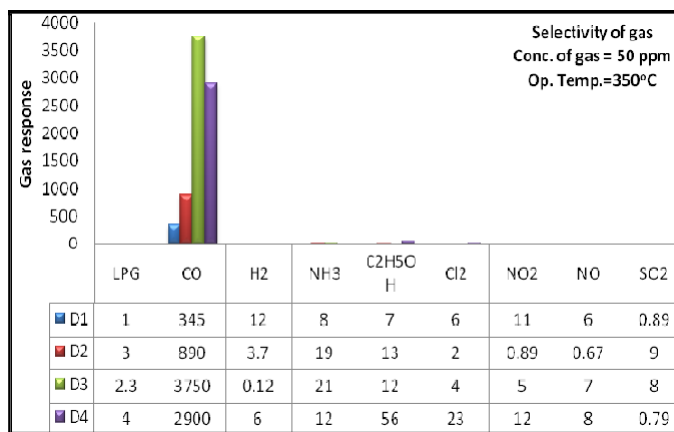
#### **Gas response:**

Figure 2 shows the variation in response with the operating temperature to 50 ppm of CO for D1, D2, D3 and D4 samples. For all the samples the response increases with increase in operating temperature and reach maximum ( $S=3750$  for sample D3) at  $350^\circ \text{C}$  and falls with further increase in operating temperature [3].



**Fig. 2.** Gas response of Tin oxide thin films with operating temperature.

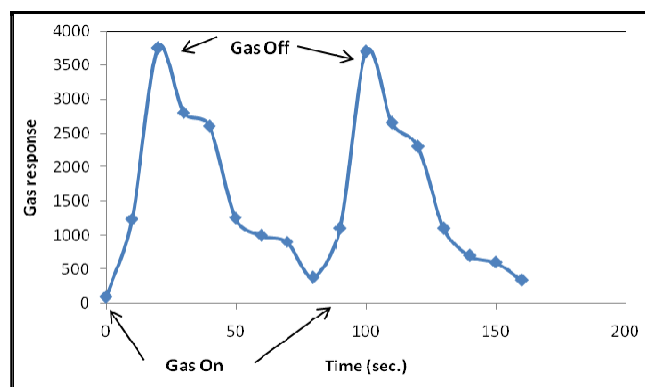
**Selectivity:**



**Fig. 3.** Selectivity of Tin oxide thin films for different gases.

Fig. 3 shows the histogram for comparison of the sensitivity to various gases for D1, D2, D3 and D4 at the optimum operating temperature 350° C.

**Response and recovery of the sensor:**



**Fig. 4.** Response and recovery of the sensor.

The response and recovery of the nanocubes SnO<sub>2</sub> most sensitive thin film (D3) sensor on exposure of 50 ppm of CO<sub>2</sub> at 350° C are represented in Fig. 4. The response is quick (30 s) and recovery is fast (60 s).

### Conclusions:

Tin oxide thin films could be prepared by simple and inexpensive spray pyrolysis technique. The structural property confirm that the as-prepared Tin oxide thin films are nanostructured in nature. Tin oxide thin film of sample D3= 3750 was most sensitive to CO gas to the gas concentration as 50 ppm at the temperature of 350° C. The sensor has good selectivity to CO against different gases. Tin oxide thin films exhibit rapid response–recovery with good stability which is one of the main features of this sensor.

### Acknowledgements:

The authors are thankful to The Principal, Shri. V. S. Naik Arts. Commerce and Science College, Raver for kind cooperation and for providing necessary laboratory facilities for this work.

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## A Study of 1991 economic reforms in India

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### Introduction:

Economic reforms have meant macro economic variables adjustment in the economy by bringing about reforms of structural adjustment measures at micro level and stabilization measures at macro level. These adjustments have led to radical changes in the existing policies. The need of adjustment was felt due to failure of economic mechanism in a country which slowly engulfed the entire sectors or the sectors critical to economic growth and development in an economy. The reasons for adjustment in the economy or economic reforms included external and internal instabilities.

India faced a crisis of unprecedented severity in the early 1990s. The budget deficit had increased from 0.9% of GDP in 1980-81 to 2.1% of GDP in 1990-91. The revenue deficit during the same period had gone up from 0.2 percent of GDP and 3.5 percent. The gross fiscal deficit had reached the level of 8.4 percent of GDP in 1990-91 from 7.5 percent in 1984-85. By August 1991, the inflation rate had climbed to a peak of 17 percent. The internal debt of the government had reached the level of 53 percent of GDP at the end of 1990-91 as against 35 percent of GDP at the end of 1980-81. Foreign exchange reserves dwindled to a level that was less than the cost of two weeks' worth of imports. The specter of default on short-term external loans loomed and led to a downgrading of India's credit rating. The government approached the World Bank and the International Monetary Fund for assistance and also undertook systemic reforms.

The major thrusts of the reforms of 1991 related to measures to address the macroeconomic and balance of payments crisis through fiscal consolidation and limited tax reforms, removal of controls on industrial investment and on imports, reduction in import tariffs, creation of a less unfavorable environment for attracting foreign capital, prudent management of movements in the exchange rate while allowing market forces to play a major role in its determination, making the rupee convertible for current account transactions and finally, opening energy and telecommunication sectors for private investment.

### **Reforms in Industrial Policy**

Industrial policy has seen the greatest change, with most central government industrial controls being dismantled. The list of industries reserved solely for the public sector—which used to cover 18 industries, including iron and steel, heavy plant and machinery, telecommunications and telecom equipment, minerals, oil, mining, air transport services and electricity generation and distribution—has been drastically reduced to three industries: defense aircrafts and warships, atomic energy generation and railway transport. Industrial licensing by the central government has been almost abolished, except for a few hazardous and environmentally sensitive industries. The requirement that investments by large industrial houses needed a separate clearance under the Monopolies and Restrictive Trade Practices Act to discourage the concentration of economic power was abolished, and the act itself is to be replaced by a new competition law that will attempt to regulate anticompetitive behavior in other ways.

### **Reforms Trade Policy**

Trade policy reform has also made progress, though the pace has been slower than in industrial liberalization. Before the reforms, trade policy was characterized by high tariffs and pervasive import restrictions. Imports of manufactured consumer goods were completely banned. For capital goods, raw materials and intermediates, certain lists of goods were freely importable, but for most items where domestic substitutes were being produced, imports were only possible with import licenses. The criteria for issue of licenses were nontransparent; delays were endemic and corruption unavoidable. The economic reforms sought to phase out import licensing and also to reduce import duties.

### **Tax Reforms**

The Chelliah Committee has produced a remarkable analysis of the weakness of India's taxation system. Since 1991 several efforts have been made through the annual budget process to achieve tax reforms.<sup>18</sup> These have focused on: expanding the tax base by including services; reducing rates of direct taxes for individuals and corporations; abolishing most export subsidies, lowering import duties; rationalizing sales tax and reducing the cascading effect of central indirect taxes by introducing a Modified Value Added Tax and a soon-to-be implemented nationwide Value Added Tax; rationalizing both direct and indirect taxes by removing unnecessary exemptions; providing for tax incentives for infrastructure and export-oriented

sectors, including setting up special Economic Zones; and simplification of procedures and efforts for improving the efficiency of the tax administration system especially through computerization.

### **Labour sector reforms**

Greater competition should be injected in the labour market by allowing a 'hire and fire' policy, unambiguously linked to productivity and profitability of the micro enterprises. These measures would be of great help in improving the presently wide-spread inefficiency oriented 'work culture', especially in public enterprises.

### **Agricultural sector reforms**

The second wave of reforms must reduce the perennial anti-agricultural bias by permitting freer exports of all 'agricultural' products, including cereals, in which India has a dynamic comparative advantage, especially under the new rules set by the World Trade Organisation. This would entail rising food prices domestically, and the government will have to manage the political economy of discontent of urban consumers of food grains. This new policy reform will unleash a high growth rate for agriculture on which nearly two thirds of India's population is still dependent for employment.

### **Foreign Direct Investment**

Liberalizing foreign direct investment was another important part of India's reforms, driven by the belief that this would increase the total volume of investment in the economy, improve production technology and increase access to world markets. The policy now allows 100 percent foreign ownership in a large number of industries and majority ownership in all except banks, insurance companies, telecommunications and airlines.

### **Conclusion**

India has embarked on a program of far-reaching economic reforms which, if carried forward, will help ensure significantly higher rates of economic growth and greater success in reducing poverty. Success in completing the reforms requires both difficult decisions and calculated political and economic risks. The importance of exports of goods, non-factor services and labour services has increased. There are increasing capital inflows as well as outward FDI. These are only some of the priority areas emerging from this paper. There are many others related to reforms in energy pricing, management of scarce water resources, and managing the challenge of urbanization. Constraints of space have ruled out exploring these issues.

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## Data Article

# Green synthesis of *N*-substituted benzimidazoles: The promising methicillin resistant *Staphylococcus aureus* (MRSA) inhibitors



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## ABSTRACT

The current investigation describes the synthesis of *N*-substituted phenyl acetamide benzimidazole based derivatives **3(a-f)** and their systematic analysis against Methicillin Resistant *Staphylococcus aureus* (MRSA). These compounds were characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR spectrometry, elemental analysis and Mass. The derivative 2-(1*H*-benzimidazol-1-yl)-*N*-(3-nitrophenyl) acetamide (**3f**) exhibited significant potent antibacterial activity (6 fold more potent as compared to the standard drug Sultamicillin) against the MRSA (ATCC 4330). The structural correlation indicates that *m*-nitro phenyl at *N*-position of benzimidazole strongly favours the anti-MRSA activity compared to the *p*-nitro phenyl.

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## Specifications Table

Subject area	Organic Chemistry
Compounds	<i>N</i> -Substituted Benzimidazoles
Data category	Spectral, synthesized
Data acquisition format	NMR, IR, Mass spectra etc.
data type	analyzed
Procedure	<i>N</i> -Substituted Benzimidazoles derivatives were prepared, analysed and evaluated for the anti-MRSA inhibitory activity
Data accessibility	Manuscript and supplementary data enclosed with this article

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## 1. Rationale

Although the advent of modern antibiotics has stemmed the number of deaths due to bacterial infections, the increased occurrence of drug-resistant bacterial infections is a major global health concern. *Staphylococcus aureus* (*S. aureus*) is a Gram-positive, round shaped bacterium that is capable of causing various serious and even fatal infections. *S. aureus* resistance to antibiotics has already been identified and is associated with considerable mortality. Currently, more than 60% of *S. aureus* isolates are resistant to methicillin (methicillin-resistant *S. aureus*/MRSA) [1].

According to the report of Centers for diseases control and prevention (CDC) of March 2019, it was estimated that nearly 1,19,000 non-invasive MRSA infection involving both healthcare and community associated infection, causing more than 20,000 deaths in the year 2017 [2]. Roughly one third of healthy human individuals carry *S. aureus*, and around 2% of people carry MRSA [3]. MRSA is responsible for several difficult-to treat infections in human being including skin and soft tissue infections, septicemia, endocarditis, pneumonia, enteritis, meningitis, osteomyelitis as well as toxic shock syndrome, and represent a significant global health threat, resulting in extensive mortality and burden on global healthcare systems [4,5].

In a response to antimicrobial stress, almost all clinical MRSA isolates produce  $\beta$ -lactamase and a penicillin-binding protein with low affinity for  $\beta$ -lactam antibiotics [6]. Vancomycin is deemed as the last-resort antibiotic for the treatment of MRSA infections, but MRSA has already developed resistance to vancomycin [7].

Thus, it's imperative to novel antibiotics with potency against MRSA benzimidazole ring displays an important heterocyclic pharmacophore in drug discovery. These compounds carrying different substituents in the benzimidazole structure are associated with a wide range of biological activities including anticancer [8-10], antiviral [11-13], anti-bacterial [14-17], antifungal, [18,19] antihelmintic [20,21], anti-inflammatory [22], antihistaminic [23], proton pump inhibitor [24], antioxidant [25,26], antihypertensive [27] and anticoagulant [28] properties.

Literature survey provides various highly active *N*-substituted benzimidazole derivatives several folds higher activity towards the MRSA as compared to standard drugs. Guven et al., reported a new class of *N*-phenyl-substituted benzyl ethers benzimidazole (i) and evaluated for its antimicrobial potential against MRSA (MIC: 6.25  $\mu\text{g/mL}$ ) [29]. Mehboob et al., reported *N*-benzyl substituted benzimidazole (ii) a class of second generation benzimidazole derivatives and screened for its antibacterial activity against MRSA (MIC: > 12.5  $\mu\text{g/mL}$ ) [30]. Ozden et al., synthesized a chain of benzimidazole-5-carboxylic

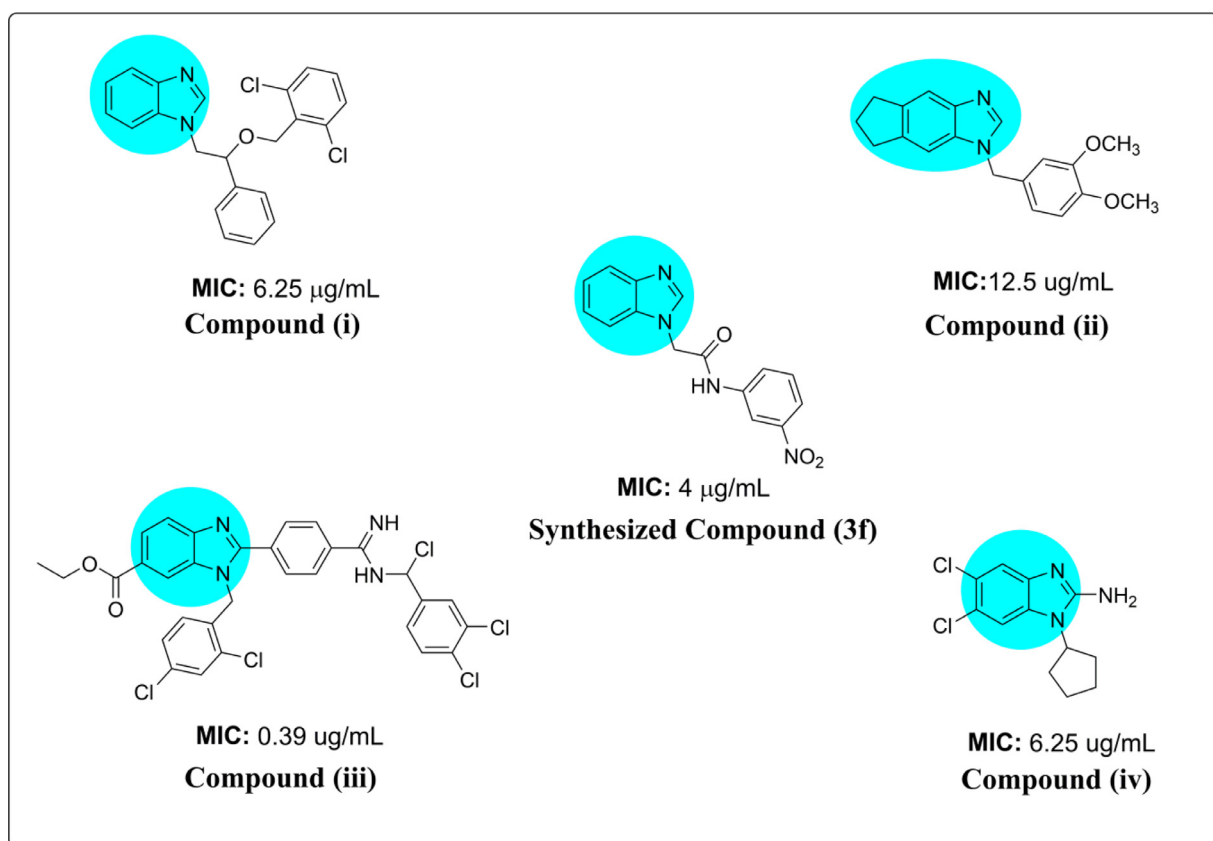
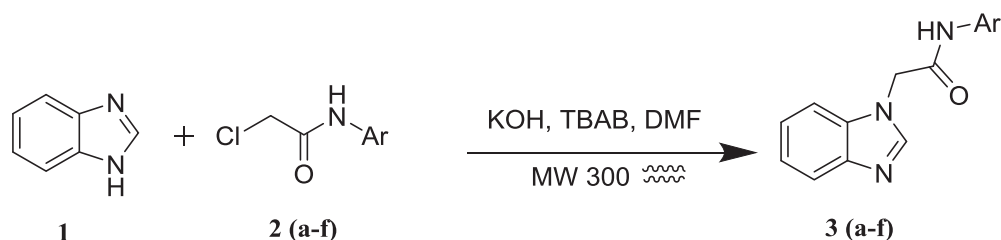
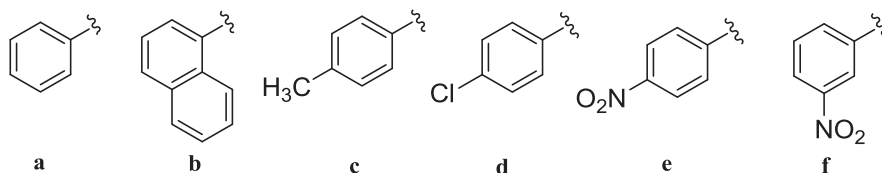


Fig. 1. Reported and proposed *N*-substituted benzimidazoles as MRSA inhibitors [29-32].



Where Ar:



**Scheme 1.** Synthetic route for *N*-substituted benzimidazole derivatives.

**Table 1**  
Physical data and time required for the microwave oven synthesis.

Compound Code	Ar	Molecular Formula	M. P. ( °C)	Reaction time (Min)	Yield (%)
3a	-C <sub>6</sub> H <sub>5</sub>	C <sub>15</sub> H <sub>13</sub> N <sub>3</sub> O	224–226	30	83
3b	-C <sub>10</sub> H <sub>7</sub>	C <sub>19</sub> H <sub>15</sub> N <sub>3</sub> O	202–204	35	88
3c	- <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>16</sub> H <sub>15</sub> N <sub>3</sub> O	218–220	30	81
3d	- <i>p</i> -Cl C <sub>6</sub> H <sub>4</sub>	C <sub>15</sub> H <sub>12</sub> ClN <sub>3</sub> O	252–254	30	78
3e	- <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub> O <sub>3</sub>	266–268	40	70
3f	- <i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub> O <sub>3</sub>	230–232	35	72

acid alkyl esters (iii) and evaluated for its antimicrobial activity against MRSA (MIC: 0.78 µg/mL) [31]. Tuncbilek et al., designed some novel benzimidazole derivatives (iv) and screened for their antimicrobial MRSA potential (clinical and standard isolates), displayed the excellent antibacterial activity as comparable to reference drugs (sultamicillin) (MIC: 6.25 µg/mL) (Fig. 1) [32]. In view of these emerging resistance problems, there is an urgent need for new anti-MRSA compounds and hence current study described new series of *N*-substituted benzimidazoles as MRSA inhibitors.

## 2. Result and discussion

### 2.1. Chemistry

The title compounds **3(a-f)** were synthesized by green chemistry approach as depicted in **Scheme 1**. Benzimidazole was dissolved in DMF containing KOH and catalytic amount of TBAB. Different substituted chloroacetanilide **2(a-f)** was introduced in this reaction mixture and irradiated to microwave until the completion of reaction. Physical data of *N*-substituted benzimidazole derivatives and time required for micro-oven synthesis is given in a **Table 1**.

In the present work *N*-substituted benzimidazole derivatives were prepared according to the indicated reactions in **Scheme 1**. Spectral data was found in full concurrence with proposed structure within the scheme. The synthesis of the title compound **3(a-f)** was confirmed by the presence of IR band at ~ 3350 cm<sup>-1</sup> (NH stretching) and ~ 1675 cm<sup>-1</sup> (C=O stretching) sharp singlet in <sup>1</sup>H NMR at ~10.00 ppm corresponding to -NH- and occurrence of singlet at ~ 5.00 ppm integrating for 2 protons of methylene. <sup>13</sup>C NMR gave significant information to affirm the number of carbon types. <sup>13</sup>C NMR shows significant peaks at ~ 47.31 (-CH<sub>2</sub>-) ppm and ~ 165.1 (>C=O of amide) ppm and affirmed the formation of title compound **3(a-f)**. Further elemental analysis and Mass data confirms the formation of title compound **3(a-f)**.

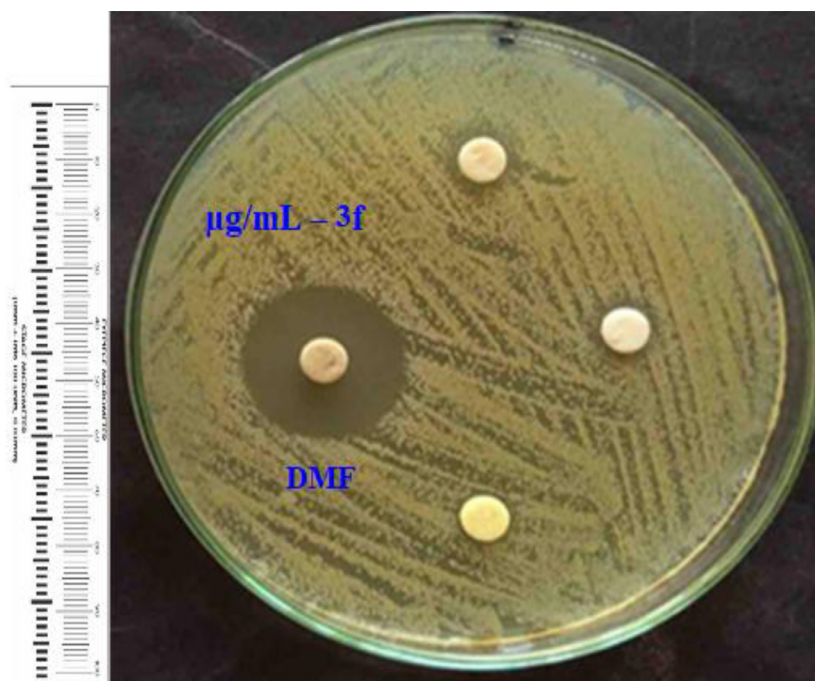
In general, the reactions are very clean, without any side product in every run. In fact, the crude products obtained are of high purity (>90% by <sup>1</sup>H NMR) with remarkable yields and do not require any chromatographic separation. Recrystallization from hot ethanol provides analytically pure sample. Most significantly, the whole operation involves very less/no organic solvent at any stage. Such simple, efficient and cost effective method is described for the synthesis of *N*-substituted benzimidazole derivatives. This simple, facile and environmentally benign safe procedure is advantageous in terms of experimentation, yield of product, short reaction time. Additionally, this protocol is adaptable to parallel synthesis and generation of combinatorial library of potentially bioactive *N*-substituted benzimidazole derivatives.

**Table 2**

The zone of Inhibition and MIC values of synthesized compounds against MRSA strain (*Staphylococcus aureus*; ATCC 4330).

Compound	Zone of Inhibition in mm (Conc. 5 $\mu\text{g}/\text{mL}$ )	MIC ( $\mu\text{g}/\text{mL}$ )	Cytotoxicity IC <sub>50</sub> ( $\mu\text{M}$ ) <sup>a</sup>
3a	10.32	128	ND
3b	9.54	128	ND
3c	9.33	128	ND
3d	7.56	64	324
3e	7.64	64	328
<b>3f</b>	<b>22.5</b>	<b>04</b>	<b>298</b>
<b>Sultamicillin</b>	<b>8.74</b>	<b>25</b>	ND

<sup>a</sup> Cytotoxicity activity was determined on mammalian Vero cell line.



**Fig. 2.** Zone of Inhibition of the Compound **3f** against the MRSA (*Staphylococcus aureus*; ATCC 4330).

## 2.2. MRSA antibacterial activity and cytotoxicity study

The synthesized compounds were evaluated against the MRSA *Staphylococcus aureus* (ATCC 4330). Their antimicrobial activity was compared with Sultamicillin as standard drug. All the results of Zone of inhibition and MIC are shown in **Table 2** and **Fig. 2**. The results of antimicrobial activity revealed that compounds were capable of inhibiting the growth of the MRSA *in vitro* having MIC values between 4 and 128  $\mu\text{g}/\text{mL}$ . Among the synthesized derivatives compound **3f** was found to be the potent candidate of the series with MIC of 4  $\mu\text{g}/\text{mL}$  followed by compound **3d** and **3e** with MIC of 64  $\mu\text{g}/\text{mL}$  as compared to the standard drug Sultamicillin (MIC of 25  $\mu\text{g}/\text{mL}$ ). On the other hand compound **3a**, **3b** and **3c** showed moderate activity against MRSA with MIC 128  $\mu\text{g}/\text{mL}$ . The synthesized potent compounds of the series were further screened for cytotoxicity (IC<sub>50</sub>) in a mammalian Vero cell line (**Table 2**). All the tested derivatives showed lower toxicity with IC<sub>50</sub> values >298  $\mu\text{M}$  and none of the synthesized compounds displayed significant activity against the mammalian Vero cell line at concentrations <100 mM. These outcomes are vital, as compounds with increased cytotoxicity are appealing in the development of new chemical entities for the treatment of MRSA. A brief structural correlation indicates that *m*-nitro phenyl at *N*-position of benzimidazole strongly favours the anti-MRSA activity compared to the *p*-nitro phenyl. Overall it's observed that electron withdrawing group favours the anti-MRSA activity as compared to the electron donating group or unsubstituted phenyl at *N*-position of benzimidazole.

## 3. Experimental

All the solvents and chemicals have been provided by Spectrochem and Sigma-Aldrich. The reactions have been monitored with the aid of pre-coated silica gel TLC aluminium sheets. Melting points were established using an Analab Scientific

Melting point apparatus. FTIR spectra were documented utilizing FTIR-8400S Shimadzu spectrometer.  $^1\text{H}$ NMR (DMSO/ $\text{CDCl}_3$ ) spectra of the compounds have been determined by Bruker Avance-II spectrometer at 400 MHz. Chemical shifts have been assessed relative to the internal standard TMS and are reported in  $\delta$  ppm. The FAB mass spectra were recorded on a Jeol SX 102/Da-600 mass spectrometer and Elemental analyses were performed on a Perkin Elmer Series II CHNS Analyzer 2400.

### 3.1. General procedure for the synthesis of *N*-substituted benzimidazole derivatives 3(a-f)

Benzimidazole (0.0059 mol) was dissolved in (2 ml) DMF containing KOH (0.0059 mol) and TBAB (0.00059 mol) as a catalyst. In this reaction mixture substituted chloroacetanilide (1 gm, 0.0059 mol) was introduced. This was subjected to microwave irradiation for enough intervals of time using resting interval of one minute after every 20 s of irradiation (power 300 W). The completion of reaction was checked by TLC (Benzene: Ethanol, 9.5:0.5), the mixture was poured in water (20 ml) and formed precipitate was filtered and recrystallized from the methanol.

#### 3.1.1. 2-(1*H*-benzo[d]imidazol-1-yl)-*N*-phenylacetamide (3a)

Obtained in solid form; Yield: 83%; IR data frequency ( $\text{cm}^{-1}$ ): 3288 (N-H stretching), 1680 ( $>\text{C} = \text{O}$  stretching), 1385 (Ar-C-N stretching), 732 (mono substituted benzene);  $^1\text{H}$  NMR ( $\delta$  ppm,  $\text{CDCl}_3$ ): 5.01 (2H, s,  $-\text{CH}_2-$ ), 7.07 to 8.08 (9H, m, Ar-H), 10.07 (1H, s, -N-H);  $^{13}\text{C}$ -NMR (DMSO  $d_6$ ): 39.51(DMSO), 47.31 ( $-\text{CH}_2-$ ) 145, 134,145 ( $\text{C}_2$ ,  $\text{C}_8$ ,  $\text{C}_9$ , benzimidazole) 110, 119, 122, 123, 128 (benzene carbons) 165.1 ( $>\text{C} = \text{O}$  of amide); Elemental Analysis (% observed): C, 72.01; H, 5.31; N, 16.81; O, 6.12. (Calculated for  $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}$ : C, 71.80; H, 5.21; N, 16.72; O, 6.37); HRMS (EI)  $m/z$  calcd.  $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}$ : 251.1059; found 251.1062 [M+].

#### 3.1.2. 2-(1*H*-benzo[d]imidazol-1-yl)-*N*-(naphthalen-1-yl)acetamide (3b)

Obtained in solid form; Yield: 88%; IR data frequency ( $\text{cm}^{-1}$ ): 3267 (N-H stretching), 1671 ( $>\text{C} = \text{O}$  stretching), 1372 (Ar-C-N stretching);  $^1\text{H}$  NMR ( $\delta$  ppm,  $\text{CDCl}_3$ ): 5.22 (2H, s,  $-\text{CH}_2-$ ), 6.75 to 8.17 (12 H, m, Ar-H), 10.07 (1H, s, -N-H);  $^{13}\text{C}$ -NMR ( $\delta$  ppm, DMSO  $d_6$ ): 47.22 ( $-\text{CH}_2-$ ), 145, 134,143 ( $\text{C}_2$ ,  $\text{C}_8$ ,  $\text{C}_9$ , benzimidazole), 110, 119, 122, 126, 128, 133, 134 (carbon atoms of benzene and naphthalene), 166.41 ( $>\text{C} = \text{O}$  of amide); Elemental Analysis (% observed): C, 75.79; H, 5.09; N, 13.85; O, 5.39 (Calculated for  $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}$ : C, 75.72; H, 5.02; N, 13.95; O, 5.31); HRMS (EI)  $m/z$  calcd.  $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}$ : 301.1215; found 301.1219 [M+].

#### 3.1.3. 2-(1*H*-benzo[d]imidazol-1-yl)-*N*-(*p*-tolyl)acetamide (3c)

Obtained in solid form; Yield: 81%; IR data frequency ( $\text{cm}^{-1}$ ): 3253 (N-H stretching), 1680 ( $>\text{C} = \text{O}$  stretching), 819 (*p*-disubstituted);  $^1\text{H}$  NMR ( $\delta$  ppm,  $\text{CDCl}_3$ ):  $\delta$  3.11(3H, s,  $-\text{CH}_3$ ), 5.20 (2H, s,  $-\text{CH}_2-$ ), 6.74 to 8.04 (08 H, m, Ar-H), 10.02 (1H, s, -N-H);  $^{13}\text{C}$ -NMR (DMSO): 47 ( $-\text{CH}_2-$ ), 20 ( $-\text{CH}_3$ ), 145, 143,136 ( $\text{C}_2$ ,  $\text{C}_8$ ,  $\text{C}_9$ , benzimidazole), 110,119,122,129,133,134 (carbon atoms of benzene), 165 ( $>\text{C} = \text{O}$  of amide); Elemental Analysis (% observed): C, 74.50; H, 5.78; N, 15.92; O, 6.09 (Calculated for  $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}$ : C, 74.42; H, 5.70; N, 15.85; O, 6.03); HRMS (EI)  $m/z$  calcd.  $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}$ : 265.1215; found 265.1209 [M+].

#### 3.1.4. 2-(1*H*-benzo[d]imidazol-1-yl)-*N*-(4-chlorophenyl)acetamide (3d)

Obtained in solid form; Yield: 78%; IR data frequency ( $\text{cm}^{-1}$ ):1093 (Ar-Cl stretching), 3325(N-H Stretching), 1685 ( $>\text{C} = \text{O}$  stretching), 827 (*p*-di substituted);  $^1\text{H}$  NMR ( $\delta$  ppm,  $\text{CDCl}_3$ ):  $\delta$  5.63 (2H, s,  $-\text{CH}_2-$ ),  $\delta$  7.04 to 8.81 (9H, m, Ar-H),  $\delta$  10.38 (1H, s, -NH);  $^{13}\text{C}$ -NMR (DMSO  $d_6$ ): 48 ( $-\text{CH}_2-$ ), 144, 135, 139 ( $\text{C}_2$ ,  $\text{C}_8$ ,  $\text{C}_9$ , benzimidazole), 110, 117, 121, 133, 134 (carbon atoms of benzene), 163 ( $>\text{C} = \text{O}$  of amide); Elemental Analysis (% observed): C, 62.98; H, 4.02; N, 14.61; O, 5.51 (Calculated for  $\text{C}_{15}\text{H}_{12}\text{ClN}_3\text{O}$ : C, 63.04; H, 4.24; N, 14.71; O, 5.60); HRMS (EI)  $m/z$  calcd.  $\text{C}_{15}\text{H}_{12}\text{ClN}_3\text{O}$ : 285.0669; found 285.0662 [M+].

#### 3.1.5. 2-(1*H*-benzo[d]imidazol-1-yl)-*N*-(4-nitrophenyl)acetamide (3e)

Obtained in solid form; Yield: 70%; IR data frequency ( $\text{cm}^{-1}$ ): 3253 (N-H Stretching), 1690 ( $>\text{C} = \text{O}$  stretching), 1248 (C-N stretching), 1525, 1348 ( $\text{NO}_2$  stretching), 842 (*p*-di substituted);  $^1\text{H}$  NMR ( $\delta$  ppm,  $\text{CDCl}_3$ ):  $\delta$  5.22 (2H, s,  $-\text{CH}_2$ ),  $\delta$  7.10 to  $\delta$  8.20 (9 H, m, Ar-H),  $\delta$  11.02 (1H, s, -N-H);  $^{13}\text{C}$ -NMR (DMSO  $d_6$ ): 46 ( $-\text{CH}_2-$ ), 142, 136, 138 ( $\text{C}_2$ ,  $\text{C}_8$ ,  $\text{C}_9$ , benzimidazole), 111, 116, 120, 132, 136 (carbon atoms of benzene), 160 ( $>\text{C} = \text{O}$  of amide); Elemental Analysis (% observed): C, 60.76; H, 3.99; N, 18.88; O, 16.27 (Calculated for  $\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}_3$ : C, 60.71; H, 4.08; N, 18.92; O, 16.21); HRMS (EI)  $m/z$  calcd.  $\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}_3$ : 296.0909; found 296.0902 [M+].

#### 3.1.6. 2-(1*H*-benzo[d]imidazol-1-yl)-*N*-(3-nitrophenyl)acetamide (3f)

Obtained in solid form; Yield: 72%; IR data frequency ( $\text{cm}^{-1}$ ): 3200 (N-H Stretching), 1703 ( $>\text{C} = \text{O}$  stretching), 1259 (C-N stretching), 1525, 1348 ( $\text{NO}_2$  stretching) 740 (*m*-di substituted);  $^1\text{H}$  NMR ( $\delta$  ppm,  $\text{CDCl}_3$ ):  $\delta$  5.20 (2H, s,  $-\text{CH}_2$ ),  $\delta$  7.08 to  $\delta$  8.22 (9 H, m, Ar-H),  $\delta$  11.09 (1H, s, -N-H);  $^{13}\text{C}$ -NMR (DMSO  $d_6$ ): 40 ( $-\text{CH}_2-$ ), 139, 138, 136 ( $\text{C}_2$ ,  $\text{C}_8$ ,  $\text{C}_9$ , benzimidazole), 110,115,120,130,137 (carbon atoms of benzene), 159 ( $>\text{C} = \text{O}$  of amide); Elemental Analysis (% observed): C, 60.74; H, 4.01; N, 18.85; O, 16.15 (Calculated for  $\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}_3$ : C, 60.71; H, 4.08; N, 18.92; O, 16.21); HRMS (EI)  $m/z$  calcd.  $\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}_3$ : 296.0909; found 296.0915 [M+].

### 3.2. Procedure for the MRSA antibacterial activity

Initially antibacterial testing was performed using disc diffusion assay. The compounds are further evaluated for their effective minimum inhibitory concentration (MIC) [33]. The methicillin-resistant *Staphylococcus aureus* (ATCC 4330) MRSA strain was employed in this antibacterial study. For this, pure culture of *Staphylococcus aureus* (ATCC 4330) was picked with a loop, and the growth was transferred into a tube containing 5 ml of a nutrient broth medium having composition ( $\text{gL}^{-1}$ ) sodium chloride, 5.0; beef extract 10.0; peptone 10.0 (pH 7.2). The broth culture was incubated at 37 °C until it achieves or exceeds the turbidity of the 0.5 McFarland standards (usually to 6 h). The turbidity of the actively growing broth culture is adjusted with sterile saline or broth to obtain turbidity optically comparable to that of the 0.5 McFarland standards. This result in a suspension contains  $2 \times 10^8$  CFU/ml of bacterial cells. Within 15 min after adjusting the turbidity of the inoculum suspension, a sterile cotton swab was dipped into the adjusted suspension. The suspension was spread on the surface of a nutrient agar plate by streaking the swab over the entire sterile agar surface. This procedure was repeated by streaking several times, rotating the plate approximately 60 rpm each time to ensure an even distribution of inoculum. Stock solutions [1000 microgram per ml] of each newly synthesized compound were prepared in DMF. The sterile discs of 6 mm diameter were used in this assay. The disc diffusion assay was carried out by taking concentration 100 microorganism per disc. The discs immersed with compounds were dispensed onto the surface of the inoculated agar plate. Also, Sultamicillin (5 microgram/disk) [Hi-media, Mumbai, disc diameter 6 mm] moistened with DMF was placed on agar plate as standard. Each disc was pressed down to ensure complete contact with the agar surface. The plates were placed in a refrigerator at to 8 °C for 30 min after the discs are applied. Then the plates were incubated in incubator at 37 °C for 24 h. After 24 h of incubation, each plate was examined.

### 3.3. Minimum inhibitory concentration (MIC)

For determination of minimum inhibitory concentration (MIC) various concentration *Viz* 1024; 512; 256; 128; 64; 32; 16; 8; 4; 2; 1; 0.5; 0.25 and 0.125  $\mu\text{g/ml}$  were prepared and allowed to interacted with *Staphylococcus aureus* (ATCC 4330) suspension containing  $2 \times 10^8$  CFU/ml of bacterial cells in double strength Nutrient broth having composition ( $\text{gL}^{-1}$ ) sodium chloride, 10.0; beef extract 20.0; peptone 20.0 (pH 7.2). Each tube was incubated at 37 °C for 24 h [33].

### 3.4. Cytotoxicity

The selected set of compounds which showed potent activity against MRSA strains were also evaluated for their cytotoxicity on VERO cell Lines by MTT assay as per the procedure reported by Falzari et al. [34].

## 4. Conclusion

Based on the anti-microbial outcomes it is clearly revealed that the structural modification at *N*- position of benzimidazole **3(a-f)** will be beneficial in the field of anti-methicillin-resistant *Staphylococcus aureus* for the designing the effective antibacterial bioactive molecules. The newly synthesized compound was identified as 2-(1*H*-benzimidazol-1-yl)-*N*-(3-nitrophenyl) acetamide (**3f**) has a potent anti-MRSA activity 4  $\mu\text{g/mL}$  as compared to the standard drug Sultamicillin (MIC of 25  $\mu\text{g/mL}$ ). Compound **3f** was 6 times more potent as compared to the standard drug Sultamicillin and found to be non-cytotoxic. A brief structural corollationship indicates that *m*-nitro phenyl at *N*-position of benzimidazole strongly favours the anti-MRSA activity compared to the *p*-nitro phenyl. The attention-grabbing conclusions avowed in this investigation will contribute to open new avenue for researchers to design future generation novel and potent benzimidazole containing drugs.

### Author disclosure

None.

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### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.cdc.2020.100344](https://doi.org/10.1016/j.cdc.2020.100344).

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