

## Nitrogen-containing Fused Heterocycles: Organic Synthesis and Applications as Potential Anticancer Agents



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**Abstract:** The fused Nitrogen heterocyclic compounds and their derivatives have grown in prominence over the past several decades as a result of their significant medical value. The adaptable and easily synthesized N-Heterocyclic scaffolds are particularly exciting in both synthetic organic chemistry and the biological sector due to their powerful pharmacological properties, which are taken into consideration while considering their numerous uses. For the synthesis of N-heterocycles and their derivatives, several attempts were undertaken to create a variety of synthetic protocols. The N-Heterocyclic compounds provide a variety of adaptable structures for specific biological applications and represent novel, broad-spectrum antibacterial and anticancer agents. They typically have minimal toxicity profiles. The majority of these N-Heterocycles have demonstrated more cytotoxicity than the effective anticancer medication cisplatin. The design, synthesis, structural characterisation, and biological uses of N-Heterocycles are reviewed in this work. In this article, the developments made in this specific field are comprehensively examined.



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### 1. INTRODUCTION

Heterocyclic compounds [1-8] are a fundamental branch of organic chemistry that has its origins in organic synthesis and medicinal chemistry [9-14]. The physicochemical qualities are greatly influenced by the kind and size of the ring structures, as well as the substituent groups of the core scaffold [15-23]. Heterocyclic compounds play an important role in a variety of medicinal applications, including antibacterial [24-26], antiviral [27], antifungal [28], anti-inflammatory [29], and anti-tumor drugs [30-33].

The ongoing identification of novel heterocyclic scaffolds gives new tools for modulating or modifying a variety of disease states [34-38]. A novel scaffold has the advantage of disrupting a signal pathway or blocking an enzyme's active site [39-43]. Synthesis of novel heterocycles using better and easier methodologies [44-50], therefore, attracts synthetic organic chemists' attention. A medium-sized ring-fused heterocycle has a variety of biologically significant properties [51-53]. Furthermore, attaching a suitable substitute as well as adding another fused five- or six-member ring to the scaffold has greatly increased activity [54].

N-containing heterocycles [55-58] are compounds with a distinct structural motif that is abundant in natural products including

hormones, alkaloids, and vitamins [59-62]. Pharmaceuticals, natural goods, pigments, organic materials, and biologically active compounds all contain N-heterocycles [63]. For their various actions, heteroaromatic chemical compounds such as benzimidazole, benzothiazoles, indole, acridine, oxadiazole, imidazole, isoxazole, pyrazole, triazoles, quinolines, and quinazolines have sparked a lot of interest in the development and pharmacology in recent years [64-68]. By suppressing cell growth and inducing cell differentiation and apoptosis, these N-heterocyclic compounds have anticancer effects in a variety of cancers [69-72].

The N-heterocycles are the most commonly used structural skeletons of medications in the market. Indeed, at least one nitrogen atom can be found in 84 percent of all molecules, while at least one nitrogen heterocycle being found in 59 percent [73]. Furthermore, the use of heterocycles in drug discovery was stressed in a recent study published by Martins and collaborators [74] on oncological medications approved by the FDA between 2010 and 2015. During that time, 26 of the 40 newly approved chemotherapeutic medicines have heterocyclic fragments in their molecular structure. Nitrogen-based heterocycles accounted for 73 percent of these heterocycles, vastly outnumbering nitrogen-oxygen (15%), oxygen (8%), and nitrogen-sulfur (4%) heterocycles.

Despite their broad spectrum of biological activities, including anticancer activity, there is still a need for creative, practical, and effective methods for nitrogen-containing heterocyclic synthesis,

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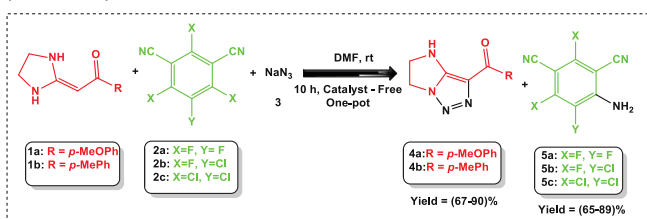
which has become a major aim in modern organic synthesis. Furthermore, the development of drug resistance to cancer chemotherapeutic drugs by chance poses serious medical issues [75]. Drug resistance, either inherent before treatment (intrinsic) or acquired after treatment (acquired), is responsible for the majority of cancer relapses and is one of the leading causes of cancer death [76]. As a result, the discovery of innovative medications with fewer side effects and broad spectrum capabilities is unavoidable if cancer treatment is to improve [77].

## 2. 1,2,3-TRIAZOLE DERIVATIVES

### 2.1. Heterocycle-fused 1,2,3-triazole Derivatives

#### 2.1.1. Synthetic Strategy

Yan *et al.* [78] synthesised a series of heterocycle-fused 1,2,3-triazoles by 1,3-dipolar cycloaddition of heterocyclic ketene animals or N, O-acetal with sodium azide and polyhalo isophthalonitriles in a one-pot reaction at room temperature without a catalyst (Scheme 1).



Scheme 1. Synthesis of heterocycle-fused 1,2,3-triazole derivatives.

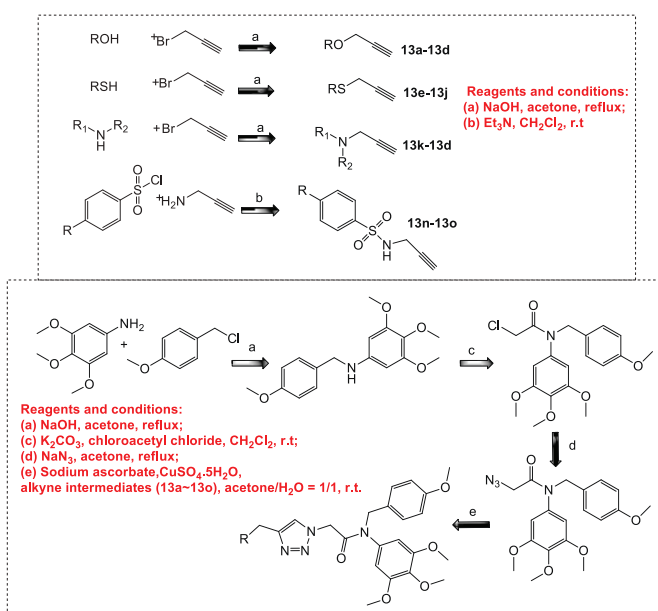
#### 2.1.2. Biological Activity

A series of heterocycle-fused 1,2,3-triazoles were tested *in vitro* against a panel of human tumour cell lines. The most effective derivative was discovered to be 4-methoxyphenyl substituted 1,3-oxazoheterocycle fused 1,2,3-triazole, with IC<sub>50</sub> values of less than 1.9 g/mL against A431 and K562 human tumour cell lines.

### 2.2. 1,2,3-triazole Hybrid Moieties

#### 2.2.1. Synthetic Strategy

Fu *et al.* [79] developed and synthesised structurally different trimethoxyphenyl-1,2,3-triazole hybrids (Scheme 2).



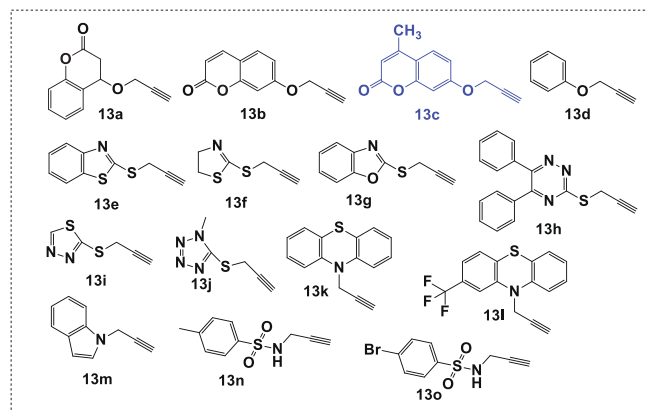
Scheme 2. Synthesis of trimethoxyphenyl-1,2,3-triazole hybrids.

#### 2.2.2. Biological Activity

The synthesized products were tested for antiproliferative efficacy against three cancer cell lines (PC3, MGC803 and HepG2) (Table 1). Trimethoxyphenyl-1,2,3-triazole containing the coumarin fragment

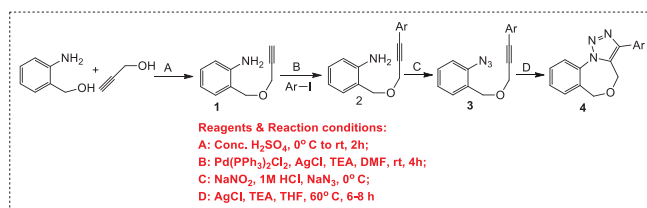
**13c** showed higher antiproliferative action than the anticancer medication colchicine, with IC<sub>50</sub> values ranging from 0.13 μM to 1.74 μM. The lead Compound (**13c**) inhibits MGC803 cell growth and colony formation, induces G2/M phase arrest by inhibiting CDK1 expression, and promotes apoptosis *via* regulating the DR5 and Bcl-2 families. Furthermore, tubulin polymerization was substantially suppressed by (**13c**), which interacted with the colchicine site.

Table 1. Chemical structure of synthesized lead moieties of trimethoxyphenyl-1,2,3-triazole hybrids.



### 2.3. Triazolo-benzoxazepine Derivatives

Banerji *et al.* [80] synthesised small triazolo-benzoxazepine scaffolds employing one-pot four-step synthetic approach incorporating the click reaction (Scheme 3) and tested them against several cancer cell lines. The MTT assay revealed that these compounds have low micromolar anticancer activity, and phase contrast, fluorescent, and confocal pictures were used to confirm cell death.



Scheme 3. Synthesis of Triazolo-benzoxazepine scaffolds using a one-pot four-step synthetic methodology involving click reaction.

### 2.4. N-substituted-3-mercapto-1,2,4-triazoles, triazolo [1,3,4]thiadiazines and triazolo [1,3,4]thiadiazoles

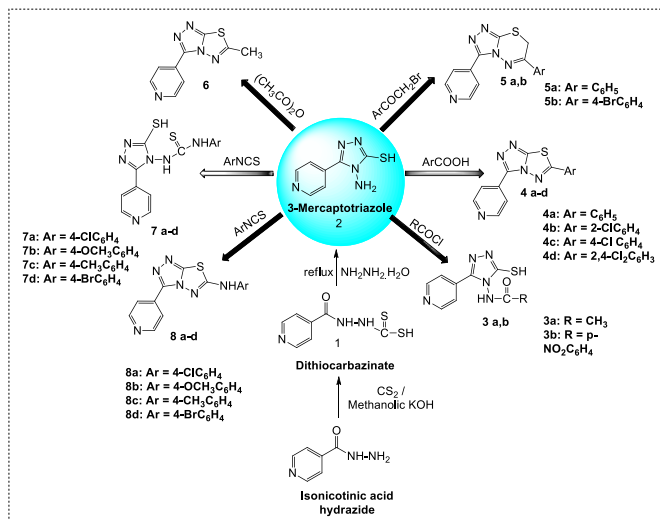
#### 2.4.1. Synthetic Strategy

Kamel and co-workers [81] synthesized a series of novel N-substituted-3-mercapto-1,2,4-triazoles (**3a-3b**, and **7a**, **7e**, **7d**), triazolo [1,3,4]thiadiazines (**5a**, **5b**), and triazolo [1,3,4]thiadiazoles (**4a**, **4e**, **4d**, **6** and **8a**, **8e**, **8d**) starting with isonicotinic acid hydrazide (Scheme 4). On the basis of spectrum data and elemental studies, the structure of the newly synthesised chemicals was validated.

#### 2.4.2. Biological Activity

All compounds were tested for anticancer activity *in vitro* against six human cancer cell lines as well as normal fibroblasts. Most cell lines showed considerable cytotoxicity to seven of the

examined scaffolds (**3a**, **3b**, **4c**, **5a**, and **8b**, **8e**, **8d**). Compound (**4c**), among these derivatives, had a cytotoxic impact on a gastric cancer cell line that was comparable to the standard CHS 828 ( $IC_{50}$  14.25  $\mu$ M). Normal fibroblast cells (WI38) were only slightly affected ( $IC_{50}$  > 10.00  $\mu$ M).

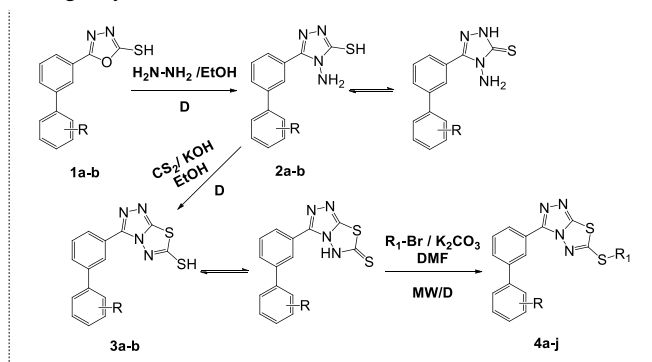


**Scheme 4.** Synthesis of N-substituted-3-mercapto-1,2,4-triazoles (**3a,b**, and **7a-d**), triazolo[1,3,4]thiadiazines (**5a,b**) and triazolo[1,3,4]thiadiazoles (**4a-d**, **6** and **8a-d**).

## 2.5. Alkyl Derivatives of 3-(substituted-(1,10-biphenyl)-3-yl) [1,2,4]triazolo [3,4-b] [1,3,4]thiadiazole-6-thiol

### 2.5.1. Synthetic Strategy

Ramprasad and coworkers [82] used conventional and microwave irradiation methods to synthesize a series of S-alkyl derivatives of 3-(substituted-(1,10-biphenyl)-3-yl) [1,2,4]triazolo [3,4-b] [1,3,4]thiadiazole-6-thiol (**4a-j**) (Scheme 5). In comparison with the conventional method, the microwave method produced a faster and higher yield.



**Scheme 5.** Synthesis of alkyl derivatives of 3-(substituted-(1,10-biphenyl)-3-yl)[1,2,4]triazolo[3,4-b][1,3,4]thiadiazole-6-thiol.

### 2.5.2. Biological Activity

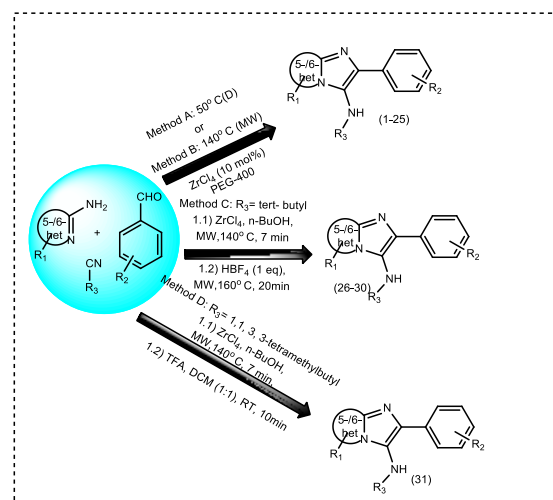
The MTT assay was used to test these substances for anticancer activity *in vitro*. The moiety (**4c**) was the most promising anticancer agent in the HT29 cell line, with an  $IC_{50}$  value of 12  $\mu$ M.

## 3. BENZIMIDAZOLE DERIVATIVES

### 3.1. N-Fused Aminoimidazoles

#### 3.1.1. Synthetic Strategy

Baviskar *et al.* [83-85] employed multicomponent protocol to make N-Fused aminoimidazoles using different approaches (Scheme 6).



**Scheme 6.** Methods of preparation of investigational compounds as potential topoisomerase II $\alpha$  inhibitors.

### 3.1.2. Biological Activity

N-Fused aminoimidazoles were tested *in vitro* against human topoisomerase II $\alpha$  (hTopoII $\alpha$ ) in decatenation, relaxation, cleavage complex, and DNA intercalation assays. These scaffolds showed substantial anticancer activity in kidney and breast cancer cell lines, as well as low toxicity to normal cells, higher potency in kidney cancer cell lines than etoposide and 5-fluorouracil, and potent suppression of cell migration. In the G1/S phase, several chemicals were discovered to have an apoptotic impact.

## 3.2. Benzimidazole Associated with Triazolo-thiadiazoles and Triazolothiadiazines

### 3.2.1. Synthetic Strategy

Two series of Benzimidazoles were synthesised by Husain *et al.* [86] in combination with triazolo-thiadiazoles (**5a-q**, **5r**, **5s**, and **5x-a**) and triazolothiadiazines (**5t-5w**) to produce promising anticancer agents (Scheme 7).

### 3.2.2. Biological Activity

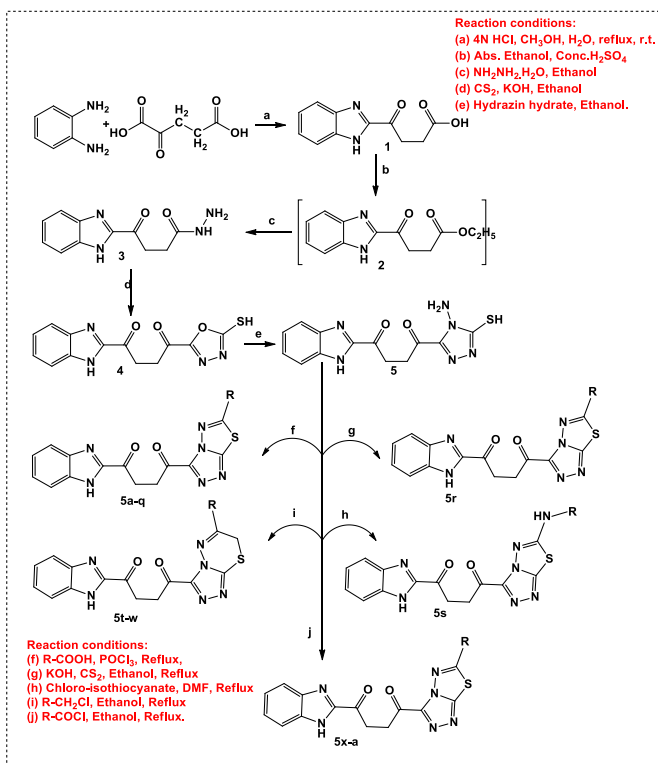
The National Cancer Institute (NCI) tested the *in vitro* anticancer activities of synthesised compounds against the NCI60 cell line panel, and the results showed good to remarkable broad-spectrum anticancer activity. Compound (**5h**) (NCS: 760452, **1**) is one of them. 3-(6-(2,4-dichlorophenyl)-[1,2,4]triazolo [3,4-b]-3-(6-(2,4-dichlorophenyl)-[1,2,4]triazolo [3,4-b]-3-(6-(1,3,4]thiadiazol-3-yl)propan-1-one) inhibited growth significantly, with  $IC_{50}$  values ranging from 0.20 to 2.58  $\mu$ M, and was found to have superior selectivity for leukaemia cell lines. It was then screened at 10-fold dilutions of five different concentrations (0.01, 0.1, 1, 10, and 100  $\mu$ M). **5h** could be used as a lead compound in the development of new anticancer agents.

## 3.3. Benzimidazole Associated with Oxadiazole and Triazolo-thiadiazoles

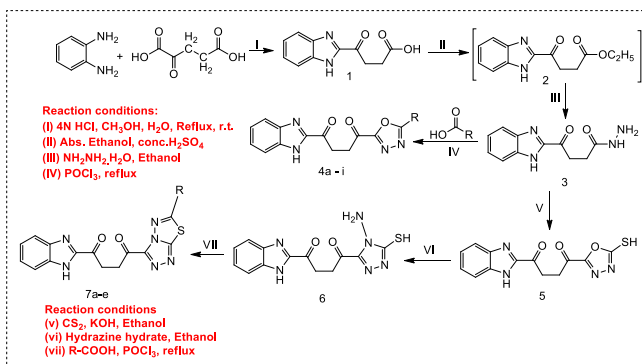
### 3.3.1. Synthetic Strategy

Husain *et al.* [87] effectively synthesised two new series of benzimidazole-bearing oxadiazole [1-(1H-benzo [d]imidazol-2-yl)-3-(5-substituted 1,3,4-oxadiazol-2-yl)propan-1-ones (**4a-l**)] and triazolo-thiadiazoles [1-(1H-benzo [d]imidazol-2-yl)-3-(6-hydroxybenzo [d]imidazol-2-yl)-6-hydroxybenzo [d]imidazol-2-yl)-6-hydroxybenzo [d]imida (substituted) - [1,2,4] triazolo [3,4-b] [1,3,4]thiadiazol-3-yl)propan-1-one (**7a-e**)] triazolo [3,4-b] [1,3,4]thiadiazol-3-yl)propan-1-one (**7a-e**)] triazolo [3,4]thiadiazol-

3-y with the goal of developing effective anticancer medicines from 4-(1H-benzo [d]imidazol-2-yl)-4-oxobutanehydrazide (3) (Scheme 8).



**Scheme 7.** Synthesis of Benzimidazole associated with triazolo-thiadiazoles (5a-q, 5r, 5s and 5x-a) and triazolothiadiazines (5t-w).



**Scheme 8.** Synthesis of benzimidazole bearing oxadiazole[1-(1H-benzo[d]imidazol-2-yl)-3-(5-substituted-1,3,4-oxadiazol-2-yl)propan-1-ones (4a-l)] and triazolo-thiadiazoles [1-(1H-benzo[d]imidazol-2-yl)-3-(6-substituted)-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazol-3-yl)propan-1-one (7a-e)]

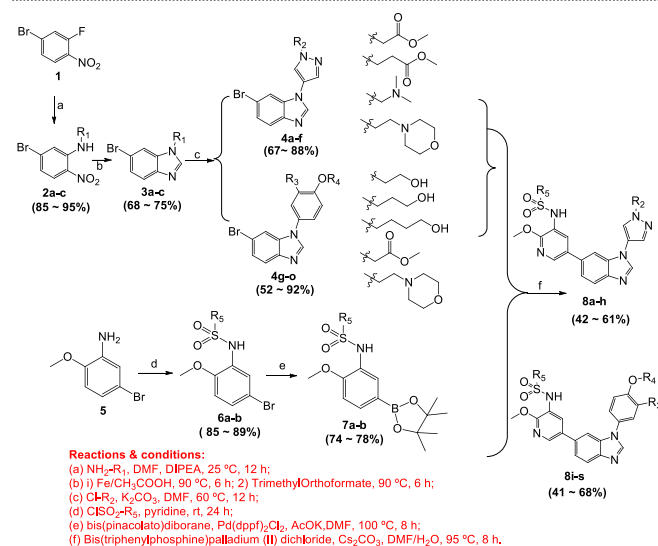
### 3.3.2. Biological Activity

The anticancer activity of produced compounds was tested *in vitro* against the whole NCI60 human cell line panel at the National Cancer Institute (NCI) in the United States, according to their methodology; the results revealed good to outstanding anticancer activity. Compound (4j, NCS: 761980) showed significant growth inhibition and was screened at 10-fold dilutions of five different concentrations (0.01, 0.1, 1, 10, and 100 μM) with IC<sub>50</sub> values ranging from 0.49 to 48.0 μM. It was found superior for non-small cell lung cancer cell lines like HOP-92 (IC<sub>50</sub> 0.49, TGI 19.9, IC<sub>50</sub> >100 and Log<sub>10</sub> IC<sub>50</sub>- 6.30, Log<sub>10</sub> TGI- 4.70, Log<sub>10</sub> IC<sub>50</sub>>-4.00).

## 3.4. 1H-benzo [d]imidazole Derivatives

### 3.4.1. Synthetic Strategy

Ding *et al.* [88] developed a library of 1,6-disubstituted-1H-benzo [d]imidazole derivatives using multistep synthesis (Scheme 9).



**Scheme 9.** Synthesis 1,6-disubstituted-1H-benzo[d]imidazole derivatives.

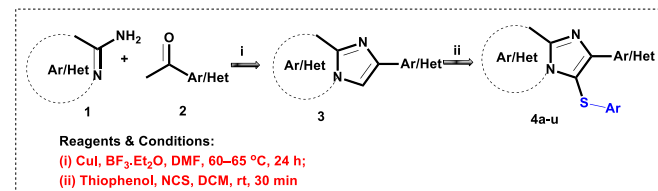
### 3.4.2. Biological Activity

The synthesized compounds were investigated *in vitro* for their antiproliferative efficacy against the T47D, HCT116, and MCF-7 cancer cell lines. The scaffold (8i), which has a 2,4-difluoro substitution pattern on the sulfonyl phenyl ring, demonstrated substantial action against the T47D, HCT116, and MCF-7 cancer cell lines, with IC<sub>50</sub> values of 0.36 μM, 0.14 μM, and 0.31 μM, respectively. Furthermore, in HCT116 cells, the active scaffold (8i) significantly suppressed cell growth by suppressing PI3K kinase and blocking the PI3K/Akt pathway.

## 3.5. Sulfonylated Imidazo [1,2-a]pyridines

### 3.5.1. Synthetic Strategy

Chitrakar *et al.* [89] described the design, synthesis, and investigation of the anticancer properties of sulfonylated 2-phenylimidazo [1,2-a] pyridines and their analogues (Scheme 10).

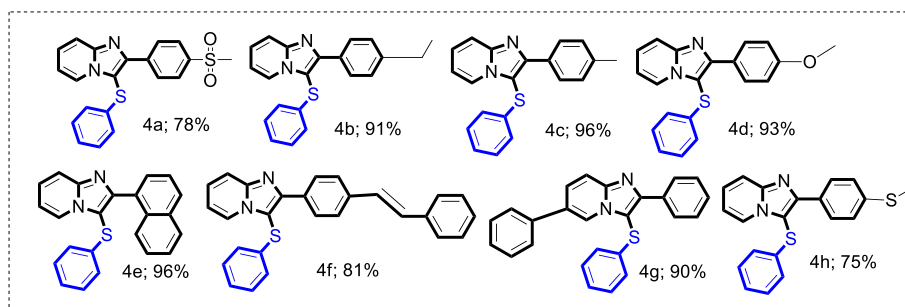


**Scheme 10.** Synthesis of sulfonylated imidazo[1,2-a]pyridines.

### 3.5.2. Biological Activity

The MTT assay was used to test the anticancer activity of twenty sulfonylated imidazo [1, 2-a] pyridine derivatives (Table 2) in seven different human cancer cell lines, MDA MB 231 (breast), HepG2 (liver), Hela (cervical), A549 (lung), U87MG (glioblastoma), SKMEL-28 (skin melanoma), and DU-145 (prostate). Compounds (4e) (naphthalene), (4f) (styrene), and (4h) (thiomethyl) in the series demonstrated potent activity against human liver cancer cells HepG2. Cell cycle analysis revealed that these compounds arrested the cell cycle at the G<sub>2</sub>/M phase and induced apoptosis in HepG2 human liver cancer cells.



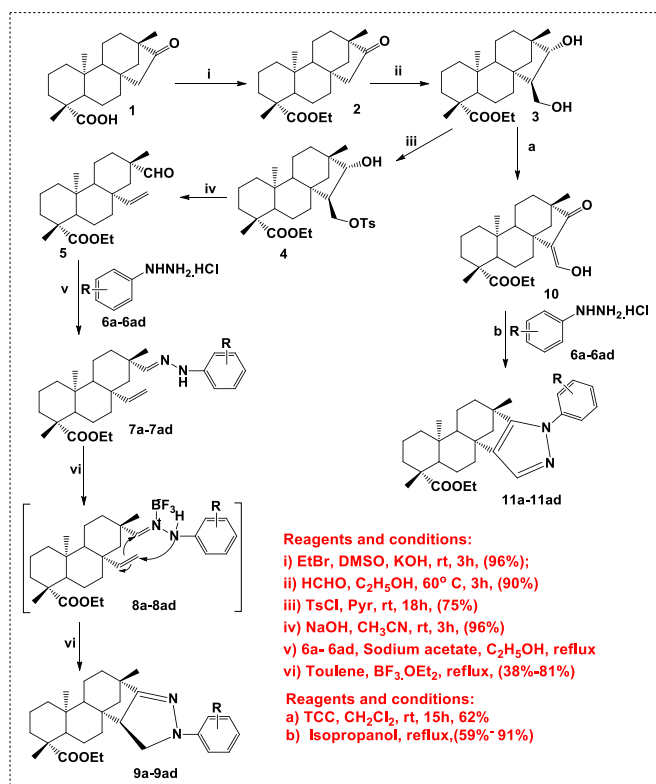
**Table 2.** Chemical structure of synthesized sulfinylated imidazo[1,2-a]pyridine analogues.

## 4. FUSED PYRAZOLINE AND PYRAZOLE DERIVATIVES

### 4.1. Isosteviol-fused Pyrazoline and Pyrazole Moieties

#### 4.1.1. Synthetic Strategy

Zhu *et al.* [90] developed two series of new isosteviol-fused pyrazoline and pyrazole derivatives *via* intramolecular 1,3-dipolar cycloaddition and condensation reactions, respectively (Scheme 11).



**Scheme 11.** Stereoselective synthesis of novel isosteviol-fused pyrazoline and pyrazole Scaffolds *via* intramolecular 1,3-dipolar cycloaddition and condensation reaction.

#### 4.1.2. Biological Activity

The four human cancer cell lines (SGC7901, A549, Raji, and HeLa) were investigated *in vitro* for their antiproliferative activity of structurally similar pyrazoline and pyrazole derivatives. The findings demonstrated that isosteviol-fused pyrazole derivatives had significant cytotoxic properties. When compared to cisplatin (IC<sub>50</sub> values 7.56, 17.78, 17.32, and 14.31 μM, respectively), 2,4-di-Cl-phenylpyrazole derivative (7) had improved cytotoxicities with IC<sub>50</sub> values of 2.71, 3.18, 1.09, and 13.52 μM against SGC7901, A549, Raji, and HeLa.

### 4.2. Pyrazolythiazole Derivatives

#### 4.2.1. Synthetic Strategy

Abbas *et al.* [91] developed a novel series of pyrazolythiazole derivatives by reacting 5-(4-fluorophenyl)-3-aryl-4,5-dihydropyrazole-1-carbothioic acid amide derivatives with various reagents (Scheme 12).

#### 4.2.2. Biological Activity

The anticancer activity of all synthesized compounds was tested against a breast cancer cell line. Eight of the investigated drugs' derivatives demonstrated effective action against MCF7. In comparison to tamoxifen, some of the investigated compounds demonstrated substantial activity against the breast cancer cell line (MCF7). Compounds (14g, 7c, 7d, 14f, 7e, 5a, 6b, and 14d) have IC<sub>50</sub> values of 8.10, 8.11, 8.33, 8.65, 8.77, 9.30, 9.60, and 9.90 μg/mL, respectively, and are equivalent to tamoxifen (IC<sub>50</sub>=8.00 μg/mL). The structure-activity relationship revealed that the anti-tumor efficacy of these compounds is strongly linked to the type of substituent at positions 4 and 5 of the thiazole ring, as well as position 3 of the pyrazole ring.

## 5. NITROGEN-PHOSPHORUS HETEROCYCLES AND PHOSPHONATES

### 5.1. Synthetic Strategy

Abdou *et al.* [92] synthesised substituted N, P-heterocycles and derived phosphonates efficiently in a tandem process without intermediate isolation (Scheme 13). The reaction of dialkyl phosphites with Schiff base, Kabachnik–Field intermediates, which are produced *in situ* from 2-amino-4,6-di-tert-butylphenol and substituted benzaldehydes in a dry THF/FeCl<sub>3</sub> (10%) solution, yielded fused oxazole-2-phosphonates in moderate yield (≈55%). By directly applying the same P(III) reagent to the parent Schiff bases, the latter products could be produced in an excellent yield (≥76%). When the Schiff bases were allowed to react with hexaalkyltriamporphosphites at room temperature, oxazaphosphinine-2-amines were extracted in high yields (≈77%). When the same reagents were applied to another imino derivative, more P-heterocycles and phosphonates were produced.

### 5.2. Biological Activity

The anticancer properties of the produced scaffolds were tested biologically and found to be potent. Bioassay data shows that N, P-heterocycles generated have exceptional anticancer efficacy against seventeen human carcinoma cell lines, including breast, prostate, and melanoma (compounds 11a and 11b). Several phosphonates (compounds 6a and 6b) have been discovered to have anti-breast cancer action particularly in MDA-MB-435 cell lines, while other

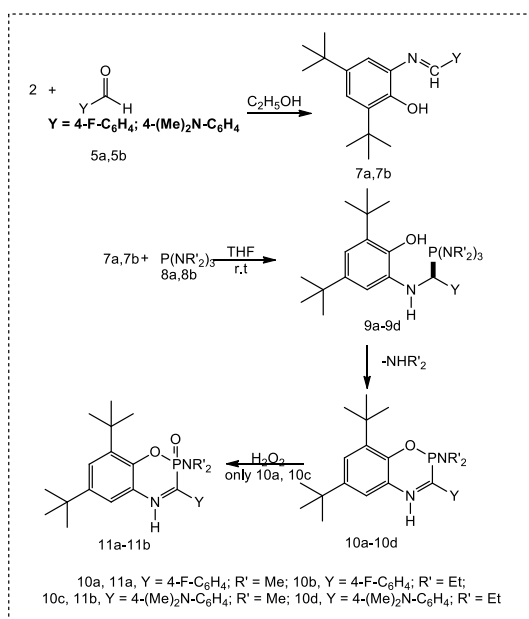
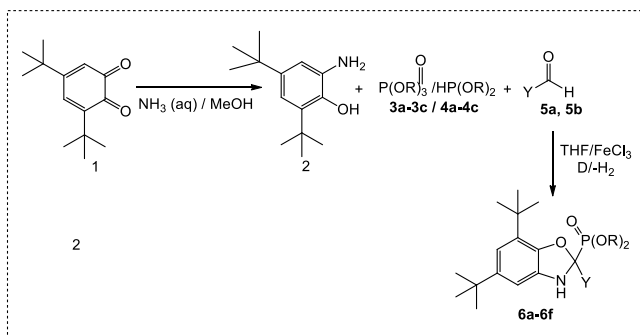


## 8. QUINOLINE AND THEIR HYBRID DERIVATIVES

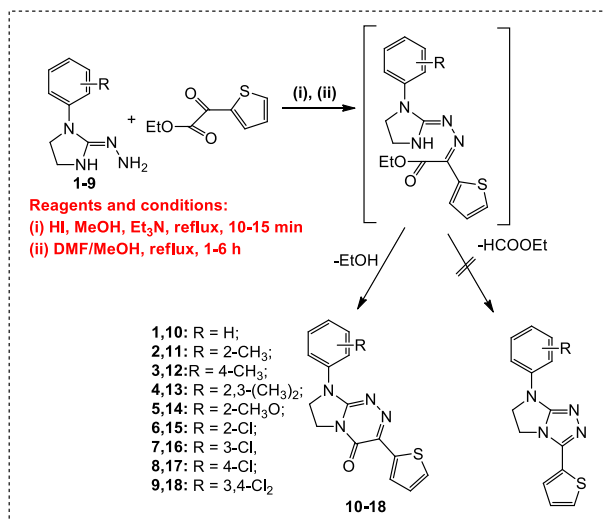
### 8.1. Quinoline Scaffolds

#### 8.1.1. Synthetic Strategy

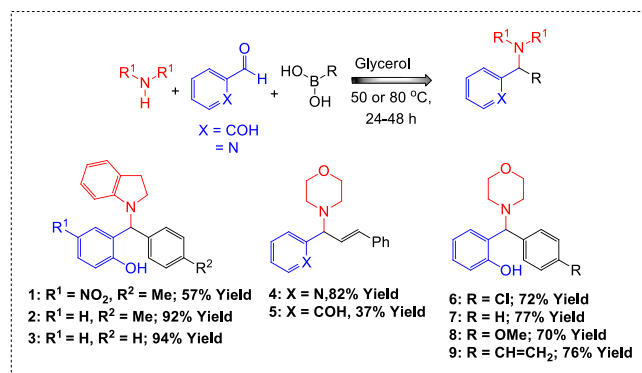
Su *et al.* [95] developed and synthesised a variety of novel quinoline compounds, which were tested for antiproliferative properties (Scheme 16).



**Scheme 13.** Synthesis of fused nitrogen-phosphorus heterocycles and derived phosphonates.



**Scheme 14.** Synthesis of a novel class of 8-aryl-3-(2-thienyl)-7,8-dihydroimidazo[2,1-c][1,2,4]triazin-4(6H)-ones (**10–18**).



**Scheme 15.** Synthesis of N-substituted indolines and morpholines.

#### 8.1.2. Biological Activity

The results showed that compounds (**4p**, **4s**, **4v**, **4x**, and **4y**) had potent antiproliferative activity against seven human tumour cell lines with IC<sub>50</sub> values of less than 10 μM, with N-(3-methoxyphenyl)-7-(3-phenylpropoxy)quinolin-4-amine (**4x**) being the most potent antiproliferative agent against HCT-116, RKO, A2780, and HeLa cell lines having IC<sub>50</sub> values of 2.56, 3.67, 3.46 and 2.71 μM, respectively. The anticancer efficacy of the representative compound (**4x**) was further examined in mice, with the results revealing that compound (**4x**) efficiently controlled tumour development (82.1%) and reduced tumour weight in animal models. Further research into the mechanism of action revealed that compound (**4x**) could inhibit colorectal cancer from growing by inhibiting the ATG5-dependent autophagy pathway. As a result, these quinoline derivatives represent a novel class of compounds that could be used to generate new anticancer medicines.

## 8.2. Benzo and Tetrahydro Benzo- [h]quinolines

### 8.2.1. Synthetic Strategy

Jafari *et al.* [96] developed and synthesised a new class of benzo- and tetrahydro benzo- [h]quinolines with a flexible (dimethylamino) ethylcarboxamide side chain as DNA intercalating anticancer drugs (Scheme 17).

### 8.2.2. Biological Activity

The synthesized compounds were tested for cytotoxicity against four human cancer cell lines: MCF7, A2780, C26, and A549. The cytotoxic activity of compounds with a slight electron donating substitution in the para-position of the phenyl ring was higher than that of the other quinolines. In general, saturated quinolines (tetrahydrobenzo [h]quinolines) were shown to be more cytotoxic than their unsaturated counterparts (benzo [h]quinolines).

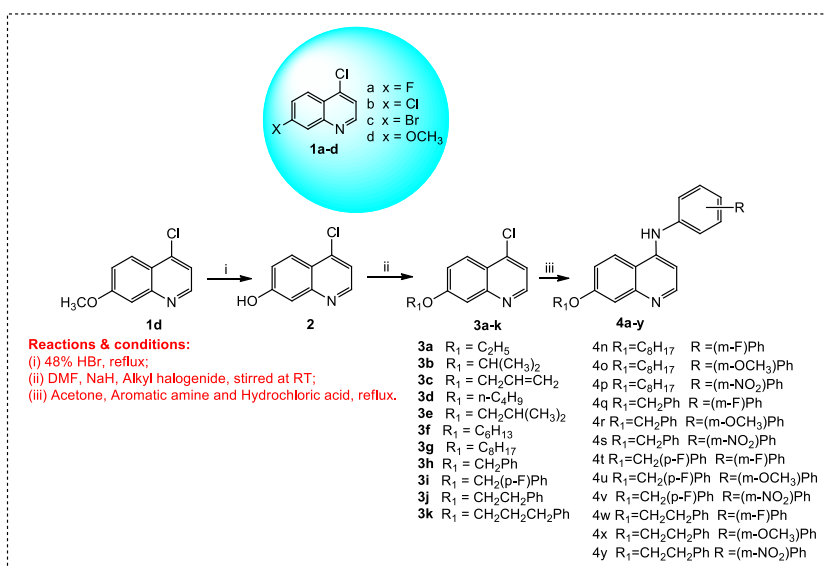
## 8.3. Pyrano [3,2-c]quinoline Derivatives

### 8.3.1. Synthetic Strategy

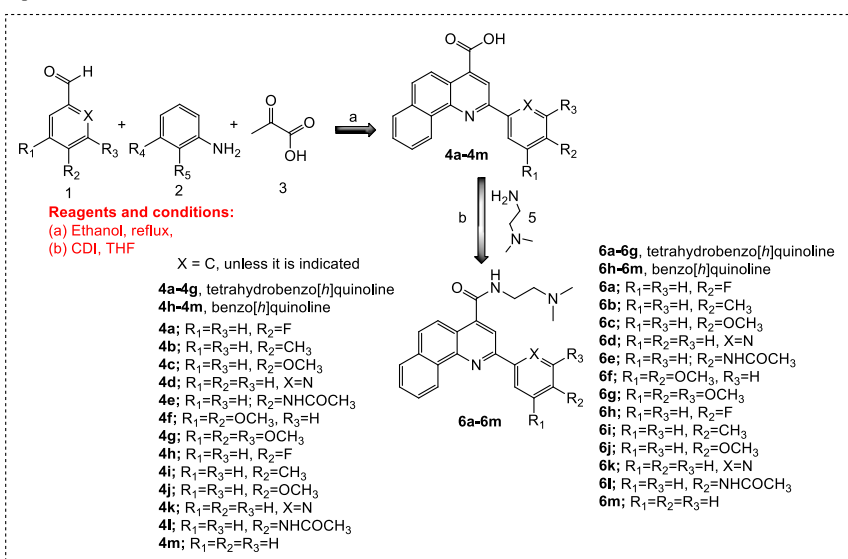
Using a one-pot multicomponent condensation between 2,4-dihydroxy-1-methylquinoline, malononitrile, and various un(substituted) aromatic aldehydes, Upadhyay and group [97] developed a variety of pyrano [3,2-c]quinoline-based structural analogues (Scheme 18).

### 8.3.2. Biological Activity

The anti-inflammatory and cytotoxic activity of the produced compounds was tested. All substances were first tested for percent inhibition of cytokine release, as well as cytotoxicity activity and 50% inhibitory dose (IC<sub>50</sub>). The capacity of the compounds to decrease TNFα production in human peripheral blood mononuclear cells (HPBMC) was investigated further based on the preliminary



Scheme 16. Synthesis of novel quinoline derivatives.

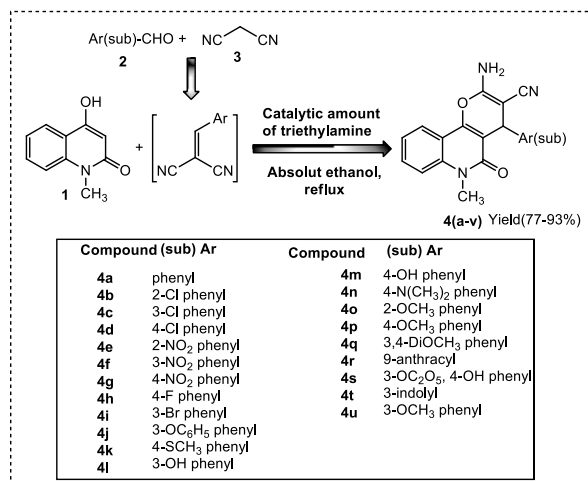
Scheme 17. Synthesis and biological evaluation of novel benzo- and tetrahydrobenzo-[*h*]quinoline derivatives.

findings. Compounds (**4c**, **4f**, **4i**, and **4j**) were identified to be the most active compounds of the series in terms of anti-inflammatory and anticancer activities, according to the screening results. The structure-activity correlation is explored, and it appears that 3-substitution on the aryl ring at C4 of the pyrano [3,2-*c*]quinolone structural motif is significant for both TNF $\alpha$  and IL-6 suppression, as well as anticancer action. Structural diversity with electron withdrawing, electron donating, sterically hindered, and heteroaryl substitution, on the other hand, had a significant impact on both inflammation and anticancer activity.

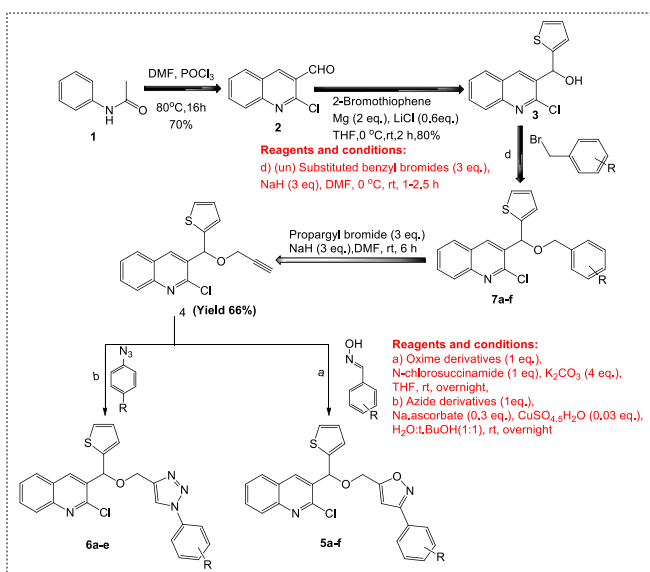
## 8.4. Thiophen-2-yl-quinoline Scaffolds

### 8.4.1. Synthetic Strategy

A series of novel 3-thiophen-2-yl-quinoline compounds based on isoxazolyl, triazolyl, and phenyl have been produced (Scheme 19). In addition, Othman *et al.* [98] announced the discovery of a new valuable synthon, (2-chloroquinolin-3-yl)-(thiophen-2-yl) methanol.

Scheme 18. Synthesis of 2-Amino-6-methyl-5-oxo-4-sub(aryl)-5,6-dihydro-4H-pyrano[3,2-*c*]quinoline-3-carbonitrile (**4a-v**).





**Scheme 19.** Synthesis of (2-chloroquinolin-3-yl)(thiophen-2-yl)methanol (**3**), 2-chloro-3-[(prop-2-yn-1-yloxy)(thiophen-2-yl)methyl]quinoline(**4**), isoxazole derivatives (**5a-f**), triazole derivatives (**6a-e**).

#### 8.4.2. Biological Activity

The antitumor activity of the synthesized products was examined. All derivatives were investigated *in vitro* against a panel of four human cancer cell lines: liver (HepG-2), colon (HCT-116), human cervical cancer (HeLa), and breast cancer (HeLa) (MCF-7). Two compounds, (**7d** and **7e**), were found as potent and selective cytotoxic agents against HeLa and MCF-7 cell lines from the synthesised library.

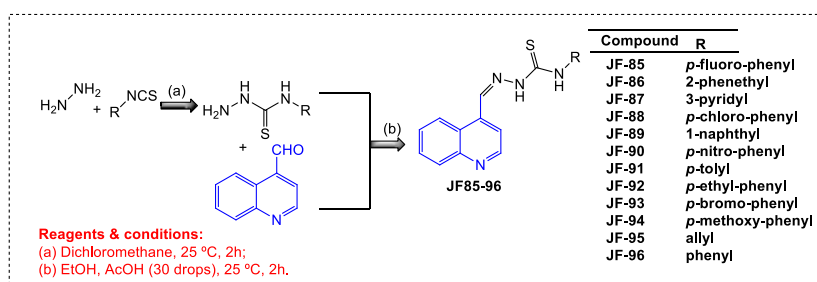
### 8.5. Quinoline-thiosemicarbazone Scaffolds

#### 8.5.1. Synthetic Strategy

Lafayette *et al.* [99] synthesized and studied the biological characteristics of twelve 2-(quinolin-4-ylmethylene) hydrazinecarbothioamide compounds (Scheme 20).

#### 8.5.2. Biological Activity

The tumor cell lines MCF7 and T-47D, all of JF's compounds showed DNA and BSA binding capabilities as well as cytotoxic action. The derivative JF-92 was singled out because it had higher Kb and Ksv values for DNA and BSA binding, indicating a possible mechanism of DNA intercalation, which was confirmed by absorption tests, CD, and molecular docking. This derivative also had a lower IC<sub>50</sub> value for MCF-7 line (0.82 μM) and partially inhibited topoisomerase IIα, making it an interfacial antitumor inhibitor.

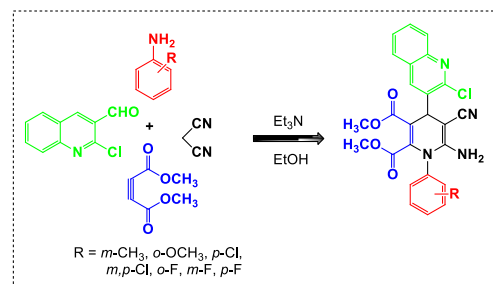


**Scheme 20.** Synthetic route of the derivatives 4-quinoline-thiosemicarbazones (JF's).

### 8.6. Quinoline Associated with Dihydropyridine

#### 8.6.1. Synthetic Strategy

Nkosi *et al.* [100] used a four-component reaction of 2-chloro-3-fomyl quinoline malononitrile, arylamines, and dimethyl acetylenedicarboxylate in the presence of a catalytic amount of triethylamine to synthesize a new series of eight quinoline bearing dihydropyridine derivatives in high yield and short reaction times (Scheme 21).



**Scheme 21.** Synthesis of novel quinoline associated with dihydropyridine.

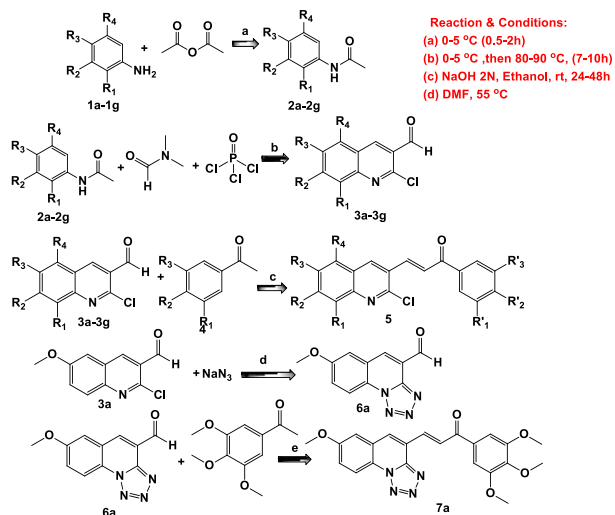
#### 8.6.2. Biological Activity

These synthesized scaffolds were tested for their biological activity in A549 lung cancer cell line and for antibacterial activity. **A2**, **A3**, **A4**, and **A8** all have shown antiproliferative activity, with (**A4**) having maximum toxicity at 250 μg/mL and (**A8**) having high toxicity at 125, 250, and 500 μg/mL, respectively.

### 8.7. Quinoline-chalcone Hybrid Derivatives

#### 8.7.1. Synthetic Strategy

Mirzaei and colleagues [101] have developed a new class of quinoline-chalcone hybrids (Scheme 22).



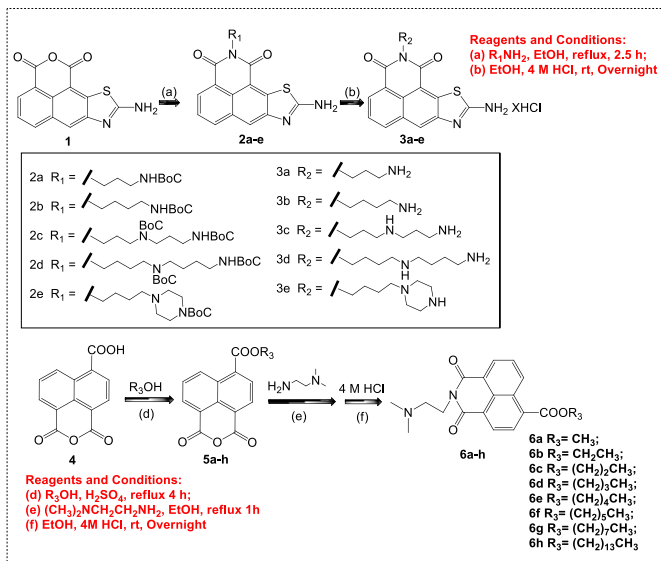
**Scheme 22.** Synthesis of quinoline-chalcone hybrids.

### 8.7.2. Biological Activity

All the compounds were tested for cytotoxicity against four human cancer cell lines: A2780 (human ovarian carcinoma) and A2780/RClS (Cisplatin resistant human ovarian carcinoma), MCF-7 (human breast cancer cells), MCF-7/MX (Mitoxantrone resistant human breast cancer cells), and normal Huvec cells. The link between the structure and action of produced chemicals was examined. The benzoyl group of quinolines (**5e**, **5g**, and **5j**) demonstrated considerable cytotoxic effects on both resistant cancer cells and their parents. The antiproliferative activity of compounds (**5g** and **5j**) was the highest, with  $IC_{50}$  values ranging from 2.32 to 22.4  $\mu$ M. They were also discovered to be tubulin inhibitors, causing cell cycle arrest in the G2/M phase as well as apoptosis. In four cancer cell lines, compound (**5j**) caused higher G2/M phase arrest than compound (**5g**). Finally, molecular dynamics simulations and molecular docking investigations of compound (**5j**) into tubulin's colchicine-binding site revealed that this compound may interact with tubulin's active site.

## 9. SYNTHESIS AND BIOLOGICAL ACTIVITY OF NAPHTHALIMIDE DERIVATIVES

Ge *et al.* [102] developed two types of naphthalimide compounds and tested their anti-hepatocellular carcinoma properties *in vitro* (Scheme 23). Compound (**3a**) suppressed cell migration in SMMC-7721 and HepG2, and additional *in vivo* testing with two animal models indicated that compound (**3a**) substantially inhibited primary H22 tumour development (52.6%) and potently disrupted lung metastasis (75.7%) without noticeable systemic toxicity at the therapeutic dose. Compound (**3a**) suppressed malignant liver cell development primarily by triggering G2/M phase arrest, according to mechanistic studies. (**3a**) might have unregulated the cell cycle-related protein production of cyclin B1, CDK1, and p21, and restricted cell migration by elevating E-cadherin and attenuating integrin  $\alpha 6$  expression, according to Western blotting investigations.

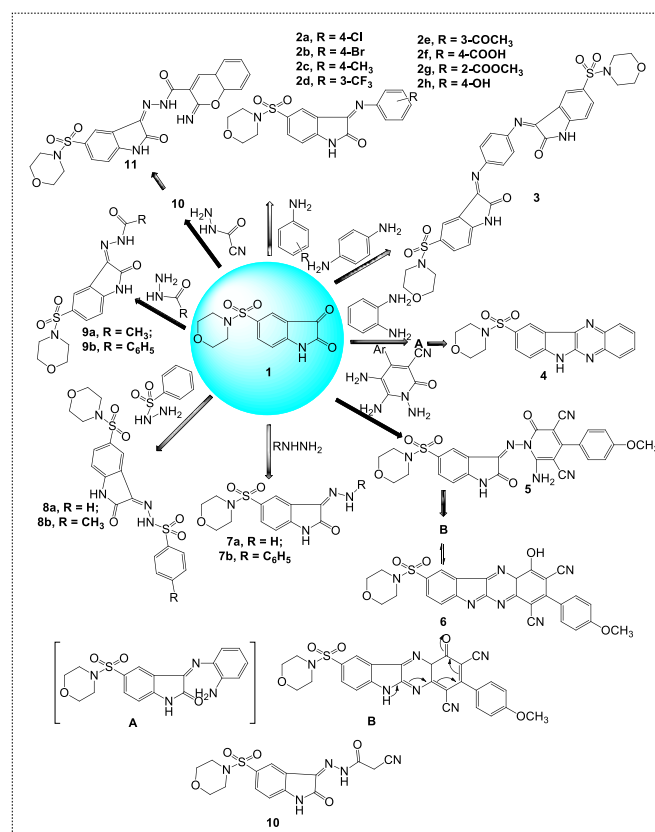


Scheme 23. Synthesis of Naphthalimide Derivatives (**3a-e**) & (**6a-h**).

## 10. 5-(MORPHOLINOSULFONYL) ISATIN DERIVATIVES

### 10.1. Synthetic Strategy

Ammar *et al.* [103] developed and synthesised a new class of 5-(morpholinosulfonyl) isatin derivatives (Scheme 24). Analyses of spectral and elemental data were used to characterise the novel compounds.



Scheme 24. Synthesis of Schiff's bases of 5-(morpholinosulfonyl)isatin and indolo[2,3-b]quinoxaline derivatives (**2a-h** and **3-6**) & hydrazones and hydrazides (**7a-11**) of 5-(morpholinosulfonyl)isatin.

### 10.2. Biological Activity

The synthesized compounds were tested using the SRB assay on four cancer cell lines, including HepG2, HCT116, CACO, and MCF7, as well as a non-cancerous human cell line, to see if they were cytotoxic. The normal generated cell line was not cytotoxic ( $IC_{50} > 130 \mu$ M). In three of the cell lines evaluated, HepG2, HCT116, and CACO compounds (**3**, **6**, **10**, and **11**) had  $IC_{50}$  values less than 10  $\mu$ M. On HepG2, CACO, and HCT116, compounds (**2h**, **5**, and **7b**) had  $IC_{50}$  values that were less than or almost equivalent to 10  $\mu$ M, respectively. On MCF7, compounds (**3** and **6**) had  $IC_{50}$  values of less than 12  $\mu$ M. These  $IC_{50}$  values are comparable to those of doxorubicin, which has an  $IC_{50}$  range of 4.5 to 8.28  $\mu$ M in the cell lines studied. With  $IC_{50}$  values less than 2  $\mu$ M, all of these intriguing compounds displayed inhibitory efficacy against EGFR. The most powerful EGFR inhibitors, (**7b**)  $IC_{50} = 46 \mu$ M and (**10**)  $IC_{50} = 23 \mu$ M, were found to produce G2/M phase cell cycle arrest and apoptosis.

## 11. SPIRO DERIVATIVES

### 11.1. Hybrid Spiro Compounds

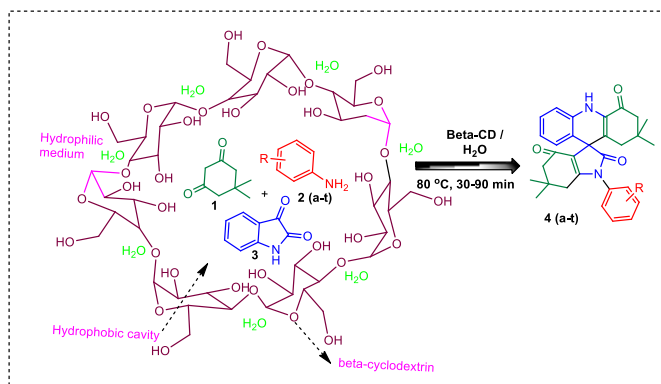
#### 11.1.1. Synthetic Strategy

Chate *et al.* [104] developed a series of novel hybrid compounds called spiro [pyrimido [5,4-b]quinoline-10,5'-pyrrolo [2,3-d]pyrimidine] (Scheme 25) using beta-cyclodextrin (Beta-CD) as a novel catalyst under greener conditions.

#### 11.1.2. Biological Activity

The synthesized scaffolds were tested *in vitro* against four human cancer cell lines: A431, PC3, MCF7, and MCF-10A. The fused heterocycles (**4m**, **4q**, and **4t**) having a chloro or trifluorome-

thyl group on the benzene ring were shown to be the most effective compounds against a human breast cancer cell line, with  $IC_{50}$  values ranging from 7.82 to 9.88  $\mu\text{M}$ . (MCF-7). Compound (**4q**) was shown to be the most effective derivative against the human breast cancer cell line studied, being more active than standard and having cytotoxic activity specific for MCF7.

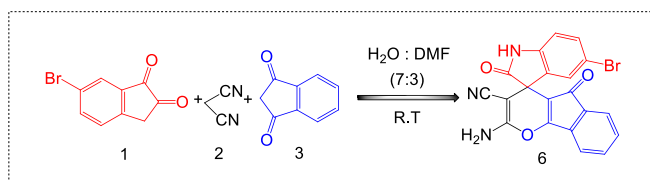


**Scheme 25.** Synthesis of 3,3,6,6-tetramethyl-10-phenyl-3,4,6,7-tetrahydro-1*H*-spiro [acridine-9,30-indoline]-1,20,8(2*H*,5*H*,10*H*)-trione.

## 11.2. Indeno-spiro Compounds

### 11.2.1. Synthetic Strategy

Patravale *et al.* [105] described a sustainable, catalyst-free, bio-oriented multicomponent synthesis of 2-amino-3-cynospiro (5*H*-indeno [1,2-*b*]pyran-4,3'-indoline)-2',5'-dione using isatin, malononitrile, and 1,3-indandione. This study describes a simple method for synthesising indeno-spiro compounds (Scheme 26).



**Scheme 26.** Synthesis of 2-amino-3-cyno-5-bromospiro(5*H*-indeno[1,2-*b*]pyran-4,3'-indoline)-2',5'-dione.

### 11.2.2. Biological Activity

The synthesized compounds were tested against breast carcinoma cell lines (MCF7 and MDA-MB-435) as well as normal Vero monkey cell lines. The bromo- and chloro-substituted indeno-fused spirooxindole derivatives were found to have selective potency against the MDA-MB-435 cancer cell lines, with  $IC_{50}$  values of 1.8 and 2.1  $\mu\text{M}$ , respectively. The compounds were also tested against the normal Vero monkey cell line, which demonstrated good to excellent selectivity against cancer cell inhibition. Furthermore, *in vitro* confocal microscopy cell imaging of selected compounds revealed cellular shrinkage and apoptosis in cancer cells, implying that indeno-fused spirooxindoles can be investigated as selective oestrogen negative receptors with a favourable safety profile.

## 12. QUINAZOLINE DERIVATIVES

### 12.1. Substituted Quinazoline Analogues

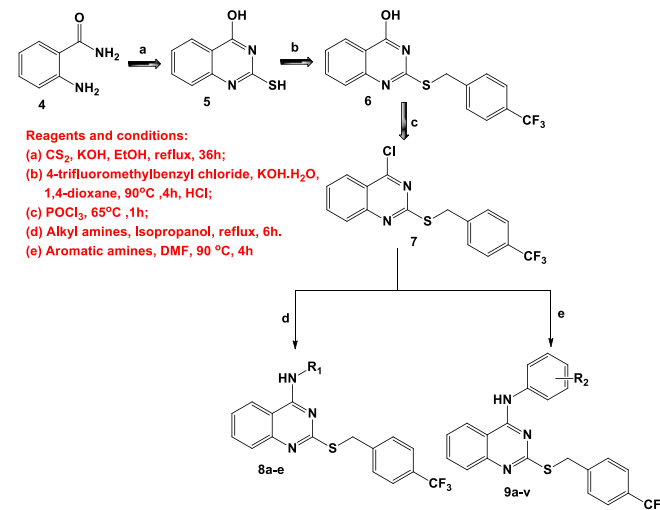
#### 12.1.1. Synthetic Strategy

Li *et al.* [106] (Scheme 27) developed a library of 2,4-disubstituted quinazoline conjugates.

#### 12.1.2. Biological Activity

The MTT assay was used to screen the derivatives for anti-cancer activity against five human cancer cell lines, including

breast (MCF-7 and MDA-MB-231), gastric carcinoma (HGC-27 and MGC-803), and prostate (PC-3) cancer cells. When compared to regular gefitinib ( $IC_{50} = 7.34 \mu\text{M}$ ), the trifluoromethyl derivative (**9n**) showed the most promising anticancer activity ( $IC_{50} = 5.10 \mu\text{M}$ ) with the MCF-7 breast cancer cell line.



**Scheme 27.** Synthesis of 2,4-disubstituted-quinazoline derivatives.

## 12.2. Benzimidazole-quinazolinone Hybrid Scaffolds

### 12.2.1. Synthetic Strategy

Fan *et al.* [107] (Scheme 28) produced benzimidazole-quinazolinone hybrids.

### 12.2.2. Biological Activity

The MTT assay was used to assess the synthesized compounds for cytotoxicity and Aurora-A kinase inhibitory activity. All three cancer cell lines tested demonstrated good cytotoxicity activity, with  $IC_{50}$  values ranging from 0.38 to 18.13  $\mu\text{M}$  for breast cancer (MDA-MB-231), prostate cancer (PC3), and neuroblastoma (SH-SY5Y). The morpholinoethyl compound (**7h**), for example, showed outstanding activity with  $IC_{50}$  values of 0.38  $\mu\text{M}$  (MDA-MB-231), 1.09  $\mu\text{M}$  (PC3), and 0.77  $\mu\text{M}$ , respectively (SH-SY5Y). Compound (**7h**) had a promising inhibitory effect on Aurora-A kinase ( $IC_{50} = 21.94 \mu\text{M}$ ). Furthermore, by inhibiting Aurora-A kinase, compound (**7h**) triggered G2/M phase cell cycle arrest and cell death.

## 12.3. Indenoquinoxaline and pyrazine derivatives

### 12.3.1. Synthetic Strategy

Tantawy *et al.* [108] synthesised some indenoquinoxaline and pyrazine compounds (Scheme 29).

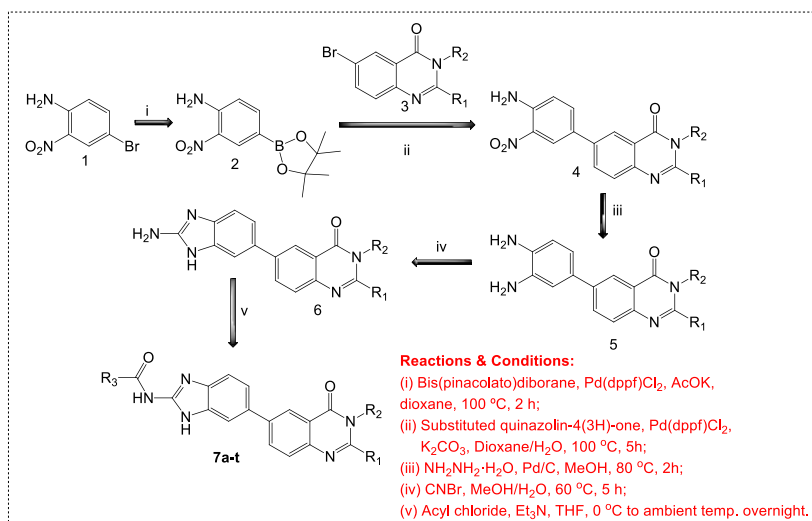
### 12.3.2. Biological Activity

The newly synthesised compounds were screened for cytotoxicity against MCF7 and A549 cell lines using the MTT assay. Compounds (**6**, **8a**, **9**, **10**, and **11**) have a strong cytotoxic effect. Especially compound (**11**), which has  $IC_{50}$  values of 5.4 and 4.3  $\mu\text{M}$ , respectively, against MCF7 and A549 cells.

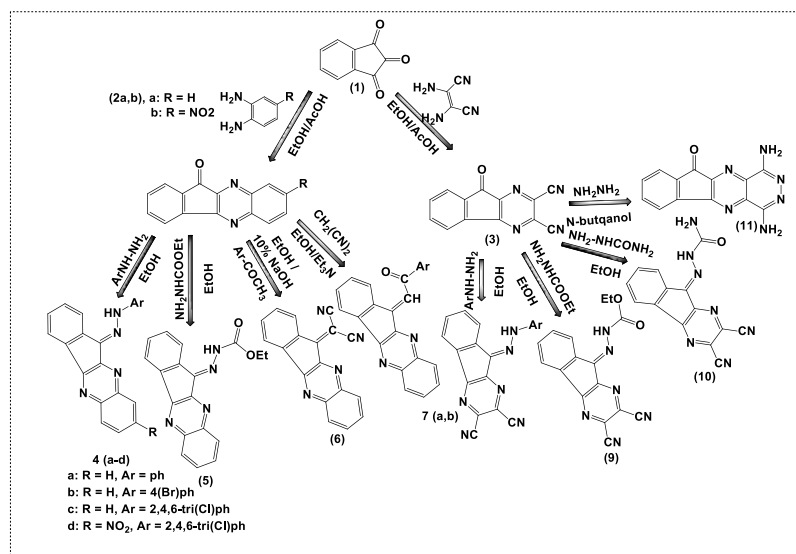
## 13. TETRACYCLIC ACRIDONES WITH AMIDE FRAMEWORKS

### 13.1. Synthetic Strategy

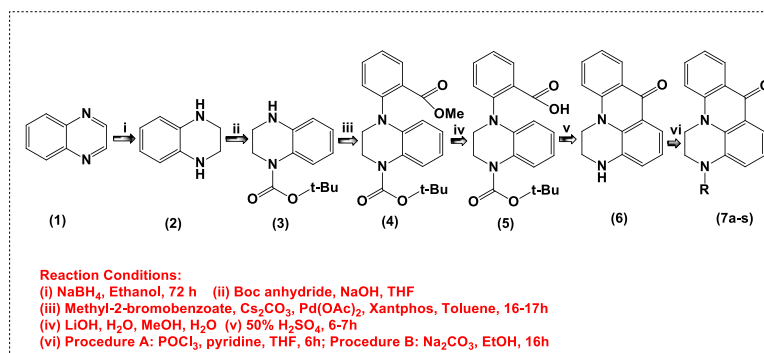
Valigeti and group [109] developed and synthesised a set of tetracyclic acridones with amide frameworks (Scheme 30), including 3-(alkyl/aryl/heteroaryl)-2,3-dihydropyrazino [3,2,1-de]acridin-7(1*H*)-ones.



**Scheme 28.** Synthesis of 6-(2-amino-1H-benzo[d]imidazol-6-yl)quinazolin-4(3H)-one derivatives.



**Scheme 29.** Synthesis of indenoquinoxaline and pyrazine derivatives.



**Scheme 30.** Synthesis of 3-aryl/aro-yl-2,3-dihydro-1H,7H-pyrazino[3,2,1-de]acridin-7-one derivatives.

### 13.2. Biological Activity

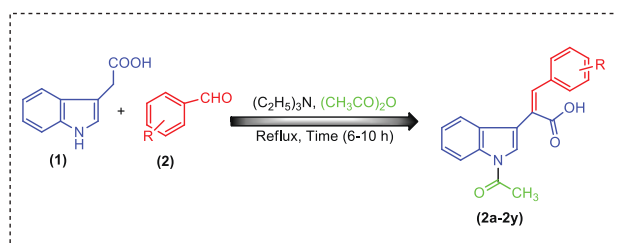
The synthesized compounds containing cyclopropyl-acetyl, benzoyl, p-hydroxybenzoyl, p-(trifluoromethyl)benzoyl, p-fluorobenzoyl, m-fluorobenzoyl, picolinoyl, 6-methylpicolinoyl, and 3-nicotinoyl groups were found to be potent against the HT29, MDAMB231 and HEK293T cancer cell lines.

### 14. 2-(1-ACETYL-1H-INDOLE-3-YL)-3-(PHENYL) PROPI-ONOIC ANALOGUES

#### 14.1. Synthetic Strategy

Kumar *et al.* [110] synthesized twenty-five new combretastatin 2-(1-acetyl-1H-indole-3-yl)-3-(phenyl) propenoic acid analogues (Scheme 31) using triethyl amine with acetic anhydride at reflux condition (2a to 2y).



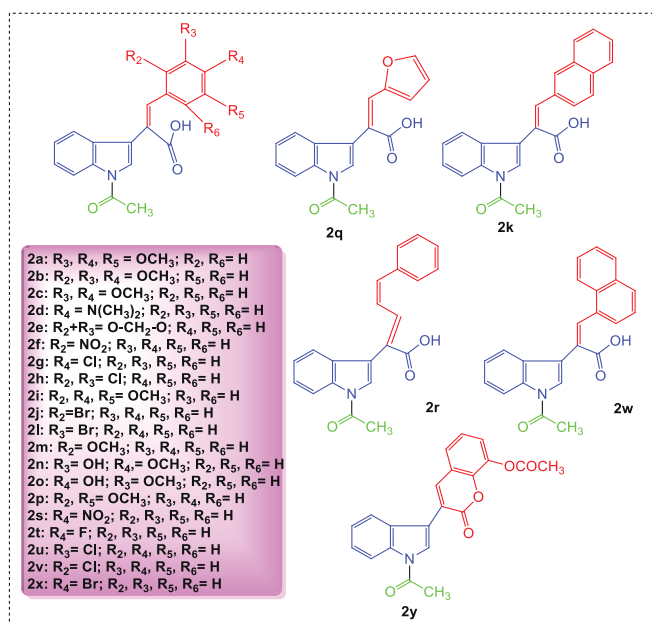


**Scheme 31.** Synthesis of 2-(1-acetyl-1H-indole-3-yl)-3-(phenyl) propenoic analogues.

## 14.2. Biological Activity

The Combretastatin 2-(1-acetyl-1H-indole-3-yl)-3-(phenyl)propenoic acid analogues (**2a** to **2y**) (Table 3), bearing an indole moiety in place of ring (A) of combretastatin (CA-4), were tested for anticancer activity against cancer cell lines such as THP1 (leukaemia), A549 (lung), IGROV1 (ovary), HEP2 (liver), MCF7 (breast), and DU145 (prostate). Compounds (**2d** and **2y**) both demonstrated anticancer action against THP1 and MCF7, with IC<sub>50</sub> values of 0.80 and 0.37 μM, respectively, and (**2y**) had an IC<sub>50</sub> of 3.60 μM, which was comparable to paclitaxel.

**Table 3.** Chemical structure of synthesized 2-(1-acetyl-1H-indole-3-yl)-3-(phenyl) propenoic analogues.



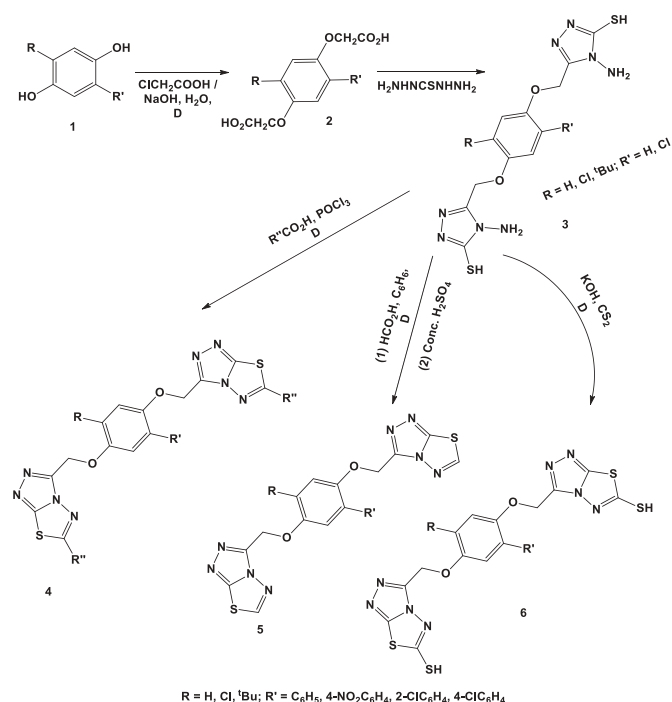
## 15. BIS-PHENOXYACETIC ACIDS

### 15.1. Synthetic Strategy

Shivarma *et al.* [111] synthesised a series of bis-phenoxyacetic acids (**2**) from matching unsubstituted/substituted 1,4-quinols (**1**). In a one-pot procedure, bis-phenoxyacetic acids (**2**) were fused with thiocarbohydrazide to get bis-[4-amino-5-mercapto-1,2,4-triazol-3-yl-methyleneoxy]phenylenes (**3**) (Scheme 32). N-bridged heterocycles (**4** to **6**) were obtained in good yields by reacting bis-triazoles (**3**) with different reagents.

### 15.2. Biological Activity

The anticancer activity of the newly synthesised compounds was tested against a panel of 60 cell lines drawn from seven cancer types: lung, colon, melanoma, renal, ovarian, CNS, and leukaemia. Some of the substances studied have anticancer characteristics that were promising.



**Scheme 32.** Synthesis of bis-[4-amino-5-mercapto-1,2,4-triazol-3-ylmethyleneoxy]phenylenes (**3**); 1,4-bis-(6-aryl-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazol-3-ylmethoxy)phenylenes Scaffold (**4,5,6**).

## CONCLUSION

The structural variety provided by the fused N-heterocyclic frameworks has proven advantageous in the discovery of novel therapeutics by enhancing pharmacology and other physical and chemical properties. Numerous medications are now being used to treat numerous types of cancer with significant therapeutic efficacy. N-heterocyclic framework in medicinal chemistry has received a lot of attention. The vast majority of benefits of pharmaceuticals containing nitrogen in the medical area, such as simple production, low toxicity, fewer side effects, high bioavailability, reduced drug resistance, strong biocompatibility, *etc.*, motivate efforts for more research and development. The synthetic approach in the present drug development and design system, therefore, depends heavily on the characteristics of these scaffolds. We extensively discussed the recent status of the families of nitrogen-based heterocyclic molecules in this review, including 1,2,4-triazole, fused aminoimidazole, Bis-phenoxyacetic acids, benzimidazole with oxadiazole and triazolo-thiadiazoles, pyrazole, pyrimidine, quinoline, and quinazoline derivatives, among many others, with highly promising biological properties like anticancer and other therapeutic properties. We have also investigated several synthetic routes, including green chemical protocols for their production. The biological investigations of the molecules under discussion provided a deeper comprehension of both the arrangement of various substituents on their N-heterocyclic skeleton and the various substituents present responsible for their efficiency. These key details support the great potential of different fused N-heterocycles and indicate a wide range of possible uses for these intriguing moieties due to their variety of molecular targets. We think that this review paper will be helpful in promoting the synthesis and anticancer development of nitrogen-based medicines that are sustainable, effective, and have few adverse effects against a variety of malignancies.

## LIST OF ABBREVIATIONS

- hTopoIIa = Human Topoisomerase IIa  
 NCI = National Cancer Institute  
 HPBMC = Human Peripheral Blood Mononuclear Cells  
 Beta-CD = beta-Cyclodextrin

## CONSENT FOR PUBLICATION

Not applicable.

## FUNDING

None.

## CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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Declared none.

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**PHYTOCHEMICAL SCREENING, ANTIOXIDANT AND ANTIBACTERIAL  
ACTIVITIES OF *PHYSALIS MINIMA* AND *LANTANA CAMERA* WILD MEDICINAL  
PLANTS**

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**ABSTRACT**

Medicinal plants have great value for the treatment and cure various diseases. Now scientific research has expanded our knowledge to discovered chemical composition and active constituents present in medicinal plants. Present research work was undertaken to the phytochemical, antioxidant and antibacterial activity of *Physalis minima* and *Lantana camera*. Phytochemical screening of all medicinal plants has been done with the use of solvent methanol, ethanol and water. Extracts of leaves were obtained by soxhlet extraction to find out the active constitution of plants. Phytochemical analysis of leaves extract has discovered the presence of medicinally important phytochemicals such as Saponin, Steroid, Tannin, Anthocyanin, Coumarin, Flavonoid, Diterpine, Phenol, Phlobatannin and Chalcone. The antioxidant of leaves extracts was assessed based on the radical scavenging effect of the stable 1,1-diphenyl-2-picrylhydrazyl (DPPH). Antibacterial activity of aqueous and ethanolic extracts of *P. minima* and *L. camera* was studies for standard bacteria one Gram-positive (*Bacillus Subtilis*) and Gram-negative (*Escherichia coli*). The optimum inhibition zone size value for both the bacteria *Bacillus Subtilis* and *Escherichia coli* are 02 mm in *P.minima* and *L.camera*. The methanol and ethanol extracts of both plant show significant antioxidant and antibacterial activity. The

diversity of phytochemicals founds in *P. minima* and *L. camera* leaves could serve as a source of useful drugs.

**Keywords:** *P. minima*, *L. camera*, Phytochemical, Antioxidant, Antibacterial Activity

## INTRODUCTION

Medicinal plants are plants that have all their parts leaves, stems, roots and flowers used for therapeutic purposes. Then desperately need to conservation of medicinal plants and cultivation of wild medicinal plants. Herbal wild medicinal plants are easily available, less expensive, no side effect and more efficient make them more attractive as therapeutic agents when compared to modern medicine [1, 2]. India has top ranked herbal medicinal producer because Indian plant biodiversity is the largest source of herbal plant medicine [3]. In the world there are 60 to 80 % of people in world use medicinal plants and their products for therapeutic purposes [4]. The medicinal value of these plants lies in the bioactive phytochemical constituents present in plants and that are beneficial to humans. Many active phytochemical like flavonoids, terpenoids, vitamins, alkaloids etc. were found to be responsible for these activities [5]. Present research work was undertaken on the phytochemical, antioxidant and antibacterial activity of *Physalis minima* and *Lanthena camera*. The methanol and ethanol extracts of both plants show significant antioxidant

and antibacterial activity. The diversity of phytochemicals found in *P. minima* and *L. camera* leaves could serve as a source of useful drugs.

## MATERIALS AND METHODS

Collection of plant materials *P. minima* and *L. camera* were collected from roadside area of near Lakhandur Tahsil of Bhandara district. The plant materials were identified by D. N. Lanjewar, Department of Botany, Yashwantrao Chawhan arts, commerce and science college Lakhandur. The *P. minima* and *L. camera* leaves was washed with tap water and used for the present study. Leaves were cut into small pieces, shade dried and ground to make fine powder. Process for Extraction 500 gm of each powder of the leaves were taken along with the 1000 ml of distilled water in a container. The mixture was shaken continuously with used of rotary shakers and place in a dark for 72 hour with occasional shaking. After 72 hour the mixture was filter and filtrate was concentrated to one third of the original amount. The resultant was used for phytochemical, antibacterial and antioxidant analysis [6].

### Phytochemical analysis

The ethanol extract of leaves of *P. minima* and *L. camera* was used for qualitative phytochemical analyses. Phytochemicals such as flavonoids, tannins, steroids, glycosides, saponins, phenolic compounds, terpenoids and alkaloids are analyzed [5].

### Antioxidant Activity By 1, 1-diphenyl-2-picrylhydrazyl (DPPH)

The antioxidant activity of the ethanol extracts of *P. minima* and *L. camera* leaves were assessed based on the radical scavenging effect of the stable DPPH [7, 8]. 0.005% of DPPH was prepared in ethyl alcohol and 4 ml of this DPPH solution was mixed with 4 ml of ethanolic plant extract solutions. These solution mixtures were kept in dark for 30 min and optical density was measured at 517 nm using UV Visible spectrophotometer. 4ml ethanol with 0.005 DPPH solutions was used as blank. The optical density was recorded in spectrophotometer and % inhibition was calculated using the following formula.

$$\text{Percentage (\%)} \text{ Inhibition of DPPH (\% AA)} \\ = A - B \times 100 / A$$

Where A=Optical density of the blank and B=Optical density of the sample.

Extraction concentration providing 50% inhibition IC<sub>50</sub> values was calculated maximum and minimum values of %AA

### Antibacterial activity (disk diffusion method)

Antibacterial activity was carried out to examine the sensitivity of some bacterial species against plant extracts of *P. minima* and *L. camera* leaves with a comparing the antibiotics for it by Disk Diffusion Method [9]. These bacteria included Gram-positive (*Bacillus Subtilis*) and Gram-negative (*Escherichia coli*).

## RESULTS AND DISCUSSION

### Phytochemical analysis

Preliminary screening of phytochemicals of ethanol extract of leaves of *P. minima* and *L. camera* are carried out as follows [10-12].

**Saponin:-** 5 ml plants extract was mixed with 20 ml of double-distilled water then agitated in graduated cylinder For 15 min formation of foam indicates Saponin.

**Steroid:-** 1ml extract was dissolved in 10 ml of CHCl<sub>3</sub> and 1ml of concentrated H<sub>2</sub>SO<sub>4</sub> acid was added from the side of a test tube. The upper layer turns red and the H<sub>2</sub>SO<sub>4</sub> layer showed yellow with green fluorescence. This indicates the presence of steroids.

**Tannin:-** 4ml extract was treated with 4 ml Ferrous chloride formation of green color indicates that presence of condensed tannin.

**Anthocyanin:-** 2 ml of aqueous extract is added to 2 ml of 2N HCl & NH<sub>3</sub>, the



appearance of pink-red turns blue-violet indicates the presence of anthocyanin.

**Coumarin:-** 3 ml of 2N NaOH was added to 2ml of aqueous extract formation of yellow color indicates coumarins.

**Proteins:-** Extract was treated with a few drops of concentrated nitric acid formation of yellow indicates the presence of proteins.

**Flavonoid:-** Extract was treated with 2N NaOH solution, formation of intense yellow color indicates presence of Flavonoid.

**Diterpine:-** Extract were dissolved in water and treated with 10 drops of  $\text{Cu}(\text{OAc})_2$  solution, formation of emerald green color indicates the presence of Diterpine.

**Phenol:-** Test extract were treated with 4 drops of Alcoholic ferrous chloride solution.

Formation of bluish black color indicates the presence of Phenol

**Phlobatannin:-** when extract plant sample is boiled with dilute 0.1N HCl was taken red ppt was obtained as evidence for presence of Phlobatannin.

**Chalcone:-** 2ml of Ammonium Hydroxide was added to 0.5 ml ethanolic extract, the appearance of the red color showed the presence of Chalcone.

**Carbohydrate:-** Extract were dissolved individually in 5ml of distilled water and filtered. The filtrate was used for the following test. Filtrate was treated with 2 drops of alcoholic a-naphthol solution, the formation of violet ring at the junction indicates the presence of carbohydrates

(Table 1).

Table 1: Test of Phytochemical

Test of Phytochemical	<i>P. minima</i> Leaves	<i>L. camera</i> leaves
Saponin	+	-
Steroid	+	+
Tannin	+	+
Anthocyanin	+	+
Coumarin	+	+
Protein	-	+
Flavonoid	+	+
Diterpine	+	+
Phenol	+	+
Phlobatannin	+	-
Chalcone	-	+
Carbohydrate	+	+

Note: + = Present and - = Absent

### Antioxidant Activity

The stock solution 1 mg/ml of ethanol extracts and DPPH solution was prepared. The required dilutions from 0.01 mg/ml to 0.1 mg/ml were prepared by appropriate

dilutions [7, 8]. The optical densities of bank DPPH solution and sample solution can be calculate and found. With use of optical density of both solution percent antioxidant activities were calculated in Table 2.

Table 2: Optical Density and % Antioxidant Activity for Ethanolic Extract of *P. minima* leaves: (O.D. of Black DPPH = 0.585)

Conc.mg/ml	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1
O.D. of <i>P. minima</i>	0.432	0.353	0.274	0.216	0.201	0.187	0.131	0.112	0.104	0.075
%AA <i>P.minima</i>	26.15	39.65	53.16	63.07	65.64	68.03	77.6	80.85	82.22	87.17

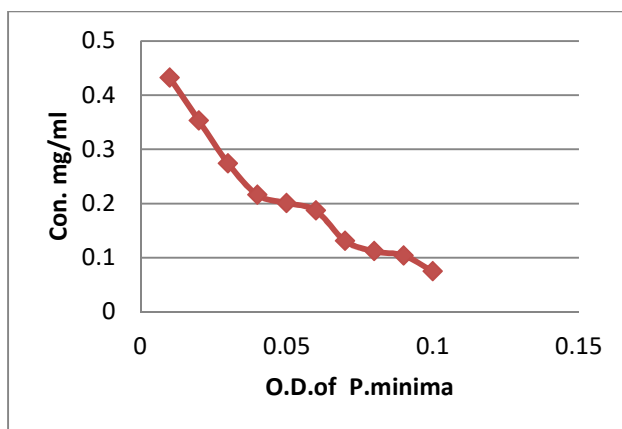


Figure 1: Decrease in Optical Density of Sample with Increase in Concentration of Ethanolic Extracts of *P. minima* leaves

Table 3: Optical Density and % Antioxidant Activity for Ethanolic Extract of *L. camera*: (O.D. of Black DPPH = 0.585)

Conc.mg/ml	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1
O.D. of <i>L. camera</i>	0.412	0.345	0.261	0.214	0.198	0.179	0.127	0.107	0.095	0.042
%AA <i>L. camera</i>	29.57	41.02	55.38	63.41	60.15	69.4	78.29	81.7	83.76	92.82

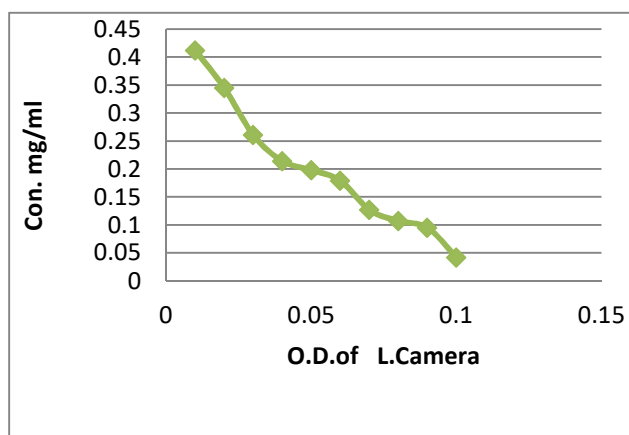


Figure 2: Decrease in Optical Density of Sample with Increase in Concentration of Ethanolic Extracts of *L. camera* leaves

Increase in Percent Antioxidant Activity with Increase in Concentration for ethanolic extract of *P. minima* leaves. Calculation of

$$\begin{aligned}
 &IC_{50} \text{ Value for } P. minima \text{ leaves : } = \max - \frac{1}{2} \\
 &(\max - \min) \\
 &= 87.17 - \frac{1}{2} (87.17 - 26.15)
 \end{aligned}$$

=56.66

IC<sub>50</sub> value from graph corresponding ethanolic extract of *P. minima* leaves is 0.036 mg/ml.

Increase in Percent Antioxidant Activity with Increase in Concentration for ethanolic extract of *L. camera* leaves. Calculation of IC<sub>50</sub> Value for *L. camera* leaves : = max – ½ (max-min)

= 92.82 – ½ (92.82 – 29.57) = 61.20

IC<sub>50</sub> value from graph corresponding ethanolic extract of *L. camera* leaves is 0.052 mg/ml.

#### Antibacterial Activity:-

The examined bacterial species included Gram-positive (*Bacillus Subtilis*) and Gram-negative (*Escherichia coli*). Sterile discs 6 mm prepared from Whatman filter paper No. 1 were made to absorb 50 µg of the test samples [13]. Standard reference antibiotic discs (Nitrofurantoin 30 µg, and Nalidixic acid 30 µg) for bacterial species were used as positive control and solvent discs (Distilled water and Ethyl Alcohol) were used as negative control [14]. The bacterial isolates were first grown in a nutrient broth for 18 h

before use and standardized to 0.5 McFarland standards (1.5 x 10<sup>8</sup> cfu / mL)(15). Mueller-Hinton agar was prepared on the plates as the medium for the test organism [16]. The bacterial inoculums were spread evenly onto the surface of the agar plate using the sterile cotton bud and then the extracts discs, 20% DMSO impregnated discs and standard antimicrobial discs were situated on the inoculums agar superficial. The antimicrobial activity was interpreted from the size of the diameter of the zone of inhibition measured to the adjacent mm as experiential from a clear zone surrounding the disc.

Methanol and ethanol extract for *P. minima* and *L. camera* leaves are effective to antibacterial activity while aqua extracts are less effective. The optimum inhibition zone size value for both the bacteria *Bacillus Subtilis* and *Escherichia coli* are 02 mm in both plants. In case optimum inhibition zone size value of antibiotic Nitrofurantoin is 06 mm and Nalidixic acid is 5mm were the details results for antibacterial activity are shown as shown in **Table 4**.

Table 4: The effectiveness of three elements (Plant extracts, Antibiotics and bacteria)

Medicinal Plants		Bacterial Species	Antibiotic	Bacterial Species	Antibiotic
		<i>Bacillus Subtilis</i> (mm)	Nitrofurantoin (mm)	<i>Escherichia coli</i> (mm)	Nalidixic Acid (mm)
<i>P. minima</i>	Aqus Extr.	01	02	0.5	02
	Methanol Extr.	02	04	02	03
	Ethanol Extr.	02	05	01	04
<i>L. camera</i>	Aqus Extr.	0.5	01	0.25	01
	Methanol Extr.	01	04	01	05
	Ethanol Extr.	02	06	02	05

Legend: (mm) = Millimeter

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**CONCLUSION**

- Phytochemical screening of selected wild medicinal plants clearly reveals that the maximum classes of photochemical are present in *P.minima* and *L.camera*
- The *P.minima* and *L.camera* Leave extracts demonstrate good DHHP radical activity with IC<sub>50</sub> value for *P.minima* is 0.036 mg/ml and *L. camera* is 0.052 mg/ml which show good antioxidant activity.
- Leaves extract of *P.minima* and *L.camera* are exhibited significant antibacterial activity for bacterial species including Gram-positive (*Bacillus Subtilis*) and Gram-negative (*Escherichia coli*). The optimum inhibition zone size value for both the bacteria *Bacillus Subtilis* and *Escherichia coli* are 02 mm in *P.minima* and *L.camera*.
- Phytochemicals in plant extract serve as a source of drugs that are useful in the medicine of some diseases caused by bacteria and also as antioxidant agents.

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# REVIEW OF DISCOVER ADULTERATION IN SOME COMMON FOODS ITEM BY BIOCHEMICAL QUALITATIVE ANALYSIS

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**Abstract:** Food is one most important basic need for all leaving organism, which useful for growth and maintnus. Now day's foods are contain by different adulterants. Adulteration is a substance which reduces the vital importance of foodstuff. Some of the common adulterants are sugar or jiggery in honey, Starch and melamine in milk, Red lead salts and brick powder in chilli powder, Metanil yellow colours in turmeric powder, Malachite green in vegetable, Mineral oil and castor oils in edible oils, Vanaspati ghee in butter, Lead chromate in pulse, Chalk powder in wheat flour, Prussian blue coloring substances in tea powder, Chicory in coffee powder, Papaya seed in black pepper etc. which is causes various diseases such as epidemic dropsy, glaucoma, cardiac arrest, paralysis, brain damage, anemia, abortion, cancer etc. The aim is to evaluate the presence of adulterant from daily uses food materials like honey, milk, sugar, chilli powder, turmeric powder, green vegetable, edible oil, butter, pulses, wheat flour, tea powder, coffee powder and black pepper which we collected from different local grocery stores and discover food adulterants by biochemical qualitative analysis. The colour change of the sample indicate the according to the reagents is indicates the presence of different adulterants. This information can help to grow the food safety and also people can be aware about the food brands for a healthy life which are very beneficial to our society and our future.

**Keywords:**-Foods, Adulterants, Diseases, Biochemical analysis, Food Safety, Healthy life

## I. Introduction

Food, sleter and cloth are basic needs for every living being. Food is the very necessity needs of life because which are use for growth and various life processes. Food contains important nutritional constituent carbohydrates, vitamins and proteins [1]. Almost all foods are of plant or animal origin. Many plants or plant parts such as roots, leaf, flower and fruit are eaten as food. There are around more than 2,000 plant species which are cultivated for food, and many have several distinct cultivars. Maize, wheat, and rice together account for 87% of all grain production worldwide. Animals are also used as food which included such as meat, milk cheese, butter and honey [2].

Nowadays, Food can be contaminated by different adulterants. Food adulteration is the process in which the quality of food is lowered either by the addition of inferior quality material or by extraction of valuable ingredient [3]. There are four different types of food adulteration included intentional adulteration, incidental adulteration, metallic adulteration and packaging



hazard [4]. In intentional adulteration substances that look similar to the constituents of the food are added to it, to increase its weight and gain more profit. Example- mixing of pebbles, stones, marbles, sand, mud, filth, chalk powder, contaminated water etc. Incidental adulteration occurs due to negligence while handling food. Example- residues of pesticides in grains, larvae growth, presence of droppings of rodents, etc [5,6]. In metallic adulteration addition of metallic materials into food like lead or mercury is metallic adulteration. It may happen accidentally or even intentionally. The packing materials in which the food is packed may also interfere and mix with the constituents of the food, leading to packaging hazards [7]. Various food adulteration methods included mixing, substituting, using decomposed food, additions of toxic substances, misbranding, and artificial ripening. Also important reason for food adulteration are overgrowing population, urbanization, industrialization, decrease the land of agriculture, environmental hazards, and depleting natural resources then decrease food production [8].

In India normally the adulteration in food is done either for financial gain or due to carelessness and lack in proper hygienic condition of processing, storing, transportation and marketing. Such types of adulteration are quite common in developing countries. Food adulteration has a great impact on our health. Be it any kind of adulteration, prolonged consumption of this type of food is very harmful to the body [9]. Consuming such food increases the toxicity in the body. As the nutritional value of the adulterated food goes down, such food is no longer nutritive for the body. The addition of chemical adulterants and colours many times proves to be fatal [10]. Adulterated food may also affect our internal organs directly leading to heart, kidney, liver, and many more organ disorders and failure. Which is causes various diseases such as epidemic dropsy, glaucoma, cardiac arrest, paralysis, brain damage, anemia, abortion, cancer etc. The Present research work to evaluate the presence of adulterant from daily uses food materials like honey, milk, chilli powder, turmeric powder, green vegetable, Edible oil, Butter, Pulses, wheat flour, tea powder, coffee powder and black pepper which we collected from different local grocery stores and discover food adulterants by biochemical qualitative analysis [11]. The colour change of the sample indicate the according to the reagents is indicates the presence of different types of adulterants. This information can help to grow the food safety and also people can be aware about the food brands for a healthy life which are very beneficial to our society and our future [12].

## II. Materials & Methods

Food materials like honey, milk, sugar, chilli powder, turmeric powder, green vegetable, edible oil, butter, pulses, wheat flour, tea powder, coffee powder and black Pepper which we collected from different departmental and local grocery stores. Some reagents like Iodine reagent, Con. HCl, Sucrose, 0.5N ethanolic KOH, Con. HNO<sub>3</sub>, Solvent ether, Resorcinol, Carbon tetra-chloride (CCl<sub>4</sub>), Con. H<sub>2</sub>SO<sub>4</sub>, Chloroform, Aniline, some apparatus such as Test tube, Beaker, Conical flask, Watch glass, Glass rod, Funnel, Burette, Pipette, Wash bottle and some paper such Filter paper, Litmus Paper, Cotton plug, blotting paper, were collected which were used for chemical tests. Biochemical qualitative analyses are done for detecting presence of

adulterants [13].

### III. Result & Discussion

Biochemical qualitative analyses of some food are as follows.

#### 1. Food:- Honey

Common adulterant: - Sugar

Biochemical qualitative analysis: - Take 5 ml of honey in a porcelain dish. Add aniline chloride solution (3 ml of aniline dissolved in 7 ml of HCL) and stir well. Orange red colour indicates presence of sugar[14].

#### 2. Food:- Milk

a) Common adulterant:- Starch

Biochemical qualitative analysis: - Take a little amount 3ml of the sample in a test tube. Add a drop of 1% aqueous solution of iodine. Blue or deep blue colorations indicate starch in milk .

b) Common adulterant:- Melamine

Biochemical qualitative analysis: - Take a little amount 5 gm of the sample in a test tube. Add a little amount of soybean powder. After 5 minute, dip a red litmus paper that are change in colour from red to blue indicate the use of Melamine in milk [15].

#### 3. Food:- Sugar

a) Common adulterant:- stone powder or white sand

Biochemical qualitative analysis :- A small amount of sugar was taken in a test tube and shaken with little water. Pure sugar dissolved in water but insoluble stone powder or white sand didn't dissolve.

b) Common adulterant:- washing soda

Biochemical qualitative analysis :-To a small amount of sugar in a test tube , few drops of diluted HCl were added. A brisk effervescence of carbon dioxide confirmed the presence of washing soda in the given sample of sugar[16].

#### 4. Food:- Chili powder

a) Common adulterant:- red lead salts

Biochemical qualitative analysis:- To a sample of chili powder, dil. Nitric Acid was added. The solution was filtered and two drops of potassium iodide were added into it. Yellow ppt. obtained indicated the Presence lead salts in a chili powder.

b) Common adulterant:- brick powder

Biochemical qualitative analysis :- A small amount of given red chili powder was added in a beaker containing water. Settling of some powder at the bottom & floating pure chili powder over water indicates the presence of brick powder in a given sample[17].

#### 5. Food:- Turmeric powder

Common adulterant:- Metanil Yellow colours

Biochemical qualitative analysis Add a few drops of HCl to turmeric in water. Instantly the solution will turn to violet colour [18].

#### 6. Food:- Green vegetables.

Common adulterant:- Malachite green

Biochemical qualitative analysis:- Take a vegetable and rubbing moistened white cotton plug. Green colour impressions on cotton plug indicates the presence of Malachite green[19].

### 7. Food:- Ice cream

Common adulterant:- Baking Soda

Biochemical qualitative analysis Take small Sample of ice cream in beaker add drop of Hydrochloric acid or some lemon juice on this, bubbles are observed if Baking Soda is present[20].

### 8. Food:- Edible oil

Common adulterant: - argemone oil

Biochemical qualitative analysis: - take 1 ml of the oil in test tube after add mixture of 1 ml of 2% salicylic acid in methanol and 2 ml of conc.  $\text{HNO}_3$ , followed by 0.5 ml of conc.  $\text{H}_2\text{SO}_4$  this mix shake indicate crimson red or deep orange-red colour develops within 20-30 sec- which indicate argemone oil adulteration is present [21].

### 9. Food:- Butter

Common adulterant:- Starch and hydrogenated vegetable oils

Biochemical qualitative analysis: - Take 2 gm butter in test tube after add 2-3 drops of iodine solution appeared blue colours indicate presence adulterated in butter [22].

### 10. Food:- Pulses

Common adulterant:- Metanil Yellow and Lead Chromate

Biochemical qualitative analysis:- Take 5 gm of the pulses sample with 5 ml of water in a test tube and add a few drops of concentrated Hydrochloric Acid. A pink colour shows presence of adulterations metanil yellow and lead chromate [23].

### 11. Food:- Wheat Powder

Common adulterant:- chalk powder.

Biochemical qualitative analysis:- You can check for the presence of adulterant chalk powder by adding 2 to 3 ml dil. HCl to the wheat powder sample in a test tube. Chalk powder creates effervescence in test tube [24].

### 12. Food:- Tea powder

a) Common adulterant:- Cashew husk

Biochemical qualitative analysis:- Spread a few tea leaves sample on a blotting paper, sprinkle some water on them. Once done, remove the tea leaves and wash the blotting paper under tap water. Observe the colour stains on blotting paper indicate presence of Cashew husk adulterant in tea.

b) Common adulterant:- iron fillings

Biochemical qualitative analysis:- For this you will need a magnet. Spread out a small quantity of tea leaves on a glass plate and gently move the magnet above the tea leaves. If the tea leaves are pure then the magnet will be clean. However, adulteration will manifest when iron fillings get stuck to the magnet.

c) Common adulterant:- some colorant

Biochemical qualitative analysis:- a glass of water. Ensure that the water is either cold or at room temperature but not hot. If the tea is pure then there will be no change in the water's colour. If the tea leaves have some colorant added to it, the colour will immediately change to red, so beware [25].

### 13. Food:- Coffee Powder

Common adulterant:- Chicory

Biochemical qualitative analysis:- Drop a pinch of coffee powder on it gently. If the powder floats for some time before sinking, it is coffee. If the powder sinks quickly, it is chicory or some other seed. If it readily diffuses brownish or yellowish colour, it contains Caramel or Chicory [26].

### 14. Food:- Black Pepper

Common adulterant:- papaya seeds

Biochemical qualitative analysis:- Add some amount of black pepper to a glass of water. Pure black pepper settles at the bottom. In the adulterated black pepper, papaya seeds float on the surface of water [27].

## IV. Conclusion

From the above review and discussions adulteration present in some common foods such as honey, milk, sugar, chilli powder, turmeric powder, green vegetable, edible oil, butter, pulses, wheat flour, tea powder, coffee powder and black pepper which we collected from different local grocery stores. Also explain some biochemical method which discovered food adulteration in the food items. Food adulteration can cause tremendous affect on health without our knowledge. Adulteration can be prevented by few alerting steps of our society. Hike of price of food items should be checked by government. While purchasing food items, selection of wholesome and non-adulterated food is necessary to make sure that such food do not cause and health problems. Though presence of adulterants cannot be ensured by visual examination as toxic contaminants are present in very low level but visual examination before purchase can ensure absence of insects, fungus and other foreign materials. The consumer should avoid buying food from places which do not maintain proper hygiene conditions. Both local and branded food stores should be inspected by government bodies. The above general consciousness is simple and easy to initiate for our healthy life. If we tend to actively participate in these changes then we can bring about a healthy and non venturous future for the upcoming generations.

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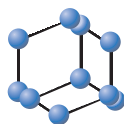
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## REVIEW ARTICLE

BENTHAM  
SCIENCE

# Synthesis of Oxygen and Nitrogen Containing Heterocycles using Zirconium Dioxide/Mixed Oxide Nanoparticles as Reusable Green Catalysts: A Comprehensive Update



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**Abstract:** The remarkable improvements in organic synthesis facilitated by zirconium dioxide-based nanoparticles are updated and summarized in this review. The ZrO<sub>2</sub> acts as a versatile heterogeneous nanocatalyst and is used in various elementary organic reactions and many multicomponent reactions. The employment of these catalysts in organic synthesis leading to bio-active scaffolds provides the opportunity to carry out the reactions using facile synthetic protocol under mild environments that furnish the equivalent products in high yields and shorter reaction times. According to reports in the literature, ZrO<sub>2</sub>-based catalysts were removed from the reaction mixture and recycled many times.



Trimurti L. Lambat

**Keywords:** Green chemistry, ZrO<sub>2</sub> nanoparticles, heterogeneous nanocatalyst, O & N-heterocycles, bio-active scaffolds, reusable green catalyst.

## 1. INTRODUCTION

Green synthesis routes have recently attracted significant attention leading to important developments in the fields of click reactions [1] and green chemistry [2-9], with the advances of environmentally and proficient benign protocols [10-15] being in focus. As catalysts, nanoparticles (NPs) demonstrated superiority to conventional catalysts in several aspects relevant to sustainable development [16-18]. Additionally, NPs were extensively investigated for potential use in nanomedicine, particularly for drug delivery [19] and early detection of cancer cells. Mesoporous nanomaterials were also employed for a variety of organic reactions [20]. The high specific area and active surface sites in nanomaterials render these materials more important than their bulk counterparts for a wide range of science and technology applications [21].

Metal oxides are frequently employed as solid catalysts that can either function as the active phase or the supports [22], exhibiting favorable catalytic activity and providing perhaps the largest class of heterogeneous catalysts [23-30]. In addition to metal oxides, metals are also widely employed in chemical synthesis [31-40]. The catalytic activity of transition and noble metals is attributed to the electronic configuration of the outer valence electrons [41]. Further, mixed metal oxides account for many solid catalysts frequently used in the pharmaceutical industry [42, 43].

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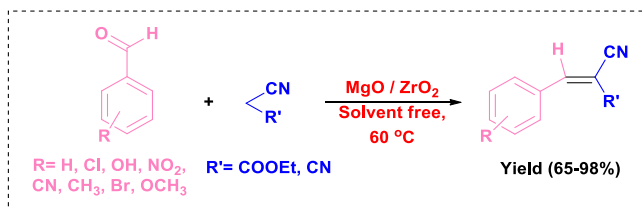
Zirconium dioxide (zirconia, ZrO<sub>2</sub>) demonstrated efficacy and potential for a number of significant applications, including catalysis, fuel cell electrolytes, buffer layers for superconductor development, oxygen sensors, gate dielectrics, and ceramics wear-resistant optical coatings [44-55]. This oxide can exist in three structural phases, monoclinic, tetragonal, and cubic [56], which exhibit different catalytic activities.

The surface of ZrO<sub>2</sub> NPs [57] can support active hydroxyl groups and oxyanions and contains Zr<sup>4+</sup> ions, enabling zirconia to function as a dual acid-base catalyst [58]. Even though the employment of ZrO<sub>2</sub> NPs for the preparation of biologically active blocks *via* solvent-free multicomponent reactions was rarely addressed [59, 60], The development of green synthesis methods and research on the synthesis of isatin-based heterocycles were reported. [61-75]. The interesting properties of sulfated zirconia, including its cost-effectiveness, thermal stability, and super acidity, render these materials industrially important for a number of reactions [76]. In addition, zirconia NPs were reported to improve the mechanical properties of ceramics [77] and modify their electrical, thermal, magnetic performance and optical properties [78]. Further, nanoscale zirconia exhibited catalytic activity for the dehydration of alcohols, the selective synthesis of dimethyl carbonate, the selective oxidation of methanol, and redox activity [79-85]. For creating zirconia NPs, several synthesis methods have been used, including but not limited to hydrothermal, sol-gel, chemical vapour deposition (CVD), and sputtering approaches [86-90].

One of the most extensively researched reactions in organic synthesis, organic transformations employing zirconium dioxide/mixed oxides are well displayed on the surface of zirconium dioxide/mixed oxides under various reaction circumstances. Zirconium dioxide/mixed oxides serve an equally significant role in the overall catalyst system used as other heterogeneous catalysts do. We will briefly discuss the use of zirconium dioxide and mixed oxides in this review's synthesis of fine chemicals, organic synthesis, and industrial, and green chemistry.

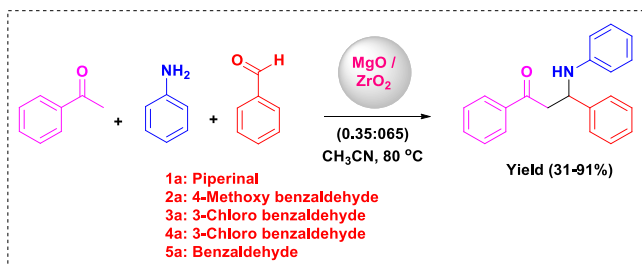
## 2. SYNTHESIS VIA MgO/ZrO<sub>2</sub> AS A CATALYST

Gawande & coworkers [91] in 2006 introduced MgO/ZrO<sub>2</sub> as a novel green catalyst for the Knoevenagel condensation of ethyl cyanoacetate with aromatic aldehydes and malonitrile (Scheme 1). The structural characterization of the catalyst indicated that the crystallization of the catalyst oxide components is highly dependent on the sintering temperature. X-ray diffraction pattern (XRD) of the catalyst sintered at 600°C revealed the existence of a cubic MgO and a monoclinic ZrO<sub>2</sub> phases, as well as evidence of the presence of a secondary tetragonal ZrO<sub>2</sub> phase. Before utilizing the catalyst in the 60°C, solvent-free processes, the catalyst was ground to a particle size of 0.5 to 0.7 μm. The catalyst gave relatively high yields of the products. It exhibited a high degree of recyclability, whereas, in the case of 4-fluoro benzaldehyde, the yield (95%) decreased slightly to 91% after the fifth cycle of reusing the catalyst.



**Scheme 1.** Knoevenagel condensation of an aromatic aldehyde with ethylcyanoacetate and malonitrile.

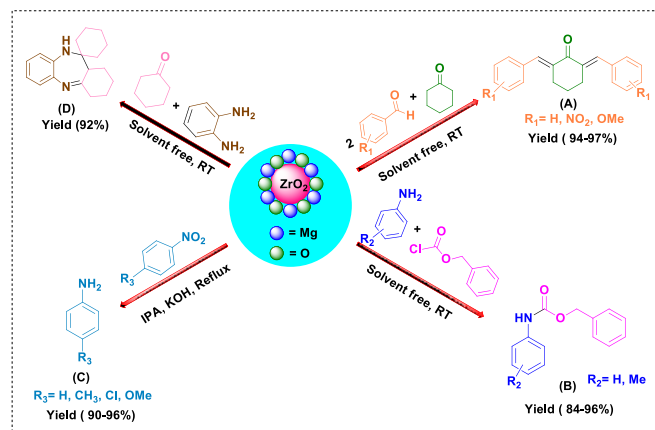
In 2010, Nagrik *et al.* [92] described an efficient three-component one-pot condensation of ketones, aldehydes, and amines using MgO/ZrO<sub>2</sub> catalyst for Mannich reaction for the synthesis of β-amino carbonyl compounds (Scheme 2). The yield depended on the ratio of the two oxides in the catalyst, and the highest yield of 91% was achieved at the MgO/ZrO<sub>2</sub> molar ratio of 0.35/0.65. It was demonstrated that the catalyst could be used repeatedly for five runs without significantly losing its catalytic activity.



**Scheme 2.** Synthesis of β-amino carbonyl compound by Mannich reaction via MgO/ZrO<sub>2</sub> catalyst.

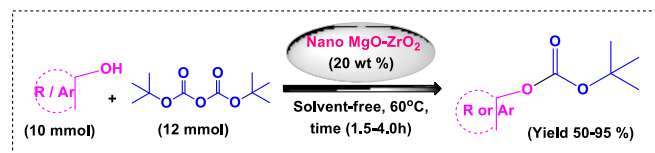
Later in 2011, Gawande *et al.* [93] have prepared MgO–ZrO<sub>2</sub> (MZ) catalyst by an ultra-dilution method, and tested its versatility for a number of organic reactions (Scheme 3). The XRD pattern indicated the presence of Monoclinic ZrO<sub>2</sub> and cubic MgO phases in the catalyst. The catalyst provided superior to outstanding yields of the products. For example, it gave 94-97% yield in the cross-aldol condensation of aromatic aldehydes with cyclohexanone, and

84-96% yield in the *N*-benzyloxycarbonylation of amines by using 10 wt.% of the catalyst. According to reports, catalyst weight percentages up to 10% led to an increase in catalytic activity, after which no significant improvement was observed. Also, the catalyst was found to be effective up to six successive cycles of the synthesis of the target products.



**Scheme 3.** Organic reactions catalyzed by MgO–ZrO<sub>2</sub> (A) Cross-Aldol condensation under solvent-free condition, (B) *N*-Benzyloxycarbonylation of amine under solvent-free condition, (C) Reduction of aromatic nitro compounds, (D) 1,5-benzodiazepine synthesis by using cyclohexanone and orthophenylenediamine.

MgO–ZrO<sub>2</sub> NPs were used by Gawande *et al.* [94] in 2012 to establish a straightforward solvent-free chemoselective *O*-tert-Boc protection of phenols & alcohols. (Scheme 4). This method's advantages include using a heterogeneous, reusable catalyst, superior chemoselectivity, enhanced substrate compatibility, high reaction rates, operational simplicity, and moderate reaction conditions. The size of the catalyst is in the nano range (20–35 nm), according to the TEM investigation of MgO–ZrO<sub>2</sub> mixed metal oxides. Under solvent-free conditions at 60°C, the reusability of the catalyst was tested for the reaction of phenol with Boc anhydride. The catalyst was filtered out and rinsed twice or three times after the reaction was finished. with ethyl acetate, dried at 120°C in an oven for 3 hours, and then used again for the reaction. Even after six cycles, the catalytic activity reduced marginally.



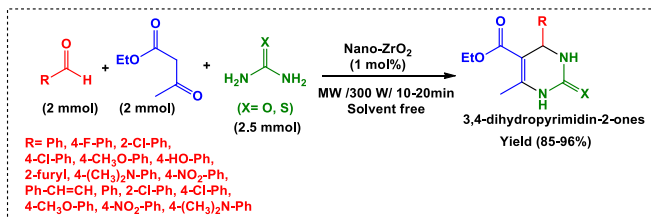
**Scheme 4.** *O*-tert-Butoxycarbonylation of phenol by using nano MgO–ZrO<sub>2</sub> catalyst.

## 3. SYNTHESIS USING ZrO<sub>2</sub> NANOPARTICLE AS A CATALYST

Bhojgowd *et al.* [95] (Zirconium nitrate with alanine were combined in stoichiometric proportions in aqueous solutions to synthesize nano crystalline-ZrO<sub>2</sub>) developed nanocrystalline zirconium (IV) oxide (nc-ZrO<sub>2</sub>) with a bulky surface area in 2011 (Scheme 5). For characterization of nc-ZrO<sub>2</sub>, SEM, powder XRD and surface area measurements were used. The powder XRD results show that the nc-ZrO<sub>2</sub> possesses a pure tetragonal phase. The crystallite size and BET surface area computed using Scherrer's formula were determined to be around (53-57 nm) and 275 m<sup>2</sup>/g, respectively. SEM image revealed the microporous character of the powder. The synthesis of 3,4-dihydropyrimidin-2-ones was accomplished without solvents in the microwave (MW)-aided multi-component,

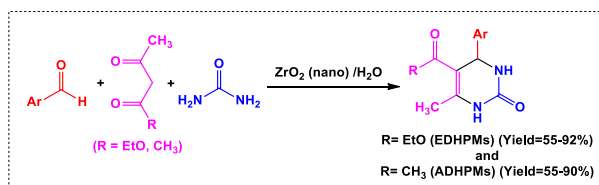
one-pot Biginelli condensation reaction of ethylacetoacetate, aryl aldehydes and urea or thiourea (DHPMs). In this reaction scenario, DHPMs are produced quickly (10–20 minutes) and in good to exceptional yields (85%–96%).

By using repeated filtering, the catalyst may be readily removed from the mixture, repeated washings with distilled water and ethanol, and dried under vacuum for 2–3 hours before re-use. The recycled catalyst was employed five times to get 5-ethoxycarbonyl-4-(phenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one with no discernible yield loss. For 1–5 cycles, the yields were 96%, 93%, 93%, 90%, and 89%, respectively; the drop in yield could be attributed to substrate adsorption on active sites. The catalyst was filtered out of the reaction mixture and replenished after each reaction.



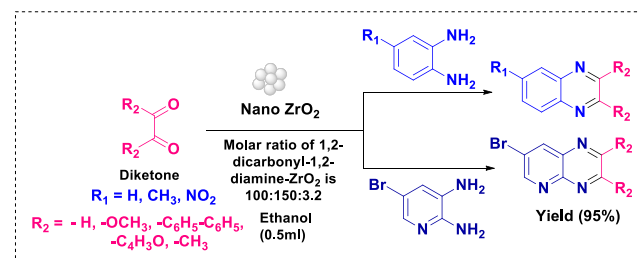
**Scheme 5.** Synthesis of 3,4-dihydropyrimidin-2-ones by Biginelli condensation of aldehyde, ethylacetoacetate and urea or thiourea using ZrO<sub>2</sub> as a nanocatalyst.

Farhadi *et al.* [96] discovered a simple and efficient one-pot three-component reaction of various aromatic aldehydes, β-keto compounds, and urea in the presence of a catalytic quantity of nano-ZrO<sub>2</sub> catalyst in the presence of water in 2013 (Scheme 6). The results show that by employing nano-ZrO<sub>2</sub> as a catalyst, several aldehydes may be converted to their corresponding 3,4-dihydropyrimidin-2(1H)-ones in good to exceptional yields, comparable to the SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> catalyst.



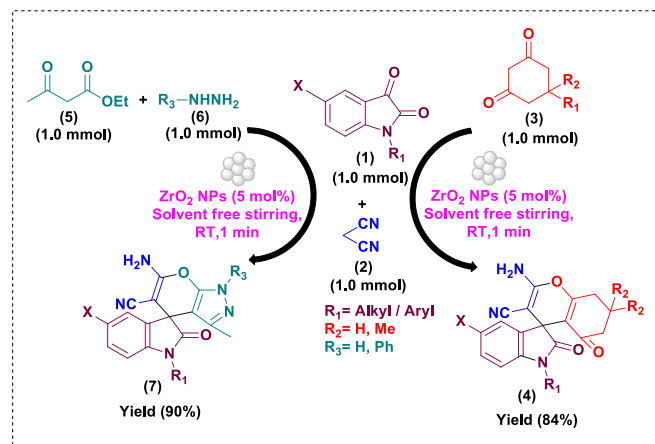
**Scheme 6.** Nano-ZrO<sub>2</sub>-catalyzed synthesis of monosubstituted derivatives of 3,4-dihydropyrimidin-2(1H)-ones.

In 2014 Jafarpour *et al.* [97] described the synthesis and characterization of monoclinic ZrO<sub>2</sub> nano catalyst using the sol-gel technique. The catalyst was used for the condensation of 1,2-diamines with Quinoxaline and pyridopyrazine heterocyclic compounds may be made using 1,2-dicarbonyl chemicals (Scheme 7). The catalyst displayed high activity, which also produced products with acceptable to exceptional yields (up to 96%). Without noticeably losing much of its catalytic activity, the catalyst was recycled and utilized for up to five further cycles.

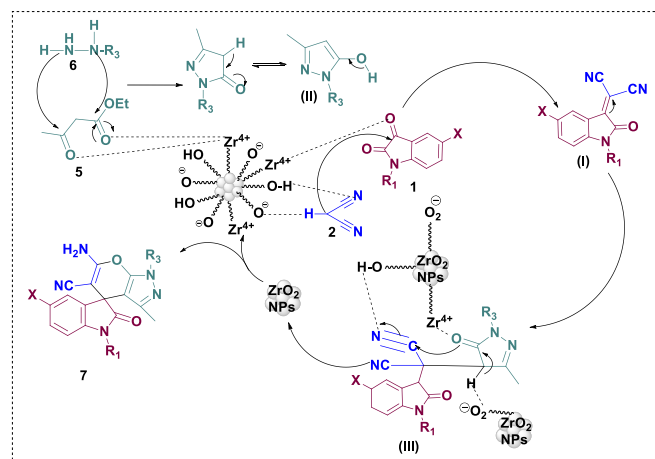


**Scheme 7.** Synthesis of quinoxaline derivatives and pyrido pyrazines in the presence of m-ZrO<sub>2</sub> nanoparticles in ethanol.

In 2015, Bodhak *et al.* [98] examined the effectiveness of the catalysis using ZrO<sub>2</sub> NPs for the synthesis of multi-functionalized spirooxindole derivatives using two different condensation protocols. They compared the results with reactions performed by using different catalysts and solvents in one-pot multi-component reactions. The study revealed the superiority of zirconia nano catalyst, which provided 84% and 90% yields of spiro[4H-pyran-3,3'-oxindoles] and spiro[indoline-3,4'(1H')-pyrano-[2,3-c]pyrazol-2-ones in an amazingly short time of 1 min. by using 5 mol.% of the catalyst (Scheme 8). Only a small increase in the yields (86% and 91%) was seen when using a greater catalyst loading of up to 20 mol%. The study also showed that the catalyst may be used again for up to five runs without substantially reducing activity. The suggested mechanisms of the spirooxindole compounds' formation are demonstrated in Figs. (1 & 2) below.



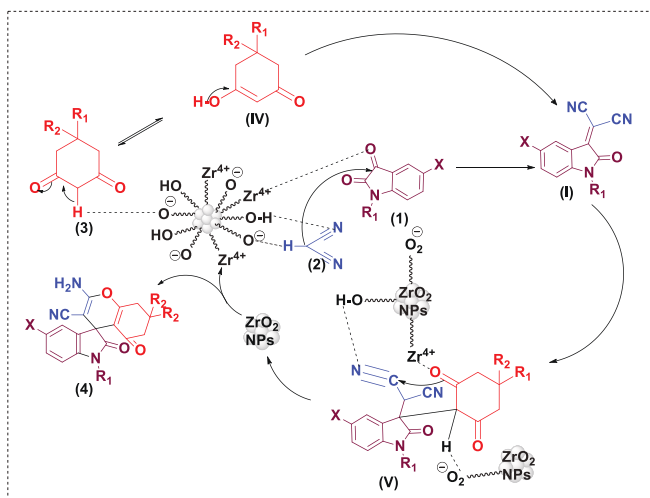
**Scheme 8.** Synthesis of spiro[4H-pyran-3,3'-oxindoles] (4) and spiro[indoline-3,4'(1H')-pyrano-[2,3-c]pyrazol-2-one derivatives (7).



**Fig. (1).** possible mechanism for the preparation of spirooxindoles (7).

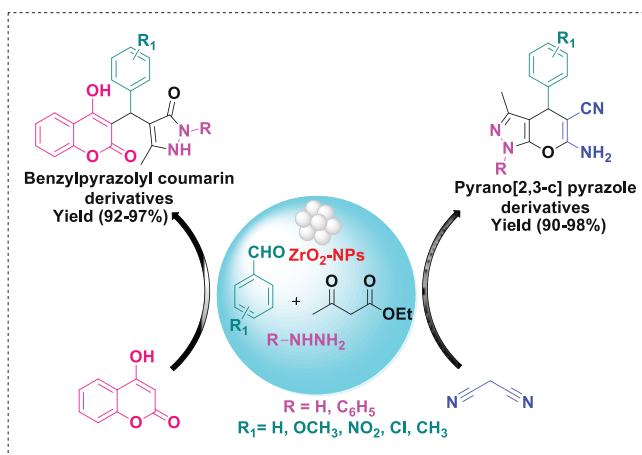
At the surface of the ZrO<sub>2</sub> NPs, the hydroxyl, oxide and Zr<sup>4+</sup> ions enable the NPs to function as a dual acid-base catalyst for the reactions. The reactants are adsorbed at the active sites of the NPs surfaces, leading to a significant increase of the local concentration of the reactants, and resulting in a significant acceleration of the rate of reaction. The catalyst's acid-base properties facilitate the first Knoevenagel condensation of malononitrile (2) with isatins (1), which leads to the production of the common intermediate (I). Next, intermediate (I) undergoes Michael-type condensation with intermediate (II) to generate the intermediate, and pyrazole intermediate (II) originates in situ from the reaction of ethylacetoacetate (5) and hydrazine (6). (III). Finally, Intermediate

(III), assisted by the acidic and basic nature of the surface sites of the  $ZrO_2$  NPs, undergoes intra-molecular electrophilic cyclization followed by tautomerization, resulting in the formation of spirooxindoles (7). In a similar fashion, the intermediate (I) undergoes Michael-type addition with the enol form of cyclohexane-1,3-diones (IV), leading to the formation of intermediate (V), which subsequently transforms into spirooxindoles (4) assisted by the catalytic activity of the zirconia NPs.



**Fig. (2).** Probable mechanism for the preparation of spirooxindoles (4).

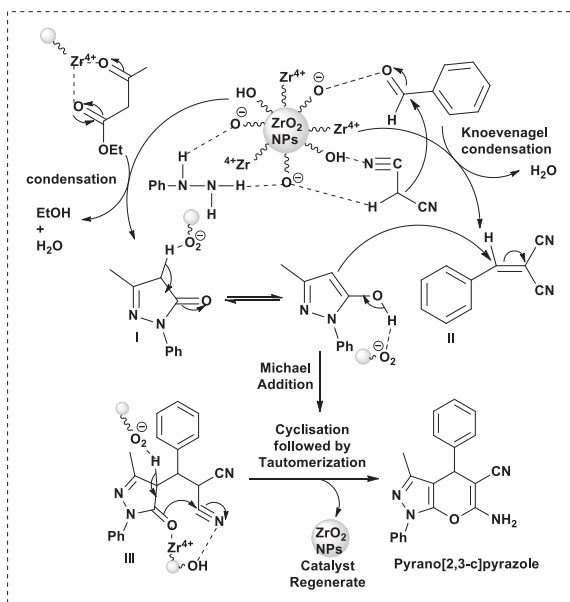
Subhash Banerjee *et al.* [99] and collaborator reported the synthesis of  $ZrO_2$  NPs catalyst with tetragonal symmetry to be used in a synthesis of bioactive pyrano[2,3-*c*]pyrazole and benzylpyrazolyl coumarin derivatives *via* a one-pot multicomponent reaction at room temp. (Scheme 9). The authors investigated the effects of experimental conditions, including the catalyst loading, reaction time and solvent, and obtained high yields (92-98%) of the products in 2-10 min. Further, the authors demonstrated the high catalytic of the catalyst even after recycling for up to 10 successive runs. The authors concluded that the catalytic activity of the tetragonal phase of  $ZrO_2$  NPs is higher than that of the monoclinic phase.



**Scheme 9.** Synthesis of benzylpyrazolyl coumarin and pyrano[2,3-*c*] pyrazole scaffolds *via*  $ZrO_2$  NPs as a catalyst.

The active hydroxyl, oxide, and  $Zr^{4+}$  ions bound to the surface of the  $ZrO_2$  NPs enable their dual activity as Lewis acids or bases, which is how the  $ZrO_2$  NPs play a part in the MCR for the synthesis of pyrano[2,3-*c*]pyrazoles. In (Fig. 3), a potential pathway for the production of pyranopyrazole derivatives aided by  $ZrO_2$  NPs is

shown. First, pyrazolone (I) and 2-phenyldienemalononitrile (II) intermediates are simultaneously formed by cyclo-condensation and Knoevenagel reaction, respectively, promoted by the  $ZrO_2$  NPs (Fig. 3). The activation of (I) by the Lewis basic (O) sites of the NPs leads to the formation of these two intermediates, which subsequently undergo Michael type addition to yield the enolate intermediate (III). Lastly, the NPs' Lewis acidic and basic sites help promote intramolecular electrophilic cyclization and tautomerization, which results in the required pyrano[2,3-*c*]pyrazole derivative. The manufacture of pyrano[2,3-*c*]pyrazole utilizing a step-by-step process, where the precursors (I) and (II) were synthesized individually from the corresponding starting materials *via*  $ZrO_2$  NPs as a catalyst, allowed the authors to demonstrate the viability of the proposed mechanism. The resulting reaction of these two precursors in the presence of  $ZrO_2$  NPs produced the required pyrano[2,3-*c*]pyrazole derivative, supporting the viability of the proposed process.



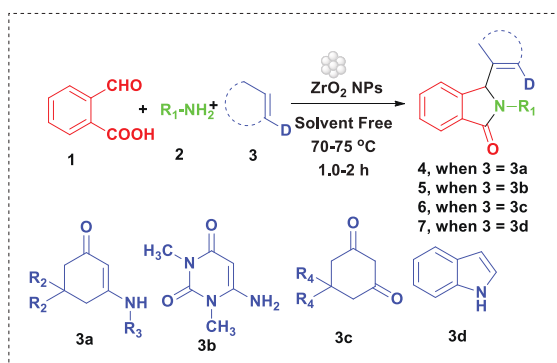
**Fig. (3).** probable mechanism for  $ZrO_2$  NPs-catalyzed synthesis of 6-amino-3-methyl-1,4-diphenyl-1,4-dihydro-pyrano[2,3-*c*]pyrazole-5-carbonitrile.

A straightforward one-pot three-component reaction catalyzed by  $ZrO_2$  NPs in solvent-free conditions was introduced by Debnath *et al.* [100] for the synthesis of multi-functionalized 2,3-disubstituted isoindoline-1-ones. The active surface sites of the  $ZrO_2$  nanoparticles facilitating the dual acid-base functionality of the catalyst were reported to be efficient in the condensation of 2-carboxybenzaldehyde, aliphatic amines and nucleophile (enamines/6-amino 1,3-dimethyluracil/1,3- cyclohexadiones/ indole) to produce 2,3-disubstituted isoindoline-1-ones with high yields (Scheme 10). The reported additional advantages of the adopted methodology include simplicity, short reaction time and low temperature, avoiding the use of hazardous solvents, wider substrate scope, and the recyclability of the catalyst for successive cycles of the reaction.

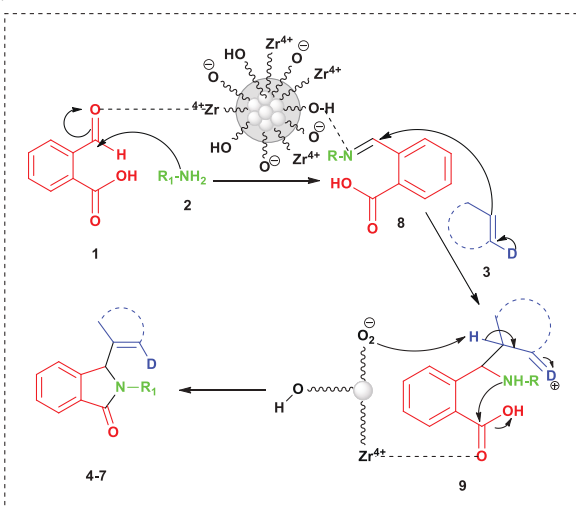
In the presence of  $ZrO_2$  NPs in solvent-free conditions, the authors postulated a likely mechanism for the synthesis of the isoindoline-1-one derivatives 4-7 (Fig. 4). The active sites on the surface of the  $ZrO_2$  NPs, which function as a dual acid-base catalyst, have been suggested by other researchers in the discussion above as an aid to condensation processes. The 2-carboxybenzaldehyde (1) and aliphatic amines (2) are condensed to produce intermediates in a



first step in which the  $Zr^{4+}$  ion at the surfaces of the NPs functions as a potent Lewis acid acceptor and triggers the carbonyl group (**8**). The intermediate is then created *via* a Michael-type addition involving (**8**) and the nucleophile (**3**) that is catalysed by  $ZrO_2$  NPs (**9**). To produce the end products, the intermediate (**9**) is then made easier to cyclize and tautomerize intramolecularly by the acidic and basic sites of  $ZrO_2$  NPs (isindoline-1-ones).

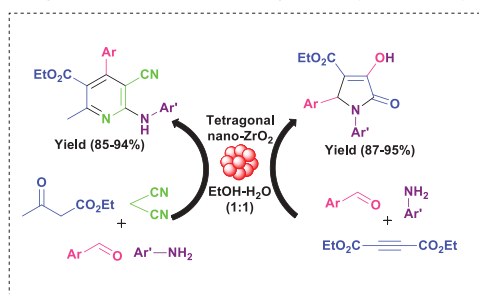


**Scheme 10.** Synthesis of multi-functionalized isindoline-1-one derivatives (4-7).



**Fig. (4).** A probable mechanism for the formation of isindoline-1-one derivatives.

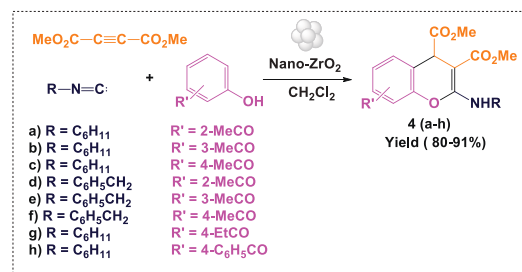
Saha *et al.* [101] in 2016 further explored the catalytic activity of tetragonal *t*- $ZrO_2$  NPs for the synthesis of poly-substituted 6-arylamino pyridines and 2-pyrrolidone derivatives (Scheme 11). The authors reported a high yield of the products, and the recyclability of the catalyst revealed a small reduction of the yield (92% to 83%) after eight successive runs using the recycled catalyst.



**Scheme 11.** Tetragonal nano- $ZrO_2$  catalyzed synthesis of functionalized pyridine and 2-pyrrolidinone derivatives.

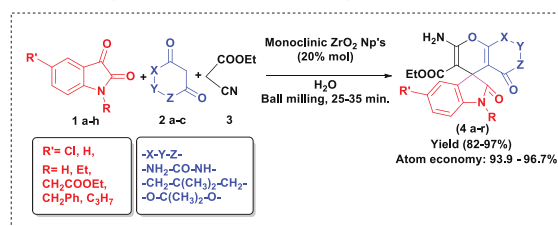
In order to synthesise novel functionalized chromenes, Zonouzi *et al.* [102] developed a fresh, succinct, and effective procedure

(Scheme 12).  $ZrO_2$  nanoparticles with a specific surface area of  $25 \text{ m}^2/\text{g}$  (100 nm particle size (TEM),  $d = 5.89 \text{ g/Lit}$ ) substantially altered and regulated the reaction's pathway. The anticipated findings, indenes, were not generated; rather, chromene derivatives were.



**Scheme 12.** Preparation of some new 2-amino-4H-chromenes using nano-sized zirconium oxide.

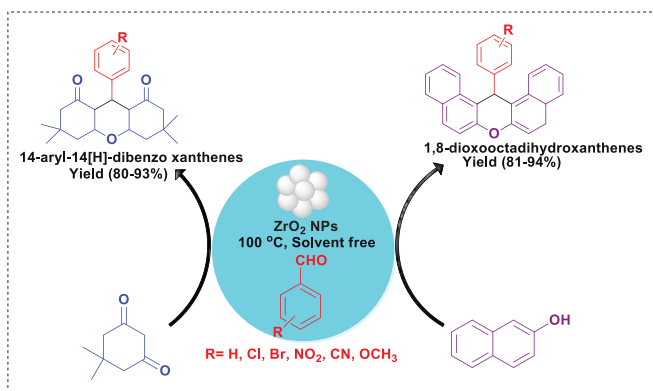
On the other hand, Bajpal *et al.* [103] reported an efficient green protocol for employing a monoclinic *m*- $ZrO_2$  NPs catalyst in a multicomponent reaction of isatin derivatives with ethyl cyanoacetate and 1,3-dicarbonyl compounds in a ball mill to create substituted spirooxindoles (Scheme 13). The approach was put out as a workable synthesis strategy for industrial-scale manufacturing in medicinal chemistry. Under ideal reaction circumstances, the reusability of the *m*- $ZrO_2$  NPs was investigated. The catalyst showed good catalytic activity in subsequent reactions up to 10 runs, at which point the yield marginally dropped from 97% to 90%. It was also reported that calcination of the recycled catalyst at  $750^\circ C$  after washing and drying resulted in an improvement of the yield (from 90% in the 9<sup>th</sup> cycle to 95% in the 10<sup>th</sup> cycle).



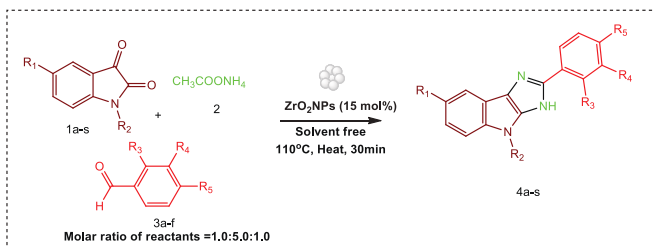
**Scheme 13.** Synthesis of Spirooxindole using *m*- $ZrO_2$  NPs catalyst by Ball milling method.

Recently, Bansal *et al.* [104] also used  $ZrO_2$  NPs catalyst for effective solvent-free one-pot synthesis of biologically active xanthenes derivatives (Scheme 14). For this purpose, the coprecipitation technique prepared tetragonal *t*- $ZrO_2$  NPs with sizes in the range of 8-11 nm and average pore size of  $\sim 3 \text{ nm}$ . Xanthenes derivatives were achieved with high yields (80-94%) within 16-33 min. by the use of a *t*- $ZrO_2$  nanocatalyst. The catalyst was demonstrated high yielding up to four additional runs.

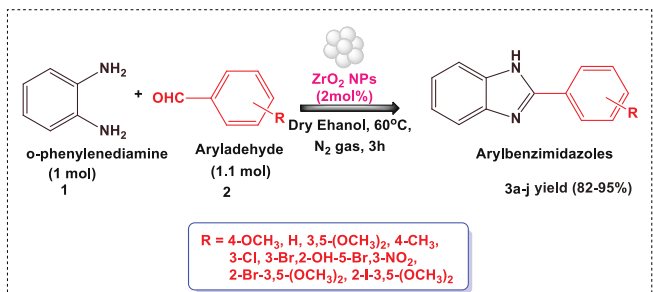
Singh and his coworker [105] in (2019) developed an ecologically friendly and highly effective approach for the synthesis of modified imidazoles employing a multicomponent reaction of isatin derivative products with ammonium acetate and aromatic aldehydes under solvent-free conditions. (Scheme 15). Because of the cheap and widely available starting materials, easy methodology, and bioactive nature of imidazoles, this strategy is beneficial to medicinal chemistry. Due to the presence of various *m*- and *t*-phases in the sample, some aggregation of the NPs can be seen in the TEM micrograph of the sample. After each reaction, the catalyst was filtered, washed, air-dried, and reused for the next reaction up to run number ten. The study revealed that there is no discernible loss in product yield during subsequent reuse, demonstrating  $ZrO_2$  NPs' reusability and recyclability.



**Scheme 14.** Synthesis of 14-aryl-dibenzo xanthenes and 1,8-dioxooctadihydroxanthenes by using  $ZrO_2$  NPs.



**Scheme 15.** Nano  $ZrO_2$  catalyzed synthesis of imidazole derivatives.



**Scheme 16.** Nano  $ZrO_2$  catalyzed synthesis of 2-aryl benzimidazoles.

Recently, a zirconia-based nano-catalyst (Nano- $ZrO_2$ ), with intermolecular C-N bond formation for the synthesis of various benzimidazole-fused heterocycles in a concise method is reported by Rao *et al.* [106] (Scheme 16). The robustness of this reaction is demonstrated by the synthesis of a series of benzimidazole drugs in a one-pot method. More importantly, the nano- $ZrO_2$  catalyst showed excellent recyclability of up to five cycles in dry ethanol.

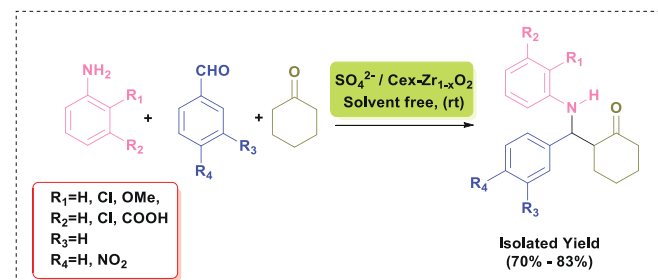
To check the reusability of nano- $ZrO_2$ , when the reaction of o-PDA (ortho-Phenylenediamine) with various substituted aromatic aldehydes was over, the product formed was extracted with ethyl acetate and the catalyst was purified. It was washed with ethyl acetate repeatedly, dried, and reused for the reaction of o-PDA with various aryl aldehydes.

#### 4. SYNTHESIS USING CRYSTALLINE NANO-SULFATED-ZIRCONIA (SZ) AS A CATALYST

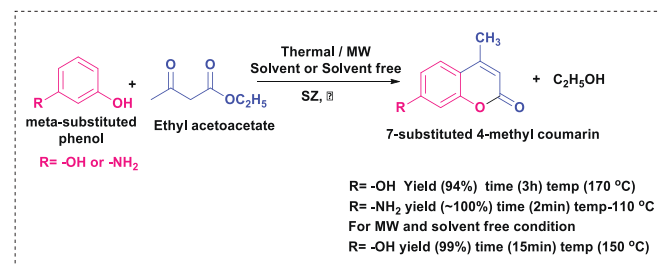
Reddy *et al.* [107] invented the synthesis of an interesting solid super-acidic  $SO_4^{2-}/Ce_xZr_{1-x}O_2$  catalyst by co-precipitation of cerium ammonium nitrate and zirconium nitrate to produce cerium and zirconium hydroxide gel, which was subsequently added with  $H_2SO_4$  to impregnation the sulfate ions on the Ce-Zr hydroxide surface. In the three-component Mannich-type reactions at room temperature without using solvents, the sulfated  $Ce_xZr_{1-x}O_2$  catalyst

demonstrated significant catalytic activity and produced product yields ranging from 72% to 83%. (Scheme 17).

Tyagi *et al.* [108] described employing a nano-crystalline sulfated-zirconia catalyst made using the sol-gel method and calcining it at  $600^\circ C$  to produce coumarin derivatives. The sulfated zirconia catalyst's XRD pattern showed a purely tetragonal crystalline phase with nano-crystallite sizes between 9 and 16 nm. The catalyst has high catalytic activity for the solvent-free Pechmann reaction's production of 7-substituted 4-methyl coumarins (Scheme 18). The authors reported higher reactivity of *m*-aminophenol compared to *m*-hydroxy phenol, where 100% conversion of *m*-aminophenol with ~100% selectivity of 7-amino 4-methyl coumarin was obtained at  $110^\circ C$  within 2 min. On the other hand, 94% yield of 7-hydroxy 4-methyl coumarin was obtained after 3 h at  $170^\circ C$  using a phenol-to-catalyst weight ratio of 80. Compared to thermal heating, where the slow diffusion rate of the reactant molecules in polar nitrobenzene and non-polar toluene solvents resulted in slow kinetics of the reaction, the authors concluded that the solvent-free microwave-assisted synthesis of the hydroxy derivative is an advantageous alternative which provides an excellent yield of 99% in a much shorter time of 15 min at a lower temperature ( $150^\circ C$ ). The reported synthesis of coumarins is economically feasible, since small amounts of sulfated-zirconia catalyst were required, and the activated catalyst was reusable for several successive runs (up to six cycles).



**Scheme 17.**  $SO_4^{2-}/Ce_xZr_{1-x}O_2$  catalyzed three-component Mannich-type reactions.

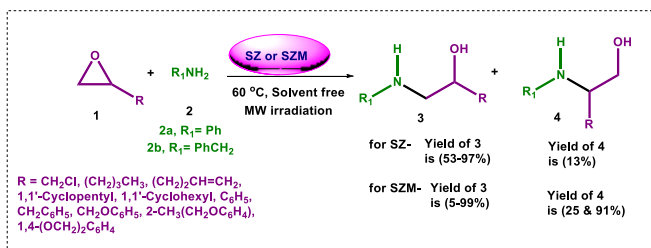


**Scheme 18.** Synthesis of 7-substituted 4-methyl Coumarin by Pechmann reaction using nano crystalline sulfated-Zirconia (SZ) as a catalyst.

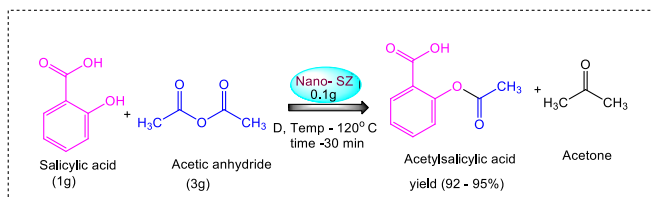
Negron-Silva *et al.* [109] described a solvent-free approach for the regioselective synthesis of  $\beta$ -amino alcohols using sulfated zirconia (SZ) and sulfated zirconia over MCM-41 (SZM) as catalysts (Scheme 19). The employment of microwaves in the synthesis reduced the time significantly and improved the yield compared to conventional heating. The catalysts were recovered and reactivation at  $550^\circ C$  for 1 h, and subsequently reused for at least three successive cycles without a significant decrease in the yield and regioselectivity. The results of the study revealed that reactivating of the SZ catalyst resulted in the development of a secondary monoclinic phase along with the original tetragonal phase. However, the authors reported evidence that the reactivation of SZM destroyed the MCM-41 phase, and concluded that the sulfated zirconia drove the catalytic activity, be it tetragonal or monoclinic.



Tyagi *et al.* [110] in 2010 used solid acid catalysts such as nano-crystalline sulfated zirconia, sulfated titania, zeolite H-beta, H-Y, H-ZSM-5, and acid-treated K-10 clay to synthesize acetylsalicylic acid, often known as aspirin or Ecotrin, in an environmentally friendly way (Scheme 20). The tetragonal phase of sulfated zirconia was discovered to have a crystallite size of 11 nm. Nano-crystalline sulfated zirconia had the highest catalytic activity of all the solid acid catalysts examined and was shown to be efficient in a small amount to produce an excellent yield (95 wt percent) of acetylsalicylic acid crystals. The yield of the thermally regenerated catalyst was comparable to that of the fresh catalyst. After washing with acetone, drying at 110°C for 2 hours, and activation at 450°C for 2 hours, the spent sulfated zirconia catalyst was recovered from the reaction mixture and reused under comparable reaction conditions. Until the fifth reaction cycle, a thermally regenerated catalyst gave the same yield of acetylsalicylic acid as the fresh catalyst.

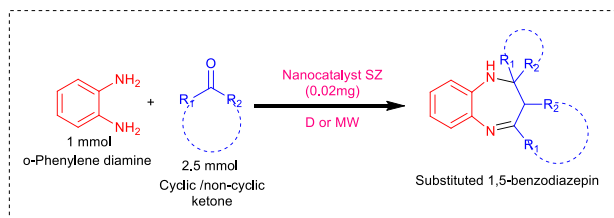


**Scheme 19.** Ammonolysis of Oxirane using sulfated Zirconia (SZ) and Sulfated Zirconia over MCM-41 catalyst (SZM).



**Scheme 20.** Synthesis of acetyl salicylic acid by O-acetylation of salicylic acid with acetic anhydride over solid acid catalyst.

Gondaliya *et al.* [111] also employed sulfated ZrO<sub>2</sub> NPs catalyst for the synthesis of 1,5-benzodiazepine derivatives by conventional and microwave-assisted protocols (Scheme 21). The catalyst was prepared by the sol-gel method and heat treatment at 600°C, and the structural analysis indicated a structural transformation from the monoclinic phase of the un-sulfated zirconia to the triclinic phase. The conventional heating method provided high yields of the products in 40-50 min, whereas the microwave-assisted method provided the yields in a much shorter time of 2-4 min. Also, the catalyst was reusable for 3-4 successive reactions.

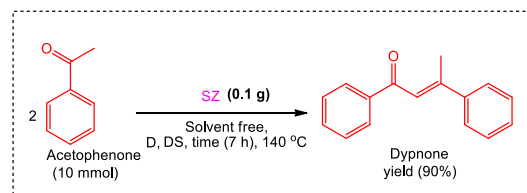


**Scheme 21.** Synthesis of 1,5-benzodiazepine derivatives using Sulfated-Zirconia as a nanocatalyst in solvent-free conditions by conventional and microwave methods.

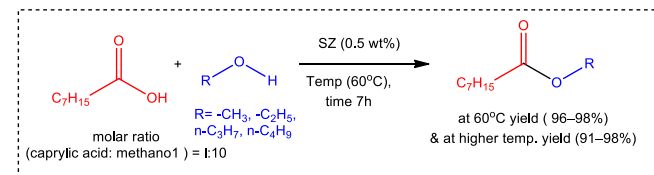
Saravanan *et al.* [112] investigated the solvent-free self-condensation of acetophenone to dypnone using a Nano-crystalline sulfated zirconia catalyst produced by a two-step sol-gel technique (Scheme 22). The catalyst had a maximum dypnone selectivity of 92 percent and 68.2 percent acetophenone conversion at 170°C after

7 hours of calcination at 650°C. The used SZ-650 catalyst was recovered from the reaction mixture, properly washed with acetone, and dried at 120°C overnight before being re-used for another reaction cycle under comparable reaction conditions to investigate its reusability.

Saravanan *et al.* [113] examined the catalytic activity of a nano-crystalline sulfated zirconia catalyst produced by the sol-gel process. They described using various analytical techniques for the esterification of caprylic acid with various short-chain alcohols (Scheme 23). At 60°C, the lower catalyst concentration (0.5wt%) resulted in 96-98% caprylic acid conversion with methanol and 100% selectivity for methyl caprylate. At 60°C, conversion decreased with increasing carbon chain lengths of alcohols, such as ethanol, n-propanol, and n-butanol, but increased dramatically (91-98 percent) at higher temperatures. Due to the water generated during the reaction, the catalyst's activity dropped marginally with each of the next five reaction cycles. To test the catalyst's reusability, it was extracted from the reaction mixture, washed with methanol, dried, and activated at 45°C for 2 hours before being employed in another reaction cycle.



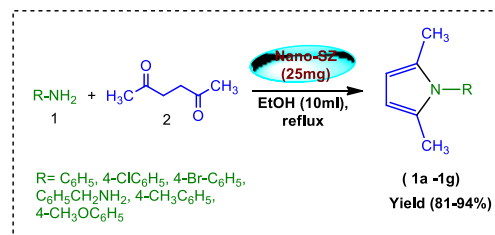
**Scheme 22.** Synthesis of dypnone by self-condensation of ACP over sulfated zirconia catalyst using Dean-Stark (DS) apparatus



**Scheme 23.** Esterification of caprylic acid with various alcohols using nano-sulfated zirconia as a catalyst.

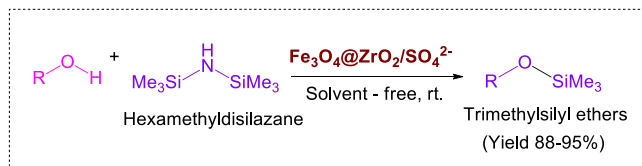
Abbas *et al.* [114] devised a novel and effective one-pot green synthesis method for producing Pyrrole by using Sulfated Zirconia as a solid acid nano crystalline catalyst in ethanol as a solvent at moderate temperature Scaffold from the Paal-Knorr condensation reaction (Scheme 24). The advantages of this unique procedure are easy availability, stability, reusability, catalyst eco-friendliness, high to exceptional yield, and simple experiment setup.

After the reaction was completed, the catalyst was separated by filtering, washed three times with 5 mL acetone, then rinsed numerous times with doubly distilled water before being dried at 110°C. The recovered catalyst was then utilized in the following run. Three successive runs revealed that the catalyst may be reused multiple times without losing significant activity.



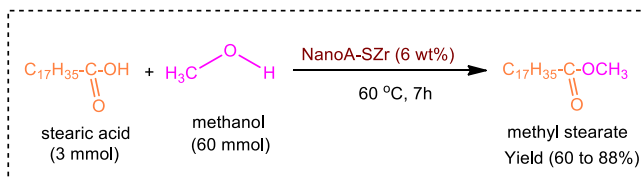
**Scheme 24.** Synthesis of N-substituted pyrrole derivatives by the condensation reaction of 2,5-hexandione with aromatic amine using sulfated zirconia as a nanocatalyst.

Ghafari *et al.* [115] discovered that nanomagnetic sulfated zirconia ( $\text{Fe}_3\text{O}_4@\text{ZrO}_2/\text{SO}_4^{2-}$ ) can be employed as a magnetic solid acid catalyst for the conversion of alcohols to their corresponding trimethylsilyl ethers using hexamethyldisilazane (HMDS) at ambient temperature and in a solvent-free environment (Scheme 25). This process has a number of advantages, including a simple set-up method, quick reaction times, high product yields, and facile catalyst recovery and reusability.



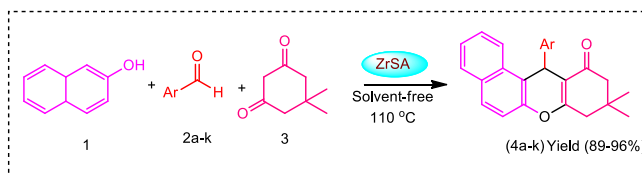
**Scheme 25.**  $\text{Fe}_3\text{O}_4@\text{ZrO}_2/\text{SO}_4^{2-}$  catalyzed silylation of alcohols using HMDS.

Saravanan *et al.* [116] used the sol-gel method to make a sulfated aerogel zirconia (A-SZr) solid acid catalyst, which was then supercritically dried in the n-propanol solvent (Scheme 26). Under the same reaction conditions, the A-SZr catalyst showed higher activity than other heterogeneous acid catalysts such as ion-exchange resins, Nafion, and acid clay; it also showed similar activity with conventional Brønsted ( $\text{H}_2\text{SO}_4$ ) and Lewis ( $\text{ZrOCl}_2$ ) acids, emphasizing its potential to replace homogeneous acid catalysts.



**Scheme 26.** Esterification of stearic acid with methanol using Aerogel sulfated zirconia as a nanocatalyst.

The catalytic effect of Zirconia Sulfuric Acid (ZrSA) nanoparticles, which are formed *via* the combination of  $\text{ZrO}_2$  with chlorosulfonic acid, was examined in the production of tetrahydrobenzo[a]xanthene-11-ones by a one-pot three-component reaction of naphthol, aromatic aldehydes, and dimedone by Nakhaei *et al.* [117] (Scheme 27). Several reaction conditions were examined in the presence of ZrSA nanoparticles as catalysts. The findings revealed that ZrSA has a strong catalytic activity for the synthesis of tetrahydrobenzo[a]xanthene-11-ones, with high yields of the desired products. The catalyst was also recyclable, implying it could be reused at least three times without losing its catalytic activity. Overall, this innovative catalytic technique for the synthesis of tetrahydrobenzo[a]xanthene-11-ones avoids the use of hazardous organic solvents and offers rapid access to the required compounds under solvent-free conditions at 110 °C following a simple workup procedure.

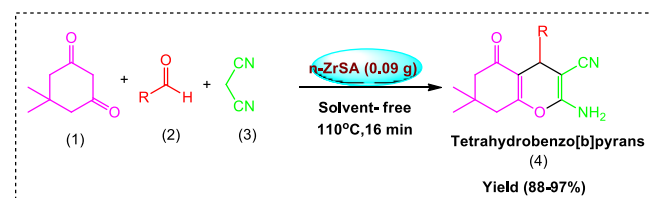


**Scheme 27.** ZrSA catalyzed synthesis of tetrahydrobenzo[a]xanthene-11-ones.

Nakhaei *et al.* [118] investigated the use of n-ZrSA to catalyze the synthesis of tetrahydrobenzo[b]pyrans from dimedone, aldehydes, and malononitrile in a one-pot, three-component reaction at 110 °C under solvent-free conditions (Scheme 28). The procedure was quick and high yielded, and the set-up was simple. After easy

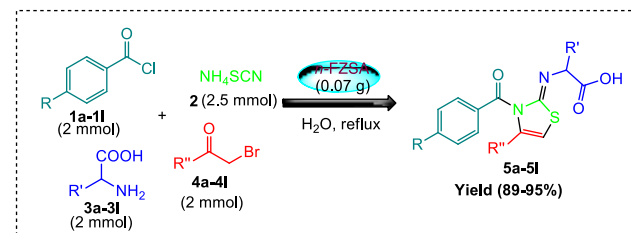
handling, the catalyst can be recycled and reused at least four times without losing its catalytic activity. The technique is also favorable in that it is a quick reaction in a solvent-free environment making it ecologically benign.

After the transformation was completed, the catalyst was filtered through a sintered glass Büchner funnel under heated temperatures. A small amount of hot ethanol was used to wash the catalyst. The combined filtrate was allowed to cool to room temperature before being used. Filtration was used to recover the precipitated solid, which was then recrystallized from ethanol to produce high quantities of tetrahydrobenzo[b]pyrans.



**Scheme 28.** ZrSA nanoparticles catalyzed synthesis of tetrahydrobenzo[b]pyrans.

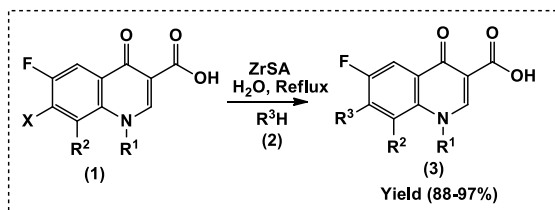
Nakhaei *et al.* [119] synthesized a  $\text{Fe}_3\text{O}_4$  magnetic core with a zirconia shell containing sulfonic acid groups ( $\text{Fe}_3\text{O}_4@\text{ZrO}_2\text{-SO}_3\text{H}$ ) that were employed as an efficient acidic catalyst in the synthesis of thiazole derivatives from acyl chloride, ammonium thiocyanate, amino acids, and alkyl bromides. In the production of thiazole derivatives,  $\text{Fe}_3\text{O}_4@\text{ZrO}_2\text{-SO}_3\text{H}$  showed strong catalytic activity (Scheme 29). After refluxing and a simple workup procedure, this innovative catalytic approach for thiazole derivatives allowed rapid access to the target chemicals in high yields in aqueous media. The new process for synthesizing thiazole derivatives is a major advance above what is already available. The catalyst could be utilized at least four times without losing its effectiveness (96, 95, 94, 94%). An external magnet was used to extract the catalyst, which was then washed in hot ethanol (10 mL). The mixture was kept at room temperature after half of the solvent was evaporated. The precipitated solid was filtered out and recrystallized from ethanol to obtain the corresponding product.



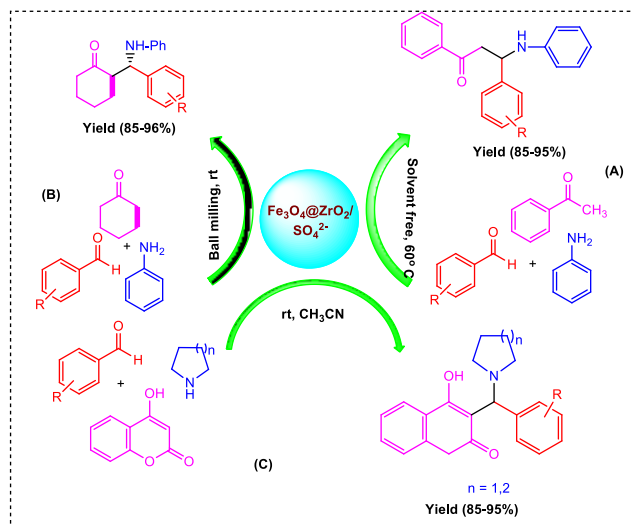
**Scheme 29.** Synthesis of thiazole derivatives in the presence of n-FZSA.

Nakhaei *et al.* [120] synthesized a variety of antibacterial fluoroquinolone compounds by amination of 7-halo-6-fluoroquinolone-3-carboxylic acids with a variety of piperazine derivatives and (4aR,7aR)-octahydro-1H-pyrrolo[3,4-b]pyridine in the presence of ordinary or magnetized water (Water treated with a magnetic field, often known as magnetised water acting as green solvent) under reflux conditions (Scheme 30). ZrSA has high catalytic activity in the formation of fluoroquinolone derivatives in two different types of water, according to the findings. On the other hand, the magnetized water functioned better. The catalyst was also recyclable, implying it could be reused at least three times without losing any catalytic activity. Overall, this innovative catalytic technique for synthesizing fluoroquinolone derivatives allows for rapid access to the necessary compounds in refluxing water after a simple workup procedure while avoiding hazardous organic solvents.

Ghafuri *et al.* [121] devised an efficient Mannich-type reaction technique for the production of  $\beta$ -amino carbonyl compounds and benzylamino coumarin derivatives in high yields (Scheme 31). The research is divided into two parts.  $\beta$ -Amino carbonyl derivatives were produced in a solvent-free environment in the first section. At room temperature, benzylamino coumarin compounds were produced in the other part. Short reaction periods, low cost, easy workup, mild reaction conditions, excellent yields, ease of recovery and reusability of the catalyst with five runs without considerable loss of activity are all advantages of the current technique.

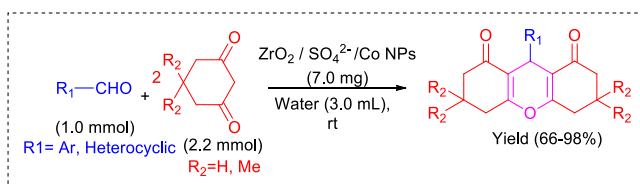


**Scheme 30.** Synthesis of fluoroquinolone derivatives in the presence of ZrSA under refluxing ordinary or magnetized water.



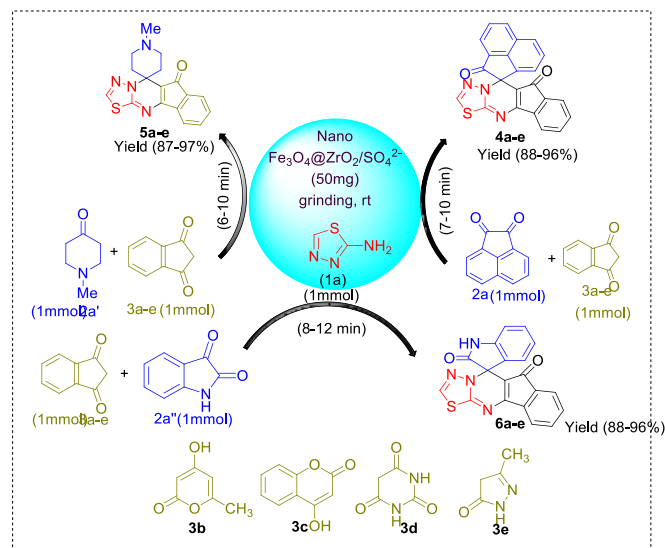
**Scheme 31.** Synthesis of  $\beta$ -amino carbonyl derivatives through Mannich reaction of various (A) aldehydes with aniline and acetophenone catalyzed, (B) aldehydes, anilines and cyclic ketones (C) aldehydes, amines and 4-hydroxycoumarin catalyzed by  $\text{Fe}_3\text{O}_4@Zr\text{O}_2/\text{SO}_4^{2-}$ .

Nasseri and co-authors [122] prepared sulfated zirconia incorporated with cobalt ( $\text{ZrO}_2/\text{SO}_4^{2-}/\text{Co}$ ) as a catalyst for the synthesis of 1,8-dioxo-octa-hydro xanthene derivatives using a one-pot multicomponent reaction under mild conditions (Scheme 32). The catalyst consisted of both monoclinic and tetragonal phases with a mean size of 13 nm. The adopted methodology revealed a wide scope for the condensation of aldehydes bearing different functional groups with dimedone and/or 1,3-cyclohexadione in water at room temperature and gave good-to-high yields in short reaction times. The catalyst was recovered and efficiently reused several times (at least eight consecutive runs) without appreciable loss of its activity.



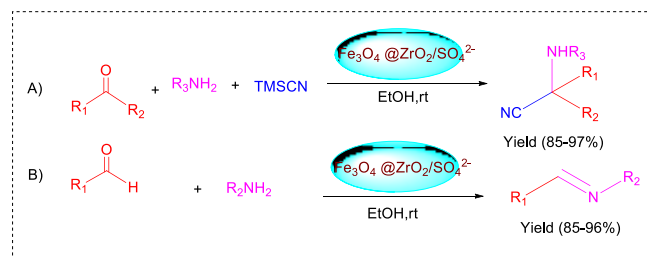
**Scheme 32.** Synthesis of 1,8-dioxo-octahydroxanthene catalyzed by  $\text{ZrO}_2/\text{SO}_4^{2-}/\text{Co}$  NPs.

Taylor *et al.* [123] described a multicomponent reaction of 2-amino-1,3,4-thiadiazole, isatin/N-methyl-4-piperidone/1,2-acenaphthylenedione and carbonyl compounds for the synthesis of spiroheterocycles spiroannulated with 1,3,4-thiadiazolo[3,2-a]pyrimidine (Scheme 33). The reaction was carried out by solvent-free grinding at room temperature, and catalyzed by magnetite-supported nanocrystalline sulfated zirconia ( $\text{Fe}_3\text{O}_4@Zr\text{O}_2/\text{SO}_4^{2-}$ ), which is magnetically recoverable for further use. The cubic (magnetite) and tetragonal (SZ) phases were confirmed by XRD. The synthesis route was environmentally benign and gave excellent yields of products. The yields did not decrease appreciably when the recovered catalyst was used for five successive cycles (only 4% decrease was reported after the 5<sup>th</sup> cycle).



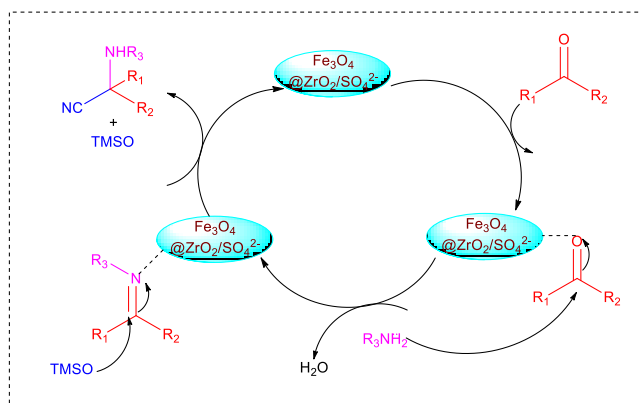
**Scheme 33.** Synthesis of spiroheterocycles spiroannulated with 1, 3, 4-thiadiazolo[3, 2-a]pyrimidine.

In 2015, Ghafuri *et al.* [124] prepared sulfated zirconia supported on magnetic nanoparticles and its catalytic activity was investigated in one-pot three-component green synthesis of  $\alpha$ -aminonitriles using various aldehydes and ketones at room temperature in ethanol (Scheme 34). This protocol has various advantages: simple work-up, short reaction time, high product yields and easy recovery and reusability of the catalyst up to five times without any considerable loss of catalytic activity. The TEM and SEM micrographs showed a homogeneous structure of  $\text{Fe}_3\text{O}_4@Zr\text{O}_2/\text{SO}_4^{2-}$  with  $\text{Fe}_3\text{O}_4$  core and average particle size of about 30 and 25 nm, respectively. The authors suggested a mechanism for the formation of  $\alpha$ -aminonitriles (Fig. 5). According to this mechanism,  $\text{Fe}_3\text{O}_4@Zr\text{O}_2/\text{SO}_4^{2-}$  catalyzes the *in situ* formation of the imine intermediate by activating the oxygen atom of the carbonyl group. In the presence of the catalyst, the imine carbon is attacked by cyanide to give the product.

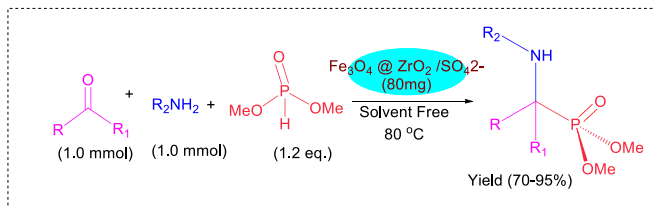


**Scheme 34.** The Strecker reaction of carbonyl compounds and amines with TMSCN catalyzed by  $\text{Fe}_3\text{O}_4@Zr\text{O}_2/\text{SO}_4^{2-}$  (A), synthesis of imines by  $\text{Fe}_3\text{O}_4@Zr\text{O}_2/\text{SO}_4^{2-}$  (B).

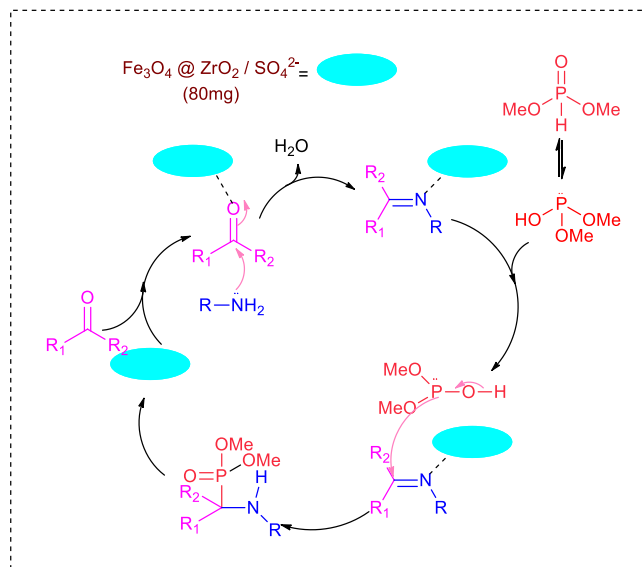
In addition, Ghafuri *et al.* [125] also synthesized the magnetite-supported SZ ( $\text{Fe}_3\text{O}_4@Zr\text{O}_2/\text{SO}_4^{2-}$ ) catalyst, which was used for the synthesis of  $\alpha$ -aminonitriles derivatives in Kabachnik-Fields reaction (Scheme 35). The catalyst gave good to excellent yields of 5 subsequent reactions without appreciable loss of its catalytic activity. The authors provided a proposed mechanism for the synthesis of  $\alpha$ -aminophosphonate using the  $\text{Fe}_3\text{O}_4@Zr\text{O}_2/\text{SO}_4^{2-}$  catalyst (Fig. 6). They suggested that the catalyst facilitates the formation of imine intermediate by activating the carbonyl group. Subsequently, the carbon of imine is attacked by phosphite leading to the formation of the desired product.



**Fig 5.** A plausible mechanism for the synthesis of  $\alpha$ -aminonitriles catalyzed by  $\text{Fe}_3\text{O}_4@Zr\text{O}_2/\text{SO}_4^{2-}$ .



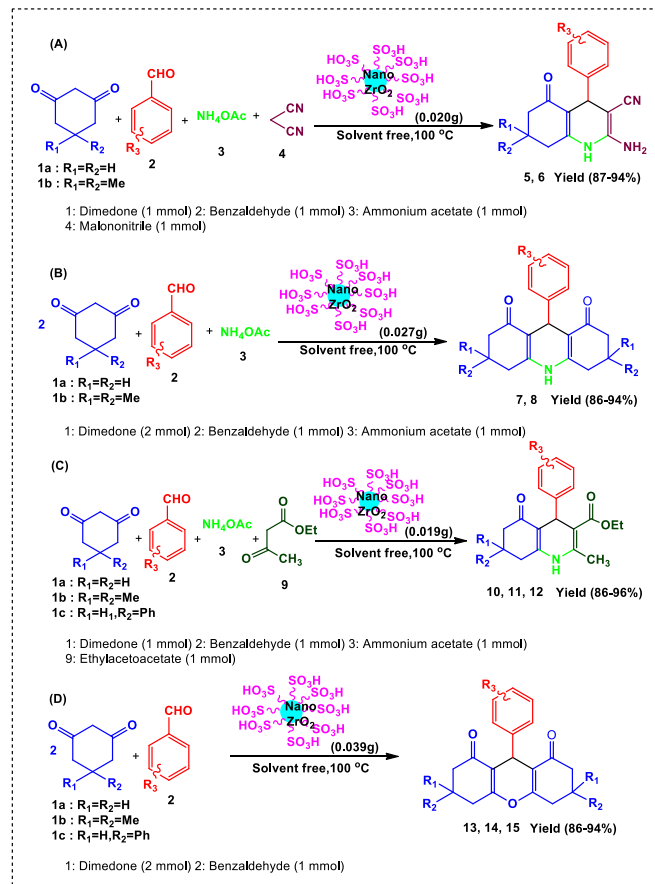
**Scheme 35.** Kabachnik-Fields reaction catalyzed by magnetite-supported sulfated zirconia ( $\text{Fe}_3\text{O}_4@Zr\text{O}_2/\text{SO}_4^{2-}$ ).



**Fig (6).** The proposed mechanism of the Kabachnik-Fields reaction in the presence of a  $\text{Fe}_3\text{O}_4@Zr\text{O}_2/\text{SO}_4^{2-}$  catalyst.

In 2016, Amoozadeh *et al.* [126] synthesized the heterogeneous acidic  $Zr\text{O}_2\text{-SO}_3\text{H}$  nanocatalyst (35-40 nm) for organic synthesis.

The catalyst efficiently provided high yields of hexahydroquinoline, 1,8-dioxo-octahydroacridine, polyhydroquinoline, and 1,8-dioxo-octahydroxanthene derivatives (Scheme 36). The reactions were carried out under solvent-free conditions at 100 °C using the one-pot multicomponent protocol. The catalyst ( $Zr\text{O}_2\text{-SO}_3\text{H}$ ) was recovered and reused for 5 successive reactions and showed only a slight decrease in the yield from 94% to 90% in a typical reaction.



**Scheme 36.** Synthesis of (A) hexahydroquinolines, (B) 1,8-dioxo-decahydroacridines, (C) polyhydroquinolines, and (D) 1,8-dioxo-octahydroxanthenes using nano- $Zr\text{O}_2\text{-SO}_3\text{H}$  catalyst.

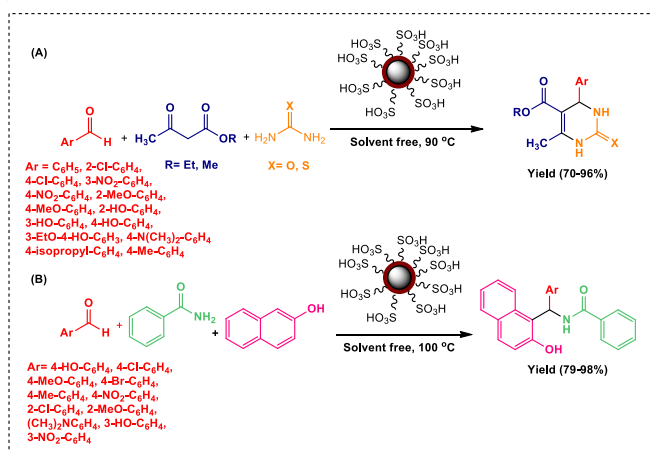
More recently, the magnetically separable core-shell  $\text{Fe}_3\text{O}_4@Zr\text{O}_2\text{-SO}_3\text{H}$  nanoparticle catalyst (n-FZSA) was introduced by Hosseini and Kolvari [127] as a novel heterogeneous solid acid catalyst. The catalytic activity of the prepared n-FZSA was evaluated in a one-pot multicomponent reaction for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones (Scheme 37). The reaction was carried out at 90 °C under solvent-free conditions. The n-FZSA catalyst exhibited a high catalytic activity with a negligible decrease of the yield (from 96% to 95%) up to the 3<sup>rd</sup> successive reaction using the recovered catalyst and a higher decrease (from 96% to 86%) upon reusing the catalyst for 6 successive cycles.

Hejazi *et al.* [128] employed  $Zr\text{O}_2/\text{Fe}_3\text{O}_4\text{-MNPs}$  as a reusable heterogeneous catalyst to establish a convenient, suitable, and environmentally acceptable technique for synthesizing quinoline derivatives via a Friedländer reaction (Scheme 38). Green reactions, simple and straightforward setup, excellent product yields, and short reaction times are all advantages of this technique. Furthermore, the catalyst could be retrieved and reused three times without losing its catalytic activity utilizing an external magnetic field.

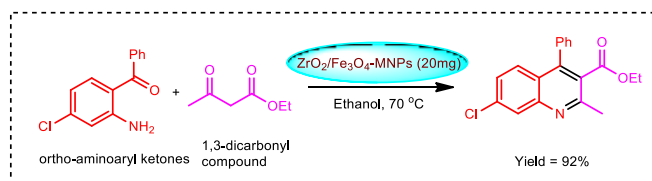


## 5. SYNTHESIS USING NiO-ZrO<sub>2</sub> NANOCATALYST

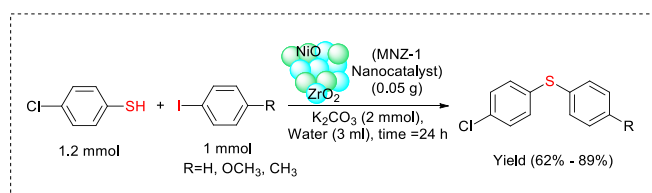
Pal and Bhaumik [129] reported the synthesis of mesoscopic self-assembled NiO-ZrO<sub>2</sub> nano-catalyst (MNZ-1) using a non-ionic surfactant *via* evaporation self-assembly and calcination at 773 K for 5-6 h. The MNZ-1 exhibited good catalytic activity for the C-S cross-coupling and synthesis of diaryl sulfides with moderately high yields from reactions of iodoaryl compounds with 4-chlorothiophenol in an eco-friendly water medium (Scheme 39). The product yield was improved significantly from 39% at room temperature to (62-89%) at 353 K. The authors reported significantly lower yields of products when the reactions were catalyzed by pure NiO or a physical mixture of pure NiO and ZrO<sub>2</sub>, and concluded that the surface area and mesoporosity of the self-assembled MNZ-1 nanocatalyst is an important factor in obtaining the higher yields.



**Scheme 37.** n-FZSA-catalyzed one-pot synthesis of (A) 3,4-dihydropyrimidinones, and (B) 1-amidoalkyl-2-naphthols.



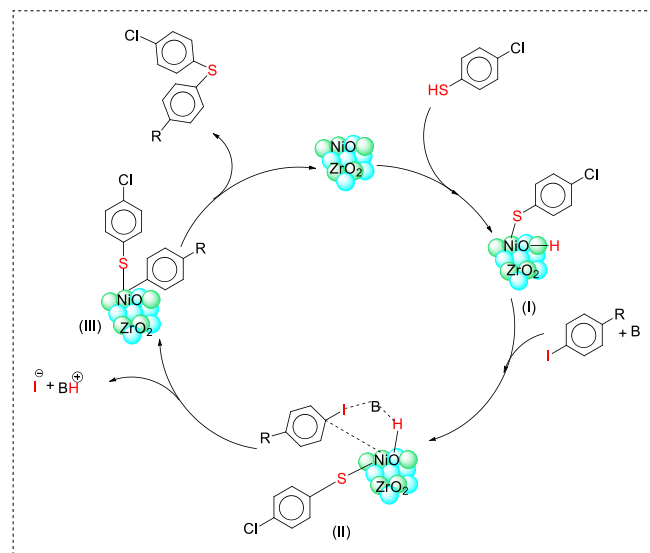
**Scheme 38.** ZrO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>-MNPs catalyzed synthesis of ethyl 2-methyl-4-phenylquinoline-3-carboxylate.



**Scheme 39.** C-S cross-coupling reaction using NiO-ZrO<sub>2</sub> nanocrystals.

The authors suggested the plausible reaction mechanism illustrated in Fig. (7) for the C-S coupling. First, the 4-chlorothiophenol forms a red colour complex with the Ni atom of the catalyst (intermediate (I)); this was confirmed by the FT-IR spectrum of the thio-Ni complex which revealed the disappearance of the characteristic S-H stretching bond of the 4-chlorothiophenol near 2550–2600 cm<sup>-1</sup>. The authors' suggestion that the thiol complexation is with the Ni rather than with the Zr ions was supported by the low activity of pure ZrO<sub>2</sub> in this reaction. Then K<sub>2</sub>CO<sub>3</sub> (B) promotes the reaction of intermediate(I) with iodobenzene leading to the formation of a six-membered ring (II) *via* the oxidative addition of the iodo compound to intermediate (I). The electron-donating substituent

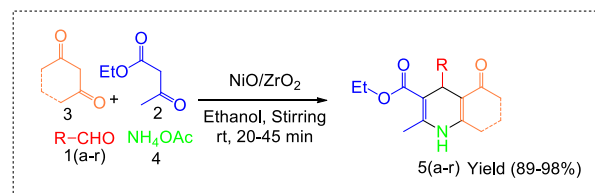
facilitates the coordination of the metal to the π-bond of the aromatic ring providing higher conversion. Finally, intermediate (II) on reductive elimination *via* intermediate (III) gives the desired product.



**Fig. (7).** Mechanism for the C-S coupling reaction.

Bhaskaruni *et al.* [130] used nickel oxide loaded on zirconia (NiO/ZrO<sub>2</sub>) as an efficient catalyst to synthesize 18 unsymmetrical 1,4-dihydropyridine derivatives (Scheme 40). With outstanding yields of 89-98% and a completion time of 20-45 minutes, the Lewis acidic character of the catalyst proved to be a good choice for the one-pot, four-component fusion reaction. According to mechanistic studies, enamine and imine functionality are two probable mechanisms for the production of 1,4-dihydropyridines with good selectivity. Two new compounds (5a, 5c) have their crystal structures described.

Up to six cycles of reusability were demonstrated with the catalyst. After each run, the catalyst was extracted from the reaction mixture, washed with ethanol, and dried at 120 °C for 2 hours. This procedure is green and cost-effective due to the room-temperature reaction and use of ethanol as a solvent.

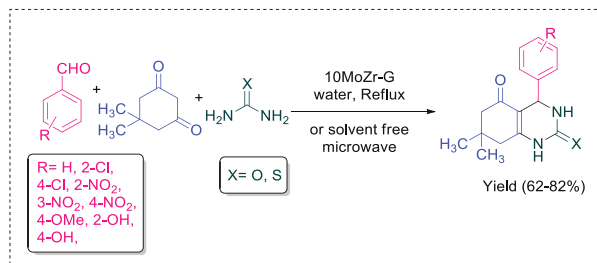


**Scheme 40.** synthesis of novel unsymmetrical 1,4-dihydropyridine derivatives.

## 6. SYNTHESIS USING OTHER METAL OXIDES/ZrO<sub>2</sub> NANOCOMPOSITES AND ZrO<sub>2</sub>-SO<sub>3</sub>H NANOCATALYST

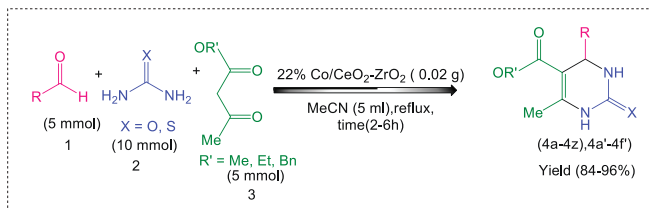
Samantaray and Mishra [131] prepared pure ZrO<sub>2</sub> and MoO<sub>3</sub>-ZrO<sub>2</sub> nanocomposite (10MoZr-G) from MoO<sub>3</sub> (10 mol.%) and ZrO<sub>2</sub> oxides by solution combustion method using different glycine fuel contents. The 10MoZr-G nanocomposite was used to catalyze the synthesis of octahydroquinazolinones by multicomponent condensation of dimedone, urea and arylaldehydes in aqueous media under solvent-free conditions using microwave irradiation (Scheme 41). The 10MoZr-G catalyst was reported to be more active than other composites prepared by using other fuel types such as urea and hexamethylene, giving a relatively high yield in a short time (180

s). The catalyst was recovered, washed with ethanol, and heat treated at 400°C for 1 h, and its catalytic activity was evaluated. The regenerated catalyst was reported to produce the target product without a significant decrease in the yield in three successive cycles.



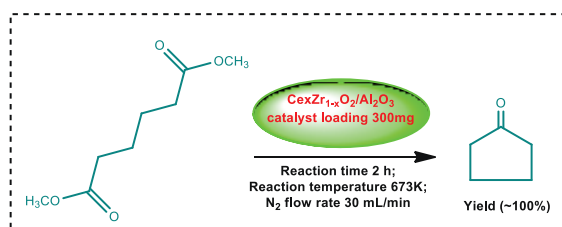
**Scheme 41.** One pot synthesis of octahydroquinazolinones using 10MoZr-G catalyst.

Biklarian *et al.* [132] created four unprecedented DHPMs 22% Co/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysed as a unique catalyst in refluxing acetonitrile using a simple modification of Biginelli's dihydropyrimidinone and thiones synthesis (Scheme 42). This approach is complementary to existing methods because of its high product yields, gentle reaction conditions, and straightforward procedure. After calcination at 800-850°C, XRD patterns of nano spherical catalysts Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> cubic structure with 32 nm crystallite size implies a 22% Co content. Furthermore, the catalyst may be easily recovered and reused (up to four times) without a significant decrease in activity, which is advantageous from a green chemical standpoint. The catalyst was filtered and rinsed with diethyl ether at the end of the process. A second or even third reaction could be performed on the recycled catalyst.



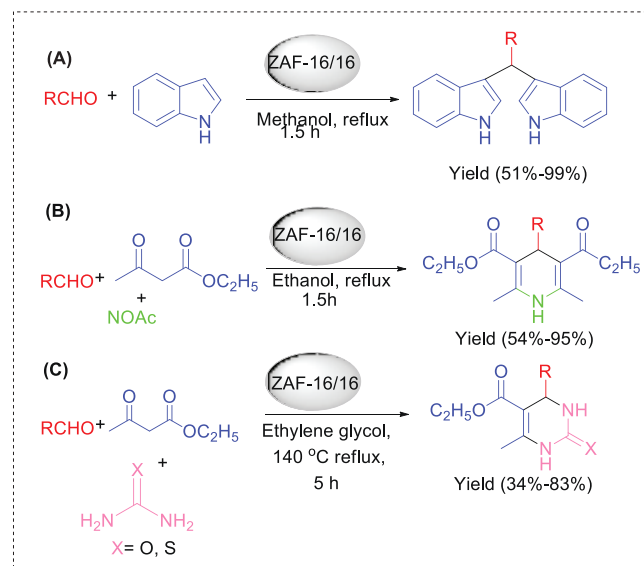
**Scheme 42.** Synthesis of 1,2,3,4-tetrahydro-2-pyrimidinones and thiones by using 22% Co/CeO<sub>2</sub>-ZrO<sub>2</sub> nanocatalyst.

Sudarsanam *et al.* [133] create an innovative and simple method for synthesising cyclopentanone, a useful industrial component (Scheme 43). As a result, Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> and Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/M (M = SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) ceria-zirconia-based nano-oxide catalysts were developed and tested for the title reaction. C, CZ, CZ/A, and CZ/S samples had average crystallite sizes of 8.9, 4.7, 3.7, and 3.4 nm, respectively. The catalytic results showed that nano-oxides based on Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> are promising heterogeneous catalysts for cyclopentanone production. Because of its advantageous physicochemical features, the Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst achieved 100% conversion with 75% targeted cyclopentanone product selectivity.



**Scheme 43.** Synthesis of cyclopentanone from dimethyl adipate by using nanostructured ceria-zirconia solid solution catalysts.

Wang *et al.* [134] reported the synthesis of a number of ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> (ZAF) nanocomposites with different zirconia and alumina molar ratios relative to magnetite (the molar ratio of which is taken as 1). The catalysts were structurally and chemically characterized in details using different techniques, and the esterification of acetic acid and n-butyl alcohol for the synthesis of n-butyl acetate as a model reaction examined their catalytic activity. The maximum conversion of 90% was obtained by using the catalyst ZAF-16/16 (ZrO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>:Fe<sub>3</sub>O<sub>4</sub> molar ratios of 16:16:1). Subsequently, the optimal catalyst ZAF-16/16 was used for the synthesis of bis-indolylmethanes and other organic reactions shown in (Scheme 44). The results of the study highlighted the importance of the proposed methodology for the synthesis of a variety of biologically active pharmacological heterocyclic compounds. The reactions gave moderate to good yields of the target compounds. On the other hand, the magnetic nanoparticles in the catalyst facilitate a simple magnetic recovery of the catalyst for subsequent reactions, which proceeded without obvious loss of the catalytic activity.



**Scheme 44.** ZAF-catalyzed reactions for (A) the synthesis of bis-indolylmethanes, (B) Hantzsch reaction, and (C) Biginelli reaction.

Mahdavi *et al.* [135] present the synthesis and catalytic activity of a ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> nano-catalyst that transforms oleic acid and methanol into fatty acid esters under high voltage circumstances in a low temperature and atmospheric pressure process (Scheme 45). This protocol's key benefits are the use of a low-cost and reusable catalyst, high yields in a short period of time, and environmental friendliness.

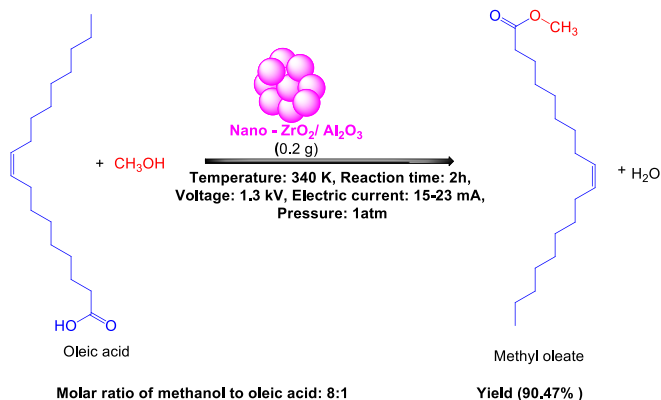
In four runs, the reusability and recycling of nano-catalyst were also examined. The findings revealed that the nano-catalyst can be reused multiple times (up to 4 runs) without losing catalytic activity. The nano-catalyst was separated, washed, and dried at 80°C for the next reaction after each reaction.

Narasimhamurthy *et al.* [136] describe the production of a nano acid catalyst ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> using urea as a fuel and the evaluation of its catalytic efficacy in the synthesis of a variety of novel substituted dihydroquinazolinones (Scheme 46).

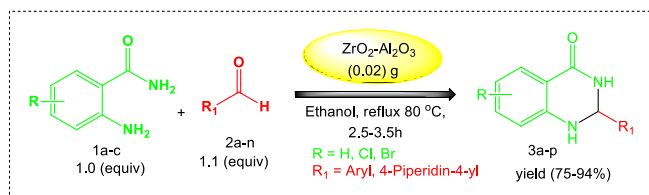
Under mild circumstances, the catalyst was shown to be a highly effective solid acid catalyst, with substantial catalytic activity in converting substituted 2-aminobenzamides to analogous 2, 3-dihydroquinazolin-4-(1H)-ones. The improved synthesis process is simple, quick, and efficient, and it has the potential to become one



of the most effective methods for obtaining pharmaceutically valuable dihydroquinazolines. Solid acid catalytic material was filtered from the reaction mixture, washed with ethanol, dried for 1 hour at 120°C, and calcined for 0.5 hours at 550°C. A reactivated solid acid catalyst was employed in the next reaction cycle to synthesize 2, 3-dihydroquinazolin-4(1H)-ones under comparable reaction conditions. The utilized solid acid catalyst was reactivated and reusability was tested four to five times.

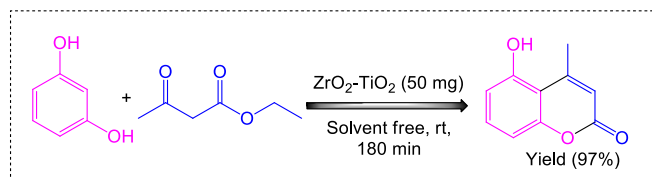


**Scheme 45.** Synthesis of fatty acid esters by using oleic acid and methanol by using Nano catalyst  $ZrO_2/Al_2O_3$  under high voltage conditions.



**Scheme 46.** Synthesis of 2,3-dihydroquinazolin-4 (1H) using  $ZrO_2-Al_2O_3$  nano catalyst.

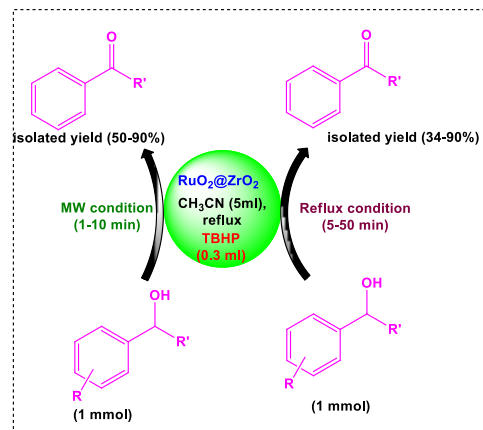
Khan *et al.* [137] describe the synthesis of coumarin in a solvent-free environment at room temperature utilising zirconia-based heterogeneous catalysts ( $ZrO_2-Al_2O_3$ ,  $ZrO_2-ZnO$ , and  $ZrO_2/cellulose$ ) (Scheme 47). In comparison to  $ZrO_2-ZnO$ ,  $ZrO_2-TiO_2$  showed the best catalytic performance for this process. The rate of reaction in a solvent-free environment is  $1.7 \times 10^3 \text{ g mol}^{-1} \text{ min}^{-1}$  at ambient temperature. At 60°C, however, the rate of reaction in ethanol is  $1.7 \times 10^2$ , and in toluene is  $5.6 \times 10^3 \text{ g mol}^{-1} \text{ min}^{-1}$ . FESEM was used to analyse the morphology of  $ZrO_2-TiO_2$ ,  $ZrO_2-ZnO$ , and  $ZrO_2/cellulose$ . The  $ZrO_2-TiO_2$  was grown as particles, while the  $ZrO_2-ZnO$  was produced in the shape of a flower.  $ZrO_2-ZnO$  was mostly formed as nanoparticles with an average size of 25–30 nm clumped together to form a flower-shaped structure.  $ZrO_2$  was developed as particles on the surface of cellulose in the case of  $ZrO_2/cellulose$ .



**Scheme 47.** Zirconia-based catalyst for the one-pot synthesis of coumarin through Pechmann reaction.

Shojaei *et al.* [138] used synthesized nanostructured  $RuO_2@ZrO_2$  as a heterogeneous catalyst and microwave irradiation in acetonitrile to establish a simple and highly efficient process for the oxidation of benzylic alcohols to the corresponding aldehydes or ketones (Scheme 48). Under mild circumstances, the catalyst has

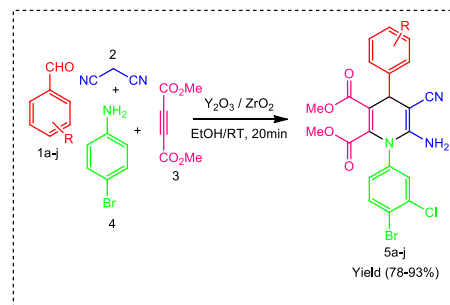
excellent activity and high conversion. After the reaction was completed, the catalyst was centrifuged and cleaned with deionized water and chloroform before being dried and reused in consecutive cycles.  $RuO_2@ZrO_2$  4 wt% can be reused three times without considerable activity loss, according to the conversion results.



**Scheme 48.** Oxidation of Benzyl alcohol by using  $RuO_2@ZrO_2$  core-shell nano particles under different conditions.

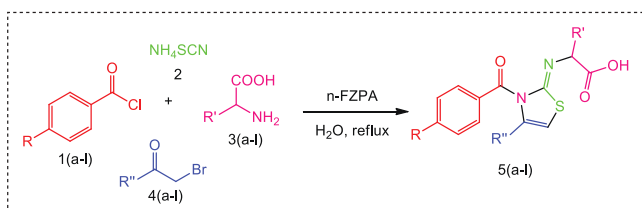
Shabalala *et al.* [139] present a very efficient approach for synthesizing 1,4-dihydropyridine compounds utilizing a 2.5%  $Y_2O_3/ZrO_2$  heterogeneous catalyst in their study. In the green solvent ethanol, substituted aldehyde, malononitrile, 4-bromoaniline, and dimethylacetylenedicarboxylate are combined in a one-pot four-component synthesis (Scheme 49). Easy set-up, green solvent, low reaction durations (less 20 minutes), energy efficient reaction conditions, no chromatographic separation procedures, and outstanding yields are all advantages of this unique methodology (88-95%).

The reaction mixture was simply filtered under vacuum, washed with ethyl acetate, and dried in a vacuum oven at 110°C for 3 hours after the reaction was completed. In the subsequent reactions, the flexibility of the recovered catalyst for reuse was examined, and no yttria leaching was observed. It can be reused for at least six runs in consecutive reactions without losing substantial yield.



**Scheme 49.** Synthesis of novel 1,4-dihydropyridine derivatives.

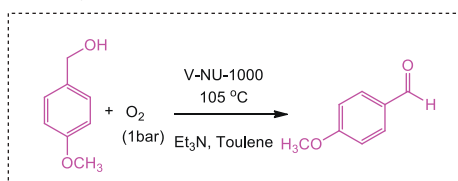
Nakhaei A. [140] developed a new method for synthesizing thiazole compounds from acyl chloride, ammonium thiocyanate, amino acids, and alkyl bromides catalysed by nano- $Fe_3O_4@ZrO_2-H_3PO_4$  (n-FZPA) in high yields in a fast reaction time using conventional or magnetised water and a simple work-up procedure (Scheme 50). Overall, the magnetised water performed better as a reaction solvent. The catalyst can be easily recycled by magnetic separation, and it can be reused up to four times without losing any catalytic activity. The catalyst is low-cost and easy to obtain, as well as stable and storable.



**Scheme 50.** Synthesis of thiazole derivatives in the presence of *n*-FZPA.

NU-1000 is a porous Zr-based metal-organic framework (Zr-MOF) that is an efficacious catalyst support due to its distinct crystal structure, protonic grafting sites on its nodes, and thermal stability, which together help with catalytic reactive site studies. Cui *et al.* [141] created V-NU-1000, a vanadium oxide catalyst based on NU-1000 synthesised by solvothermal deposition in MOFs (SIM). The catalytic activity of V-NU-1000 is investigated using 4-methoxybenzyl alcohol oxidation in an O<sub>2</sub> atmosphere, and it is discovered that it has higher conversion and selectivity than vanadium oxide supported on high surface area zirconia (V-ZrO<sub>2</sub>) (Scheme 51).

Recyclability and leaching studies show that the recollected V-NU-1000 retains equal catalytic ability to the fresh catalyst with no loss of metal loading. With a turn-over frequency (TOF) of 2.6 h<sup>-1</sup> measured at a conversion level of 3.2 percent, V-NU-1000 exhibited a conversion of about 56 percent after 8 hours. As shown by GC-MS, this catalyst is highly selective (>99 percent) for the synthesis of 4-methoxy benzaldehyde without generating the over-oxidized product 4-methoxy benzoic acid.



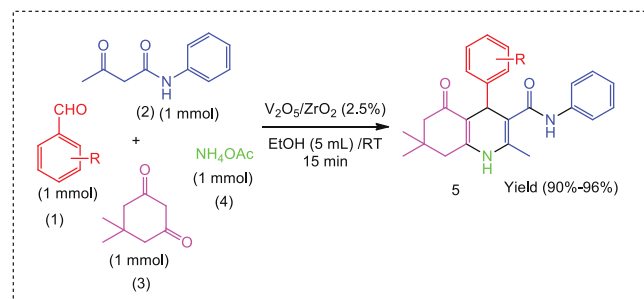
**Scheme 51.** Synthesis of 4-methoxybenzaldehyde by oxidation 4-methoxybenzylalcohol using V-NU-1000 as nanocatalyst.

By cyclo-condensation of aromatic aldehydes, 5,5-dimethyl-1,3-cyclohexanedione, acetoacetanilide, and ammonium acetate, Bhaskaruni *et al.* [142] establish a viable technique for the one-pot, multicomponent synthesis of 1,4-dihydropyridine derivatives employing aromatic aldehydes, 5,5-dimethyl-1,3-cyclohexanedione. Using ethanol as a solvent and V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> as a heterogeneous catalyst, ten novel 1,4-dihydropyridines were synthesised at room temperature (reaction time: 20 min) (Scheme 52). XRD, TEM, SEM, and BET were used to characterise the catalyst materials. Simple set-up, green solvent, short reaction times, mild reaction conditions, and good yields (90-96%) are the advantages of this unique approach. Without the use of chromatography, the reaction product can be easily isolated in pure form.

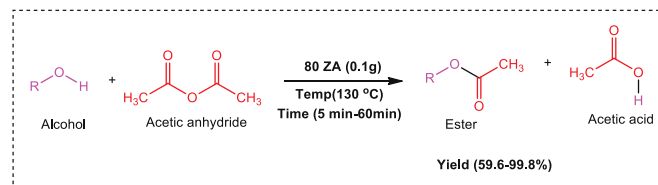
Heterogeneous catalysts have the advantage of being easily recyclable, making them a great choice, especially in terms of cost and environmental benefits. As a result, examination of the stability of catalyst recycling has been conducted. The catalyst was vacuum-separated from the reaction mixture after each run, washed with ethanol solvent, and dried for 4 hours at 120-130°C. The recycled catalyst showed no significant loss of catalytic activity even after five cycles, showing that there is no leaching or loss of vanadia throughout the process and that it is intact in the zirconia lattice.

Thimmaraju *et al.* [143] used the solution combustion method (SCM) to prepare solid acids such as Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> containing different ZrO<sub>2</sub> loadings (10-100 mol percent) and char-

acterised them for total surface acidity and crystallinity using the NH<sub>3</sub>-TPD/*n*-butylamine back titration method and powder X-ray diffraction (PXRD) technique respectively. With acetic anhydride (AA) as an acetylating agent, these solid acids were tested for their catalytic activity in the synthesis of new O-acetylated compounds from substituted phenols, pyridine alcohols, and aryl alcohols (Scheme 53). The catalyst, molar ratio of the reactants, reaction temperature, and catalyst amount were all changed to improve the reaction conditions. In this investigation, all of the solid acids utilized had good catalytic activity in the process. ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> with 80 mol% ZrO<sub>2</sub> was shown to be very active in the acetylation reaction, yielding a high yield of acetylated products. Surface acidity, crystallinity, and catalytic activity of solid acids were found to have a triangular relationship. It was discovered that these solid acids may be reactivated and reused.



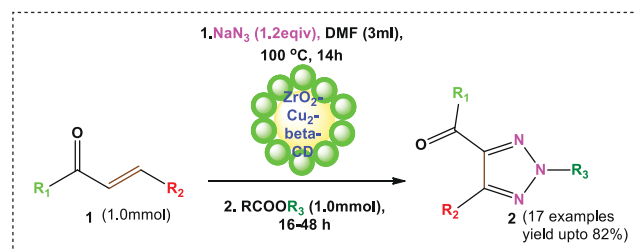
**Scheme 52.** Synthesis of 1,4-dihydropyridine moieties via V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> as a heterogeneous catalyst.



**Scheme 53.** O-acetylation of different hydroxyl compounds with AA over ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> solid acid.

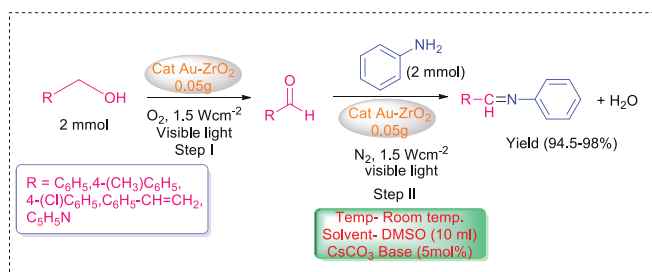
## 7. SYNTHESIS USING ZrO<sub>2</sub>-SUPPORTED Cu(II)-β-CYCLODEXTRIN AND Au/ZrO<sub>2</sub> AS A CATALYST

Girish *et al.* [144] prepared ZrO<sub>2</sub> nanoparticle-supported Cu(II)-β-cyclodextrin complex to catalyze the synthesis of N-2-substituted-1,2,3-triazoles via azide-chalcone oxidative cycloaddition and post-triazole alkylation using a one-pot multi-component stepwise approach (Scheme 54). The authors have introduced the N-2 alkylation of triazoles using different aryl-alkyl esters without any additives as a novel approach. The reported simple and atom-economical synthetic route exhibited regioselectivity and good yields (~81%). The recovered catalyst maintained its high catalytic activity for four consecutive reactions. The small decrease in the catalytic activity (81% to 77%) could be partially attributed to a small loss of the catalyst during the recovery process.



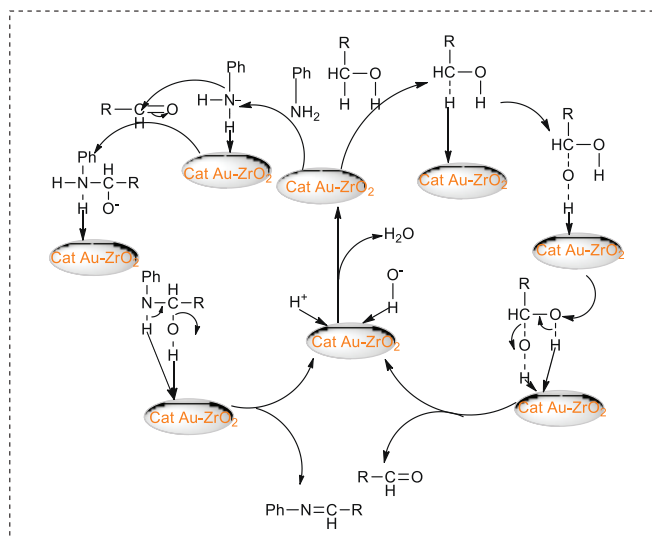
**Scheme 54.** N-2-substituted-1,2,3-triazole in the presence of ZrO<sub>2</sub>-Cu(II)-β-CD.

Motivated by the potential of Au/ZrO<sub>2</sub> NPs as an efficient photocatalyst for organic synthesis due to their limited to a small area surface Plasmon resonance (LSPR) effect, Zheng *et al.* [145] prepared Au/ZrO<sub>2</sub> nano-powders (average particle size of 5 nm) by a solution method for employment as a heterogeneous catalyst used in organic transformations. In this study reveals that the photosynthesis of imines from alcohols & aniline raised by aerobic oxidation of the alcohols by the nucleophilic addition of aniline (Scheme 55). The reaction was carried out by using dimethyl sulphoxide (DMSO) as a solvent. The imines in reactions performed with 3 wt% Au/ZrO<sub>2</sub> and irradiation by visible light at room temperature were high (over 90%) compared to reactions performed without irradiation. The reaction outcome depended strongly on the intensity and wavelength of the light, and the catalyst was recovered and reused for at least five successive reactions. The results of the study indicated that the reaction of alcohols with aniline in the presence of Au/ZrO<sub>2</sub> as the photocatalyst can proceed under environmentally friendly conditions.



**Scheme 55.** Synthesis of Imine from alcohols and aniline by using Au/ZrO<sub>2</sub> as a photocatalyst.

The alcohol was initially oxidised to an aldehyde in the presence of Au/ZrO<sub>2</sub> under an O<sub>2</sub> environment and exposure to visible light, according to the authors' probable reaction mechanism (Fig. 8). Alcohol is oxidised by the Au-NPs by the process of electron capture because of the strong electro negativity of gold. By promoting interband electronic transitions in Au NPs through the LSPR effect, visible light can catalyse the oxidation of organic molecules while also releasing energy.



**Fig. (8).** Possible mechanism for the synthesis of imines from aniline and alcohols over Au/ZrO<sub>2</sub>.

An oxygen atom can be inserted between the carbon-hydrogen bonds as a result of the Au nanoparticle pulling on the hydrogen atom bound to the carbon. As a result, a water molecule is taken

out, and aldehyde is created. An atom of hydrogen is drawn off of the amine by the catalyst, which is a nucleophilic reagent with a single pair of electrons. The amine then attacks the carbonyl group, resulting in a nucleophilic addition process (the CQ-O bond was broken, and the hemiacetal amine intermediates were obtained). The imine was eventually created after removing a water molecule from the intermediates.

## CONCLUSION

This article discusses current advancements in the synthesis of organic materials using zirconium compounds as green catalysts. The importance and benefits of zirconium compounds as catalysts or reagents in organic reactions were amply illustrated by the examples in this review appreciation of their high reactivity, distinctive selectivity and methods of recyclability. Even though these results are encouraging, much more work must yet be done in this field to investigate the potential uses of zirconium compounds fully.

## LIST OF ABBREVIATIONS

ZrO <sub>2</sub>	= Zirconium Dioxide
SZ	= Sulfated Zirconia
SZM	= Sulfated Zirconia Over MCM-41
HMDS	= Hexamethyldisilazane

## CONSENT FOR PUBLICATION

Not applicable.

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## CONFLICT OF INTEREST

Dr. Subhash Banerjee is the Executive Guest Editor of the journal COC.

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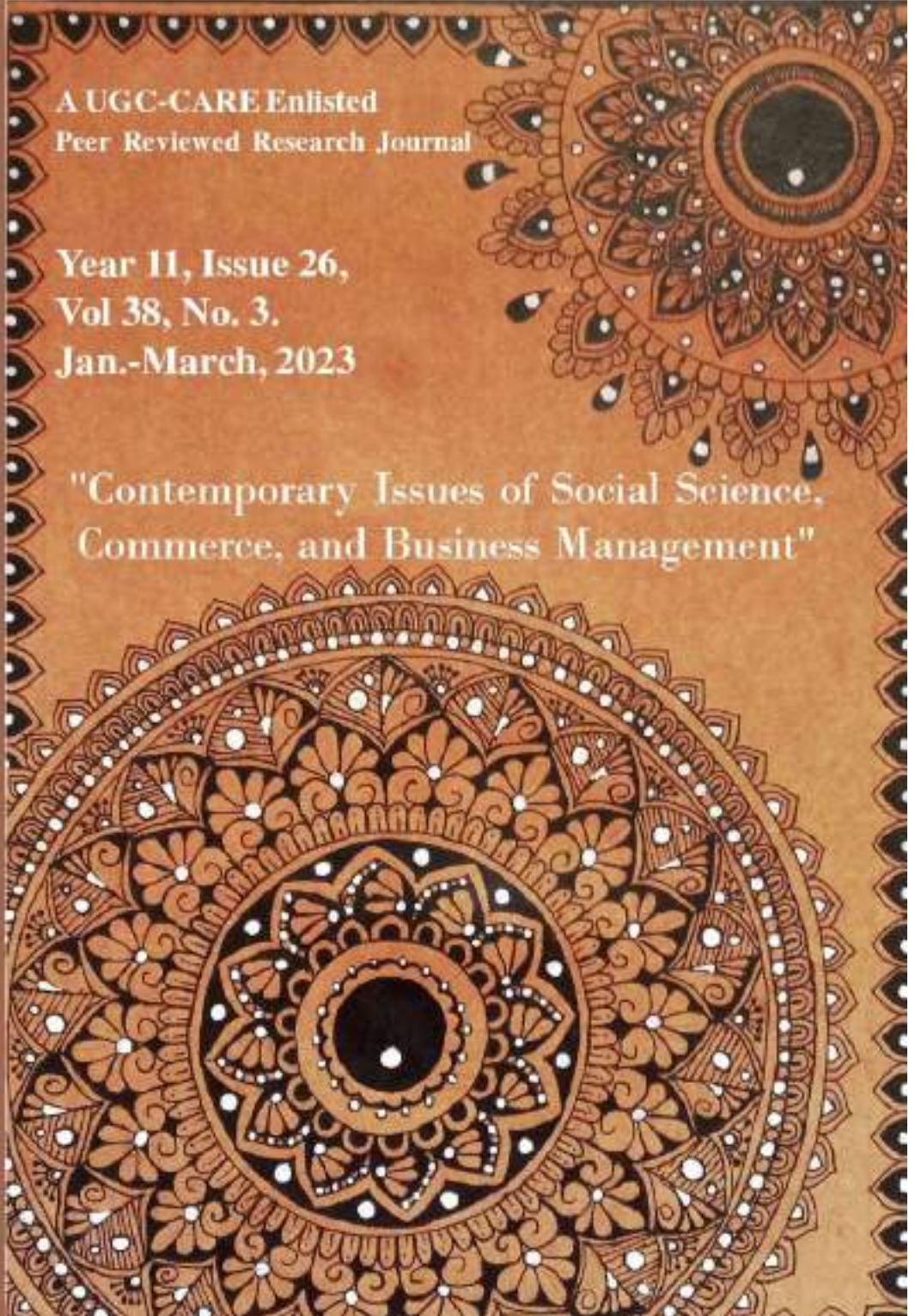
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# CONTEMPORARY ISSUES OF INDIAN AGRICULTURE SECTOR

○ **Dr. Vinod Madhao Barde\***

## ***Abstract:***

Agriculture is the Foundation of the Indian economy. There was a great importance to agriculture in 18th century. Even today also farming occupation is an important because 52% population of India are in agriculture sector as a profession. Out of total national income in India, ¼ income is from agriculture and allied sector. Agriculture was traditional and non-developed with low labour source and productivity. Farmers used to adopt old traditional method for cultivation of land. Use of chemical fertilizers was so limited. Agriculture was only cultivated for survival but not for income. During green revolution productivity has been raised in India. Due to new technology involvement in agriculture water and irrigation is most essential, which affects the uncertainty reflects concerning to the agriculture productivity. Its truth that in future also agriculture sector will play an important role in India. Currently many farmers migrated to urban areas for the searching job in industrial sector. Several farmers committed suicide the reason of crop production failure, increasing loan, water unviability. Farmers faced Emerging challenges like Rain-water uncertainty, climate changes, overburden of population, demand and supply of product, economic problem, lack of marketing knowledge, insufficient finance etc. In this research paper discuss the importance of emerging issues of Indian agriculture sector, and which scheme implemented for the farmers.

***Keywords:*** Agriculture, farmers, challenges, scheme, income.

## ***Introduction :***

India is a predominantly agricultural nation. Agriculture is important to the Indian economy. Agriculture is a tool of economic production and medium of cultural development. Agriculture is a backbone of Indian economy. There was a great importance to agriculture in 18th century. Even today also farming occupation is an important because 52% people

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of India are in agriculture sector as a profession. Out of total national income in India, ¼ income is from agriculture. Its truth that in future also agriculture will play an important role in India.

During Indian independence, agriculture was traditional and non-developed with low labour source and productivity. Farmers used to adopt old traditional method for cultivation of land. Use of chemical fertilizers was so limited. Agriculture was only cultivated for survival but not for income. Commercialization of farming had been not propagated with limited utilization of money. Indian agriculture was totally dependent on nature. Around 54.21% agriculture was dependent on monsoon in the year 2015-16. Even today also nature plays an important role in farming sector.

Due to hybridization of seeds (except wheat) the dependency on nature has been increased drastically. During green revolution productivity has been raised in India. Due to new technology involvement in agriculture water and irrigation is most essential, which affects the uncertainty reflects concerning to the agriculture productivity. Agriculture development is high and steady in irrigation facility prone area. There is total uncertainty to non-irrigated and monsoon dependent agriculture land.

#### ***Objectives of the Study :***

1. To understand the Significance of the Agriculture sector.
2. To Research the issues facing the Agriculture sector.
3. To study the scheme for the farmers.

#### ***Research Methodology***

The current study is based on secondary data that is primarily descriptive. The information gathered from the ministry of Agriculture & Farmers Welfare's, Annual Report, the Reserve Bank of India Bulletin, the Indian Economic Association, Report, the NABARD Reports, articles, books, journals, websites and government publications.

#### ***Importance of Agriculture in Indian Economy :***

An important part of the Indian economy is Agriculture. In 2021-22, 45.6% of the total work force in India will be employed in activities related to agriculture and associated sector, According to the government of India's "Annual Report of the Department of Agriculture & Farmers Welfare Ministry of Agriculture & Farmers Welfare", at current prices, agriculture's contribution to national income (Gross Value Added) that year was 18.8%. In India, agriculture is expected to contribute 14.2% of exports and 18.8% of GDP in the years 2020-21. According to the government's 2018-19 report, out of the total geographical area, 139.3 million hectares were recorded as net deeded and 197.3 million hectares as gross cropped, with a cropping intensity of 141.6%. The net area sown is 42.4% of the total area.

#### ***Scheme for the farmers :***

**PM KISAN Program :** It is program of the federal government to help land holding farmers with their financial needs. With this program, land holding farmers receive a direct benefit transfer of Rs. 6000 per year in financial benefit. In Accordance with the economic survey for 2022-23, the program covered approximately 11.3 crore farmers. This program

has aided farmers in making profitable investment in agriculture endeavors. In 2023 (Varsney& Joshi).

**PMFBY :** Pradhan MantriFasalBimaYojana, is the world's largest crop insurance programme. Every year, over 5.5 crore farmers engage in this programme. The programme guarantees that farmers will have less financial risk because they only have to pay 1.5% of the entire premium during the Rabi season and 2% during the Kharif season. Farmers paid a premium of Rs. 25,186 crore during the last six years of its implementation and received claims of rupees 1.2 lakh crore (as of 31 October 2022).

**KISAN Credit (KCC) :** In order to encourage farmers to buy agricultural inputs and services such as seeds, fertiliser, pesticides, etc. on credit, the Kisan credit card programme was created in 1998. According to the Indian Economic Survey, banks provided Kisan Credit Cards (KCC) to 3.89 crore eligible farmers as of December 30, 2022, with a KCC limit of \$4,51,672 billion (Varsney & Joshi, 2023).

**Mission for Integrated Development of Horticulture (MIDH) :** The objectives of the Mission for integrated development of horticulture is to promote increasing the horticulture production area and farmers income. In This programme, which includes fruits, vegetables, plantation crops, spices, flowers, and root and tuber crops, was introduced in 2014-15. Economic survey statistics show that on a surface area of 28.0 million hectares, a record production of 342.3 million tonnes was attained. Twelve of the fifty-five horticultural clusters designated by the Indian central government have been chosen for the Cluster Development Program trial phase.

**Challenges of Agriculture Sector :** Since the green revaluation, there has been a significant change in the country's food situation. India experienced a severe food scarcity and widespread starvation, and millions of people's lives were saved by food imports. High Yielding Varieties of wheat and paddy were made available after the green devaluation, and irrigation was increased.Improved and High Yielding Varieties were also developed in many other crops. These changes effect on land quality, ecosystem, and environment. Therefore it is imperative to discuss challenges facing Indian agriculture.

**Dependability of Rainfall :** In the more than fifty percentage parts (over 56%) of the country, agriculture is mostly dependent on rainfall, specially the summer monsoon. Inappropriately, the behaviour of summer monsoon is highly unpredictable. Therefore, the variability of rainfall is high which affects the agricultural return unfavourably. Just 54.21 percent of the total planted area is irrigated, which gives farmers greater assurance about their agricultural revenues even when the monsoon fails, as it did in 2015-16, according to the Government of India Report.

**Climate Changes :** Currently the climate change is significant factor, those effecting on agriculture productivity. Increasing temperature along with increased occurrences of unsafe weather circumstances have made climate change a major hazard to Indian agriculture sector and productivity defeat.

#### **Over burden of population :**

Indian agriculture is characterised by a significant population burden. A total of 46% of the nation's population is either directly or indirectly reliant on agriculture.At present,

due to the CORONA pandemic heavy burden on agriculture. Per head availability of agriculture land has decreasing, but the rate of population increasing, hence dependability on agriculture of population is increased.

**Economic Problems:** Indian farmers are basically poor, it is not possible to buy agricultural machinery, use of new technology, improved seeds. Therefore, it is not possible to do new experiments in agriculture and to practice modern agriculture. Due to the high indebtedness of the farmers, after deducting the expenses from the income, the remaining amount does not meet even his primary needs, so the poor farmer is getting poorer.

**Demand and Supply:** If the farmers hark work is supported by nature, the farm yields huge income, at a time when supply is high, demand is low, and thus prices are low. Adequate godowns have not yet been created by the government in Indian to store the goods without selling them at falling prices when the cost of the increased production falls. In fact, it seems to be ignored at the government level. While promising to double the production of the country's farmers, there has been no substantial achievements in the last decade in terms of building basic facilities for it. As a result, due to the neglect of the storage of agriculture produce, crores of goods are seen to be worthless. In the five years from 2017 to 2022, more than 13 thousand tons of grain was wasted due to lack of necessary facilities in the government grain godown. This is evident from the figures of the Ministry of Food and Civil Supplies of the Central Government.

**Traditional Method:** A most of the Indian farmers are still farming with old traditional tools, are overall production is growing slowly. Lack of capital required to use modern technology and tools, lack of technical knowledge and lack of support from the administration level, while implementing the plans at the government level is causing Indian farmers to fail to use new technology. It affects the total production of the farmer and it is seen that the economic condition is getting weaker.

**Lack of Marketing:** Due to the large number of middlemen in the Indian market, the farmer does not sell the crop directly to the consumer. Whereas the middlemen buy the goods from the farmers and get the brokerage money. Bargaining power is low as farmers are unorganized and their organizational power is low. Due to the lack of market prices and related information, it is seen that Indian farmers are losing profit by selling their goods in market.

### **Conclusion :**

The government's actions to increase crop and livestock productivity, guarantee certainty of return to farmers through price support, encourage crop diversification, improve market infrastructure by providing encouragement for the formation of farmer-producer societies, and promote investment in infrastructure facilities have all contributed to the sector's resilient performance over the past few years. Inadequate infrastructure, inadequate irrigation, and a lack of market expertise, particularly in rural regions, are the major issues that currently plague Indian agriculture.

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सत्राची फाउंडेशन, पटना  
शोध, शिक्षा एवं प्रकाशन की समाजसेवी संस्था

**यह संस्था -**

- साहित्यिक सम्मान देती है।
- शोध पत्रिकाएँ प्रकाशित करती है।
- पुस्तकें प्रकाशित करती है।
- सेमिनार आयोजित करती है।
- राजभाषा/राष्ट्रभाषा सेवियों को प्रोत्साहित करती है।
- शोधकर्तओं को स्तरीय शोध के लिए प्रोत्साहित करती है।
- नेट/जे.आर.एफ. के अभ्यर्थियों को निःशुल्क मार्गदर्शन देती है।
- हिन्दी साहित्य के शिक्षार्थियों को प्रतियोगी परीक्षाओं के लिए तैयार करती है।



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# Population Characteristics and its Impact on Socio-Economic Development of Gadchiroli District : A Geographical Analysis

- Prof. (Dr.) Ganesh L. Dhote \*
- Prof. (Dr.) Kishor Y. Thakare \*\*

## **Abstract**

Gadchiroli is the large district in the maharashtra state having 4.69% of the area of the state. Gadchiroli district is located in the some what eastern part of maharashtra. The west side in district wainganga river basin.its impact over the distribution of population as well as density of the population of the Gadchiroli district and East side of district cover on forest .therfour population on the region is low .Gadchiroli districts holds 1.87% of population to the state over 4.69% of its area among the 12 tehsil. Chamorchi teshil is the most population while korchi is the least population. Population live in rural area of 88.00% .The population of sc and st in district shows trend the study 2011. The % of S.C. population 11.25%. while S.T. population 38.70%.In this census 2011 the percent of Scheduled cast population was 11.25% and Scheduled tribes population was 38.70%. Out of Scheduled cast population of the districts 41.76% lived in rural areas and 14.44% lived in urban area. Qualitative population accelerates the socio-economic condition of the reason. Topographical accessibility helps to the people for better development while inaccessibility stands as a obstacle.

**Key Word:** population distribution, Growth, Density, Economic structure, Socio-Economic Development.

## **Introduction**

The proposed study aims to highlight the major characteristics of population and the impact of its on socio-economic development with special reference to the geographical region of the Gadchiroli districts. The study of population never be viewed in isolation. Population and other physical environmental and geographical etc. factors are

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interrelated. population its self is an important aspect. Characteristics of population involves distribution of population, growth of population, standard of living, density and economic structure.

These Characteristics are useful to understand population personality of the region. The study is related to the distribution of population.

Physical factor involves the topographical features such as mountain, plateaus and plains. The distribution of population is concerned, mountains play favorable as well as unfavorable roles. Normaley pleteaus are suitable for human settlement while plain accelerates the population growth. The Gadchiroli districts on which the study includes mountain ous and forest areas of east region.

### **Objectives of the study**

The majour objectives of the present study is to make a comprehensive and impact of socio- economic development of Gadchiroli district.

### **Hypothesis**

Population characteristics has impact on social and economic aspects of the region.

### **Data Base & Methodology**

The data collected and used for the period various census book ,districts statical abstract,socio-economical review of Gadchiroli district etc.

### **Study Area**

Gadchiroli is the large district in the maharashtra state having 4.69% of the area of the state .Gadchiroli district is located in the some what eastern part of maharashtra lying between 18°46' north to 20°50' north latitudes and 79°46' east to 80°55' east longitude. Geographical area of the district is 15433.10 sq.km. Which is 4.69 % of the total area of the maharashtra. The population as per 2011 census is 10,72,942 out of which 9,54,909 is rural and 1,18033 is urban population. The area of the district is distributed among 12 sub divisions [Tahsil] .For the administrative purpose.

Physiography is one of the dominant paeameter of physical environmental, The district includes the gondwana land its three division,easted of shoots as Tipagadh & surjagadh range ,the middle land is slope and western part of wainganga river basin. Forest cover in the districts is 77% above.

The climate of the districts is mainly monsoon type. It,s is characterized with hot summers and dry winters. The winter season which last February. The average annual rainfall in the districts is 1150.00m.m. the average temperature of the district is 41° cg during summer season and winter season lowest temprature in December 11°cg. The drainage of Gadchiroli districts deals with three major river, the wainganga in the west,Indrawati river in east- south, and Godavari rivers in west-south. Minerals, especially of economic importance are avabile in the district.The forest covered in district 76% and surjegadh range in Iron minerals on Etapalli tahisil.

### **Impact of physiography on population characteristics of the District**

Physiography or physical set of the Gadchiroli District is unique in nature. The district is a elevated tableland. It,s location to the wainganga river in west border.The physiography of the district.Indrawati river in the south border and east border surjagadh.The west side



in district wainganga river basin.its impact over the distribution of population as well as density of the population of the Gadchiroli district and East side of district cover on forest .therfour population on the region is low

Tahsil wise population [%] in Gadchiroli District -2011

**TABAL-1**

Sr. no	Name of the Tahsil	Population in [%]
1	Desaiganj	7.79
2	Armori	9.06
3	Kurkheda	8.02
4	Korchi	3.99
5	Dhanora	7.70
6	Gadchiroli	13.60
7	Chamorchi	16.69
8	Mulchera	4.27
9	Etapalli	7.63
10	Bhamragadh	3.38
11	Aheri	10.90
12	Sironcha	6.97
	District	100.00 %

*Source:*Gadchiroli district,census,report-2011

Korchi taluka bears 3.99%, Muiehera 4.22% ,Bhamragadh 3.38%, Dhanora 7.70%, Sironcha 6.97% Ettapallil 7.63%, These distributions are due to somewhat impact of the physiography of the region the region with river of waingang,pranhita,godavari,chimorchi, aheri shows 7.79% ,9.06%,13.60%,10.90% (2011) population growth .

The 2011 census record shows following distribution of density in the district. The region with low density below 100 consist korchi, Dhanora, Etapalli,bhamgradh are dominance in physiography, which shows,its impact over population density of the region. The region with high density are Desaiganj, Armori,Gadchiroli,Chimorchi are in the wainganga basins.

### **Cast wise Population**

#### **[ Schedule Caste and Scheduled Tribles ]**

Districts census handbook [2011] contains data about schedule cast and scheduled tribes. This data is usefully for plan out their socio-economic enlistment and both the planners

and administrator

**S.C. and S.T. population in Gadchiroli district- 2011.**

**TABAL-1**

Cast	Total	Rural	Urban
S.C.	11.25	10.67	15.98
S.T.	38.70	41.71	14.44

The population of s.c. and s.t. in district shows trend the study 2011. The % of S.C. population 11.25%, while S.T. population 38.70%.

Taluka	Total Population	S.C. Population	S.C. Populatin %	S.T. Population	S.T. Populatin %
Desaiganj	83,607	14138	16.91	7119	8.61
Armori	97,097	11368	11.71	23,120	23.81
Kurkheda	86,073	8963	10.41	46,826	54.40
Korchi	42,811	3442	8.04	31,333	73.19
Dhanora	82,698	3934	4.76	58,745	71.19
Gadchiroli	1,45,963	21,023	14.40	28,421	19.47
Chimorchi	1,79,120	16,135	9.01	32,623	18.21
Mulchera	45,787	2726	5.95	14,834	32.40
Etapalli	81,713	2893	3.54	66,597	81.50
Bhamragadh	36,325	1128	3.11	29,459	81.10
Aheri	1,16,992	16683	14.26	58,233	49.78
Sironcha	74,756	18,312	24.50	17,916	23.97
District	10,72,942	1,20,745	11.25	4,15,306	38.70

In Gadchiroli district S.C. Population was 1,20,745 [11.25%] in 2011. Sironcha taluka most S.C. population 24.50% and bhamragadh taluka lowest population 3.11%.

The Gadchiroli district S.T. Population was 4,15,306 [38.70 %] and S.T. population Etapalli taluka most S.T. population 81.50% and Desaiganj taluka lowest population 8.61%. The urban area most ratio in s.c. poipulation and rural area most ratio in s.t.population.

***Scheduled Cast and Scheduled Tribe Occupational Characteristics:***

People are engaged in different works as a economic activities. These activities are

closed in three categories as primary activities (Cultivators, Agricultural labourers, livestock, Forestry, Fishing, Hunting, Plantations, and mining etc.) Secondary activities (Manufacturing, processing, rearing in household etc.), and Other activities (Trade, Transport, Communication etc. The Gadchiroli district has population of these categories accelerate their socio-economic life.

**Table-3**

Tahsil	Population		Total workers		Main workers		Primary activities		Secondary activities		Other activities	
	S.C.	S.T.	S.C.	S.T.	S.C.	S.T.	S.C.	S.T.	S.C.	S.T.	S.C.	S.T.
Desniganj	14138	7119	7127	3647	4310	2203	2675	685	161	47	1474	474
							71.98	52.65	3.73	2.13	(34.19)	(27.86)
Amori	11368	23120	6389	12885	3867	8008	2914	7656	85	110	868	922
							75.28	88.11	2.19	1.26	(21.44)	(10.41)
Kurkheda	8963	46826	5129	26894	2967	15472	2311	14053	42	157	614	1262
							77.88	91.02	10.41	1.01	(20.69)	(8.15)
Korchi	3442	31333	1985	18089	1140	10592	794	9842	39	86	307	664
							69.64	92.92	3.42	0.81	(26.92)	(6.21)
Dhanora	3934	58745	2220	34326	1626	23104	1212	21581	47	226	367	1297
							74.53	84.99	2.89	0.98	(22.57)	(5.61)
Gadchiroli	21023	28421	5226	14793	7101	9984	3557	6414	158	181	3386	3325
							50.68	64.13	2.22	1.81	(47.68)	(33.30)
Chimorchi	16135	32623	8675	18708	5824	12305	4436	10405	58	82	1330	1218
							76.16	88.66	0.99	0.66	(22.83)	(9.89)
Mulchera	2726	14834	1516	7870	719	4194	540	3754	08	35	171	405
							75.09	89.50	1.11	0.83	(23.78)	(9.66)
Etapalli	2893	66597	1443	36995	1005	26930	602	24679	24	317	379	1934
							59.89	91.63	2.38	1.18	(37.71)	(7.18)
Bhamragadh	1128	29459	658	17218	457	14279	278	13043	08	167	171	1069
							60.83	91.33	1.75	1.16	(37.41)	(7.48)
Aheri	16683	58233	8065	29182	5695	19865	4026	16466	119	155	1550	3244
							70.66	82.88	2.08	0.78	(27.21)	(16.33)
Sironcha	18312	17916	11818	10737	8568	7062	7867	6294	184	36	517	613
							91.81	89.12	2.14	0.50	(6.03)	(8.68)
Total	120745	415306	64854	232344	43279	154681	31212	156655	933	1599	11134	16427
							72.71	88.35	2.15	1.03	(25.72)	(10.62)

The Tables gives distribution of workers by three categories of economic activities in the district of 2011. The proportion of all these categories difference from tahsil to tahsil. The



closed in three categories as primary activities (Cultivators, Agricultural labourers, livestock, Forestry, Fishing, Hunting, Plantations, and mining etc.) Secondary activities (Manufacturing, processing, repairing in household etc.), and Other activities (Trade, Transport, Communication etc. The Gadchiroli district has population of these categories accelerate their socio-economic life.

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The Tables gives distribution of workers by three categories of economic activities in the district of 2011. The proportion of all these categories difference from tahsil to tahsil. The

schedule cast and scheduletribes of Primary activities is between 91.63% to 52.65% .The schedule cast Primary activities in highest is in Sironcha tahsil 91.81% and lowest Etapalli tahsil 59.89% . Secondary activities in district 2.15%.The height % is in Desaiganj 3.73% and lowest 0.99% is in Chamorchi tahsil. Other activities in district 25.72%. The highest in Etapalli 37.71% and lowest 6.03% is in Sironcha.

The scheduletribe of Primary activities is between 91.92% to 52.65% .The scheduletribePrimary activities in highest is in korchi tahsil 91.92% and lowest Desaiganj tahsil 52.65% . Secondary activities in district 1.03%.The height % is in Desaiganj 2.13% and lowest 0.50% is in Sironcha tahsil. Other activities in schedule tribe in district 10.62%. The highest inGadchiroli 33.30% and lowest 5.61 % is in Dhanora tahsil.

### **Conclusions**

Gadchiroli districts holds 1.87% of population to the state over 4.69% of its area among the 12 tahsil.Chamorshi tahsil is the most population while korchi is the least population. Population live in rural area of 88.00% the district.The districts density 74 persons per km<sup>2</sup> from 2011 the most density in desaiganj teshil 335persons per km<sup>2</sup>, and lowest density is in bhamradh tashil 28 persons per km<sup>2</sup>.

The schedule cast &scheduletribesworkers in three different categories of economics activities in the district.The Primary activities in 91.81% and schedule tribe Primary in activities in 91.92%

Scheduled cast & Scheduledtribes are made available by the census.These statistics are use full for the planning of socio-economic development in the districts by the government .In this census 2011 the percent of Scheduled cast population was 11.25% and Scheduled tribes population was 38.70%. Out of Scheduled cast population of the districts 41.76% lived in rural areas and 14.44%lived in urban area.Qualitative population accelerates the socio-economic condition of the reasion.Topographical accessibility helps to the people for better development while inaccessibility stands as a obstacle.

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# SERVICE SECTOR : A MEDICINE FOR STRONGEST INDIAN ECONOMY

○ Dr. Rita R. Raut\*

## *Abstract :*

The service sector has taken the lead in many places in India. Agriculture and industry sectors are developing at a large rate while services are being developed. Generally service work is transferred from one person to another in an invisible form. Services are also in intangible, invisible and visible form. The development of industry sector, agriculture sector, education sector, trade sector and various sectors mainly depends on service sector. The progress of other service organizations depends on the availability and readiness of the service. So, in the current situation the service areas are expanding day by day and continuously. It mainly pushed and boosted capital development, employment Generation, proper utilization of human resources, increase in technology, customer satisfaction, economic and industrial development etc. It also helps in day-to-day life cycle. In 2021-22, total expenditure on medical fare is only 2.1% of GDP as compare to Japan or other countries. The highly contribution of Travel and Tourism industry in India by 178 billion dollars to Indian GDP. The total contribution of service sector in Indian GDP is 60%. In India, the expansion of the service sector has given a major boost to job creation. It has helped a lot in solving the problem of unemployment in the country. Services are also expanding due to current globalization.

**Keywords :** Service, Indian Economy, Start Up, Digital Platforms, Employment

## *Introduction*

Services are not visible like goods. Service is the main part of any humanity and with the help of service factor, we maintain connectivity in society. In the modern era, the importance of marketing has increased and the role of the service sector is important in it. Along with goods, the demand for services has increased. But services cannot be measured like goods. Some services are not visible like medical services, entertainment service, travelling services etc. Service Sector is played an important role in developing economy

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\* HOD and Assistant Professor in Commerce Yashwantrao Chawhan College, Lakhnadur Dist-Bhandara

of India. Service sector is wide area. It includes various contents like trade, hotel, transport, storage, communication, financing, business services, personal services etc. There is need of service of schools, hospitals, administrative and accountings for development of Indian Economy. Increase in service sector of India is a unique example of traditional model of development of Indian Economy. But it providing less employment.

Agriculture and production department still contain high employment. Start-up concept provide many new employments with grateful services. It proposes digital platforms to societies which give new inspiration to young generation. Service sector increases its importance after Corona Period. It is third source of earning in Indian Economy. Service sector includes all contents which are taken by people using time and knowledge for improvement in productivity, uses, capacity, possibility, durable etc. The object of this study is to provide awareness about employment providing sector i.e., service sector which is giving positive approach in young generation.

#### **Objectives of Study :**

India has tremendous structures nearby creativity in ability development content. India Government has started the "Digital India" notion overall India. Within this concept, many peoples were coming under service factor and the purpose of India Government providing the digital platform is self - employment.

On this basis, in this study the purpose is taken according to the need of employment at present date. Some Objectives are here-

1. To provide awareness within society about service sector in India.
2. To maintain Sustainable Development through service area.
3. To provide knowledge about role of service sector in employment.
4. To study the startup features about service sector

#### **Research Methodology :**

In this study, some data is taken from secondary sources like books, newspapers, periodicals, articles, websites etc. some data is primary type was usual by online survey. As well as it primarily be contingent upon exploratory in countryside. The study is based on quantitative and qualitative methods.

#### **Review of Literature :**

The aspect of FDI i.e., foreign direct investment in India service sector(a study of post liberalization) are analyzed by most of the scholars and researchers that are Dr. Arjun Singh Sirari and Mr. Narendra Singh Bohra.2011 examined the role of FDI in service sector.

Indian Economy and service sector: When the importance of online increased during the Corona period, online services were increased according to the needs of households. When the importance of online increased during the Corona period, online services were increased according to the needs of households. And the benefit of this is the increase in the number of unicorns that offer large-scale online services. Out of which a large number of employments were generated. It shows that the demand for service sector is more. More than 6 lakh jobs created by unicorns in India. It includes Ola, Big Basket, Paytm and so on.

The economy is depending upon three criteria which are agriculture, industrial and



service. Out of these the third sector is very helpful for creating employment and to boost Indian economy by giving contribution in many fields like medical, tourism, leisure's etc. In 2020-21, the gross value added at current price is 53.89% of total India's GAV. Industry Sector contribute% as well as agriculture sector contributes 20.19% in GAV. gets highest range in country's Net National Product. As usual the agriculture sector mostly contributed sector in Indian Economy.

The following table shows the sector wise GAV in India and their shares.

**Table No.1.1 GAV in Indian Economy (2020-21)**

Sr.No.	Sectors	GAV Rupees in Crore.	Shares in %
1	Public Administration, Defense and other services	2,761,996	15.42
2	Financial Real Estate and prof. services	3,950,786	22.05
3	Trades, hotels, transport, communication and services related to broadcasting	2,941,477	16.42
<b>Total GAV at basic prices</b>		<b>9,654,259</b>	<b>53.89%</b>

Source : Ministry of Statistics and Programme Implementation 2020-21

From above table, there is 53.89% in shares of Indian Economy. Financial Real Estate and prof. services contribute 22.05% in it. Agriculture sector contributes 20.19% in GAV same as Industry Sector contributes 25.92% in GAV.

The contribution of service sector in Indian GDP is increased for continuously according to many peoples. Foreigners are taking interest in Indian Service Facilities because India has a big group of skilled worker, low charges and high education. Practically, it is a quality which is liked by people in other country. So, on this basis, many other countries are started out sourcing in business services and in IT sector services. Due to this, service facilities have been providing a boosting power to Indian Economy and the result is shown in GDP growth.

#### **FDI and Service Sector :**

FDI increases job opportunities in country and help to create skill-based thing. It also boosts Indian export system and encourage to international organization for entering domestic market. In March 2021, FDI in insurance sector is increases from 49% to 72%. FDI helps in reforming economy of many countries and it is very essential factor for growth economic globalization. FDI means investing in a company in another country. RBI controls FDI under FEMA. FDI inflow of foreign currency into India leads to creation of infrastructure in India, increase in productivity and in turn increase in employment. The service sector accounts for the largest share of foreign investment inflows to India. In the first half of 2021-22, foreign direct investment of USD 16.73 billion has flowed into services sector. "The Economic Survey report shows a significant increase in foreign direct investment in financial, business, outsourcing, research and development, computer technology testing and analysis and education sub-sectors. Currently ENCUBED announced a new R&D Center of Excellence at Palava.

### **Trade in Service Sector :**

Services are the backbone of the global economy, accounting for more than two-thirds of global GDP and attracting three-quarters of FDI. Globally, new job creation takes place on a large scale. Service trade has become very important. First sea trade was seen only then insurance trade increased. Service is mainly seen in it. Now the importance of IT sector is increases day by day. Specially in communication technology, services are popular by peoples. It brings new service pattern in society. That's why some companies are economically developed. It includes legal, engineering, professional services, computer services, telecommunication etc. GATTS provides special rules for service market which help to determine the status of transaction whether it is residents or non-residents. Basically the "the mode of supply" is known for the service provide on the basis of transactions between supplier and customer at territorial place which contracts about the trade services. India has a lion's share in exporting services globally. In 2020, India has taken place in First Ten's list in service exporter. In 2020, services are covered at 4.1% contribution in commercial services as compared to 2019 which was 3.4%. The Net export growth rate in 2021-22 is 22.8%.

In the year 2021-22, the IT sector will provide 5 million jobs in India and account for 51% of services exports. IT sector provide more than 290 M&As by focusing digital platforms. Industry and digital revenue contribute five times more than service sector in Indian economy by various new skills in employees.

### **Start-Up and Digital platforms :**

Currently, start-ups have taken over the services marketing. The start-up helped the youth to find employment. Many service professionals have gained a foothold in the market. Many service professionals have gained a foothold in the market. Among the various ecosystems in India, startups are becoming important. Among the various ecosystems in India, startups are becoming important. The services sector has captured the market share in the Indian economy. The services sector has captured the market share in the Indian economy. Service base business growing fastest in India because it contributes in GDP growth, employment, trade, and in investment also. There is also major contribution of E-Commerce in pie. By Morgan Stanley study says in 2020 that the business of E-Commerce market has been increases from \$ 102 billion to \$ 119 billion. Many start-ups in India having advantages because of service based businesses. There are some reasons for successful a start-up project like low capital cost, faster to launch, lower business risk, flexibility and adaptability etc. There is some successful service-based startups in India are Zomato, Practo, Rentomojo etc. Zomata is working for search a particular restaurant by online and provide choices for taking decision within 1 million options in 23 countries. This service is launched in 2008 by providing service to 3,31,200 restaurants in 19 countries. Practo is known for health tech company with more than 1 lakhs doctors and more than 20 million patients across the worlds. Rentomojo is providing online rental facility for furniture.

### **Service Sector and Sustainable Development :**

Sustainable development is achieved by managing the natural processes of things. Business of services in it is certainly a pollution-free matter. Big factories have to be set up



for the production of goods and this leads to destruction of the structure of nature. Service businesses can avoid these side effects. Service marketing plays its role after the goods are manufactured. Services include travel, hoteling, medical as well as religious and social culture. It receives a large amount of foreign investment. Service sector is based on online mode also. Hence it is similar to digital economy. Service can reach everywhere by from online to offline way, so, each and every person can get the benefits of any products at any place. ITU's contributed in 17 SDGs goals. It is also taking place in service area. Service Area provide a huge number of services which are paperless also. So, day by day the importance of service sector is increasing through various platforms which are helpful in growth in digital economy.

### **Conclusion**

The service sector plays an important role in developing Indian Economy as well as digital economy. It is helpful in creating digital jobs, pollution free environment, increasing FDI. It is also helpful in maintaining sustainability. IT sector and Banking Sector are providing best services to people by many securing applications. Due to service sector, from urban to rural area all types of people can involve and make themselves economically strong. One thing is it is difficult in requirement of skill which are not properly gathered. Visionary people need to be change for implementation of the sector.

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○ Dr. Rita R. Raut\*

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# Self-Help Groups in India an Effective Tool for Women Economic Empowerment and Poverty Eradication

○ Dr. Mahendra B. Wasker \*

## Abstract

People experiencing challenging conditions are found to be stronger when organized as a group and more empowered when given the chance to engage in an environment that is free, open, and non-threatening. Due to unequal access to governmental, social, and economic resources in India, which has led to high infant mortality rates, low nutritional standards, and low rates of female literacy, women are regarded as the "unsung heroines" of the country. In order to overcome these challenges, rural women needed to be grouped in order to develop their skills and increase their capacity for interaction, thought, inspiration, and action with a self-sufficient mindset. Government and non-governmental organizations (NGOs) have established self-help groups (SHGs) to inform women about their constitutional rights, dietary requirements, and political participation.

**Keyword:-** SHG members, women groups, women, self.

## Introduction

People facing challenging circumstances are found to be stronger when organized collectively and more empowered when certain the chance to participate in unrestricted, open, and non-threatening environment, according to community groups. It is predicated on the idea that it is malleable.

### Empowering women

In India, the term "women's empowerment" is popular. India as a nation is dedicated to promoting women. Even ignorant and undeserving men felt superior to women who did not earn them, despite the fact that women are viewed as "unsung heroines who work from dawn to dusk." Since then, the government has worked diligently to eradicate different biases.

In India, women play a variety of responsibilities both within the family and in society at large. Innovations that cater to women's practical requirements as well as their strategic

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interests are essential in response to these roles and responsibilities. To guarantee these success enabling mechanisms must go along with innovations. This is the path to a change in society that will strengthen women.

#### Coming together

It was urgently necessary to group these rural women in order to showcase their skills. The groups initially lacked initiative because of low self-confidence, a dearth of capital to launch new businesses, and poor credit worthiness. Due to their unequal access to political, social, and economic means, women had suffered. Low female reading rates, high infant mortality rates, and subpar nutritional standards were the direct results of this. It was discovered that working with specific women did not result in any beneficial changes to their standard of living. In order to improve the women's capacity to communicate, think critically, motivate others, and act in a self-sufficient way, we thought it was essential to encourage the women to establish self-help groups.

#### Ways with self-help

The key to empowering women is educating them about their legal rights, health and nutrition, gender equity, and the legislative process. There was a real need for the groups to lead training courses so that they could acquire skills and boost their confidence. By organizing different skill-based, income-oriented training programmes in agricultural operations, significant efforts were made to instill entrepreneurial essence and information among the rural farm women. Members were encouraged to cut back on unnecessary expenses and save between 100 and 200 rupees each month, depositing the funds in a joint account run by the elected group leaders.

In all these mechanisms about the empowerment of women, Government and NGOs are unanimously established Self-Help Group (SHG) to strengthen the women. If the woman becomes independent in financial aspect, she will independently start her business and build up her career. Keeping this in view, it is essential to understand what Self Help Group is and its functioning.

#### Self-Help Groups

Self-Help Groups are a small, volunteer group of underprivileged individuals, ideally from the same socioeconomic bracket. They become entrepreneurial thanks to the microcredit provided. It may consist of only males, only women, or even a mix of both. However, it has been observed that Co's groups perform better in all of the crucial SHG's

Concept of Self-Help Group was established by Mridul Yunus in Bangladesh. Later on, the concept through sea change in the social and financial fields. In India, during 1974-80, in the states like Karnataka and Andhra Pradesh, there were small saving groups of women and they continued the structure of groups to them. Thus, they created the group norms and guidelines. In India, self-help groups started out in this way. From dependency towards independency and from interdependency towards interdependency, is the definition of Self Help Group. SHG is not any kind of scheme nor any project. But it is a group which



imparts progressive education to women. To bring sea change in the psychological, argumentative and financial condition of the members is the motive behind the establishment of these groups. To make its members financially independent is the thought behind the SHG. To bring about improvement in financial condition of the family through the saving, to think about the crisis in the society, to maintain amount for the business-all these can be possible with the help of SHG.

Self Help Groups is a collection of pastoral poor people who offered to form clubs in an effort to end poverty among their members. They make a commitment to save consistently and combine their funds into the Group Corpus, a collective fund. Members of the organization consent to using these common funds as well as any additional funds they might obtain through collective management. When forming groups, the following basic principles are taken into account:

A self-help club typically has between 10 and 20 members. However, this number may range from 5 to 20 in challenging parts like deserts, mounts, and areas with dispersed and sparse populations, as well as in cases of minimal irrigation and people with disabilities.

However, if necessary, up to 20% and, in exceptional circumstances, up to 30% of the individuals in a group may be drawn from families just above the poverty line who live continuously with BPL families and if they are acceptable to the BPL. Participants in the gathering. Multiple people from the same household cannot be included in the same group. An individual shouldn't belong to more than one group at a time. The managing and decision-making, which normally shouldn't be left entirely in the hands of APL families, must involve the BPL families actively. Additionally, members of the Self-Help Group who earn more than the federal poverty level are not allowed to serve as office holders (Group Leader, Assistant Group Leader).

In order to adhere to it, groups should create a code of conduct (a code of group leadership). Regular meetings that function democratically and allow for the open exchange of ideas and members' participation in the decision-making process should be held on a regular basis (either weekly or biweekly). Every meeting should be able to have an agenda that the group can use to make choices.

Members should consistently save money to develop their bodies. At routine group meetings, the group should be able to receive any required minimum savings amount from each participant. The Group's company funds are the savings that are thus gathered.

Loans to the member should be advanced using the group corpus that was identified. The organization should create financial management guidelines that cover the process for approving loans as well as the interest rates and repayment schedule.

All lending decisions should be made by the participants in the group meetings using a participatory decision-making method.

The group ought to be able to prioritize loan applications, establish repayment plans, determine the appropriate rate of interest for loans given, and carefully watch over the loanee's repayment of loan installments.

It is preferable for the Group to have a Group Account at a bank branch in the same region where Members can deposit any outstanding amounts after a payment has been made.

Simple basic records like a minute's book, attendance register, loan ledger, general ledger, cash book, bank passbook, and individual passbook should be kept by the organization. What do women's self-help groups do?

Facilitate members to participate in government schemes.

Encourage children, especially girls, to go to school.

Celebrate important days.

Attend Gram Sabha (village group) meetings

Assist in the health campaigns and veterinary camps

Develop unity and self-confidence among the group members

Form a platform where groups can interact to accumulate and share new knowledge and techniques

Inculcate the habit of savings and initiate income-generating activities

Create a space for women's participation in socio-economic development

Social awareness

As the capacities and capabilities of the self-help group members grow, their communities feel for the first time able to address social issues to the pertinent government agencies. These issues include:

(The need for safe drinking water, street lights, public sanitation and roads

(The scrubbing of public spaces

(Receiving land patta (deeds) for houses

(Finding inexpensive lodgings or restrooms

**Gaining strength**

Rural women's lifestyles, attitudes, and approaches have undergone radical change as a result of the establishment of women's self-help organizations.

- They are managing their own insurances. They take part in making decisions for the home.
- They have the ability to participate in societal issue decisions.
- They are able to assist other members of their community and are more responsible to their needs and those of their society.
- They can communicate with representatives of government agencies, NGOs and banks to get their wants and rights met.
- In accumulation to generating income for themselves as a group, their strength and unity have opened up new opportunities for improvements in society.



- They have learned novel techniques in tanning and other tasks.
- The importance of a child's schooling is recognized especially girls. By giving their children more nutrient-rich food and the appropriate vaccinations, women are protecting both their own and their children's health.
- The women are ambassadors for the development message, raising awareness throughout their complete family and community.

### Suggestions & Recommendations

1. It is necessary to try to encourage individual women to become a SHG.
2. Government, social organizations, NGOs should try to encourage the participation more and more women from all strata of society in SHG.
3. It is necessary to conduct a special drive for women to encourage them to save at least 40% of their earnings every month.
4. Innovative methods should be implemented while conducting the meetings of SHG during the peak periods of agricultural work.
5. Member should be trained and informed about book-keeping and accounting, time to time transactions and audit.
6. Government should issue considerable grants every year for SHG.
7. Government should provide special grants to SHG for Emergency Conditions.
8. SHG should conduct regular literacy drive for the female women in the village. As such, Adult Literacy Classes should be conducted for the adult illiterate members in the village.
9. There should be strict supervision on whether the members are utilizing the amount of loan for their genuine need. In such, there should be watch on the timely repayment of loan. In case of any fault, the repayment of the loan should be done in one stroke.
10. Special awards should be given to members and office bearers of SHG for their exemplary work in the field.
11. Women members should produce seasonal goods. The product should be sold on the center established by District Rural Development Mechanism.

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## V.S. Naipaul's Perspective on Contemporary India through 'India: A Million Mutinies Now'

○ Dr. Rakesh Vishwanath Talmale\*

### Abstract

The research paper is an attempt to explore V.S. Naipaul's perspective on contemporary India which he had experienced in the decade 1980-1990. His travelogue 'India: A Million Mutinies Now' is the third book of his visit to India. It is a mirror of contemporary India having truthful picture of Indian social, religious and political scenario. He frankly but truthfully depicts the 'mutinies' of India like religious, regional, commercial and caste-based. In his travel he meets with number of people and places showing positive aspects in progress in various fields. V.S. Naipaul's is satisfied with the present Indian scenario than his experience in previous visit explored in two books.

**Keywords:** Contemporary, Colonial, Indian, Travelogue, Third world

Vidiadhar Surajprasad Naipaul is an elegant writer of West Indies. His father was migrated from India to West Indies. He was born and brought up at Trinidad. He is famous for his comic and autobiographical writings. In his 50 years of writing career, he wrote thirty books both fiction and non-fiction genre. He was born in 17<sup>th</sup> August 1932 in a Brahmin family. His father was an English language journalist who wrote short stories in the 'Trinidad Guardian'. His father encourage him for the writing career but before he could achieve success, his father passed away in 1953. He started writing with novel at the age of 18 but could not get a willing publisher. His debut work 'The Mystic Masseur' (1957) is about a bright youth's pursuit to become writer.

V.S. Naipaul's post-colonial writing created controversy in literary world. He was keen to explore the legacy of colonialism of the British Empire. The novels he wrote were based on the colonial as well as ex-colonial societies. The novels were

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marked with the problems of the colonized people and the impact of colonisation on them. His travelogues containing series of three books 'An Area of Darkness' (1964), 'India: A Wounded Civilization' (1977) and 'India: A Million Mutinies Now' (1990). Naipaul's attraction to homeland India urged him to write about contemporary scenario of India through these travelogues. These books contained impact of colonisation on India and recently emerged as third world. He skillfully transformed the travelogue into text, mainly post-colonial text. These text revealed passionate picture of contemporary India. The last travelogue 'India: A Million Mutinies Now' is fine picture of realistic India 1980 to 1990.

V.S. Naipaul's started literary career in 50's in Britain. He established himself as a novel writer, so he got a fellowship of Trinidad and Tobacco government. He returned to Caribbean exploring the novel and travelogue writing. It was the time when anti-colonial movements were reaching at its height. 'India: A Million Mutinies Now' conveys the post-colonial and home coming ideas of Naipaul. It is a recommendation of his love-hate relationship for India. He expresses his detachment with India mostly sensitive than negative. He expresses view on India as a leading Third World which differs from his last visits. He observes modernity and traditional aspects in homogeneous ways. These are the harmonious principals prevailed oneness rather than showing different aspects.

India as a hybridized cultural formation where Hinduism and Parliamentary democracy, mantras and transistor, radios, bullock carts and nuclear power can co-exist perfectly. (Cronin, 1989, 113)

This travelogue explains various changes and developments found in India. Though, India's journey is in right direction, it is far away to reach level of developed country. Naipaul explores 'million mutinies' of India will help to flourish it like western countries. Naipaul conveys

'What the mutinies were also helping to define was the strength of the general intellectual life and wholeness and humanism of the values to which all Indians now feel they could appeal and – strange irony – the mutinies were not to be wished away. They were part of the beginning of a new way for many millions, and part of its restoration. (Naipaul, 150, 518)

Naipaul explores number of mutinies of India containing regional, religious, commercial, caste based etc. The movements like Naxalite, Dalits, Dravidian, Khalistani terrorists, South Indian are explosive one but not stumble block in the uniformity of India. Unlike this, Naipaul wondered to experience agricultural,



Babasaheb Ambedkar the huge crowd emerged on road sides. He met with Shivsena leaders who were staunch follower of Hinduism and aggressively putting forward their ideology. Naipaul saw wretched condition of Muslim community. He visited to Mohammad Ali road highly populated with Muslim community. He met with Anwar, an educated young man. Anwar had great belief in Islam who thought that illiteracy in Muslims caused greatly in their progress. He says,

It is inevitably that they will fight for Islam. It is contradictory roll. They will continue their criminal activities, but at the same time they will read the Koran, and do the namaaz, five times a day. The community does not admire these people, but the people are enchanted by the way the dons behave with the common muslims.

(Naipaul, 1990, 43)

In this ways, Naipaul put focus on the dark side, chaos and the mutinies in India. The societies are separated on the basis of religion, caste, region and languages. On account of this, Indian people have the strong belief in powerful patriotic ideas which bind them in single thread of uniformity.

But, in the present scenario of 2023, India seems fanatical changes on social, political, religious and cultural fields. Due to lack of ruling visionary people, it seems that India is getting backward on number of fronts. Unlike V.S. Naipaul's views of powerful 'Third World', it emerges great anxiety in the scholarly world that India is making somewhat pessimistic regression in every walk of life.

To conclude it can be said that V.S. Naipaul observes in 'India: A Million Mutinies Now' the colonization and its positive picture on the multiple horizon of contemporary India. Despite mutinies, India seems strong unified, homogenous and bounded nation. He meets and observes people thinking about modernization and globalization. At last, we can say that Naipaul strongly feels that India is flourishing as a powerful and progressive third world.

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# गोंदिया जिले की ग्रामीण अधिवासों का भौगोलिक अध्ययन-2011

- संतोष कुमार पी. ठाकरे\*
- डॉ. किशोर वाय. ठाकरे\*

## संक्षिप्त :

प्रस्तुत अध्ययन का मुख्य उद्देश्य ग्रामीण वस्तियों के प्रकार और अध्ययन क्षेत्र को प्रभावित करने वाले कारक की पहचान करना है। ग्रामीण वस्ती के विस्तृत विश्लेषण के लिए, बर्नार्ड (1931) की संकेन्द्रण सूचकांक (Degree of Concentration) पद्धति का उपयोग करके गणना की गई है। वर्तमान अध्ययन मुख्य रूप से द्वितीयक डेटा पर आधारित है और इसे गोंदिया जिले की जनगणना पुस्तिका 2011 से एकत्रित किया गया है। इन गणना किए गए सूचकांक से पता चलता है की गोंदिया तहसिल में संकेन्द्रण सूचकांक मध्यम है। इसका मुख्य कारण यह है कि गोंदिया तहसिल के पश्चिम में पहाड़ी और पूरब एवं दक्षिण में जंगल व्याप्त भाग है। कृषकों ने अपने कृषि कार्यस्थल पर ही घर (निवास स्थान) बना लिए है। जहाँ कृषि कार्य हेतु सिंचाई की सुविधा है। अध्ययन क्षेत्र के पूरब, दक्षिण और पश्चिम दिशा में संकेन्द्रण सूचकांक मुख्य रूप से कम है। इसका मुख्य कारण यह है कि इस दिशा भाग में भी पहाड़ी, बीहड़ स्थलाकृति, जंगल व्याप्त क्षेत्र अधिक है। जहाँ सिंचाई की सुविधा है वहाँ कृषक कार्यस्थल में ही घर (निवास स्थान) बनाकर रहते है। इसी वजह से छोटी-छोटी बस्तियों का निर्माण हुआ है। यह बस्तिया मुख्यरूप से तिरोडा, गोरेगांव, आमगांव, सड़क/अर्जुनी, अर्जुनी/मोर. सालेकसा तथा देवरी तहसिल में पाई जाती है। इन तहसिलों में कम गुणवत्ता वाली भूमि और अन्य कारणों से भी यहाँ एकाकी/ प्रकीर्ण प्रकार की बस्तियाँ है।

**बीज शब्द :** ग्रामीण अधिवास, संकेन्द्रण सूचकांक, एकाकी अधिवास, अपखंडित या पुरवा युक्त अधिवास।

## प्रस्तावना :

अधिवास मानव द्वारा निर्मित सांस्कृतिक भूदृश्यों में सर्वाधिक महत्वपूर्ण और स्पष्ट रचना होती है, जिसे वह अपने निवास के लिए, काम के लिए, विभिन्न सामग्रियों के संग्रह के लिए या सामाजिक सांस्कृतिक एवं राजनीतिक क्रियाओं को सम्पन्न करने के लिए निर्मित करता है। भूगोल में, अधिवास अध्ययन का एक

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\* शोधकर्ता, यशवंतराव चव्हाण महाविद्यालय लाखांदूर (संशोधन केन्द्र) भूगोल विभाग प्रमुख रा.तु.म.नागपूर विश्वविद्यालय, नागपूर यशवंतराव चव्हाण महाविद्यालय लाखांदूर।

\* मार्गदर्शक, यशवंतराव चव्हाण महाविद्यालय लाखांदूर (संशोधन केन्द्र) भूगोल विभाग प्रमुख रा.तु.म.नागपूर विश्वविद्यालय, नागपूर यशवंतराव चव्हाण महाविद्यालय लाखांदूर

महत्वपूर्ण स्थान है क्योंकि अधिवासों को मनुष्य और पर्यावरण के बीच संबंधों की एक मौलिक अभिव्यक्ति के रूप में देखा जाता है। (शर्मा 2015)। बस्तियों को जनसंख्या सघनता का बिंदू माना जाता है। निवास स्थान या अधिवास वह स्थान है जहाँ, लोगों ने अपना स्थायी निवास स्थापित किया। सामाजिक-आर्थिक विशेषताओं, व्यावसायिक संरचना, जीवन के तौर तरीके, जनसंख्या आकार के आधार पर मानव बस्तियों को दो प्रकारों में वर्गीकृत किया गया है। वे प्रकार ग्रामीण और शहरी इस प्रकार है। ग्रामीण बस्तियाँ वे बस्तियाँ हैं, जहाँ के लोग अधिकतर कृषि और कृषि संबंधी गतिविधियों में लगे रहते हैं। जबकी शहरी बस्तियाँ वे बस्तियाँ हैं, जिनके निवासी गैर-कृषिगत गतिविधियों में लगे रहते हैं (आर.एल.सिंह 2002)। ग्रामीण और शहरी बस्तियों को उनके उप-प्रकारों में वर्गीकृत किया गया है। उसके लिए अनेक भूगोलवेत्ताओं और विद्वानों द्वारा विभिन्न विधियों का परिचय दिया जाता है। जो उनके प्रकारों को वर्गीकृत करती हैं। ओरोसेल (1920), बर्नार्ड (1931), पावलोव्स्की (1938), डेवोबेरी (1943), ट्रेवार्था (1946) मंडल (1972), हडसन (1976), गिलग (1996), और अन्य कई भूगोलवेत्ताओं ने ग्रामीण बस्तियों के प्रकारों की विभिन्न मानदंड और सांख्यिकीय तरीके के आधार पर व्याख्या की है। बस्तियों की सघनता बस्तियाँ निर्मित क्षेत्र के तहत कुछ क्षेत्र को इंगित करती है। (नंदी और मिस्त्री 2018), आर.एल.सिंह (1955), ने बस्तियों के मुख्य चार प्रकार बताये हैं जैसे-सघन बस्तियाँ (Compact Settlement) अर्ध-सघन बस्तियाँ (Semi compact) पुरवा युक्त बस्तियाँ (Semi Sprinkled) और प्रकीर्ण या एकाकी बस्तियाँ (Dispersed) सभी मानव बस्तियाँ एक दूसरे से भिन्न हैं और यह आसपास के वातावरण पर निर्भर करता है। इसलिए ग्रामीण बस्तियाँ मानव अधिवास सुविधाओं और पर्यावरण का पारंपारीक संबंध दर्शाती है (सिंह 1961) भारत में बस्तियों का ढांचा केन्द्रीकृत से परिक्षिप्त या बड़े गावों के लिए टोला आकार में विविधतापूर्ण है (Dey & Bhaduri 2016)। सघन अधिवास अधिकतर अत्यधिक उत्पादक जलोढ़ मैदान में पाए जाते हैं, जबकि बिखरी हुई बस्तियाँ आम तौर पर अत्यधिक (चरम) जलवायु क्षेत्र, पहाड़ी इलाके, घने जंगल, घास के मैदान, खराब कृषि भूमि, व्यापक खेती के क्षेत्र और ऐसे क्षेत्र जहाँ यह आवश्यक है कि, किसान को गाँव के बजाय अपनी कृषि भूमि पर रहना चाहिए में पाई जाती है (मजीद हुसैन 2018)। ग्रामीण अधिवासों का प्रकार एवं प्रतिरूप पूर्णतः क्षेत्र की भौतिक और सामाजिक-आर्थिक स्थिती पर निर्भरकरता है। इसलिए पृथ्वी की सतह पर हर जगह बस्तियों को समान नहीं देखा जाता है।

### साहित्य समीक्षा :

अधिवास भूगोल यह मानव भूगोल की एक मूलभूत ज्ञानशाखा है। आधुनिक अधिवास भूगोल का अध्ययन कई भूगोलवेत्ताओंने किया है। उसमें रिचथोफेन, विदाल-द-ब्लाश, डिमांजीयन, ब्रूनज, फिंच, ट्रिवार्था, डॉक्सियाडिस, डिकिनसन, डॉ. आर.एल.सिंह, आर.वाय.सिंह, जयराम यादव, ऐसे भूगोलवेत्ताओं का समावेश है। ब्लाश ने सघन एवं एकाकी अधिवासों की जानकारी दी है। 1909 में ब्योपेट ने युक्रेन, 1910 में चोर्ले ने फ्रान्स, 1993 में रॉबर्ट ग्रैण्डमेन ने जर्मनी के ग्रामीण अधिवासोका विस्तृत अध्ययन किया है।

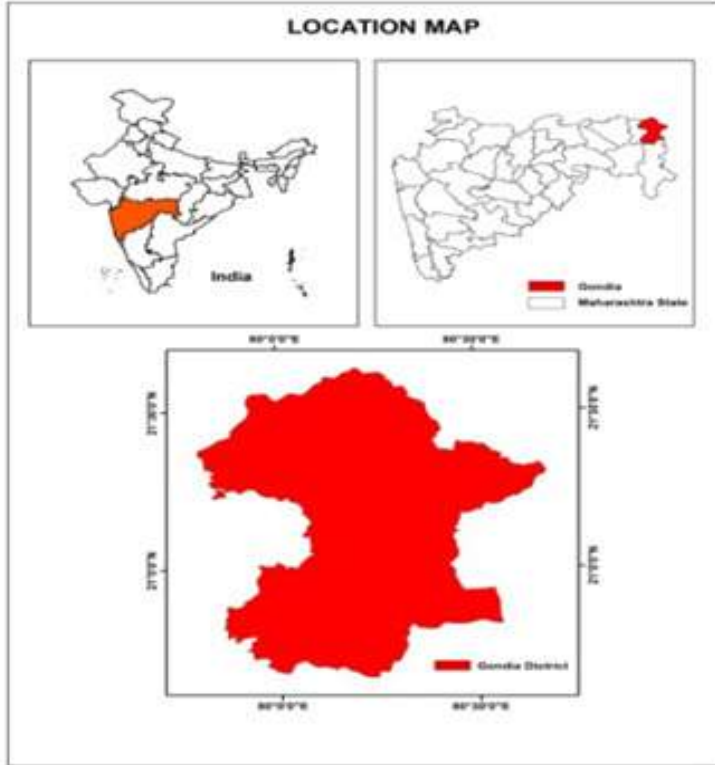
भारत में भौगोलिक अध्ययन की शुरुआत बहुत देरी से हुई। सर्वप्रथम स्पेट ने अपनी किताब 'भारतीय गांव' सी.डी.देशपांडे के सहयोग से लिखी। 1967 में आर.सिंह, एस.बोस, 1970 में एस.पी.सिंह, 1971 में टी.पी.पाटील इन्होंने अनेक ग्रामीण अधिवासों का अध्ययन किया। श्रीनिवास इनकी "India's Village" यह किताब बहुत ही महत्वपूर्ण है। अयोध्याप्रसाद ने छोटा नागपुर, एस.आर. चौधरी ने खानदेश के ग्रामीण अधिवासों का विस्तृत अध्ययन किया है। इस प्रकार कई विद्वानों ने ग्रामीण अधिवासों का अध्ययन किया है।

### अध्ययन क्षेत्र :

गोंदिया जिला महाराष्ट्र राज्य के विदर्भ प्रांत के पुरब में बसा है। 1 मई 1999 को भंडारा जिले का विभाजन हुआ और नवनिर्मित गोंदिया जिले की स्थापना हुई। गोंदिया जिले का अक्षारीय विस्तार 20035'



उत्तर से 21045' उत्तर और देशांतरीय विस्तार 79045' पुरब से 80045' पूरब है। गोंदिया जिले में आठ तहसिल है। वे गोंदिया, गोरेगांव, तिरोडा आमगाव, सालेकसा, देवरी, सडक/अर्जुनी एवं अर्जुनी/मोरेगांव इस प्रकार है। क्षेत्रफल की दृष्टि से देखा जाए तो देवरी सबसे बड़ा एवं आमगांव सबसे छोटा तहसिल है। गोंदिया जिले के पूरब दिशा में राजनांदगांव जिला (छ.ग), पश्चिम दिशा में भंडारा जिला, उत्तर दिशा में बालाघाट जिला (म.प्र.) एवं दक्षिण दिशा में गडचिरोली जिला (म.रा.) इनकी सिमाएं स्पर्श करती है।



Map No. 1

जिले का कुल भौगोलिक क्षेत्रफल 5234 चौ. कि.मी (2021 चौ.मैल) है। यह राज्य के क्षेत्रफल का 1.70 प्रतिशत है महाराष्ट्र राज्य के 36 जिलों में क्षेत्रफल की दृष्टि से गोंदिया जिले का 29 वा स्थान है। 2011 की जनगणना के आकड़ों के अनुसार जिले की जनसंख्या 1322507 है। यह राज्य के कुल जन संख्या का 1.18 प्रतिशत है। जनसंख्या के बारे में सोचा जाए तो विश्व की 47.87 प्रतिशत (2011), भारत की 68.84 प्रतिशत (2011), महाराष्ट्र की 54.78 प्रतिशत (2011) और गोंदिया जिले की 88.05 प्रतिशत जनसंख्या ग्रामीण भाग में रहती है। जिले में जनसंख्या घनता एक चौ.कि.मी. में 253 (2011) है। जबकि महाराष्ट्र राज्य के 36 जिलों की जनसंख्या के दृष्टि से जिले का स्थान 29 वा है और घनता की दृष्टि से 24 वा स्थान है। जिले में सबसे अधिक घनता गोंदिया तहसिल में 422 प्रति चौ.कि.मी. है। जबकि सबसे कम घनता 97 प्रति चौ.कि.मी. देवरी तहसिल में है। जिले में लिंग अनुपात 999 है। यह अनुपात ग्रामीण भाग में 1001 और शहरी भाग में 988 है। जिले में देवरी एवं गोरेगांव तहसिल में सबसे अधिक 1014 लिंग

अनुपात है। जिले में 13.31 प्रतिशत अनुसूचित जाती और 16.20 अनुसूचित जनजाति (2011) जनसंख्या है। जिले में जंगल क्षेत्र, 2715.48 चौ.कि.मी. है। यह जिले के कुछ भौगोलिक क्षेत्रफल का 51.88 प्रतिशत है। अध्ययन क्षेत्र में 942 (2011) ग्रामीण बस्तियाँ हैं।

### **उद्देश्य :**

वर्तमान अध्ययन का मुख्य उद्देश्य अध्ययन क्षेत्र को प्रभावित करने वाले भौगोलिक एवं सांस्कृतिक इकाई के अनुसार ग्रामीण अधिवासों के प्रकार और उनकी पहचान करना है।

### **परिकल्पना :**

गोंदिया जिले के ग्रामीण अधिवासों पर भौगोलिक एवं सांस्कृतिक इकाईयों का प्रभाव पड़ा है।

### **डेटाबेस एवं कार्यप्रणाली (Database and Methodology):**

वर्तमान अध्ययन मुख्य रूप से आंकड़ों के द्वितीयक स्रोत पर आधारित है। द्वितीयक डेटा गोंदिया जिले का सामाजिक आर्थिक समालोचन (सार) 2011, गोंदिया जिले की जनगणना पुस्तिका 2011, और Website से लिया गया है। गोंदिया जिले के तहसिलों को ग्रामीण बस्ती के स्थानिक विश्लेषण के लिए एक इकाई के रूप में लिया गया है। संदर्भ प्रयोजन के लिए कुछ किताबों, शोध पत्रों, Website के लेखों का भी उपयोग किया गया है। विश्लेषित डेटा को कोरोप्लेथ मानचित्र के साथ विश्लेषित किया गया है। ग्रामीण अधिवास प्रकारों के मापन की मात्रात्मक विधि का उपयोग किया गया है। जिसमें ग्रामीण अधिवासों के संकेन्द्रण सूचकांक मापन हेतु बर्नार्ड (1931) द्वारा प्रस्तावित सूत्र का उपयोग किया गया है।

$$S \times M$$

$$K =$$

$$N^2$$

**Where,**

K=Degree of Concentration

S= Area of the Tahsil

M= Total Number of House in the Tahsil

N = Number of Settlement Groups in the Tahsil

### **गोंदिया जिले में ग्रामीण अधिवासों के प्रकार (Types of Rural Settlement in Gondia District):**

ग्रामीण अधिवासों को उनकी स्थिति, आकारिकी (Morphology) समूहन तथा गृह-अन्तरण आदि के आधार पर विभिन्न वर्गों में विभक्त किया जाता है, अर्थात् ये किसी बस्ती के भवनों के बीच रिक्त स्थानों के द्योतक होते हैं। अतः गृहों की दूरी व उनकी सघनता अधिवासों के प्रकारों में भेद का प्रमुख आधार माना जा सकता है। इस आधार से ग्रामीण बस्तियों के चार प्रकार/भेद होते हैं।

#### **1. एकाकी या प्रकीर्ण (Dispersed Settlement)**

ऐसे अधिवासों में मकानों का बसाव बिखरा हुआ मिलता है। इस प्रकार की बस्तियां सामान्यतः खेतों के द्वारा एक-दूसरे से अलग होती हैं। इन मकानों के मध्य की भूमि पर कृषि कार्य भी होता है। बिखरी हुई बस्तियों को पृथक बस्तियों के रूप में भी जाना जाता है। छोटा आकार, जिसमें एक घर से लेकर घरों का एक छोटा समूह इस बस्ती की एक विशेषता है। गोंदिया जिले में इस प्रकार की बस्तियां ज्यादातर तिरोडा, गोरेगांव, आमगांव, सालेकसा, सडक/अर्जुनी, अर्जुनी/मोर., देवरी तहसिलों में देखी जाती हैं। इस समूह की श्रेणी का संकेन्द्रण सूचकांक 1500 से नीचे है। इस प्रकार की बस्तियों के निर्माण एवं विकास के कारक निम्न हैं। जिसमें बिहड़ स्थलाकृति, खड़ी ढलान, कम भुजल स्तर और कम गुणवत्ता वाली मिट्टी आदि हैं।

ये बस्तियां आकार में छोटी तथा जंगल तथा पहाड़ी क्षेत्रों में बिखरी हुई हैं। बीहड़ स्थलाकृति (Rugged topography), पहाड़ी और जंगल क्षेत्र की वजह से कनेक्टीविटी कम है। खासकर जिले की पूरब दिशा और दक्षिण दिशा। पूरब दिशा में सालेकसा तहसिल है। जो पूर्णतः पहाड़ी जंगल से व्याप्त है। देवरी तहसिल जिले के दक्षिण दिशा में है। इस तहसिल में भी पहाड़ और जंगल हैं। इसी वजह से कनेक्टीविटी कम है। संपूर्ण गोंदिया जिले का विचार किया जाए तो यह जिला पिछड़ा आदिवासी जिला है, यहाँ की भूमि गुणवत्ता भी कम, भू-जल स्तर नीचे है, जिले में ऊपरी तहसिलों में से कुछ जैसे-आमगांव, सडक/अर्जुनी, अर्जुनी/मोर। सालेकसा इन तहसिलों में तालाबों द्वारा जल सिंचाई होने की वजह से खेती सिंचित है। इस क्षेत्र में घर एक दूसरे से बहुत दूर हैं। बस्तियाँ छोटी एवं दूर हैं। अधिकांश हिस्सा आदिवासी है। इन बस्तियों में प्राथमिक व्यवसाय; जैसे, कृषि, पशुपालन, खोदकाम, वनउपज इकट्ठा करना; जैसे- मोहफूल, आवला, हिरडा, बेहड़ा, शहद, चार ऐसे अन्य कई प्रकार की वनऔषधी और फलफूल इकट्ठा करके गांव-गांव में जाकर बेचना जैसी आर्थिक गतिविधियोंका बोलबाला है। कृषक कृषि कार्यस्थल में घर बनाकर रहते हैं। इसलिए यहाँ एकाकी बस्तिया पाई जाती हैं।

**TableNo-1 Gondia District : Types of Settlement 2011  
(Based on Bernards Method of degree of concentration)**

Sr. No.	Tahsil	Area (Sq.Km.)	No.of Village	Number of House hold	N	Index (K)	Type
1.	Tirora	607.24	123	33865	15129	1359	D
2	Goregaon	484.42	99	28046	9801	1386	D
3	Gondia	612.19	147	55373	21609	1569	SP
4	Amgaon	333.32	81	28404	6561	1443	D
5	Salekasa	450.88	91	20026	8281	1090	D
6	Sadak Arjuni	651.42	108	26543	11664	1482	D
7	Arjuni/Morgaon	988.21	159	34856	25281	1362	D
8	Deori	1040.23	134	24944	17956	1445	D

(Source –Computed by Researcher with help of census data 2011)

(Note–C-Compact, SC-Semi Compact, SP-Semi Sprinkled & D- Dispersed)

**Table No. 2 Gondia District: Types of Settlement 2011  
(Based on Bernards method of degree of concerntation)**

Sr. No.	Types of Settlement	Range (Index)	Tahsil	Total No. of Settlement	Total Area (%)
1.	Compact (C)	Above 4500	—	—	—
2.	Semi Compact (SC)	3000-4500	—	—	—
3.	Semi Sprinkled (SP)	1500-3000	Gondia	147	11.85
4.	Dispersed (D)	Bellow 1500	Goregaon, Amgaon, Tirora, Salekasa, Deori, Sa dak/Arjuni, Arjuni/Mogaon	795	88.15



## अपखंडित अधिवास :

जिस ग्रामीण अधिवास में गांव की सीमा के भीतर ही बसाव बिखरा हुआ मिलता है अर्थात गांव के घर एक-दूसरे से थोड़ी दूरी पर बने होते हैं अथवा छोटे-छोटे पुरवे या नगले थोड़ी-थोड़ी दूरी पर बसे होते हैं तथा कोई भी केन्द्रीय ग्राम नहीं होता उसे अपखंडित बसाव कहा जाता है। इस प्रकार के अधिवास को एकाकी अधिवास नहीं कहा जा सकता। क्योंकि अमेरिकन या यूरोपीय 'फार्मगृह' के समान विपरीत इन छोटी-छोटी बस्तियों में एक ही परिवार का होना आवश्यक नहीं है। दूसरे इनमें सामाजिक संघटन, श्रम विभाजन एवं सामुदायिक भावना पाई जाती है। प्रो. सिंह ने ऐसी बस्तियों को पुरवो का अधिवास या

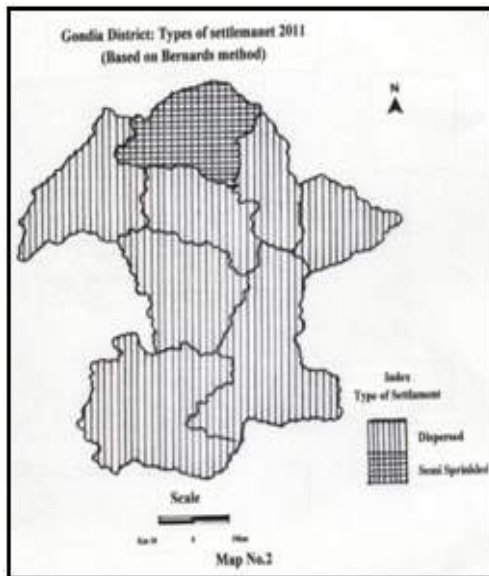
अपखंडित (Fragmented) अधिवास कहा है। यह बस्तियां आकार में छोटी होती हैं एवं कृषि योग्य भूमि के निकट होती है। इन बस्तियों का संकेद्रण सूचकांक 1500 से 3000 होता है। मुख्य रूप से इस प्रकार की बस्ती का वितरण अध्ययन क्षेत्र के गोंदिया तहसिल में पाया जाता है। इस प्रकार की बस्तियाँ गोंदिया शहर जो कि जिला मुख्यालय है के आसपास के क्षेत्र में पाई जाती है। बस्ती का यह प्रकार मुख्य रूप से गोंदिया तहसिल के कृषि योग्य भूमि के पास पाया जाता है। गोंदिया तहसिल में मुख्य रूप से राईस मिल ज्यादा होने की वजह से भी इस प्रकार की बस्तीया यहाँ पाई जाती है। संपूर्ण गोंदिया जिला कृषि प्रदान है। और यहाँ धान/चावल का उत्पादन अधिक मात्रा में होने की वजह से राईस मिल उद्योग को बढ़ावा मिलने की वजह से भी यह बस्तीया यहाँ पाई जाती हैं। कृषक

कृषी कार्यस्थल में ही घर (निवास स्थान) बनाकर रहते है। और इनकी छोटी-छोटी बस्तीया होती है। गोंदिया तहसिल में जिला मुख्यालय होने की वजह से अन्य व्यवसाय भी यहाँ थोड़ी-थोड़ी मात्रा में पनम (फलफुल) रहे है। इन बस्तियों की प्रमुख विशेषतः यह है कि इनमें गरीबों के घर अधिक मात्रा में पाये जाते हैं और पूरे क्षेत्र में फैले है। तथा सड़को की गुणवत्ता कम है एवं कनेक्टिविटी भी कम है।

## अर्ध-सघन अधिवास :

अर्ध-सघन अधिवास में प्रकीर्ण एवं सघन अधिवासों के बीच की अवस्था से सम्बन्धित विशेषताओं का विकास होता है। जो समाजोन्मुखी तथा समाज विमुखी शक्तियों की अन्योन्य क्रिया का प्रतिफल माना जाता है। ऐसी बस्तियों में आवास बहुत सघन रूप से जुड़े नहीं होते और एक साथ गुंथे हुए होते हैं। यह एक सामान्य बात है (Mandal & Roy 2020)। ऐसी बस्तियों की विशेषता यह है कि छोटी लेकीन सघन होती है। इस अधिवास के मूल केन्द्र (Nucleus) पर बसे प्रमुख अधिवास के अतिरिक्त गांव की सीमा के भीतर कुछ-कुछ दूरी पर एक या अनेक पूरवे (Hemlets) बसे होते हैं। इन अधिवासों का संकेन्द्रण सूचकांक/एकाग्रता मान 3000 से 4500 तक होता है। गोंदिया जिले में किसी भी तहसिल में यह प्रकार देखने को नहीं मिलता। क्योंकि यहाँ बड़े कृषक नहीं और बड़ी मात्रा में व्यापारी कृषि नहीं की जाती।

**सघन या पुंजीत अधिवास :** ऐसी बस्तियों में मकान एक दुसरे के पास बनाये जाते है। इनका विकास नदी



घाटियों तथा उपजाऊ मैदानों में होता है। यहाँ रहने वाले लोगों का व्यवसाय समान होता है। तथा यह समुदाय समूह बनाकर रहते हैं। इस गुच्छित (Clustered) प्रकार की बस्तियों में ग्रामीण घरों के संहत (Dense) खण्ड पाये जाते हैं। इन बस्तियों में सामान्य क्षेत्र स्पष्ट रूप से निकटवर्ती खेतों, घरों (बाड़ों) तथा चरागाहों से अलग होता है। इस प्रकार की बस्तियाँ अत्यंत उपजाऊ जलोढ मैदानी (Alluvial Plain) क्षेत्रों में पाई जाती हैं। सघन अधिवास स्थायी कृषि उत्पाद भूमि और अनुकूल जलवायु परिस्थितियों का उत्पाद है (Patil, 2019)। अध्ययन क्षेत्र में इस प्रकार की भौगोलिक परिस्थिति उपलब्ध नहीं होने की वजह से ग्रामीण अधिवास का यह प्रकार देखने नहीं मिलता।

### परिणाम

बर्नार्ड (1931) विधि द्वारा सरल सूत्र का उपयोग करके संकेन्द्रण सूचकांक की गणना की गई है। आर. एल.सिंह ने ग्रामीण अधिवासों के 1) एकाकी 2) अपखंडीत 3) अर्ध-सघन 4) सघन या पूंजीत यह चार प्रकार बताये हैं। उनमें से बर्नार्ड के संकेन्द्रण सूचकांक के अनुसार गोंदिया जिले में 1) एकाकी 2) अपखंडीत ये दो ही प्रकार दिखाई देते हैं। अध्ययन क्षेत्र का संकेन्द्रण सूचकांक तालीका संख्या 2 और अधिवासों के प्रकार मानचित्र संख्या 2 में दर्शाये गए हैं। यही मुख्य परिणाम अध्ययन क्षेत्र में दिखाई देते हैं।

### सुझाव (Suggestion):

अध्ययन क्षेत्र ग्रामीण और कृषि प्रधान होने के बावजूद भी कुछ सुविधाओं के अभाव में विकास दिखाई नहीं देता। अध्ययन क्षेत्र की ग्रामीण क्षेत्र और कृषि क्षेत्र का विकास होना जरूरी है। तभी यहाँ की कृषकों की आर्थिक समस्या दूर होगी। पक्की सड़कें हर ग्रामीण बस्ती एवं कृषि कार्यस्थल तक बनना जरूरी है। कृषि आधारित व्यवसाय को शुरू करना जरूरी है; जैसे, अध्ययन क्षेत्र की मुख्य फसल चावल है। यहाँ राईस मिल इन्डस्ट्रीज है, चावल से व्यावसायिक दृष्टि से अन्य उत्पाद बनाने का उद्योग निर्माण होना जरूरी है। पहाड़ी क्षेत्रों का विकास होना जरूरी है। जंगलों में आवश्यक फल एवं औषधि वृक्ष लगाना चाहिये। जिन ग्रामीण बस्तियों में जल सिंचाई की सुविधा नहीं है वहाँ के कृषकों को आर्थिक सहायता देना चाहिए ताकि वह अपने कृषि कार्यस्थल में कुआँ एवं बोरवेल का खोदकाम कर, जल स्रोत निर्माण कर सके। सरकार की जो कई अलग-अलग सुविधाएँ हैं उनकी जानकारी आज भी ग्रामीण अधिवासों तक नहीं पहुँची है। जब कि वह जानकारी पहुँचना जरूरी है। इसकी जवाबदारी सरकार ने बस्तियों के प्रतिष्ठित, सामाजिक व्यक्तियों को देनी चाहिए और उन व्यक्तियों ने वह पूरी जानकारी ग्रामीण जनता तक पहुँचाना चाहिए। ऐसी सुविधाओं का उपयोग करने पर, गोंदिया जिले में अर्द्धसघन और सघन अधिवासों के यह दो प्रकार दिखाई नहीं देते वे अधिवासों के प्रकार ऊपर दिये गये सुझाव से शायद भविष्य में दिखाई दे सकते हैं।

### निष्कर्ष :

शोध कार्य का समग्र विश्लेषण इंगित करता है कि अध्ययन क्षेत्र की बस्तियों के विकास में भौगोलिक एवं सांस्कृतिक इकाई का प्रभाव दिखता है। भौगोलिक एवं सांस्कृतिक इकाईयों के प्रभाव से अध्ययन क्षेत्र में अधिवासों के एकाकी और अपखंडित यह केवल दो ही प्रकार हैं। अध्ययन क्षेत्र के गोंदिया तहसिल में अपखंडित अधिवास और तिरोडा, आमगाव, गोरेगाव, अर्जुनी/मोर., सड़क अर्जुनी, देवरी एवं सालेकसा इन तहसिलों में एकाकी अधिवास है।

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## SPORTS AND EMPLOYMENT: OPPORTUNITIES AND GROWTH IN CAREER

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### Abstract

Employment is the continuous employment of the country's current workforce in economic activity. Employment, working and employment indicate employment. Employment is an important concept for both the labor market and the economy in general. Sports the executives is an interdisciplinary field, drawing on parts of advertising, law, money and management. A particular graduate degree assists understudies with creating fundamental abilities in business organization, financial matters, account, law, brain research and showcasing – all with a particular spotlight on the games area. It is vital satisfactory (preparing) of representatives in sport (sports organization) to stay up with the improvement of data advances and how to take full advantage of the advancement that we permit new advances. With the coming and improvement of data innovation in our nation at home and abroad are progressively the inquiry is skill sports organization (sports the executives) to satisfactorily and appropriately do their positions and how to save time and assets of their association. The vast majority of the games association tolerating the advancement of new innovation learning, create and receive new techniques (data and correspondence innovation) that will assist them with improving their items and benefits and carry them nearer to their clients.

### Introduction

An overview of sports associations in the early 21st century involves the use of methods and methodologies that are evident in most business, government and philanthropic organizations today. Game executives participate in necessary arrangements, oversee large numbers of paid and voluntary employees, manage billions of dollars in broadcast contracts



deal with state aid from major competitors that in some cases require multiple normal compensations, and work deep inside: coordinates global organizations of global gambling federations, public gaming associations, government agencies, media companies, sponsors and local associations. Students seeking a career as a gaming administrator must gain an understanding of the unique highlights of the game and its joint ventures, the operating environment of sports federations and the various gaming associations that operate in the public, philanthropic and professional spheres. of the gaming industry. The rest of the episode is given to discussing those priorities and covers the exceptional parts of the board. The game is used by a large number of people all over the planet, played or watched by the majority of the entire population, and has grown from a novice to a huge industry at the world or expert level. The development and professionalism of the game has led to changes in the use, creation and management of games and associations at all levels of the game.

### Sports and Employment

Employment is the continuous employment of the country's current workforce in economic activity. Employment, working and employment indicate employment (Kamaç, 2016). Employment is an important concept for both the labor market and the economy in general. Employment has two main purposes: an economic purpose and a social purpose. The financial goal is to organize and increase production. To achieve financial goals, it is necessary to succeed in social goals. In this regard, the social goals of employment are to find work for all who want work, increase productivity, ensure labor peace and harmonize the demand and supply of work (Murat, 2007). Youth employment is very important for sustainable economic and social structure and social well-being. In this sense, countries mainly design regulations that enable young people to participate in the labor market, take steps to create a relationship between education and employment, and often develop active employment policies to ensure youth employment (Kılıç and Bülbül, 2012). There is no linear relationship between youth unemployment and the level of economic development. The fact that unemployment affects the young population of continental European countries most clearly shows that such a relationship does not exist between youth unemployment and the level of development of the country. However, there are differences in the causes of youth unemployment. Although the cause of youth unemployment in developed countries is mainly related to population distribution and development, in developing countries the main reasons are insufficient educational level and

corresponding, as they work in cooperative energy, not avoided. No craftsmanship by science, or science with creation, the portion of workmanship. Human asset the executives in sport is another hypothetical, logical and realistic methodology, which from one perspective, alludes to the administration of competitors by mentors, group of specialists and sports researchers, then again, the productive and viable administration of the whole game association by control in sport, sports supervisors, promoting administrators and sports volunteers. The executives of sports includes the investigation of confused and demonstrated information on how a games association accomplishes its objectives, obtaining, dispersing and the utilization of restricted human, material, data and monetary wellsprings of its prosperity. Sports Management as the workmanship and art observational, unstructured experience of skilled administrators of individual competitors, groups and clubs arose with the presence of the principal pro athletics association. The presence of a methodical, logical organized information on sports the board is associated with the development of professionalization of game and its standards assurance - administration market economy, and the rise of the executives science, first in the benefit area, corporate business, and afterward, and it's spreading to the area of non-benefit public and private area. Understudies keen on both business and sports can track down their optimal program with Sports Management. This degree can open up a wide range of open positions inside the games business. It can situate understudies to become specialists, group promoting chiefs, athletic division directors, mentors, wellness focus administrators, group supervisors and the sky is the limit from there.

Understudies can likewise work at various levels, from nearby games and lower levels to territorial and public game affiliations, giving a lot of development freedoms to those intrigued. A Sports Management degree can likewise help graduates discover positions at amusement focuses, recreational areas, and other related associations. It's moreover customary for understudies to be enthusiastic about the benefits and weaknesses of Sports Management at whatever point they have graduated and are looking for a wonderful calling. Advantages to this degree.

### Occupation Flexibility

As we referred to above, there are various occupation choices for Sports Management. On the off chance that you are keen on local area authority and public diversion the executives for neighborhood parks, Sports Management can help you. On the off chance that you need to fill in



Vidyapeetha as a specialist for players or a PR administrator for a group or game in emergency, this degree is phenomenal arrangement. In the event that you have your eyes set in turning into a group executive or chief, a Sports Management degree is a vital advance in arriving. The program upholds so various profession ways that it's a solid match for a wide range of interests.

### **Travel and Experience**

Sports Management can be entertaining. In the event that you like travel, investigating new areas, and visiting new urban communities, a Sports Management profession could be an incredible decision for you. Numerous vocations in the games business include going all throughout the planet for different occasions and occupation duties. It very well may be a little glimpse of heaven for understudies who need a functioning way of life that remunerates their hunger for new experiences. Goodness, and in the event that you're not actually the voyaging sort, there are still a lot of chances for overseeing sports settings and different places that include altogether less travel.

### **You Can Give Back to Your Community**

Rewarding your local area is simple with a Sports Management degree. This program gives the abilities you need to a wide range of volunteer exercises or philanthropic endeavors to energize actual wellness, make beginner groups, and substantially more. There are a couple of things, nonetheless, you should remember while seeking after this kind of degree. To begin with, in contrast to certain ventures, it can require critical exertion to arrive at center and more elevated level administration positions. Understudies ought not anticipate getting an administration position in the games business just after graduation (even those with MBAs). Second, pay can shift significantly for Sports Management occupations relying upon the position, so it tends to be hard to rely on a specific compensation. A few positions may have unpredictable hours or are occasional dependent on the kind of game. It isn't for everybody, except it very well may be exactly the thing you're searching for.

### **Career opportunities In Sports Management**

A Sports Management certificate shows understudies abilities and ideas identified with Management, Finance, Marketing, and Law identified with the games business. Sports Management classes will assist you with figuring out how to outline the business side of a games association with the utilization of the most recent patterns and advancements. You'll build up an expansive arrangement of abilities, yet the absolute most significant are basic



reasoning, critical thinking, correspondence, and thoughtfulness regarding subtleties. These will prove to be useful in any circumstance. Regardless of whether you're arranging a sponsorship contract for a nearby occasion or a multimillion-dollar bargain for a player or group you address, the capacities you create during a Sports Management degree are fundamental.

### Conclusion

It is vital satisfactory (preparing) of representatives in sport (sports organization) to stay up with the improvement of data advances and how to take full advantage of the advancement that we permit new advances. With the coming and improvement of data innovation in our nation at home and abroad are progressively the inquiry is skill sports organization (sports the executives) to satisfactorily and appropriately do their positions and how to save time and assets of their association. The vast majority of the games association tolerating the advancement of new innovation learning, create and receive new techniques (data and correspondence innovation) that will assist them with improving their items and benefits and carry them nearer to their clients. To accomplish the greatest in the game, it is important to make, adjust, arrange, and consistently to execute anongoing and last readiness of world class competitors, and alongside that, work on finding themost reasonable authoritative structures, techniques and substance of work in getting ready eliteathletes for the most elevated level agent donning accomplishments. Contemporary expressions association in the present powerful climate described by continuous changes andnumerous contenders can not make due without the executives.

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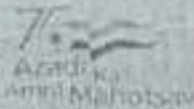
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has actively participated in two days ICSSR sponsored International Conference on "Importance  
of Sports, Physical Education & Sports Science" organized by Chintamani Mahavidyalaya,  
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He/She has presented a research paper entitled Sports And Employment:  
Opportunities And Growth In Career

We appreciate your valuable participation.

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### Studies on Zooplankton Composition and $\alpha$ -Diversity Indices at Thanegaon Reservoir, Maharashtra, India

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**Abstract:** Present study was undertaken to investigate the zooplankton diversity of Thanegaon reservoir located in Arvi tehsil of Wardha district in the Indian state of Maharashtra. Samples were collected on the monthly basis for six months during January 2020 to June 2020. In this reservoir we have studied the four major groups of zooplankton: Rotifera, Copepoda, Cladocera and Ostracoda. Rotifera was found to be the dominant group during the entire study period. The study revealed a total 34 species of zooplanktons during the entire study period, of which 19 species belong to Rotifera, 8 belong to Cladocera, 5 belong to Copepoda and 2 belong to Ostracoda. Statistical analysis of data was done by using  $\alpha$ -diversity indices. Shannon-Wiener index 4.50 to 4.72, Simpson index 0.034 to 0.043 indicated the diverse nature of the zooplankton community. Margalef richness index 5.86 to 6.23 and Menhinick index 2.40 to 2.92 indicated the good species richness. Equitability index was in the range from 0.92 to 0.95 showing much evenness of species during the study. Relative biovolume % of zooplankton and composition in terms of density was also calculated. It showed the maximum number of species during the months of January, March and June.

**Keywords:** Thanegaon reservoir, Zooplankton, Rotifera,  $\alpha$ -Diversity indices, Shannon-Wiener index, Simpson index

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### Introduction

Thanegaon reservoir (Wardha district, Maharashtra, India) is a freshwater natural lake which is filled to its maximum capacity throughout the year. Thus, this reservoir serves as a source of domestic and agricultural water for nearby areas. Thus, it becomes necessary to keep the quality of water good for these purposes. Study of

zooplankton composition is very important due to their role in the food web by linking the producers with consumers in the Lake Ecosystem and prediction of primary productivity and aquatic pollution (Nimbalkar *et al.*, 2013; Ghosh and Biswas, 2015). Many species of the zooplanktons are sensitive to pollution and thus act as a



Fig.1: Google map image of Thanegaon Reservoir.

bioindicator to monitor the quality of water (Ferdous and Muktedir, 2009; Sivalingam *et al.*, 2013). Zooplankton community constitutes the faunal composition of water bodies which are sensitive to water quality parameters and aquatic pollution (Schindler, 1987; Jose and Senthil Kumar, 2015). Thus the aim of the present investigation was to study the zooplankton composition and structure, density, dominance and abundance along with  $\alpha$ -diversity indices in the Thanegaon reservoir.

### Materials and Methods

Thanegaon reservoir (Fig. 1) is a freshwater natural lake situated at 21° 08' 48" N Latitude and 78° 28' 41" E Longitude at the elevation of 484 Mts. near Sirsi and Kharas Khanda, approximately 10 kilometers away from Karanja (Ghadge) in Wardha district, Maharashtra, India. Collection of sample was done on monthly basis for 6 months from January 2020 to June, 2020 around 7.00 to 7.30 a.m. from selected site by filtering 50 liters of the lake water by using a standard 55  $\mu$ m pore size bolting nylon plankton net. All specimens collected were preserved in 4% formalin soon after collection. Identification of the specimens was performed according to Kolisko (1974); Koste (1978); Ward and Whipple (1959); Mizuno (1964); Mizuno and Takahashi (1991), Battish (1992) and Dhanapathi (2003). Six indices were used to estimate biodiversity and species richness. Species diversity index was calculated based on

Simpson (1949) and Shannon-Weiner (1949); richness index was adopted by Margalef (1951) and Menhinick (1964) and equitability Index by Magurran (1988). Dominance index or Simpson's index of diversity was calculated using formula 1-Simpson index. The percentage relative abundance and density of the specimens was estimated by direct count.

### Statistical Analysis:

Statistical analysis was carried out using Statistical Package for Social Sciences (SPSS 10.0). Graphs were drawn using Microsoft Excel Software.

### Results and Discussion

Zooplankton diversity and  $\alpha$ -diversity indices play key roles in evaluating the trophic status of lakes and suitability of water for domestic purposes and irrigation. In the present study, zooplankton diversity belonging to Rotifera, Cladocera, Copepoda and Ostracoda have been undertaken. In the present study 19 species of Rotifera including 6 families and 9 genera, 8 species of Cladocera including 5 families and 8 genera, 5 species of Copepoda including 3 families and 5 genera and 2 species belonging to Ostracoda were noted. Overall 34 species of zooplankton were recorded (Table 1). The most abundant taxonomic group recorded during the study was the rotifer. Pereira *et al.* (2002) noted the rotifers as a most abundant group. Main abundant species of rotifer observed by them were *Keratella quadrata*, *K. cochlearis*,



Table 1: Zooplankton species identified in Thanegaon reservoir

<b>Phylum: Rotifera</b>			
S. No.	Class and Order	Family	Genus and Species
1.	Class: Monogonata Order : Ploima	Brachionidae	<i>Brachionus quadridentatus</i> Var. <i>Entzi</i>
2.			<i>Brachionus falcatus</i>
3.			<i>Brachionus forficula</i>
4.			<i>Brachionus diversicornis</i>
5.			<i>Brachionus calyciflorus</i> Var. <i>Hymani</i>
6.			<i>Brachionus platulus</i>
7.			<i>Brachionus bidentata</i>
8.			<i>Brachionus rubens</i>
9.			<i>Brachionus ureceolaris</i>
10.			<i>Keratella vulga</i>
11.			<i>Keratella tropica</i> (Apstein)
12.			<i>Platyias species</i>
13.		Colurellidae	<i>Colurella adriatica</i>
14.		Lecanidae	<i>Lecane arculata</i>
15.			<i>Monostyla bulla</i>
16.		Asplanchnidae	<i>Asplanchna intermedia</i>
17.		Gastropodidae	<i>Ascomorpha species</i>
18.	Class: Monogonata Order: Flosculariaceae	Filinidae	<i>Filinia longiseta</i>
19.			<i>Filinia apoloensis</i>
<b>Phylum: Arthropoda</b>			
20.	Subphylum: Crustacea	Sididae	<i>Diaphanasoma</i>
21.	Class: Branchiopoda Order: Cladocera	Moinidae	<i>Moinodaphnia</i> (Herrick, 1887)
22.			<i>Moina macrura</i>
23.		Daphnidae	<i>Daphnia longispina</i>
24.			<i>Cereodaphnia reticulata</i>
25.		Bosminidae	<i>Bosmina longirostris</i>
26.		Chydoridae	<i>Chydorus sphaericus</i>
27.			<i>Alona rectangula</i>
28.		Class: Hexanauplia Subclass: Copepoda Order: Cyclopoida	Cyclopidae
29.	<i>Cyclops viridis</i>		
30.	Subclass: Copepoda Order: Calanoida	Diaptomidae	<i>Skistodiaptomus</i>
31.			<i>Diaptomus</i>
32.	Class: Hexanauplia Subclass: Copepoda	Canthocamptidae	<i>Nauplius</i>
33.	Subclass: Ostracoda Order: Podocopida	Cypridae	<i>Cyprretta frontanalis</i>
34.			<i>Cypridopsis helvetica</i>

*Polyarthra vulgaris*, *Filinia terminalis* and *Hexarthra mira*. Picapedra *et al.* (2020) have identified a total of 115 taxa of zooplanktons. Rotifers were the richest group. However, the copepods were the most abundant. They have reported the inter-annual changes in zooplankton species composition from large daphnids and calanoid copepods to small cladocerans (e.g. bosminids) and generalist rotifers. Zooplankton were present in the following order of dominance;

Cladocera > Rotifera > Copepoda > Ostracoda. The zooplankton community structure showed a mixed composition of mesotrophic to eutrophic species. Among the zooplanktons, the population of cladocera was rich in density and poor in species diversity. Rotifers are the dominant in the eutrophic lakes which are indicators of eutrophication and *Brachionus* species are indicators of eutrophic conditions (Aboul-Ezz *et al.*, 1996; Baloch and Soomro, 2004; Ceirans,

2007). *Moina macrura*, *Bosmina longirostris*, *Chydorus sphaericus*, *Alona rectangula* were the dominant cladocerans in the Thanegaon reservoir. Abundance of the rotifer species like *Brachionus*, *Lecane*, *Filinia* and *Keratella* indicates the mesotrophic and semi polluted water and enrichment of nutrients in the reservoir.

Khan *et al.* (2016) have noted a total of 22 species of zooplanktons where rotifers were dominant and were represented by 15 species whereas cladocera and copepoda were represented by three species each and Ostracoda was represented by one species. 15 species of rotifers noted by them were *Asplanchna priodonta*, *Brachionus bidentata*, *Brachionus calyciflorus*, *Brachionus falcatus*, *Brachionus urceolaris*, *Cephalodella gibba*, *Habrotrocha bidens*, *Keratella tropica*, *Lecane luna*, *Monostyla bulla*, *Mytilina ventralis*, *Mytilini acanthophora*, *Platylas quadricornis*, *Rotifer tardus*, and *Filinia longiseta*. Cladocera was represented by *Ceriodaphnia cornuta*, *Chydorus sphaericus*, *Moina brachiata* and among Copepoda, *Heliodiaptomus viduus*, *Mesocyclops leuckarti*, *Tropocyclops prasinus* were noted by them and Ostracoda was represented by *Hemicypris fossiculata*. They noted the seasonal variation in zooplanktons and found maximum number of species during summer and the minimum number of species in rainy season. Density was also recorded high during the summer as compared to rainy season. Zooplankton density and relative biovolume is represented in the Figure 2 and 3, respectively. Relative biovolume, density and composition of the zooplankton community is strongly dependent on the season. Relative biovolume of cladocerans was maximum during winter season in the month of January (46.38%) while it was minimum at the end of the summer season in the month of June (40%). Maximum number of zooplankton (Org/lit) was recorded during the winter in the month of January was 166 whereas minimum number of zooplankton 105 was noted in the month of June.

Shukla *et al.* (2012) noted the zooplankton population (Org/L) during different seasons and

found maximum number of zooplankton as  $285 \pm 18.68$ /lit during pre-monsoon whereas minimum number recorded was  $215 \pm 27.33$ /lit during monsoon season. The observed Cladocerans species by them were *Bosmina longirostris*, *Cerioaphnia*, *Cypris*, *Daphnia*, *Moina* and *Macrothris*. Among the copepods they noted *Diaptomus*, *Heliodiaptomus*, *Macrocyclops*, *Nauplius* and *Vidumus*. Rotifers noted by them were *Slanchna*, *Brachionus*, *Distimus*, *Filinia*, *Keratella*, *Nothoica* and *Flurcularia*. Among protozoans they reported *Amoeba*, *Acrella*, *Centroysis* and *Paramecium*. Dagne *et al.* (2008) have noted the extremely high variation in abundance of zooplanktons which was ranging from 2 to 1000+ individuals per litre and correlated abundance of crustaceans with the increased phytoplankton production at the onset of rainy season. Rotifer biovolume was observed maximum in the month of January (28.91%) and it was found to be minimum in the month of May (22.42%) in summer season. Copepods showed their maximum biovolume in the month of February (23.56%). However, rapid decline in their biovolume was observed in the month of March (15.97%). Ostracods showed their maximum biovolume at the end of the summer in the month of June (9.52%) and minimum at the end of winter season in the month of March (5.55%) (Fig. 3). Annalakshmi and Amsath (2012) have recorded 45 species of zooplanktons in the Cauvery. They observed rotifera species as dominant (34.97%); followed by Cladocera (29.92%), Copepoda (18.27%), Protozoa (12.2%) and Ostracoda (8.72%), however, Dorak *et al.* (2014) have noted the Copepoda as a most abundant taxa (53%), followed by Cladocera (33%), and Rotifera (14%).

Values for  $\alpha$ -biodiversity indices that are Simpson index, Dominance index, Shannon-wiener index, Menhinick index, Margalef richness index and Equitability index are represented in the Table 2. Simpson index was found as low as 0.034 during June and was maximum during 0.043 in summer in the month of April while Dominance index was high as 0.96 revealed the rich diversity of species in this reservoir. Shannon-Wiener index

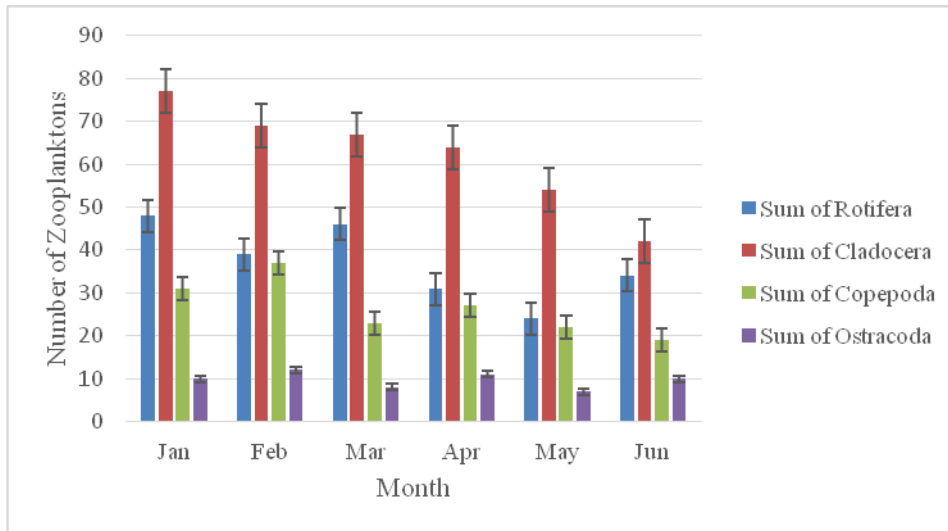


Fig. 2: Composition of zooplanktons in terms of density (Organisms lit<sup>-1</sup>).

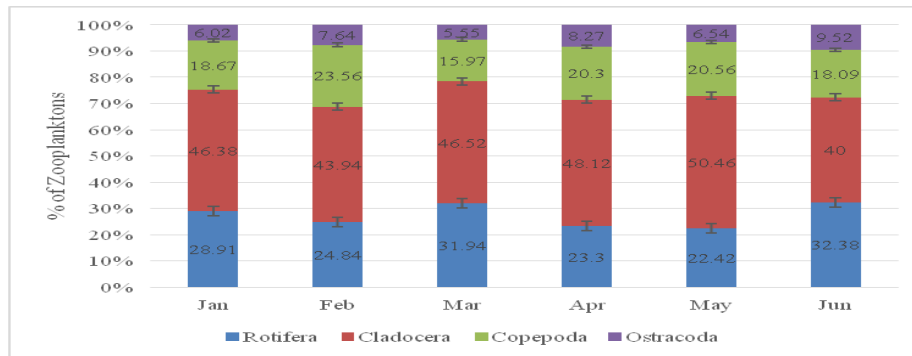


Fig. 3: Relative Biovolume (%) of Zooplanktons.

Table 2: Zooplankton community structure and  $\alpha$ - biodiversity indices of Thanegaon reservoir

Month	Simpson Index	Dominance Index	Shanon-Wiener Index	Menhinick index	Margalef Richness Index	Equitability Index
Jan	0.037	0.96	4.71	2.4	5.86	0.95
Feb	0.039	0.96	4.66	2.74	5.93	0.94
Mar	0.036	0.96	4.72	2.58	6.03	0.95
Apr	0.04	0.95	4.6	2.68	6.13	0.92
May	0.043	0.95	4.5	2.8	5.99	0.92
Jun	0.034	0.96	4.69	2.92	6.23	0.95

values were in the range of 4.50 to 4.72, Menhinick indexes were in the range of 2.40 to 2.92 and Margalef richness index values were in the range of 5.86 to 6.23 confirms the mesotrophic status of this reservoir. The

equitability index was in the range of 0.92 to 0.95 and the distribution of zooplankton species during the study was even and follows the Lorenz graph. No major fluctuation was found in the equitability index during the entire study period.



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# Historical Significance of Shankarpat in Bhandara District

- Prof. (Dr.) Bharat Vithoba Nakhate \*
- Prof. (Dr.) Ganesh Laxman Dhote \*\*

## *Abstract*

Through Shankarpata, rural life, their livestock, farm labour, agriculture-based supplementary businesses in the village are sustained. In the 21st century, the means of entertainment have changed, rural life has been destroyed and cities have blossomed, problems of urbanization have arisen. Rashtrasant Tukdoji Maharaj says, "No business in the world can stop unemployment, unemployment. Agriculture is the only occupation in which maximum number of people are given employment. The power to convince the unemployed and give them work is only in agriculture/agribusiness." While doing agriculture business in Bhandara district, Shankarpat is played as entertainment and entertainment. Farmers and rural people are brought together and agricultural culture is cultivated. Communal harmony, social unity, cultural heritage are preserved. Thus, rural culture gets a revival.

**Key Words:** Agribusiness, Sankarpat, entertainment, folk festivals, customs, culture, social unity.

## *Introduction:*

"Man's life begins with celebration and ends with celebration."

India, which is full of diversity, has different rivers, mountains, land surrounded by sea on three sides, there is no other country in the world that has such diversity. From Kashmir to Kanyakumari and Andaman and from Gujarat to Bengal, each region has a different language, religion, dress, food, festivals and culture. All the provinces have preserved their culture. All these have created a profoundly rich Indian culture.

Agriculture and animal husbandry are two major occupations in India. Starting from the Harappan civilization. Excavations have yielded physical means of entertainment in the Harappan culture. Humans have sung, played music and danced on occasions of joy as entertainment. It is from this that the need and necessity of various means of entertainment

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has arisen.

Folk culture, ethos, sports, various arts and entertainment in India changed over time. Marathi people are celebratory. Padwa, GaneshChaturthi, Dussehra, Diwali, Eid, Natal Asha along with various festivals also get to see various sports. In the Vidarbha region of Maharashtra, in fact, during the harvest season, one can see dandar, mandai, wrestling riots, animal fights, bullock cart rides i.e. Shankarapat, drama, tamasha, chaos and other means of entertainment and folk festival.

The tradition of Shankarapats is ancient in Bhandara district. E.g. Rural farmers pay attention to animal husbandry along with farming and use animals for entertainment through these Sankarpats such as Masal Cha Pat, PachgaonPalependhari Pat, Pimpalgaon (Road) Pat etc. Chariot races in Aryan period, animal fights in Harappan culture, cock fights, bull races were popular in rural areas and even today in the 21st century in the age of internet in Bhandara district, second day Shankarpat is held to celebrate Sanam during the harvest season.

### **Objective**

The main objective of this study is to study Shankarpata in Bhandara district and explain its historical importance.

Apart from this there are other objectives

- Entertainment is an important human need.
- Many devices are used for entertainment.
- Entertainment gives rise to various addictions.

### **Importance of study :**

These Shankarpats have social, cultural, economic, political and historical importance. Shankarapatas are also used as a means of preserving folk culture. Traditional history, folk songs, folk culture are preserved through dramas, dandars, gondhall, tamasha, qawwali, kustidangal. Therefore, it is necessary to study the real picture of rural life by understanding their historical significance. Agricultural labourers, rural professionals, artists, women etc. participate. Also, their participation in maintaining rural and agricultural culture is very valuable.

### **Importance of Shankarpatas**

*"Another one got the idea. He made the pair cool all around.*

*A second pair of bulls was planted. to run*

*Attracted public attention. It was fun.*

*Later Shankar pata started. Village by village.*

*It would have been better to have some purpose in it. Bullocks are fed by Devoni.*

*The competition increased the strength of the bulls. For agriculture. ...*

*But it also has side effects. Keep up the good work.*

*Bull driving season. It comes next. .*

*Agricultural work remained. Shankarpat's venture.*

*People do Kasab Karma. Nanapari. (Gram Gita)*

### **Social Significance**

Human is a social animal. Along with food, clothing, shelter, entertainment is also a



human need. Social unity in rural life, burning of social customs and socialization process etc. were maintained through Shankarapata. For hundreds of years, the culture is being preserved by filling the Shankarpat every year. Shankarapata has a lot to contribute in family life and marriage institution. Shankarapat is an important means of marriage, marriage and marriage in rural areas through watching and hospitality. On this occasion, important tasks such as seeing girls, choosing boys and coming together of two families become successful due to Shankarapata.

### ***Economic Importance***

Entertainment and entertainment are not as important as Shankar pata, but entertainment is done through night plays, tamasha, chaos, qawwali etc. The expenditure on this is in lakhs. Also in Shankarpata money is poured on gambling, sattapatti, zendi-mundi, hod etc. Race is important in Shankarapat. Apart from that, there is a turnover of lakhs of rupees, many kinds of rewards and prizes. Shankarapat is not complete without racing.

Markets, toys, observing the sky, getting innovative products. Business is done as a means of rural employment. Many rich farmers have become deshodhadi due to the hobby of Shankarpata, due to this financial turnover, politics, social causes and family system in the rural areas have also had bad effects.

### ***Historical Significance***

In the 21st century (the age of LPG and internet) where agricultural systems are being destroyed by sez; Bullocks, cows, goats, horses, buffaloes are decreasing. Humans have started eating these animals. Mechanized agriculture has come. But even in this case Shankarapat is filled on the occasion of a special festival. The contribution of rural culture is important in maintaining this tradition. The agrarian culture that changed during the British era and lost its form in the 21st century. Protecting agriculture, preserving agricultural culture means protecting the country. Rural culture is disappearing in the process of urbanization. Villages dried up, cities swelled and no one was ready to do farm work.

### ***Increasing Addiction***

Addictions like drugs, alcohol, gambling, smoking, etc. for entertainment are initially done as entertainment, then after getting used to it, it becomes a physical and mental need. The last person becomes addicted to addictions and becomes a home for various diseases. The remedies of doctors, physicians, hakims do not work. Getting used to any good or bad habit is addiction, now the whole world is concentrated in mobile due to internet, today mobile addiction has become a global problem. Many problems are arising affecting childhood, family life, social sphere, rural life, sports, etc.

### ***Communal Significance***

Shankarpats are held for celebration and entertainment, in which people of different castes, religions, sects and parties in the rural areas forget all differences and enjoy it together, thus creating an atmosphere of unity in rural life through art, entertainment, sports. Shankarpat, animal fights, folk art, drama. , Tamasha, Gondhals, Dandaretc occasions create communal harmony.

### ***Conclusion***

Due to the global pandemic corona, the people of India started to understand the

importance of their villages, agriculture, the passivity of urban life was proved.

Rashtrasant Tukdoji Maharaj while preaching through bhajans says that,-

*"Let's go to the small village, don't stay in the city,*

*Not food, but Marshell Upashi.*

*All the land is like gold, but no one has Rabena.*

*He got up and became a servant, greedy for money.*

*Who will do the work of agriculture? Speak up brother Majsi..."*

*Oh, the empty wheel spins*

*Isn't the shrine of your village?*

*A poor person living in a village, fasting,*

*Food-Satra Lavitosi Kashi.....*

*..... who serves the poor village*

*He is honored with fame. (Rashtrasant Tukdoji Maharaj)*

Tukdoji Maharaj has emphasized the importance of rural life through the above hymns. The Maharashtra government had banned Shankarpats by law in the interim, but in 2021-22 the ban on Shankarpats was lifted once again and approved. From this, the government has realized the necessity of Shankarpata.

Thus, the social, cultural, religious, economic and political importance of Shankarpata as animal husbandry, agriculture, rural life and entertainment needs to be preserved even today.

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## Acquisition of natural remanence in the basaltic laterites of Deccan volcanic province (India): Implications to palaeomagnetic studies in laterites

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### ABSTRACT

Lateritization in the Deccan basalt province (India) represents a large spectrum of chemical weathering with up to 99% of CIA values and the complete ferri- to antiferromagnetic transformations. We combined rock magnetic, palaeomagnetic, XRD, and XRF analyses to investigate the mineralogical transformations and its relationship to the acquisition of natural remanent magnetization (NRM) by sampling a 25 m thick Deccan lateritic profile from the West Coast of India. Significant amount of amorphous hematite (*ha*), crystalline hematite (*hc*), goethite and their Al- substituted forms were detected along with gibbsite and kaolinite. The domain size association of 'SP + SD and 'SP + SD + MD' in the ferri- as well as antiferromagnetic forms; and combination of *ha* and *hc* yield strong NRMs amongst these laterites. Low field demagnetization (< 5mT) allows removal of *ha*<sub>NRM</sub>; and the secondary components due to ferrimagnetic oxides can be removed at < 25 mT. Thereafter, the *hc*<sub>NRM</sub> continued to decay up to > 150 mT. Palaeomagnetic tests (Koenigsberger ratio, MDF, intensity decay and Zijderveld diagrams) indicate stable Characteristic remanent magnetizations (ChRM) due to *hc*; and the Al-substitutions does not affect the ChRM stability, depicting these laterites as excellent palaeomagnetic recorders. The stable ChRMs due to Chemical/Crystallization RMs due to '*hc*' also benchmarks the degree of maturity within the process of lateritization.

### 1. Introduction

Laterites are the manifestations of deep, prolonged, and intensive chemical weathering that occurred on differing host lithologies (Widdowson and Cox, 1996; Bourman and Ollier, 2002; Wimpenny et al., 2007, Ollier and Sheth, 2008, Babechuk et al., 2014, Ghosh et al., 2015). Selective diminution of alkali, alkaline earth elements, and silica from parent rock through the process of lateritization results in gradual enrichment of the iron and aluminium oxides and hydroxides along with some residual clays (Widdowson and Gunnell, 1999; Borger and Widdowson, 2001; Widdowson, 2007).

Widespread occurrence of laterites is observed in tropical regions particularly during the Cenozoic period (Bardossy, 1981; Gunnell, 2003). Laterites from the Indian subcontinent particularly preserve a variety of processes from different ages and host rocks (Meshram and Randive, 2011; Caner et al., 2011). Some of the pioneering and funda-

mental information on laterites is also derived from the Indian west coast occurrences (Buchanan, 1807) and were studied using physical, geochemical (Widdowson and Cox, 1996; Kısakürek et al., 2004; Babechuk et al., 2014, 2015; Suhr et al., 2018) and mineral magnetic perspective (Liu et al., 2019; Singh et al., 2020).

The prolonged process of lateritization permits sufficient time for NRM acquisition depicting them as good magnetostratigraphic recorders. However, there is ambiguity in understanding the acquisition in terms of the lateritization process. A single lateritic profile can be perceived through different superimposing processes dominated by solution and precipitation activities (Widdowson, 2007; Babechuk et al., 2014, Suhr et al., 2018). Palaeomagnetic studies in lateritic profiles therefore demand detailed mineralogical assessment in context to NRM acquisition. The renewed interest in basaltic laterites as possible analogues of Martian weathering processes (Hynek et al., 2002; Thomas et al., 2005; Greenberger et al., 2012), CO<sub>2</sub> sequestration during basaltic

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weathering (Seifritz, 1990; Schuiling and Krijgsman, 2006; Gislason and Oelkers, 2014) further demand detailed studies from ideal basaltic laterites, such as the Deccan traps. Iron oxides being the chief constituent of laterites, magnetic mineralogy and spectroscopy makes some of the most suitable approaches for such investigations.

The basalts are enriched with ferrimagnets and hence provide a complete spectrum of transformation to antiferromagnetic oxides during through the process of lateritization. The complex nature of lateritization allows many repeated and superimposed reaction series of partial to complete oxidation, hydroxylation, dissolution, and precipitation leading to the processes such as maghematization, ferryl-hydroxylation, Al-substitution, crystallization, and recrystallization. Several residual, crystalline, and amorphous minerals are produced during lateritization compelling the use of multiple spectroscopic and magnetic approaches to analyse the laterites. On the other hand, it enriches our understanding on NRM acquisition by chemical/crystallization remanent magnetizations (CRMs). This study is aimed at finding the efficacy of NRM in terms of palaeomagnetic signatures from the laterites.

The mineral/rock magnetism is a well-established approach for identification of different phases of iron oxides enabling their semi-quantitative estimates (Thompson and Oldfield, 1986, pp. 21–38; Evans and Heller, 2003, pp. 50–78; Liu et al., 2012). Intensive work has been made to delineate and differentiate dominant phases of ferrimagnetic mineralogy (i.e. magnetite, maghemite, and greigite) from the antiferromagnetic minerals. Further the studies are available to provide distinction within the antiferromagnetic phases (e.g., Dekkers and Rochette, 1992; France and Oldfield, 2000; Sangode and Bloemendal 2004; Roberts et al., 2020; Jiang et al., 2022). The antiferromagnetic minerals can carry stable remanence over a longer period makes them suitable for palaeomagnetic studies (Dunlop and Özdemir, 1997, pp. 16–42; Roberts et al., 2020). Previously, Schmidt et al. (1983) made palaeomagnetic attempts on Indian laterites and found considerable scatter in data which he then inferred mixing of normal and reverse magnetization demanding detailed mineralogical studies. Substitution of cations (e.g., Al) and amorphous to crystalline transformations within antiferromagnetic complexes (Cornell and Schwertmann, 2003, pp. 39–57; Liu et al., 2007; Hu et al., 2016) is a crucial factor in the determination of magnetic properties akin to the standard and theoretical values. Laterites being highly enriched with antiferromagnetic oxides/hydroxides such as hematite, goethite, ferrihydrites and lepidocrocite (Kisakürek et al., 2004; Meshram and Randive, 2011; Babechuk et al., 2014, 2015; Suhr et al., 2018; Singh et al., 2020) provide an opportunity to study the complex processes and their implications on NRM. Here we characterized the lateritic magnetic minerals, their concentration and domain sizes to understand its implications on NRM acquisition.

## 2. Study area

The Indian subcontinental drift from the southern to northern hemisphere continued until its collision with Asia to form the Himalayas (Klootwijk and Pierce, 1979; Courtillot et al., 1988). During this transect voluminous lavas were erupted at ~ 65 Ma ago around the Cretaceous-Tertiary (K-T or K-Pg) boundary, occupying an area of 500,000 km<sup>2</sup>, thus creating the Deccan traps (Klootwijk and Pierce, 1979) as large igneous province. This formed the substrate for the lateritization typically under the tropical humid conditions over suitable geomorphological surfaces. The studied laterites are formed over the Poladpur Formation of Deccan traps. The thickness of lava flows belonging to the Poladpur Formation varies from 3 to several 10's of meters spread over wide distances (Duraiswami et al., 2014). The studied laterites occur on the Konkan plain are known as low-level laterites (Widdowson and Cox, 1996) and are depicted in the Fig. 1a. Schmidt et al. (1983) divided Indian laterites into late Cretaceous-early Tertiary laterites and mid-to-late Tertiary laterites.

## 3. Materials and methods

Large oriented block samples (greater than 30 cm<sup>3</sup>) of laterites were collected at 5 m intervals from the freshly excavated laterites near the Chiplun area covering an entire profile of 25 m. Sample 1 and sample 7 are from the top and bottom of the profile, respectively. Samples of the fresh host basalt were obtained at the base of the profile for mineralogical and palaeomagnetic reference. All the samples were cored into standard specimen sizes keeping the orientations in-tact and the sets of palaeomagnetic and rock magnetic studies were prepared. For instance, specimens of sample number 1 are labelled 1.1, 1.2, 1.3, etc. for palaeomagnetic measurements, and 1A, 1B, 1C for rock magnetic measurements.

### 3.1. Rock magnetic measurements

Magnetic susceptibility was measured using Bartington MS2B susceptibility meter operated dual frequency ( $\chi_{lf}$  at 0.465 and  $\chi_{hf}$  at 4.65 kHz). The  $\chi_{fd}$  and  $\chi_{fd}$  % were calculated using  $(\chi_{lf} - \chi_{hf})$  and  $[(\chi_{lf} - \chi_{hf})/\chi_{lf}] \times 100$ , respectively. Anhysteretic remanent magnetization (ARM) was induced by a peak AC field of 200 mT superimposed over 0.1 mT DC bias field using Magnon alternating field demagnetizer (Germany). The values for susceptibility of ARM ( $\chi_{ARM}$ ) were calculated by normalization of ARM with DC bias field. Isothermal remanent magnetization (IRM) was imparted using ASC-IM-10–30 (USA) impulse magnetizer. The field was induced at incremental steps from 25 to 2200 mT and backfields from –10 to –1000 mT. The magnetizations were measured using Molspin (Minispin) magnetometer (Sensitivity:  $3 \times 10^{-5}$  A/m), whereas the palaeomagnetic remanence was measured using the JR-6A spinner magnetometer (AGICO, Czech) (Sensitivity:  $2.4 \times 10^{-6}$  A/m). The maximum field available in the laboratory (i.e., 2200 mT) was considered as saturation field to calculate the SIRM (Evans and Heller, 2003, pp. 50–78). The values of susceptibilities and remanent magnetizations throughout the calculations were mass normalized. Table 1 (Supplementary file) summarizes the parameters used for estimation of different parameters and Table 2 (Supplementary file) accounts the mean values of the studied parameters. Backfield data were used to calculate the coercivity of remanence ( $B_{CR}$ ). Rock magnetic and palaeomagnetic analyses were carried out at the Palaeomagnetic laboratories of Department of Geology, Savitribai Phule Pune University (SPPU) and the CSIR- National Geophysical Research Institute (NGRI), Hyderabad.

### 3.2. Hysteresis loops and thermomagnetic measurements

Set of samples were analysed for thermomagnetic, XRF and XRD studies using standard methods. Hysteresis loops and thermomagnetic curves were generated on advanced variable field translation balance (AVFTB) (Sensitivity-  $5 \times 10^{-5}$  Am<sup>2</sup>/kg, Temperature window- 0 to 800 °C) at CSIR- NGRI. The hysteresis loop parameters were analyzed using software 'rockmagalyzer' (<https://earthref.org/RockMagAnalyzer/>).

### 3.3. X-ray fluorescence (XRF)

A set of powdered samples (six samples of laterite and two samples of basalt) were used for XRF analyses to calculate the weathering indices. The analyses were made on ED-XRF SPECTRO XEPOS III unit at SPPU following the sample preparation procedure described in Kisakürek et al (2004). USGS standards AGV-1, BHVO-1, VL-1 and VL-2 were used as standards for calibration (LaBrecque and Schorin, 1987). The geochemical indices were calculated using spreadsheet provided by Babechuk et al (2014). Chemical index of alteration (CIA) and Mafic index of alteration (MIA)(oxidation) were measured using moles of oxides

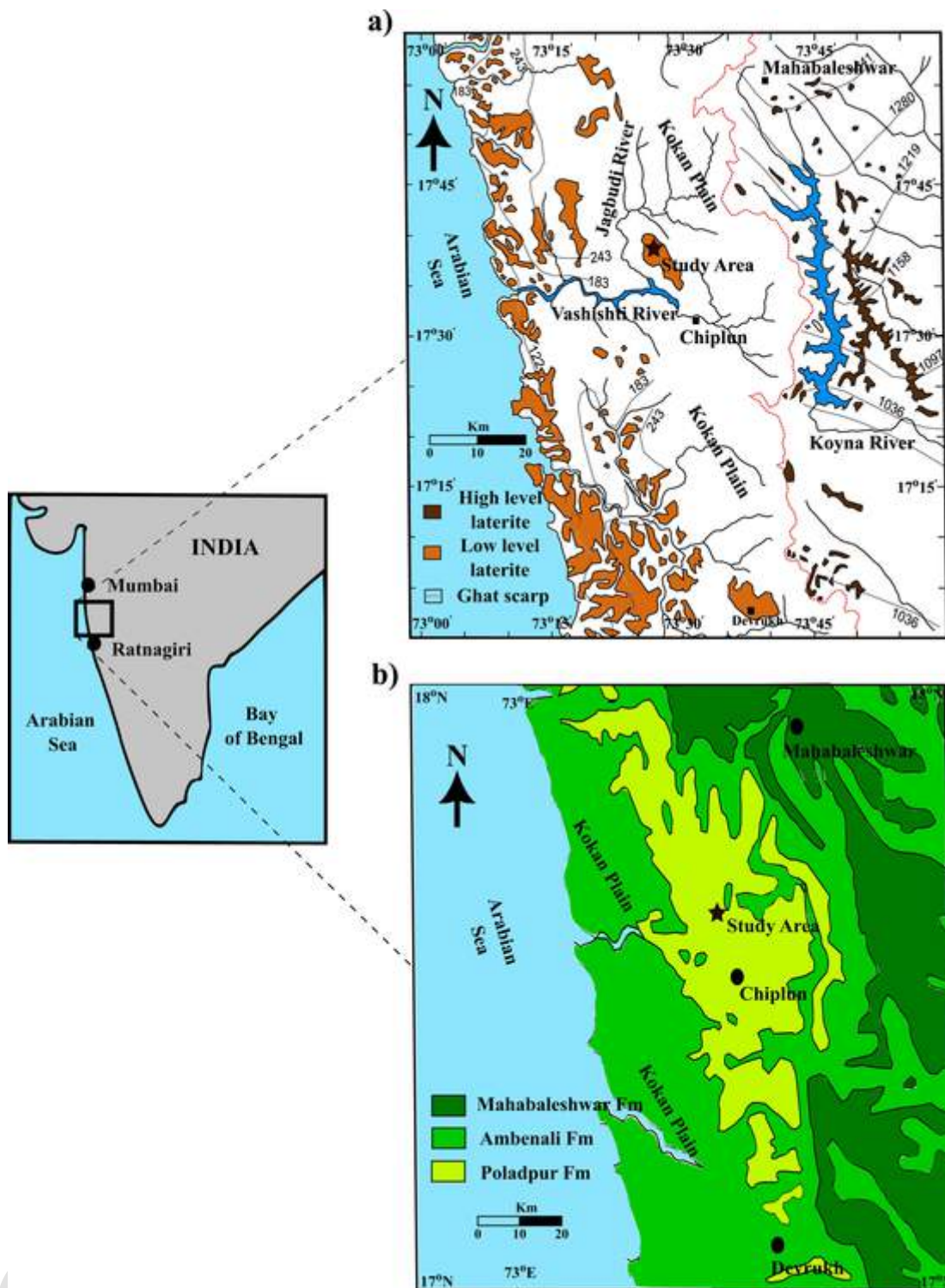


Fig. 1. Location map of the study area. a) High level (dark brown) and low level (orange) laterites separated by the Western Ghats escarpment (dashed red line). Black dot lines represent the elevation contours in meters. Inland water bodies are marked in blue colour. The study area (near Chiplun) is indicated by a black star. b) Geological map of the study area after Widdowson and Cox (1996). The Deccan trap stratigraphy is shown by shades of green colour. The studied laterites are developed on basalts belonging to Poladpur Formation of Deccan volcanic province (modified after Widdowson and Cox (1996)).

in their formulae, while oxide wt % were used in the case of the index of lateritization (IOL) with formulae given below.

$$CIA = [Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O)] \times 100.$$

$$MIA = [(Al_2O_3 + Fe_2O_{3(T)}) / (Al_2O_3 + Fe_2O_{3(T)} + MgO + CaO + Na_2O + K_2O)] \times 100.$$

$$IOL = [(Al_2O_3 + Fe_2O_{3(T)}) / (SiO_2 + Al_2O_3 + Fe_2O_{3(T)})] \times 100.$$

### 3.4. X-ray diffraction (XRD)

RIGAKU XRD Model ULTIMA IV was used to generate the XRD spectra for bulk powder samples from each unit at SPPU. The 2θ scan range



was set at 10 to 80° with a step interval of 0.02° and speed of 4 per second. Samples were measured in Cu-K $\alpha$  mode applying a voltage of 45 keV and the intensity of 40 mA. Phase identification and refinement were accomplished using Match software (<https://www.crystalimpact.com/match/>) having options for library data search to enable the mineral identifications in the bulk samples.

#### 4. Results and discussion

##### 4.1. Rock magnetism

The magnetic susceptibility ( $\chi_{lf}$ ) variation within the profile (Fig. 2a and Table 2) shows values from 31 to 105  $\times 10^{-8}$  m<sup>3</sup>/kg in Zone I, 2 to 40  $\times 10^{-8}$  m<sup>3</sup>/kg in Zone II, and 77 to 84  $\times 10^{-8}$  m<sup>3</sup>/kg in Zone III from top to bottom. The overall range of values for Zone I and III are substantially higher than that for Zone II depicting possible ferrimagnetic influence for the former compared to antiferromagnetic nature of mineralogy in Zone II. The  $\chi_{fd}$ % (approximate concentration of SP grains) is higher in Zone II relative to Zone I and III (Fig. 2b). The Zone II values range from 0.4 to 5.5%, whereas the average values for  $\chi_{fd}$ % in Zone I and III are 0.5 and 0.8%. Lateritization process favours a large-scale transformation within magnetic mineralogy by dissolution and precipitation in an oxidative regime of Eh-pH conditions. The  $\chi_{fd}$  % represents the effect of viscosity at room temperature for the superparamagnetic (SP) domain fraction with diameters less than 3–50 nm. The behaviour of SP grains is largely dependent on temperature and the time span of observation (O'Reilly, 1984, pp. 58-97). The  $\chi_{fd}$ % enrichment amongst Zone II samples suggests its formation possibly by intense dissolution-solution-precipitation activity during lateritization. The ferrimagnetic SP may arise by the dissolution of larger ferrimagnetic grains or simply by maghemitization. Whereas, Zone II is marked by the highest coercivities

( $B_{CR}$ ) and hard isothermal remanent magnetizations (HIRM) (described below) suggest the possible antiferromagnetic nature of the SP fraction. The intense antiferromagnetic transformations in laterites lead to the formation and precipitation of ferrihydrite and limonitic complexes in their amorphous states and nanoforms to produce the SP.

The  $\chi_{ARM}$  is generally related to the concentration of stable single domain (SSD) ferrimagnetic grains (Maher, 1988; Egli and Lowrie, 2002). As seen in Fig. 2c, the  $\chi_{ARM}$  is strikingly lower in Zone II compared to Zone I and III, with Zone III representing higher concentration of SSD grains of ferrimagnetic nature. The Saturation Isothermal Remanent Magnetization (SIRM) collectively depends upon the coercivity of magnetic mineral phases (Thompson and Oldfield, 1986, pp. 21-38). Magnetically hard minerals (high coercivity and low remanence) resist the applied field while soft minerals (low coercivity and high remanence) align easily along external fields. The SIRM in Zone I (max: 0.84 Am<sup>2</sup>/kg) and III (max: 0.46 Am<sup>2</sup>/kg) show exceptionally higher values than Zone II (Fig. 2d). SIRM values for Zone I and Zone III thus indicate a dominant contribution from ferrimagnetic minerals e.g. magnetite/titanomagnetite and maghemite; while Zone II indicates majority of antiferromagnetic complexes (hematite, goethite, and their substitutes). The SIRM values for Zone I are much higher than Zone III depicting significant ferrimagnetic contribution from magnetite-maghemite phases.

The S-ratio depict relative abundance of soft versus hard magnetic minerals (King and Channell, 1991). Theoretically, the values close to '1' correlate well with soft ferrimagnetic minerals like magnetite and prevailing lower values correspond to magnetically hard minerals such as hematite and goethite. In the present scenario, Zone I and III show the S ratios close to 0.9 implying dominant ferrimagnetic mineralogy (Fig. 2e). The maximum and minimum values are observed in Zone II and are within the range from 0.67 to 0.02 suggesting minor contribution of ferrimagnetic minerals in overall antiferromagnetic assemblage

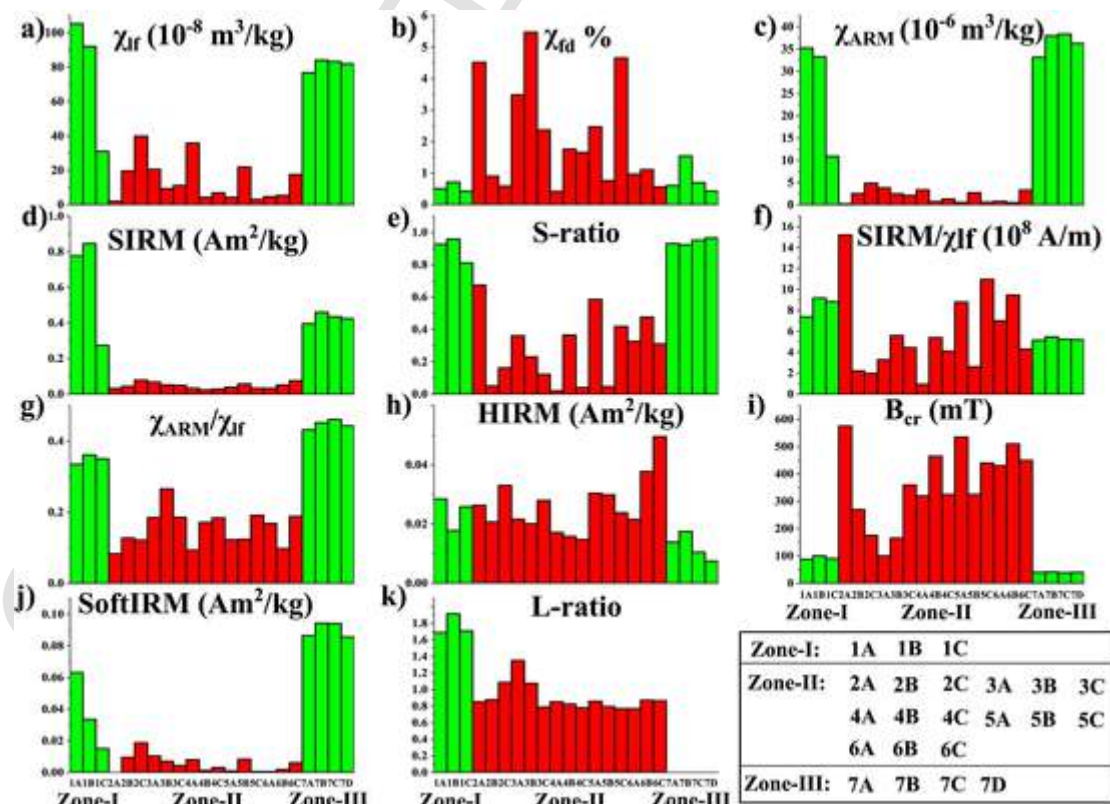


Fig. 2. Bar plots of different environmental magnetic parameters against the specimens of their respective samples. Green-coloured bars represent Sample 1 (specimens 1A, 1B, 1C) of laterite and Sample 7 (specimens 7A, 7B, 7C, 7D) of basalt, while Sample 2–6 of the typical laterites are shown in red bars. Index on the lower right side of the diagram represents zones and their corresponding specimens. The parameters employed in this study are a)  $\chi_{lf}$  ( $10^{-8}$  m<sup>3</sup>/kg), b)  $\chi_{fd}$  %, c)  $\chi_{ARM}$  ( $10^{-6}$  m<sup>3</sup>/kg), d) SIRM (Am<sup>2</sup>/kg), e) S-ratio, f) SIRM/ $\chi$  ( $10^8$  A/m), g)  $\chi_{ARM}/\chi_{lf}$ , h) HIRM (Am<sup>2</sup>/kg), i)  $B_{cr}$  (mT), j) Soft IRM (Am<sup>2</sup>/kg), k) L-ratio.

(Fig. 2e). However, the use of S-ratio for relative contribution is statistically non-linear and the interpretation is based on their non-unique nature (Heslop, 2009).

The SIRM/ $\chi_{lf}$  ratio broadly delineates the changes in domain-size; and in the present case, it is sensitive to changes in the magnetic mineral phases along with a possible contribution from paramagnetic minerals (predominantly the clay minerals). In Zone II, the combination of SIRM/ $\chi_{lf}$  and  $\chi_{ARM}/\chi_{lf}$  depict bimodal distribution due to smaller and larger SD grains (Fig. 2f, 2g). The higher values of  $\chi_{ARM}/\chi_{lf}$ , a grain size indicator depict relative enrichment of SD particles and its lower values show a bias towards SP or Multidomain (MD) particles (Liu et al., 2012).

The HIRM and Soft IRM ratios are primarily inferred for discrimination of bulk concentration of ferrimagnetic and antiferromagnetic mineralogy (Robinson, 1986; Thompson and Oldfield, 1986, pp. 21-38). Overall, the high HIRM in Zone II indicated the predominance of antiferromagnetic minerals relative to Zone III (Fig. 2h). The Soft IRM values in Zone II are 17 times lower than Zone III suggesting the relative abundance of hematite and/or goethite like mineral phases (Fig. 2j). The coercivity of remanence ( $B_{cr}$ ) is a complex parameter that depends upon mineralogy, domain states, and crystal structures (Dunlop and Özdemir, 1997, pp. 133–140). The substitution of Al or Ti in the structures of magnetic minerals however causes drastic changes in the magnetic properties (Liu et al., 2007; Liu et al., 2012). This may result in an increase or decrease in the values of saturation magnetization, coercivity, and Neel/Curie temperatures (Liu et al., 2007). The  $B_{cr}$  values are higher in Zone II (max- 575) than Zone I and Zone III (Fig. 2i). Nonetheless,  $B_{cr}$  in Zone I is twice as higher as Zone III. Low S-ratio, high  $\chi_{lf}$ , and SIRM along with high  $B_{cr}$  values thus indicate the existence of both antiferromagnetic and ferrimagnetic minerals in Zone I. Liu et al. (2007)

suggested constancy of L-ratio to reflect the absolute changes in the concentration of hematite or goethite,. For conventional use of S-ratio and HIRM, therefore we estimated the L-ratio. The values were uniform in Zone I and II, attesting the fair usage of L-ratio and HIRM (Fig. 2k).

Finally, the inferences from routine mineral magnetic analysis are summarized below.

1) The topmost Zone I is dominated by an equitable proportion of soft and hard magnetic minerals with a significant concentration of SD grains. The surficial ferrimagnetic inputs can be attributed to secondary/detrital processes as described in Singh et al (2020).

2) The intermediate Zone II represents a predominant antiferromagnetic zone with minor ferrimagnetic contribution and the predominance of SP fraction. This zone mainly represents the intense lateritization with almost complete transformation of ferrimagnetic oxides along with possible addition of antiferromagnetic complexes along with other minerals by dissolution and precipitation during intense chemical weathering enriching the antiferromagnetic oxides.

3) The lowermost Zone III represents a dominant ferrimagnetic mixture of SD and MD grains along with low antiferromagnetic contributions.

#### 4.2. Modelling of the isothermal remanent magnetization (IRM) spectra

When the samples are dominated by mixed magnetic mineralogy, detailed analysis of IRM curves can provide differentiation of admixtures (France and Oldfield, 2000; Liu et al., 2012). The values of acquired magnetization are plotted on the y-axis and corresponding field values on the x-axis. Fig. 3 thus depict that Zone II specimens are typical of antiferromagnetic nature (Dekkers and Linssen, 1989). The antiferromagnetic mineral hematite usually saturates in the fields up to 2–5 T,

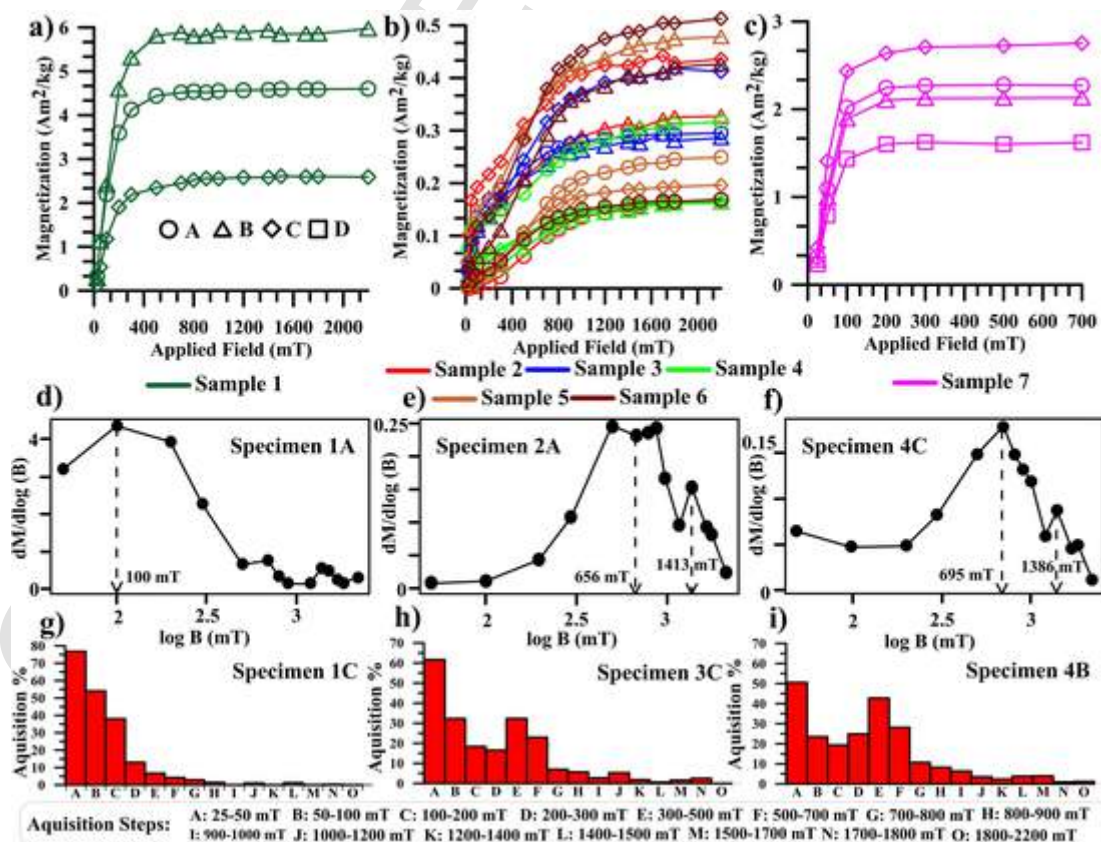


Fig. 3. The first row shows IRM acquisition (magnetization against applied field) for a sample from Zone I, Zone II, and Zone III in sequence. The second-row plots the coercivity spectra [d(M)/d(log B)] vs log B mT for specimens from Zone I (d), and Zone II (e, f). The dashed lines represent the mean coercivity values of the components. In the third row, we have plotted the RPM (relative percentage of magnetization acquisition) for specimens belonging to Zone I (g) and Zone II (h, i). Letters A to O on the x-axis represents the intervals of applied field in mT. Acquisition steps are shown at the bottom of the figure.



but the presence of goethite can increase the field of saturation up to ~6–9 T or even higher (Dekkers, 1988; Rochette et al., 2005; Liu et al., 2012). The saturation magnetization, coercivity, and Curie/Neel temperatures also depend upon the amount of substitution and degree of crystallinity (Cornell and Schwertmann, 2003, pp. 111-136; Liu et al., 2007). Thus the IRM curves for *Zone II* specimens can be subdivided into three parts depending upon the maximum magnetization induced (Fig. 3b). This proposes the variations in the mineralogy and domain size perhaps as a result of crystalline to amorphous varieties and their substitutions within the hematite dominant mineralogy along with some proportion of goethite. *Zone I* specimens show the highest enhancement compared to *Zone III*. However, *Zone III* specimens exhibit higher values of magnetization as it is dominated by ferrimagnetic minerals. This indicates a significant ferricretization in *Zone I*, while *Zone II* is dominated by lateritization.

The discrete IRM spectra are further useful for modelling the components of acquisition based upon the coercivity characters (e.g. Kruiver et al., 2001; Heslop et al., 2002; Maxbauer et al., 2016). These methods are generally applied when magnetic minerals are originated from different sources. The requirements for these methods are monotony in the data which will be achieved by increasing the IRM acquisition steps along with less magnetic interaction. As the applied field increments were less in this study, and also the magnetic minerals are grown from only one source (i.e. unimodal chemical origin), we used a plot of  $[d(M)/d(\log B)]$  against  $\log B$  (Fig. 3d, 3e, 3f) to identify mean coercivity components prior to applying further statistical procedures (e.g. smoothing, component fitting) (Tauxe et al., 1996; Maxbauer et al., 2016). The minerals that were not identified/detected by the values of coercivity from back-field application (possibly because of their lower concentration) can be separated using this plot. The plot for specimens 2A and 4C represents two coercivity components (Fig. 3e and 3f). For specimen 2A, the mean coercivity for components 1 and 2 are 656 mT and 1413 mT, respectively (Fig. 3e). Assigning the components for specific minerals depends on the source variation (eventually which will affect the magnetic signal) (Kruiver et al., 2001; Heslop et al., 2002; Maxbauer et al., 2016).

The lateritic mineralogy being antiferromagnetic (AFM) dominant, the coercivity analysis and the rate of change of IRM acquisition (RPM) appears to have been governed by the variation within the AFM phases. IRM being an indirect method, in this lateritic composition, we anticipate these different phases as a result of substitution (e.g. Aluminium-) and the grain size variations within the range of crystalline to amorphous oxides. We further examined this mineralogy using more advanced approaches in rock magnetism and the spectroscopy (i.e., XRD). In the present case, we assign the lower values of coercivity to hematite and higher values to goethite. The significant presence of goethite apart from hematite has been confirmed using x-ray diffraction analysis (presented later). The assigned value (656 mT) of coercivity is still higher than that expected for hematite (Peters and Dekkers, 2003). As stated above, the Al-substitution increases the values of coercivity for hematite and it decreases for goethite (Roberts et al., 2006; Liu et al., 2007). Similar two components were identified for specimen 4C. However, as shown in Fig. 3f, the curve initiates with elevation (x-axis) as opposed to specimen 2A. This initial enhancement implies the influence of a small/soft ferrimagnetic (FM) component which can be attested from the rate of acquisition (RPM) plots (Fig. 3i). Furthermore, specimen 1A is dominated by only one component (i.e., FM) having a mean coercivity of 100 mT, that is in agreement with the values obtained from backfield data (Fig. 3d).

The RPM for specimen 1C shows substantial acquisition up to 500 mT, depicting magnetite-maghemite-like ferrimagnetic phases (Fig. 3g). For specimen 3C, the percentage acquisition shows two trends, one up to 300 mT and the other from 300 mT upwards (Fig. 3h). Similar results were obtained for specimen 4B. This anticipates the presence of maghemite-like phases within *Zone II*. Furthermore, it also justifies the

initial peak exhibited by specimen 2A as mentioned above. We considered the possibility of maghemite (/titanomaghemites) within FM mineralogy due to the commonly occurring process of maghemitisation during weathering of magnetite/titanomagnetites sourced from the parent Deccan basalts. In a nutshell, these results indicate that *Zone II* is dominantly hematitic (Al substituted?) along with variable contributions from goethite and maghemite; and maghemite (or magnetite) is the major phase in *Zone I*.

#### 4.3. Hysteresis and thermomagnetic analysis

The hysteresis curve data are plotted for representative specimens of laterite and parent rock basalt (Fig. 4). The changes in magnetization with applied fields are measured using hysteresis loops (Thompson and Oldfield, 1986, pp. 21-38). The height, width, squareness, and steepness of the hysteresis loops are the consequence of magnetic concentration, stability, ease of magnetization, and grain interactions respectively (Maher and Thompson, 1999, pp. 29-31). Also, there is a significant impact of magnetic domain size on hysteresis curves (Dunlop and Özdemir, 1997). The laterites (Sample 2–6) typically showed wasp-waisted loops, except for Sample 1 (Fig. 4). Tauxe et al. (1996) demon-

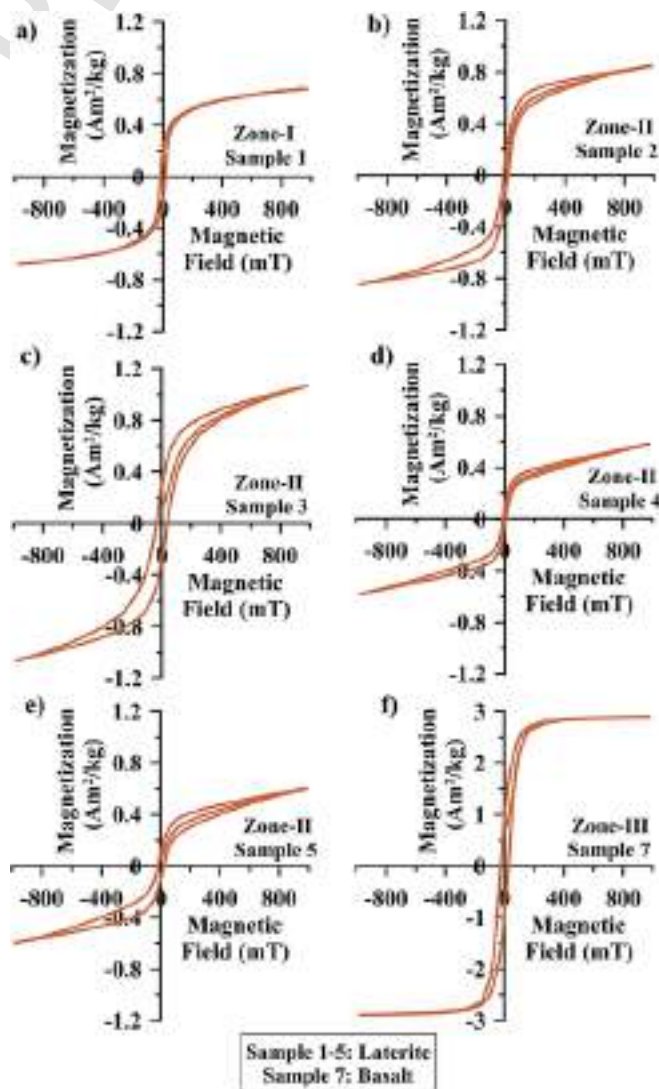


Fig. 4. Hysteresis curves for samples representing all three zones (*Zone-I, II and III*) from the studied profile. The figure shows wasp-waisted curves for laterite samples (b-e). The hysteresis curve of Sample 1 (laterite) showed similarity with the Sample 7 (basalt) (a, f).



strated that the mixtures of SP and SD grains with a size range of greater than 8 nm of SP can produce wasp-waisted curves. Also, a threshold size of 15–20 nm of SP grains along with some SD grains would create an exact shape, which is exhibited in the present scenario. There is a remarkable difference between the loops from *Zone I* (Sample 1), *Zone II* (Sample 2–6) and *Zone III* (Sample 7) as expected (Fig. 4). The hysteresis loop for Sample 1 closes at lower coercivity indicating dominant ferrimagnetic mineralogy (Fig. 4a). Lower values of coercivity can be observed in Sample 7 (basalt) compared to lateritic samples indicating SD to MD magnetite grain size population in basalt (Fig. 4f; Tauxe, 2002, pp. 35-75; Liu et al., 2012).

The graph of reduced saturation remanence ( $M_{rs}/M_s$ ) against reduced coercivity ( $B_{cr}/B_c$ ) so called 'Day Plot' has been pervasively used in many studies to discriminate the grain size variations (Day et al., 1977). Here, we used the Day-Dunlop plot as modification of the Day plot (Dunlop, 2002) shown in Fig. 5. Dunlop (2002) calculated theoretical as well as actual mixing lines for magnetite domains, with modified limits of reduced ratios in the Day plot. As seen in Fig. 5, majority of the samples of laterites fall within the range of 15 and 20 nm SP-SD mixing lines with one sample falling in 10–15 nm SP-SD mixing line. This suggests varying proportion of SP and SD grains in the lateritic samples. Furthermore, it supports the illustration given for hysteresis curves. The crystallinity of hematite determines the SD threshold size (Dekkers and Linssen, 1989).

The thermomagnetic curves (Fig. 6, discussed below) indicated that the hematites are Al-substituted. The exact delineation of critical SD size of hematite is limited by substitution (Dekkers and Linssen, 1989). However, the critical SD size for hematite could possibly be elevated to 100  $\mu\text{m}$  (Kletetschka, 2002). Basalt sample is exactly falling on the mixing line of SD-MD having 15 % of MD mixtures in SD grains of magnetite (Ti). The explanation of hysteresis loops and Day-Dunlop plot suggests that the lateritic mineralogy is dominated by SP (10–20 nm) and SD AFMs. The SP fraction appears to be abundantly the amorphous hematite apart from other poorly crystalline antiferromagnetic fractions.

The identification of magnetic minerals using their respective Curie/Neel temperature has been widely used, although magnetic enhancement and diminution effects during heating/cooling often mask

the recognition (Liu et al., 2004; Torrent et al., 2006; Zhang et al., 2010). Fig. 6 illustrates the heating and cooling cycles (marked by red and blue arrows) for laterite and basalt analysed using AVFTB. Sample 1 showed dramatic change in magnetization during heating (300–500 °C) and a large rise during cooling, in contrast to the other laterites (Fig. 6a). The final decline in magnetization around 580 °C indicates the existence of magnetite (Fig. 6a). All the remaining laterite samples show a similar pattern by sudden decrease in magnetization at 300–500 °C during heating (Fig. 6b, 6c, 6d, 6e). Removal or conversion of mineral phase with higher magnetization to that with lower one possibly explains this behaviour. During the cooling cycle, we observed a significant loss of magnetization (50–80 %) concerning initial magnetization. Liu et al. (2005) observed similar changes in thermomagnetic curves for loess samples attributing such changes to conversion (inversion) of maghemite to hematite during heating in the same temperature range as observed here. They further suggested that this behaviour could also be used as an index for the presence of SP particles. The inversion temperature have been reported from 250 °C to  $\geq 750$  °C depending upon grain size, degree of oxidation, and incorporation of impurity to the crystal structure (Dunlop and Özdemir, 1997) and the Neel temperature of hematite is 657 °C (Dunlop and Özdemir, 1997, p. 51). However as seen in Fig. 6, the heating curve drops around 640 °C depicting the lowering of Neel temperatures due to substitution. The Al-substitution could be the most common reason for lowering of the Neel temperature of hematite (Dunlop and Özdemir, 1997, pp. 69–74; Liu et al., 2007). The diamagnetic bias of Al substitution decreases the crystallinity of hematite eventually affecting its Neel temperature and coercivity (Cornell and Schwertmann, 2003, pp. 39-57; Liu et al., 2007).

Identification of goethite in the present case is demanding as Al-substitution, excess water and crystallinity could reduce its Neel temperature to room temperature (Dekkers, 1990; Liu et al., 2012). Also, dehydration of natural and synthetic goethite occurs at considerably lower temperatures, at less than 270 °C (Lewis and Schwertmann, 1979). Dekkers (1990) reported dehydration of goethite at the temperature range from 260 to 360 °C. The basalt sample has shown a gentle decrease in magnetization up to 300 °C, thereafter a small drop was observed in a temperature range of 300–400 °C (Fig. 6f). Jiang et al. (2015) suggested magnetic enhancement in synthetic samples due to iron content from clay minerals and subsequent production of magnetite. There is a possibility of titanomagnetite to be exsolved into Ti-rich and Ti-poor magnetite phases at elevated temperatures (Dunlop and Özdemir, 1997, pp. 61–66), fairly enhancing the magnetization while cooling.

#### 4.4. X-ray fluorescence analysis

The intensity and magnitude of alterations in the magnetic mineralogy of basalt could be traced using various alteration indices (Nesbitt and Young, 1984; Nesbitt and Wilson, 1992; Fedo et al., 1995; Babechuk et al., 2014). The CIA values primarily track dissolution of feldspar and higher values promote the removal of labile elements (Ca, Na and K) (Babechuk et al., 2014). CIA greater than 99% indicates complete removal of mobile elements and retention of Aluminium (Fig. 7a) (Table 3, Supplementary file). CIA values for basalt are less than 33% which are well within the basaltic weathering range (Fig. 7a). In SAF triangular diagram, all laterite samples fall in moderately to strongly lateritised fields, suggesting the deep nature of weathering in a complete profile (Fig. 7b). In the laterites from Gujarat, Meshram & Randive (2011) reported similar strong lateritization from the SAF diagrams. The IOL is a prime index of lateritization whose values in these laterites are significantly higher (greater than 70%) (Fig. 7b). Basaltic sample at the base fall in kaolinitised field in SAF diagram (this could represent the initiation of lateritization process in *Zone III*) (Fig. 7b). The basalt IOL values are consistent with values obtained by Babechuk et al. (2014). Lastly, the MIA (oxidation) represents the retention of  $\text{Fe}^{3+}$  and

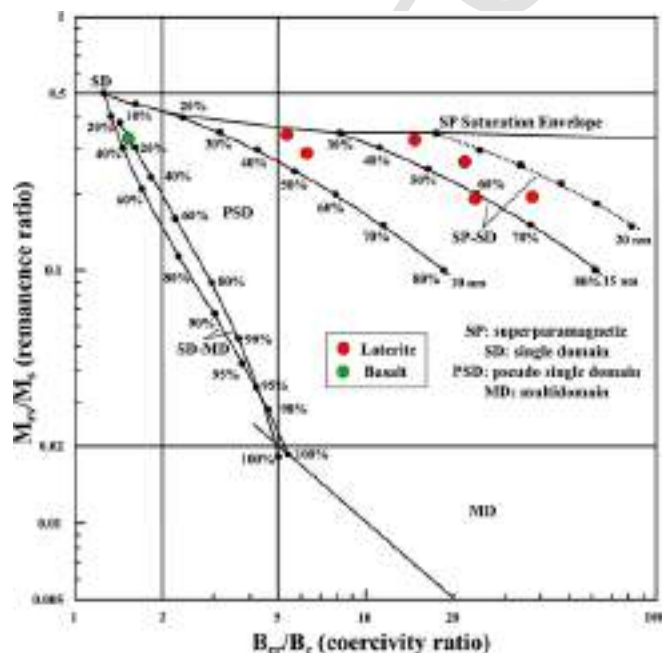


Fig. 5. Day-Dunlop plot (Day et al., 1977; Dunlop, 2002). Domain state mixing lines are adopted from Dunlop (2002). Red circles indicate laterite samples (Sample 1–6) while green circle indicate basalt sample (Sample 7).

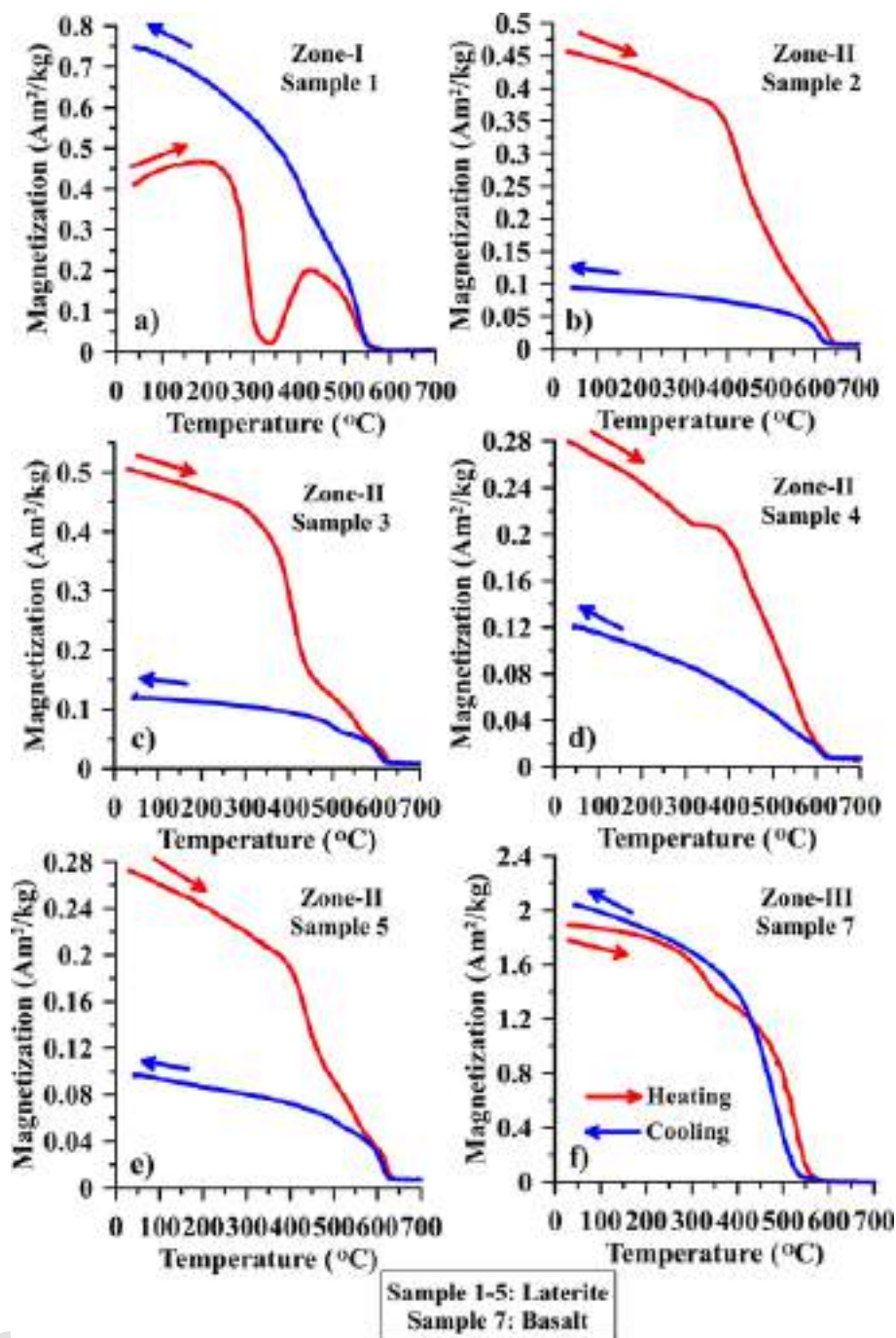


Fig. 6. Thermomagnetic curves for laterites (Sample 1–5) and basalt (Sample 7). Distinct patterns of heating are observed for samples from Zone I (a), Zone II (b-e) and Zone III (f). Laterite samples showed large differences in the magnetization after heating and cooling cycles (irreversible behaviour). Reversible curves were produced for basaltic sample (Sample 7). Red and blue arrows indicate heating and cooling curves.

aluminium over other oxides eventually noting the vital characteristics of laterite formation. As seen in Fig. 7c, all the laterite samples fall on the  $Fe_2O_3-Al_2O_3$  line indicating their enrichment and maturity.

Above mentioned alteration diagrams clearly indicate absolute maturation of the laterite profile and completion of the lateritization process. The conversion of magnetic minerals from basaltic lithology has experienced laterite weathering to the fullest possible extent. This strengthens our inference of detrital ferrimagnetic input in the highest horizons of laterites contributing to ferrimagnetism in an AFM dominant process of lateritization.

#### 4.5. X-ray diffraction analysis

The XRD analyses have been extensively practiced both quantitatively and qualitatively to study geological formations. We used Match-3 software to analyse and refine the XRD data (<https://www.crystalimpact.com/match/>). This software utilizes extensive data library search to identify the mineral phases in the sample. We found background noise in the data similar to Suhr et al. (2018) which was later assigned to the widespread occurrence of ferrihydrite and amorphous phases of hematite. Iron and aluminium oxides and hydroxides along with clay minerals were observed throughout the laterite profile. Majority of the iron oxide and hydroxide peaks occur at  $30^\circ$  ( $2\theta$ ) on-

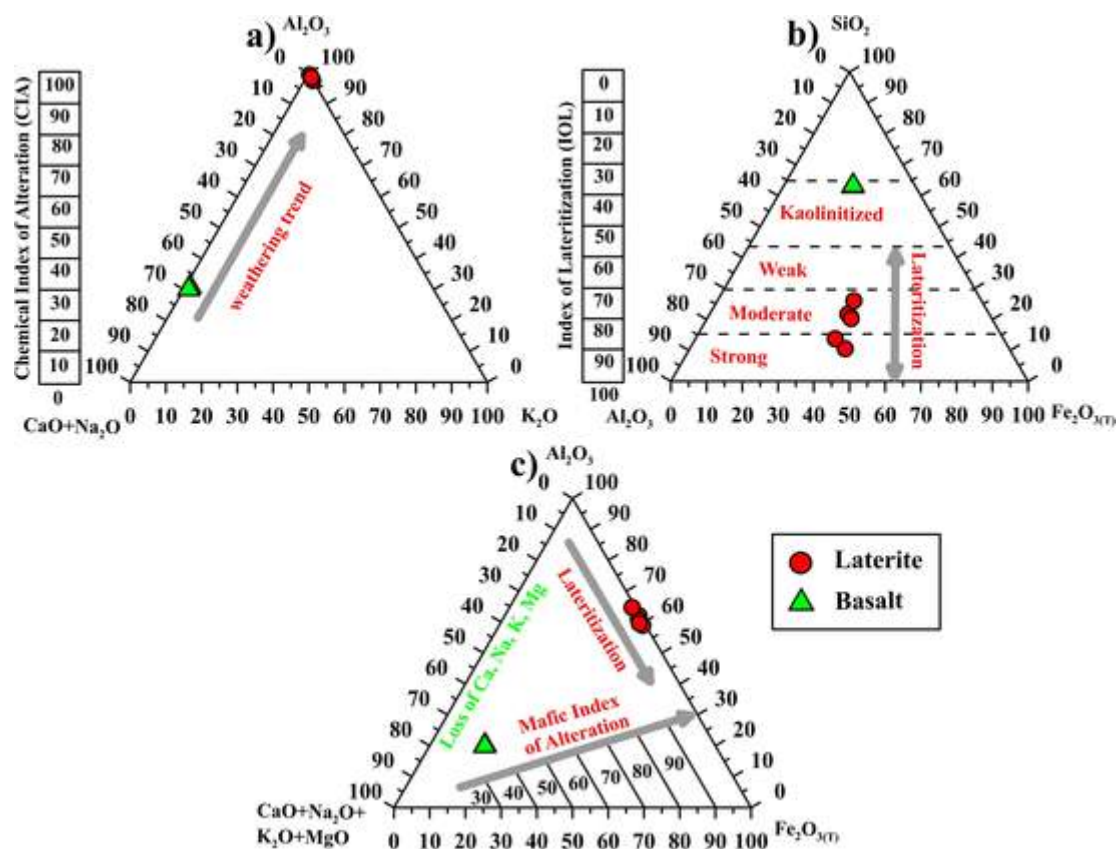


Fig. 7. Ternary diagrams indicating changes in various oxides along with weathering indices. Laterites are marked by red circles while basalt samples are shown by green triangles. The first diagram (a) is A-CN-K ternary plot along with the chemical index of alteration (CIA) (Nesbitt and Young, 1984; Nesbitt and Wilson, 1992; Fedo et al., 1995). The second diagram (b) is S-A-F ternary plot after Schellmann (1986) indicating the degree of lateritization. A-L-F ternary plot (c) indicating losses of mafic against alkali oxides (Babechuk et al., 2014).

wards. Identification of maghemite and magnetite is challenging as their maximum peaks coincide. However, magnetite does not exhibit a peak at lower values of  $2\theta$  ( $2.5^\circ$ ). Stoichiometric hematite produced characteristic peaks in the XRD spectra (Fig. 8). Furthermore, the Al-hematite peaks (d-values: 2.2076, 1.4552) are identified using software's library and the XRD spectra of Al-hematite in Roberts et al. (2006). The higher Al-substitution in hematite moves 2 thetas to higher values (Roberts et al., 2006). Furthermore, hematite and goethite peaks were checked and confirmed using XRD data of France and Oldfield (2000). XRD spectra of samples representing all the three zones are shown in Fig. 8. The minerals identified are gibbsite, Al-hematite, maghemite, goethite, hematite, ferrihydrite, and kaolinite (Fig. 8). Similar minerals were observed by Singh et al. (2020) while studying the laterites from the nearby Patan (Satara, Maharashtra) area of Deccan province. The XRD for basalt samples detected characteristic minerals of the rock (plagioclase, pyroxene, olivine, and minor quartz) (Fig. 8c). Initiation of the process of lateritization due to weathering of parent rock (formation of saprolite) could affect the primary mineral assemblage resulting in the formation of secondary clay minerals. Minor magnetic enhancement during thermomagnetic (high temperature) treatments is probably due to the conversion of these minerals into new magnetic mineral phases (e.g., magnetite; Jiang et al., 2015) (Fig. 6f).

The exact quantification of minerals by XRD spectra depends on crystal structure of the mineral phase present, their substitution, defects, polytypes, and also peak collisions (Zhou et al., 2018). Substitution and varying crystallinity are possible in laterites evident from their behaviour during thermomagnetic analysis. In this regard, laterite from Zone I and Zone II show similar mineralogy in XRD spectra but for their relative quantification, we rely on characteristic rock magnetic parameters because of earlier discussed factors.

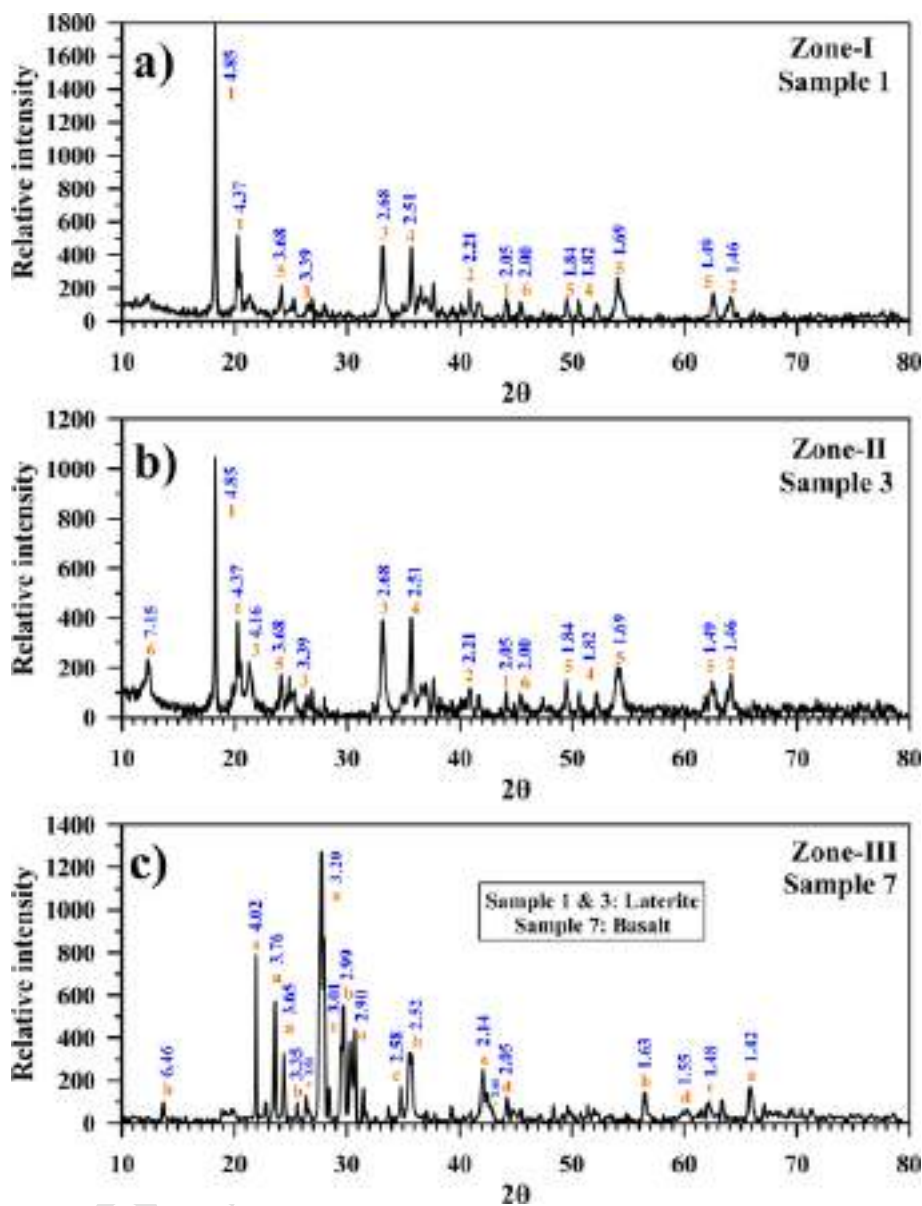
The laterite mineralogy being complex, the results produce several uncertainties in XRD spectra. A dedicated study focussing on the mineralogical aspects of laterites using advanced microscopy (scanning electron microscopy) is required for the identification of the full spectrum of minerals (magnetic and non-magnetic). Therefore, maintaining the focus upon the main objectives of rock magnetism and palaeomagnetism, further spectroscopic analysis on mineral separates were restricted and the overall information based on XRD and rock magnetism endorsed the presence of at least two varieties of hematite (crystalline and amorphous), the goethite (with substitutions); maghemite, and possible products of partial maghemitization of magnetites. Rock magnetism also suggested a mixture of SD + SP + MD and SD + SP under dominant antiferromagnetic mineralogy. Thermomagnetic data confirmed the existence of goethite, maghemite, and magnetite. XRD showed kaolinite as a dominant clay mineral along with goethite, hematite, and gibbsite and their substitutional varieties.

#### 4.6. NRM acquisition

Above mineralogical studies infer that these laterites are enriched with both amorphous and crystalline antiferromagnetic oxides as the possible agents of NRM in the form of chemical/crystallization remanent magnetization (CRM). Amongst the two, crystalline hematites are the best possible candidates for stable and characteristic remanent magnetization (ChRM). On these premises, we conducted the palaeomagnetic analysis using alternating field demagnetization on the set of representative sister samples and are described below.

We relied upon the alternating field demagnetization, as thermal demagnetization was highly susceptible to laboratory heating-induced changes due to the abundance of amorphous and poorly crystalline iron





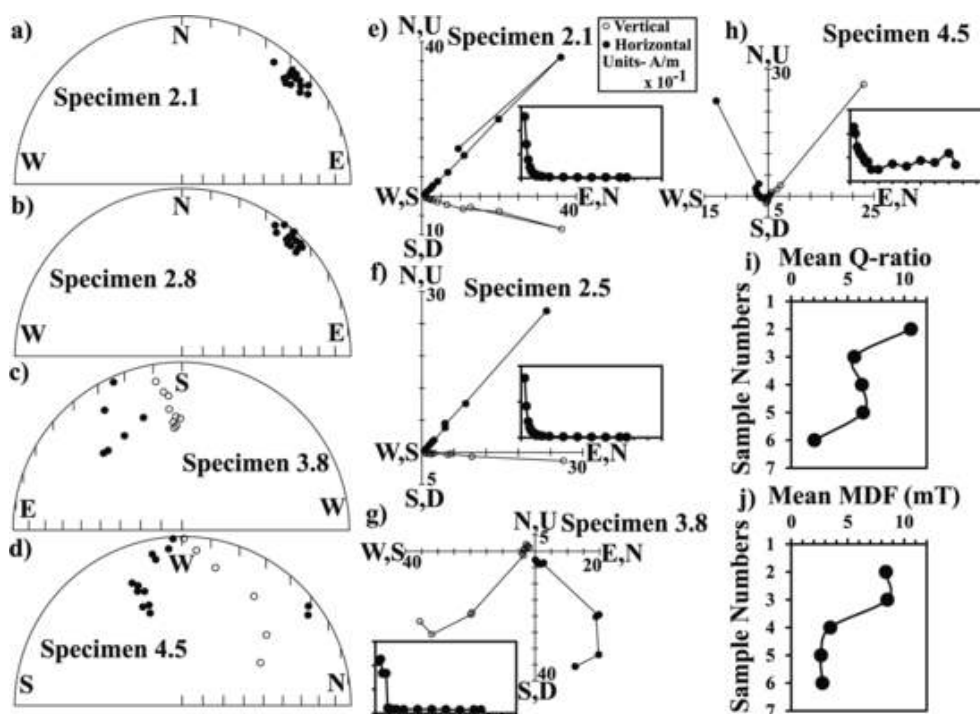
**Fig. 8.** XRD diffraction patterns of samples representing all three zones. a) Sample 1 (Zone-I) b) Sample 3 (Zone-II) c) Sample 7 (Zone-III). The characteristic minerals identified are marked by numbers for laterite (sample 3) and small letters for basalt (sample 7). The d-values for the identified peaks are shown in blue coloured text. 1-Gibbsite, 2-Al-hematite, 3-Goethite, 4-Maghemite, 5-Hematite, 6-Kaolinite, a-Plagioclase, b-Pyroxene, c-Olivine, d-Quartz, e-Magnetite.

oxide/hydroxide complexes (limonitic – ferrihydrites) and the presence of goethites resulting in strong secondary magnetization. The AF (alternating field) demagnetization on the other hand yielded convincing intensity decay as well as vector migration paths. The progressive demagnetization was carried up to the fields of 150 mT and showed stable components of remanence (Fig. 9).

We found sudden increase in magnetization at 5 mT (Fig. 9e) due to the removal of antiparallel or high angle viscous component, increasing the intensity for the resultant component. This followed a steady decay even at higher fields depicting single stable component in the NE direction. Alternating fields up to 150 mT removed large, low stability components parallel/subparallel to the NRM directed towards NE with an inclination of  $\sim 10^\circ$ . For majority of the samples, we found a trend in intensity decay partitioned into 0–25 mT and 60–150 mT. All the secondary components were removed by 25 mT depicting the ferrimagnetic components, further, there is a 90% loss of intensity by 150 mT (Fig. 9e).

The equal-area projection for the demagnetization spectra for specimen 2.1 shows a well-clustered nature with stable declination (D) and inclination (I) values. It shows the D/I values of  $10^\circ$  and  $46^\circ$ , respectively (Fig. 9a). Specimen 2.5 showed a sudden increase in intensity at the demagnetizing field of 5 mT, similar to the previous sample (Fig. 9f). Afterwards, there is complete decay or removal of remanent magnetization linearly from 5 to 25 mT. The equal-area projection shows good clustering of data with constant inclination and declination. Similar results were obtained for specimens 2.8 and 2.10. Specimens 3.1 and 3.5 showed a scattering of data in equal-area projection, although there is smooth decay in the fields of 0–25 mT and then 60–150 mT (not shown). These specimens show unimodal ChRM components without any secondary magnetization. Specimen 3.8 show stepwise decay of intensity of magnetization (Fig. 9g). Specimen 4.5 showed overlapping components with scattering in equal-area projection (Fig. 9d, 9h).

Further, in order to test the stability of NRM, we have calculated the Koenisberger ratio (Q-ratio) (Koenigsberger, 1938) using the equation  $Q = \text{NRM} (A/m) / [\chi (SI) \times H (A/m)]$ , where  $\chi$  indicates the magnetic



**Fig. 9.** The equal area projection of vector migration (a, d, c, d) and the Zijderveld diagrams (e, f, g, h; Zijderveld, 1967) for representative laterite specimens. The nature of magnetic intensity decay curve for respective specimens is shown in the inset graphs. Variation in the Koenisberger ratio (Q-ratio) (i) indicating an upward increase along with the profile. The graph between sample numbers and median destructive field of NRM indicates an upward increase in MDF along with the laterite profile (j).

susceptibility and  $H$  represents the local geomagnetic field (Table 4, Supplementary file). The Q-ratio for present samples was calculated taking local geomagnetic field value of 34.18 A/m referred from International Geomagnetic Reference Field (12th Generation) values. The values  $Q$  greater than 1 indicate remanent magnetization dominates over induced magnetization (Clark, 1997; Dunlop and Özdemir, 1997, pp. 238–239) and the contribution of remanence properties is major to the total magnetization of the rock. Fig. 9i shows an upward rise in the Q-ratio along the laterite profile suggesting that the rock possesses stable carriers that can hold stable remanence.

The median destructive field (MDF) of NRM is the magnetic field required to eliminate half the remanent saturation magnetization (Dankers, 1981; Brachfeld and Banerjee, 2000). This parameter measures remanence stability by targeting the carriers of natural and induced remanences (Brachfeld and Banerjee, 2000). It is calculated by AF demagnetizing the sample through steps until we get the one-half value of the original NRM (Table 5, Supplementary file). MDF of studied samples increases upward in profile suggesting more stable remanence carriers (Fig. 9j). Generally, lower values of MDF of NRM suggest magnetite-titanomagnetite mineral phases while higher values suggest hematite-goethite mineral phases (Dankers, 1981).

The primary remanent magnetization (ChRM) in the studied samples was thus obtained after removal of the viscous components (at less than 5 mT), while the secondary remanence due to ferrimagnetic components are removed by 25 mT (Fig. 9). This indicates that the stable CRM in laterites is attributed to a sufficiently long duration of the process of lateritization surpassing the time of lock-in remanence. The amorphous AFMs appear to have little or no influence in disturbing or overprinting the NRM and can be demagnetized at low field values of 5 mT. The study, therefore, indicated: a) suitability of laterites to acquire stable NRMs and b) Crystalline hematite as benchmark mineral to record the NRM within the complex process of lateritization.

## 5. Basaltic weathering and natural remanent magnetization

Basalts are some of the most susceptible substrates to chemical weathering under a large spectrum of Eh-pH and temperature conditions. The basaltic weathering is an effective process of  $\text{CO}_2$  sequestration (Gislason and Oelkers, 2014), while it is considered a possible analogy to the Martian weathering conditions (Greenberger et al., 2012) due to the existence of both basalt and hematite over the planet. Another very important aspect of the basalts and their weathering products is its enrichment with ferrimagnetic minerals which can have unique pathways of conversions to maghemite and hematite. Lateritization permits sufficient reaction time and porosity for fluid migrations to convert these ferrimagnetic sources into antiferromagnetic, apart from the conversion of several other Fe oxides bearing silicates to such end product. Geologically laterites contribute to significant information on the paleogeographic status of a continent. The longitudinally drifting continent like India further preserve an important record of paleolatitudes to be determined from palaeomagnetic and magnetostratigraphic approaches.

Our studies have broadly inferred the total transformation of the parent basalts into antiferromagnetic during lateritization; and ferrimagnetism if any present is because of the lateral/surficial inputs during the process of lateritization. The abundance of feldspars in these basalts is also a possible reason for the early advancement of lateritization. The feldspar weathering has created labile elements besides their larger grain size providing effective porosity for the migration of solution. Early weathering of feldspar is also the source of ionic Al- to be readily available for substitution with ferrihydrites and hence hematites and goethite. The abundance of solution due to precipitous and humid conditions near the coast further accelerated the formation of limonites and goethite; which later permitted the formation of amorphous hematites by release of hydroxyl ions. Further maturity formed the crystalline hematites as the stable and advanced stage of lateritization reached. Once formed, the crystalline hematite (hc) remained stable preserving the NRMs. The process of formation of crystalline

hematites (*hc*) from the amorphous hematites (*ha*) strengthened the CRM with sufficient time for lock-in, although a possibility of superimposition of CRMs cannot be ruled out. Our palaeomagnetic results could not trace such superimposition and almost a unimodal *hc* component was detected in these samples. However, a strong secondary component is observed due to ferrimagnetism (removed at 25 mT) which was accommodated as surficial input as discussed above.

This type of remanence acquired during the conversion of one mineral phase to another predominantly lead to growth-CRM (Haigh, 1958; Stokking and Tauxe, 1990) and can be strongly represented by primary remanence in palaeomagnetic studies (Walker et al., 1981). Hematites can be crystallized through various pathways, directly from the hydrolysis of ferric iron salts (Schwertmann and Cornell, 2000, pp. 121-134) or indirectly via the ferrihydrite → hematite reaction (Schwertmann and Cornell, 2000, pp. 121-134), later being common during the initial process of lateritization anticipating the strong CRM.

The CRM is acquired below their Curie/Neel points during the conversion of one mineral phase to another (Dekkers and Linssen, 1989; Jiang et al., 2015). CRM can be simple crystal growth (growth-CRM) or the alteration of parent magnetic minerals (alteration-CRM) (Haigh, 1958; Stokking and Tauxe, 1990). In laterites, there are several possibilities for the unstable/transitional nature of the components. Such components can arise from: i) partial transformations of detrital magnetite to maghemite, ii) partial transformation of amorphous to crystalline hematites, iii) re-lateritization of the re-deposited or precipitated laterites, iv) post formation deformation within laterite zones imparting porosity, or v) groundwater-related activity in the porous laterite. The crystalline hematites are developed only during matured stage of lateritization, and they tend to remain stably prevented from the secondary magnetization, although the deformation may cause physical scattering of directions. Alternatively, the CRM in these laterites arises from crystallization remanent magnetization (*sensu stricto*). Our study depicted the middle zone to be more mature and abundant with SD hematites, whereas the upper zone is influenced by surficial ferruginous/lateritic inputs. The CRMs therefore can be used reliably for the magnetostratigraphic approach in the Deccan laterites, when the surficial inputs, deformation, and other disturbances are restricted. The present approach of palaeomagnetism combined with mineral magnetism can be developed to understand the otherwise complex nature of timing in the lateritic processes. Determination of the timing of degree of lateritization at various stages is therefore helpful in studying various applications including CO<sub>2</sub> sequestration and Martian weathering analogy.

## 6. Conclusions

The Deccan Laterites represent peak basaltic weathering conditions by complete ferri- to antiferromagnetic transformations and further mobilizations within antiferromagnetic oxides. The combination of rock magnetism, XRD spectroscopy, palaeomagnetism, and XRF analysis provide an ideal approach to characterize the mineralogical influence over natural remanence. This integrated study inferred a set of minerals depicting partial to complete maghemitization, total hematization, goethite formation, ferrihydrite complexes, and their Al-substituted varieties in addition to gibbsite and kaolinite. The abundance of amorphous- (*ha*) and crystalline hematite (*hc*) varieties interests the palaeomagnetic studies to investigate the nature of NRMs, while the ferrimagnets are represented as secondary components. A range of domain sizes occurs with mixtures of SP + SD and SP + SD + MD, and SD remains common to most of the profile. The secondary/viscous NRM due to *ha* is removed at 5 mT and the secondary component due to ferrimagnets (magnetite or maghemites) removed at 25 mT. The *hc* component continues to decay linearly up to 150 mT depicting unicomponent behaviour after 25 mT. The palaeomagnetic tests (Koenisberger ratio, MDF, intensity decay, and Zijderveld diagrams) indicated stable directions (ChRMs) due to *hc*; and the Al-substitution does not affect the stability

of ChRM. The lock-in CRM from *hc* also benchmarks the maturity of the profile in terms of mineralogical advancement during lateritization. These laterites are thus ideal for palaeomagnetic studies and intricacies and scattered directions may arise from other secondary processes during lateritization such as internal deformation and solution/precipitation activities through secondary porosity. The ferrimagnetic abundance in basaltic laterites permits a large amount of crystalline hematite which once formed remain stable favouring reliable ChRM directions due to CRM.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catena.2023.107154>.

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## Studies on cholesterol level in wild caught females of the Emballonurid Bat, *Taphozous kachhensis* (Dobson) in relation with reproductive cycle

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### Abstract

Bats play a key role as pollinators and significantly contribute in controlling insects but very scanty information is available on their basic physiology. The aim of the present investigation was to estimate the significant differences in level of cholesterol in female *Taphozous kachhensis* during various stages of the reproductive cycle. Estimation of cholesterol level was done for twelve months representing all stages of the reproductive cycle. During lactation, quiescence, recrudescence and oestrous mean cholesterol level was found to be  $149 \pm 2.55$  mg/dL,  $154 \pm 2.76$  mg/dL,  $155 \pm 3.21$  mg/dL and  $158 \pm 3.13$  mg/dL respectively. During early pregnancy and mid pregnancy mean cholesterol level was found to be  $164.91 \pm 1.27$  mg/dL and  $161.08 \pm 3.02$  mg/dL respectively. Significant decrease in mean cholesterol level was noted during advanced pregnancy when compared with early and mid pregnancy. Mean cholesterol level was observed in the range of 137-173 mg/dL during the entire reproductive cycle in females. Present investigation revealed the significant differences in the level of cholesterol during the reproductive cycle and thus providing the information regarding basal physiological measurement of bats.

**Keywords:** bat, *Taphozous kachhensis*, chiroptera, cholesterol

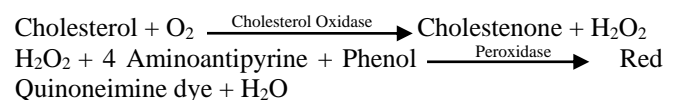
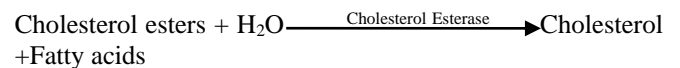
### Introduction

Order chiroptera is the second most diverse, abundant group of mammals, which is represented by more than 1421 species grouped in 21 families (Simmons and Cirranello, 2020) [12]. Study of the ecological and physiological characteristics of bats as representative of the numerous and thriving order chiroptera is important. The relatively high life expectancy of some species of bats is of great interest. Information of many unknown aspects of the basic biology and physiology of bats is scanty. Bats are of immense importance to human beings for medical research and public health. However baseline values of hematological profiles of many of the species of the bats are not studied. Physiological changes during the reproductive cycle of the bats is related with the changes in the hematological profile of these bats. The present study revealed useful information on basal values of cholesterol level during various stages of the reproductive cycle for research and conservation of this species.

### Material and methods

The present study was conducted on females of the Emballonurid bat, *Taphozous kachhensis*. Identification of the animal was done using standard monograph (Bates and Harrison, 1997) [1]. A mist net of the mesh size (10mm) was used to capture the bats. These were collected from from Ambai Nimbi, 45 kilometers from Bramhapuri (M.S.). After capturing the bats, female bats were separated and were brought to the laboratory. These were weighed on the electronic weighing balance and anesthetized with ether. Blood samples were collected from subclavian and pectoral veins without hurting the animal. Blood samples were collected and was centrifuged to separate the serum. After recovery from the anesthesia, all specimens were released in their natural habitat. Auto analyser was used for quantitative estimation of the serum cholesterol.

CHOD/PAP method was used for the estimation of serum cholesterol. Cholesterol esterase hydrolyses esterified cholesterol to free cholesterol. Hydrogen peroxide is formed from free cholesterol due to oxidation which then reacts in the presence of peroxidase enzyme with 4-aminoantipyrine and phenol which result in quinoneimine red dye complex. The intensity of the dye is directly proportional to the concentration of cholesterol present in the serum.



This kit has Cholesterol reagent (L1) and Cholesterol standard 200 mg/dL (S)

### Protocol for test

**Sample:** (0.01ml serum + Cholesterol reagent (L1) 1.0 ml

**Standard:** (0.01ml standard + Cholesterol reagent (L1) 1.0 ml

**Blank:** (0.01ml Distilled water + Cholesterol reagent (L1) 1.0 ml

Mix well and incubate the solution at 37 °C for 5 min. or at room temperature for 15 minutes. Measure the absorbance of the Standard and test sample against the blank within 60 min at 505 nm.

### Calculations

Cholesterol in mg/dL = Absorbance of test / Absorbance of Sample X 200



**Statistical analysis**

Raw data was analyzed to give mean, standard error and significance using Statistical Package for Social Sciences (SPSS 10.0). All graphs in this study were drawn using Microsoft Excel Software.

**Results**

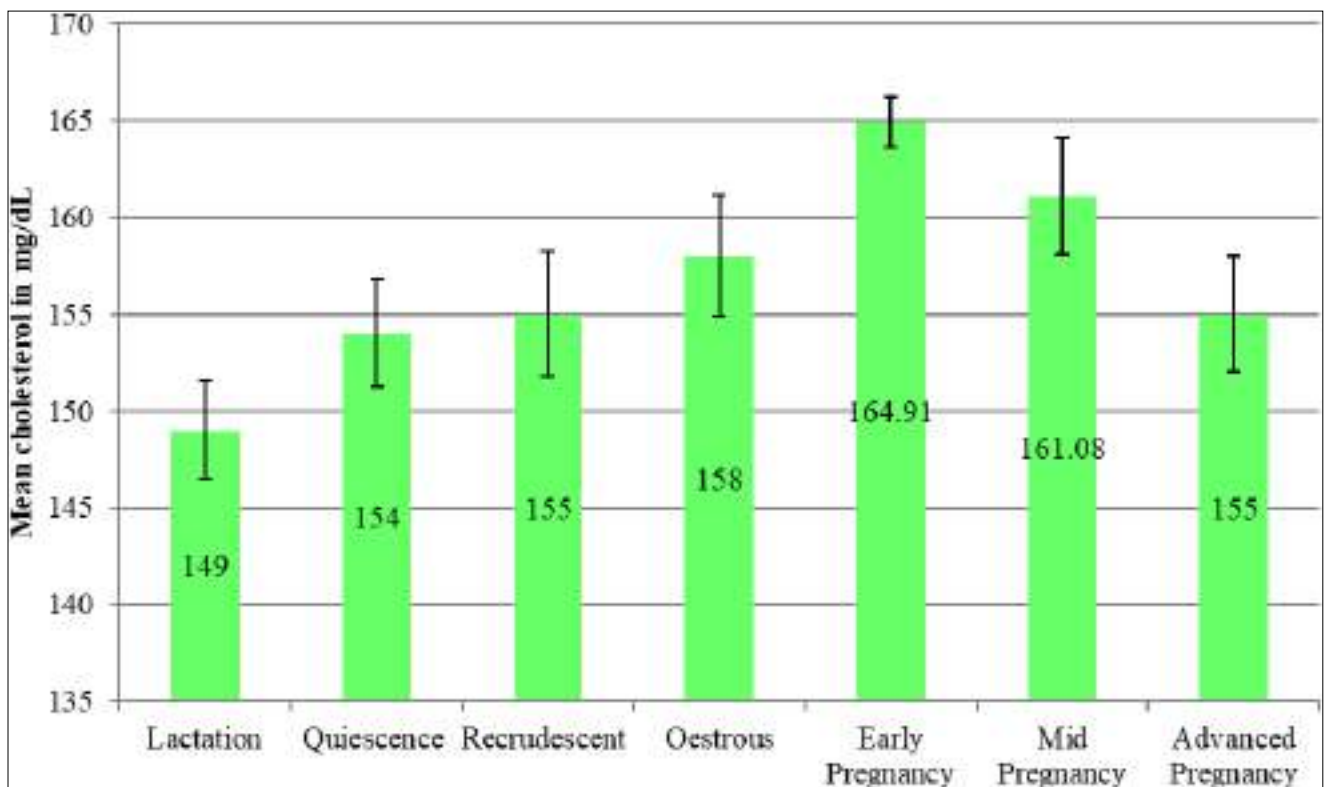
Mean cholesterol level observed during different stages of reproductive cycle in female *Taphozous kachhensis* and the P-value corresponding to F-statistic value of one way ANOVA (P = 0.0007) is presented in table 1 and 2 respectively. Histogram showing cholesterol level in female *Taphozous kachhensis* during reproductive cycle is presented in figure 1.

**Table 1:** One-way ANOVA with post- hoc Tukey HSD showing comparison of cholesterol (mg/dL) in female *Taphozous kachhensis* during reproductive cycle.

Reproductive status	No. of Bats	Cholesterol Range in (mg/dL)	Mean ± S.E	Variance	Standard Deviation
Lactation	18	137 – 170	149.00 ± 2.55 <sup>a</sup>	117.52	10.84
Quiescence	12	140 – 170	154.00 ± 2.76 <sup>a</sup>	91.63	9.57
Recrudescent	06	145 – 165	155.00 ± 3.21 <sup>a</sup>	62.00	7.87
Oestrous	06	148 – 168	158.00 ± 3.13 <sup>a</sup>	58.80	7.66
Early Pregnancy	12	158 – 170	164.91 ± 1.27 <sup>ab</sup>	19.53	4.42
Mid Pregnancy	12	145 – 173	161.08 ± 3.02 <sup>ab</sup>	109.53	10.46
Advanced Pregnancy	06	145 – 165	155.00 ± 3.02 <sup>a</sup>	54.80	7.40
Pooled Total	72		156.25 ± 1.21	106.04	10.29

**Table 2:** One-way ANOVA of seven independent groups showing P-value corresponding to F- statistic.

Source	sum of squares SS	degrees of freedom	mean square MS	F statistic	p-value
Treatment	2,225.6667	6	370.9444	4.5460	0.0007
Error	5,303.8333	65	81.5974		
Total	7,529.5000	71			



**Fig 1:** Mean cholesterol in female *Taphozous kachhensis* during reproductive cycle

During lactation, quiescence, recrudescence and oestrous mean cholesterol level was found to be 149 ± 2.55 mg/dL, 154 ± 2.76 mg/dL, 155 ± 3.21 mg/dL and 158 ± 3.13 mg/dL respectively. No significant differences were observed in mean cholesterol level during lactation, quiescence, recrudescence and oestrous stages. Significant increase in mean cholesterol level was noted during early pregnancy and mid pregnancy. During early pregnancy and mid pregnancy mean cholesterol level was found to be 164.91 ±

1.27 mg/dL and 161.08 ± 3.02 mg/dL respectively. Significant decrease in mean cholesterol was observed during advanced pregnancy when compared with early pregnancy and mid pregnancy. Pooled total mean cholesterol level during all stages of reproductive cycle in females was found to be 156.25 ± 1.21 mg/dL. During the entire reproductive cycle in females, mean cholesterol level was observed in the range of 137 – 173 mg/dL.

## Discussion

Cholesterol is a lipid which is widely distributed in various types of animal tissues. It is synthesized in the liver and is a normal component of bile and principal constituent of gallstones. Cholesterol acts as a precursor for the synthesis of various steroid hormones like adrenal corticoids and sex steroid in mammals. Total level of cholesterol is related to liver function. Increased level of cholesterol is generally found in pathological conditions like hypothyroidism, nephrosis, coronary artery disease, hyperlipoproteinemias, diabetes mellitus and many liver disorders. Low level of cholesterol occurs during malnutrition, acute infections, haemolytic jaundice, pernicious anemia and hyperthyroidism. In humans normal level of total cholesterol is between 152 to 240 mg/dL. Ageing is associated with an increase in serum total cholesterol. In the present investigation pooled mean total cholesterol in females of *Taphozous kachhensis* found to be  $156.25 \pm 1.21$  mg/dL. In females of *Taphozous kachhensis* no significant variation in total cholesterol were observed during lactation, quiescence, recrudescence, oestrous and advanced pregnancy. Significant elevated level of total cholesterol was noted during early pregnancy and mid pregnancy is associated with higher anabolic activity of the liver for the synthesis of sex steroids like 17- $\beta$  oestradiol and progesterone. Higher levels of these hormones are required for the maintenance of pregnancy. McMichael et al. (2015) [7] had noted the total cholesterol in wild black flying foxes, *Pteropus alecto* and reported significant differences in the level of cholesterol in females at  $P < 0.001$  level. They had noted the plasma total cholesterol females of *Pteropus alecto* was 17.40 mg/dL. Selig et al. (2016) [11] observed mean cholesterol level 23.5 mg/dL in straw colored fruit bats (*Eidolon helvum*). Low level of total cholesterol in pteropodid bats as compared to insectivorous bat are likely due to a low-protein diet, as cholesterol is obtained either by diet or by synthesis within liver (Widmaier et al., 1996; Heard and Whittier, 1997) [13, 4]. Moretti et al. (2021) [8] had observed very low value of triglycerides in healthy captive Egyptian fruit bat *Rousettus aegyptiacus*. Esher et al. (1973) [3] had noted 87% decrease in liver cholesterol during torpid condition in *Myotis lucifugus*. Widmaier et al. (1996) [13] had noted the high fasting plasma cholesterol level ( $215 \pm 8$  mg/dL) in insectivorous Mexican free tailed bat, *Tadarida brasiliensis mexicana* during late pregnancy and lactation. They had correlated extra ordinary high levels of cholesterol with consumption of double the amount of insect diet which is high in fat.

Normal level of total cholesterol in captive *Pteropus hypomelanus* was  $12 \pm 4$  mg/dL. Such low levels of total cholesterol was related to primary frugivorous habit associated with consumption of fruit (Widmaier et al., 1996; Heard and Whittier, 1997) [13, 4].

Heard and Whittier (1997) [4] had observed the plasma cholesterol level in *Pteropus vampyrus*, *Pteropus rodricensis* and *Pteropus hypomelanus* was  $30 \pm 14$ ,  $33 \pm 40$  and  $17 \pm 10$  mg/dL respectively. They had observed the cholesterol level in *Pteropus rodricensis* was in the range of 2 to 152 mg/dL. McLaughlin et al. (2007) [6] has found cholesterol level  $46.4 \pm 0.7$  mg/dL in wild caught flying fox, *Pteropus giganteus*. Highest range level cholesterol of *Pteropus rodricensis* shows similarity with our study. Sarmin et al. (2020) noted the cholesterol level in juvenile buckes of *Ettawa* crossbred goats in the range of 68-162

mg/dL. The high cholesterol level in this study was comparable to our finding.

Korine et al. (1999) [5] had observed the seasonal variations in the cholesterol level in fruit eating bat, *Rousettus aegyptiacus*. They have noted the total cholesterol level during winter, spring, summer and autumn were  $1.00 \pm 0.02$ ,  $1.00 \pm 0.00$ ,  $9.17 \pm 2.63$  and  $2.00 \pm 1.41$  mg/dL respectively and suggested cholesterol as a function of diet (Carroll and Kurowska, 1995; Widmaier et al., 1996; Heard and Whittier, 1997) [2, 13, 4].

Otis et al. (2011) [9] had studied the cholesterol and lipoprotein dynamics in hibernating squirrels and found similar concentrations of cholesterol during spring and summer. Cholesterol transported by lipoprotein particles in circulation. Excess cholesterol is excreted from the body in the form of bile acid by fecal excretion. They had observed a high level of cholesterol in plasma during hibernation was due to thirteen fold lower expression of cholesterol alpha-hydroxylase enzyme. Low concentration of cholesterol during winter is related to efficient use of lipoprotein in mammals essential for their survival.

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