Shirdi Sai Rural Institute's

ARTS, SCIENCE AND COMMERCE COLLEGE, RAHATA

"NAAC REACCREDITED "B++" GRADE COLLEGE"

A/P/Tal-Rahata,Dist.-Ahmednagar.(M.S.)423107

Affiliated to Savitribai Phule Pune University, Pune

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SELF STUDY REPORT-CYCLE 3rd

2018-2023

Criterion: III

Research, Innovations and Extension

Key Indicator: 3.3

Research Publication and Awards

Metric: 3.3.1 (Q_nM)

Number of research papers published per teacher in the Journals as notified on UGC CARE list during the last five years

Submitted to

NATIONAL ASSESSMENT AND ACCREDITATION COUNCIL(NAAC)

BENGALURU

Shirdi Sai Rural Institutes,
Arts, Science and Commerce College, Rahata
Tal- Rahata, Dist-Ahmednagar, Pin - 423107 (MS)
(University of Pune Affiliated ID No. PU/AN/ASC/052/1997)
NAAC RE-ACCREDITED "B++" GRADE COLLEGE

Ref. : ASCCR /

Date

DECLARATION

We the undersigned, hereby declare that all information, reports, true copies of the supporting documents, and numerical data submitted by our institution for the purpose of NAAC accreditation have been thoroughly verified by the Internal Quality Assurance Cell (IQAC). We affirm that these submissions are accurate and correct as per our records.

This declaration pertains specifically to the accreditation process for the third cycle of the institution, covering the period from 2018-19 to 2022-23.

Thank you.

Sincerely,

Dr. Vikram P. Bhalekar
IQAC Coordinator
Internal Quality Assurance Cell
Arts,Science and Commerce College, Rahata

Arts,Science and Commerce College Rahata
Tel-Rahata
Dist-A'nagar

Prof.(Dr.) Somnath S. Gholap
Principal
Arts,Science and Commerce College
Rahata,Tel-Rahata,Dist-Ahmednagar

Date-**30/07/2024**

Place- **Rahata**

Sr NO.	Title of paper	Name of the author/s	Department of the teacher	Name of journal	Calendar Year of publication	ISSN number	Link to the recognition in UGC enlistment of the Journal /Digital Object Identifier (doi) number		
							Link to website of the Journal	Link to article / paper / abstract of the article	Is it listed in UGC Care list
	Academic Year 2019-2020								
1	Additive Free Greener Synthesis of 1,2-Disubstituted Benzimidazoles Using Aqueous Extract of Acacia concinna Pods as an Efficient Surfactant Type Catalyst	Prof.Dr.S.S.Gholap	Chemistry	Polycyclic Aromatic Compounds	2019	Print ISSN: 1040-6638 Online ISSN: 1563-5333	LINK	LINK	YES
2	An expeditious synthesis of 3-methyl-4-arylmethylene-isoxazole-5(4H)-ones using aqueous extract of Acacia continua pods as a natural surfactant catalyst.	Prof.Dr.S.S.Gholap	Chemistry	Indian Journal of Heterocyclic Chemistry	2019	0971-1627	LINK	LINK	YES
3	An expeditious synthesis of 1, 3-oxazine and Betti bases catalyzed by aqueous extract of Acacia concinna pods as an efficient surfactant type	Prof.Dr.S.S.Gholap	Chemistry	Chemistry & Biology Interface	2020	2249-4820	LINK	LINK	YES

	catalyst.								
4	*N*-butylpyridinium heptachlorodialuminate as a highly efficient catalyst for the synthesis of Polyhydroquinolines under solvent-free ultrasound condition	Dr G D Shirole	Chemistry	Journal of Emerging Technologies and Innovative Research	2019	ISSN-2349-5162	LINK	Printed	UGC Approved Journal No 62759
5	Ionic liquid catalyzed one pot green synthesis of isoxazolone derivatives via multicomponent reaction	Dr G D Shirole	Chemistry	Indian Journal of chemistry Sec-B	2020	ISSN-0975-0983	LINK	LINK	YES
6	Additive Free Greener Synthesis of 1,2-Disubstituted Benzimidazoles Using Aqueous Extract of Acacia concinna Pods as an Efficient Surfactant Type Catalyst	Dr V R Kadu	Chemistry	Polycyclic Aromatic Compounds	2019	Print ISSN: 1040-6638 Online ISSN: 1563-5333	LINK	LINK	YES
7	An expeditious synthesis of 3-methyl-4-arylmethylene-isoxazole-5(4H)-ones using aqueous extract of Acacia continua pods as a natural surfactant catalyst.	Dr V R Kadu	Chemistry	Indian Journal of Heterocyclic Chemistry	2019	0971-1627	LINK	LINK	YES
8	An expeditious synthesis of 1, 3-oxazine and Betti	Dr V R Kadu	Chemistry	Chemistry & Biology Interface	2020	2249-4820	LINK	LINK	YES

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10	Ionic liquid catalyzed one pot green synthesis of isoxazolone derivatives via multicomponent reaction	A S Tambe	Chemistry	Indian Journal of chemistry Sec-B	2020	ISSN-0975-0983	LINK	LINK	YES
11	One Pot Synthesis of Lead Sulphide Thin Films	Dr V P Bhalekar	Physics	Parishodh-Engineering Skill Developement	2020	ISSN: 2347-6648	LINK	Printed	YES
12	Variational iteration techniques for nonlinear boundary value problems	Dr T K Kumkar	Mathematics	Aarhat Multidisciplinary International Education Research Journal	2020	ISSN-2278-5655	LINK	Printed	Peer Reviewed
13	Solution of Homogeneous nonlinear Advection equation by using	Dr T K Kumkar	Mathematics	Ajanta	2019	ISSN 2277-5730	LINK	Printed	UGC Approved Journal No

	variational iteration technique								40776
14	Sesonal variation of Moniezia (B) hircusae in capra hircus at Sangmner region Ahmednagar district (MS)	Dr V R Pawade	Zoology	Aarhat Multidisciplinary International Education Research Journal	2020	ISSN-2278-5655	LINK	Printed	Peer Reviewed
15	Agri-Tourism[1]An Upcoming Trends in Tourism and Advancements in Agricultural Research (An Overview Agritourist)	Prof. Dr. Rajaram nathaji Wachaure	Commerce	Ajanta	2019	ISSN 2277-5730	LINK	Printed	UGC Approved Journal No 40776
16	A Study of Regional Rural Bank in the Rural Development of Maharashtra	Prof. Dr. Rajaram nathaji Wachaure	Commerce	International Journal of Multidiciplinary E-Research Journal (Research Journey)	2020	E-ISSN: 2348-7143	LINK	Printed	UGC Approved
17	Financial Analysis of Women's Cooperative Credit Societies in Ahmednagar District	Prof. Dr. Rajaram nathaji Wachaure	Commerce	Journal of Information and Computational Science	2020	ISSN-1548-7741	LINK	Printed	YES
18	Importance of Rural Entrepreneurship	Dr S K Pulate	Commerce	Research Journey	2020	E-ISSN: 2348-7143	LINK	Printed	UGC Approved
19	A Review of Cashless policy in India	Dr S K Pulate	Commerce	Ajanta	2019	ISSN 2277-5730	LINK	Printed	UGC Approved Journal No 40776

20	Human Resource Role of Management as on the industry	Dr S K Pulate	Commerce	Aarhat Multidisciplinary International Education Research Journal	2020	ISSN-2278-5655	LINK	Printed	Peer Reviewed
21	Self-help group and Woman Entrepreneurship: A Solution to India's Slowdown	Dr J R Dighe	Economics	Research Journey	2020	E-ISSN: 2348-7143	LINK	Printed	UGC Approved Journal No 40705
22	Problems of Argo based Women Entrepreneurs in Agriculture Marketing : A Case Study of Ahmednagar District in Maharashtra	Dr J R Dighe	Economics	Research Journey	2020	E-ISSN: 2348-7143	LINK	Printed	UGC Approved Journal No 40705
23	Economic and marketing problems of women entrepreneurs in rural area A case study of Ahmednagar district in Maharashtra	Dr J R Dighe	Economics	Research Journey	2020	E-ISSN: 2348-7143	LINK	Printed	UGC Approved Journal No 40705
24	Application of GIS Techniques for Analyzing Spread of Covid-19 Disease in India	C M Bansode	Geography	Juni Khyat	2020	ISSN 2278-4632	LINK	LINK	YES
25	Detection of Land Use Land Cover Changes by Using RS and GIS Techniques a Case Study of Shrigonda Tahsil Maharashtra	C M Bansode	Geography	Juni Khyat	2020	ISSN 2278-4632	LINK	LINK	YES

	State, India								
26	Collaborative Teaching Strategies: Fostering Student Engagement and Academic Success	Dr R D Kasar	English	Shodh Sanchar Bulletin	2020	ISSN-2229-3620	LINK	Printed	YES
27	Vaishvikaran Ka Hindi Bhasha Aur Sahity per Prabhav	Dr.Ainur S Shaikh	Hindi	Research Journey	2020	E-ISSN: 2348-7143	LINK	Printed	UGC Approved Journal No 40705
28	Ajay Shukla ke Natak 'Tajmahal ka Tendar' me Vyangya	Dr D N Dange	Hindi	Research Analysis & Evaluation	2020	ISSN-2320-5482	LINK	LINK	UGC Approved
29	Vartman Pariprekshya me Vivah ka Badlata Swarup	Dr D N Dange	Hindi	Shodh Samiksha Aur Mulyankan	2020	ISSN-2320-5474	LINK	LINK	UGC Approved
30	Library Automation	Dr D T Satpute	Library	Ajanta	2019	ISSN 2277-5730	LINK	Printed	UGC Approved Journal No 40776
31	Open Source Library Management Software	Dr D T Satpute	Library	Ajanta	2019	ISSN 2277-5730	LINK	Printed	UGC Approved Journal No 40776
32	Massive Open Online Courses (MOOC) : an Overview of recent perspective	Dr D T Satpute	Library	International Multilingual Refereed Research Journal (Vidya	2019	ISSN-2319-9318	LINK	Printed	UGC Approved Journal No 62759

				Warta)					
33	RFID GENIUS	Dr D T Satpute	Library	GENIUS	2020	ISSN-2279-0489	LINK	Printed	UGC Approved Journal No 47100

IQAC Coordinator
ASC College, Rahata

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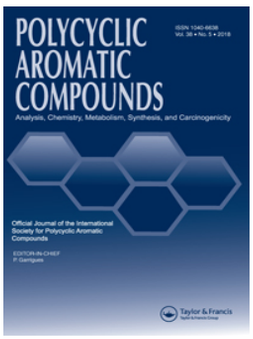
Art's,Science & Commerce College,Rahata



Polycyclic Aromatic Compounds

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Additive Free Greener Synthesis of 1,2-Disubstituted Benzimidazoles Using Aqueous Extract of *Acacia concinna* Pods as an Efficient Surfactant Type Catalyst

Vinod R. Kadu, Hemant V. Chavan & Somnath S. Gholap

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Additive Free Greener Synthesis of 1,2-Disubstituted Benzimidazoles Using Aqueous Extract of *Acacia concinna* Pods as an Efficient Surfactant Type Catalyst

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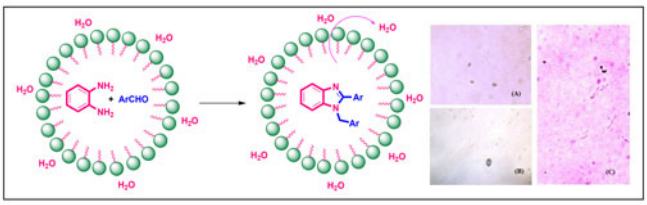
ABSTRACT

An efficient environmentally benign method for the synthesis of 1,2-disubstituted benzimidazole derivatives via one-pot multicomponent has been reported using aqueous extract of *Acacia concinna* pods as a naturally occurring surfactant type catalyst. The present surfactant medium was found superior and additive free for the condensation of o-phenylene diamine and two equivalent of aldehyde to yield 1,2-disubstituted benzimidazole derivatives in excellent yields under mild conditions. A simple, economically viable and biocompatible catalytic system suggested the possible utility of the present protocol for the large scale construction of benzimidazole derivatives.



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KEYWORDS
Acacia concinna; 12-disubstituted benzimidazoles; green methodology; multi-component reaction; natural surfactants

Introduction

The development of new catalytic systems originated from renewable sources has been enormously increasing to minimize environmental disturbance generated by the field of medicinal chemistry and production of fine chemicals. Moreover, new and efficient catalytic protocols are necessary to construct the promising classes of organic compounds for molecular and biomedical research. Nowadays, numerous natural and synthetic materials like supercritical solvent, ionic liquids, clays, enzymes and surfactants are extensively recognized as practical substitute to traditional synthetic procedures. These materials are found to be convenient to solve certain incredible synthetic problems concerning environmental aspects to some extent. In order to overcome the problems associated with existing catalysts such as environmental hazards, expensiveness, use of halogenated organic solvents, handling problems, use elevated temperature to get desired yield

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of the required organic compound etc., natural sources are found to be the best remedy. Nature offers an incredible array of biochemicals providing unique class of potential biocatalysts useful for the reactions of various organic substrates.[1–3] The synthetic utility of these materials are biodegradable and generate less waste than the conventional methods. In addition, the emphasis of Green Chemistry is towards development of designing of chemical products and processes through pollution free and eco-friendly protocols.[4] In this context, the plant cell culture of *Daucus carota* root,[5–10] soaked *Phaseolus aureus* (green grams),[11] and coconut juice (*Cocos nucifera*)[12] has been successfully utilized as biocatalysts for selective reduction of ketones. In the previous reports, aqueous extract of *Acacia concinna* has been utilized for the synthesis of 3-carboxycoumarins and Cinnamic acids via Knoevenagel condensation,[13] acylation of amines,[14] and synthesis of aryl-hydrazones.[15]

In the field of medicinal chemistry, the benzimidazole core is one of the privileged substructures for drug design due to its affinity towards the broad range of enzymes and proteins.[16] It has been displayed remarkable potential against HIV, herpes (HSV-1), RNA, influenza, and human cytomegalovirus (HCMV) viruses.[17–21] Various benzimidazole derivatives are known to have topoisomerase, smooth muscle cell proliferation and angiotensin II inhibiting properties, selective neuropeptide YY1 receptor antagonists, 5-HT3 antagonists, antitumor, antimicrobial agents.[22–27] Some of the potentially active benzimidazole derivatives such as candesartan (**A**) plays an important role in AT1 receptors binding exhibiting stronger blood pressure lowering effect, azilsartan (**B**), is as AT1 receptor antagonist for the treatment of hypertension,[24] telmisartan (**C**) is an orally active potent AT1-selective antagonist discovered by Boehringer Ingelheim in 1991[28] astemizole (**D**), is a second-generation H1-receptor antagonist discovered by Janssen Pharmaceutica in 1977,[29] mizolastine (**E**) is a non-sedating antihistaminic drug[30] and clemizole (**F**) is first-generation antihistamine drug used against itching and allergic reactions[31] (Figure 1).

The traditional synthesis of benzimidazoles involves the reaction between an *o*-phenylenediamine and a carboxylic acid or its derivatives (nitriles, amidates, orthoesters) under harsh dehydrating conditions.[32] Very recently, a literature survey revealed several methods for synthesis of benzimidazole and its derivatives using L-proline,[33] glyoxalic acid,[34] $SiO_2/ZnCl_2$,[35] $Fe(ClO_4)_3$,[36] trimethylsilyl chloride,[37] silica sulfuric acid,[38] oxalic acid,[39] mesoporous metal oxide

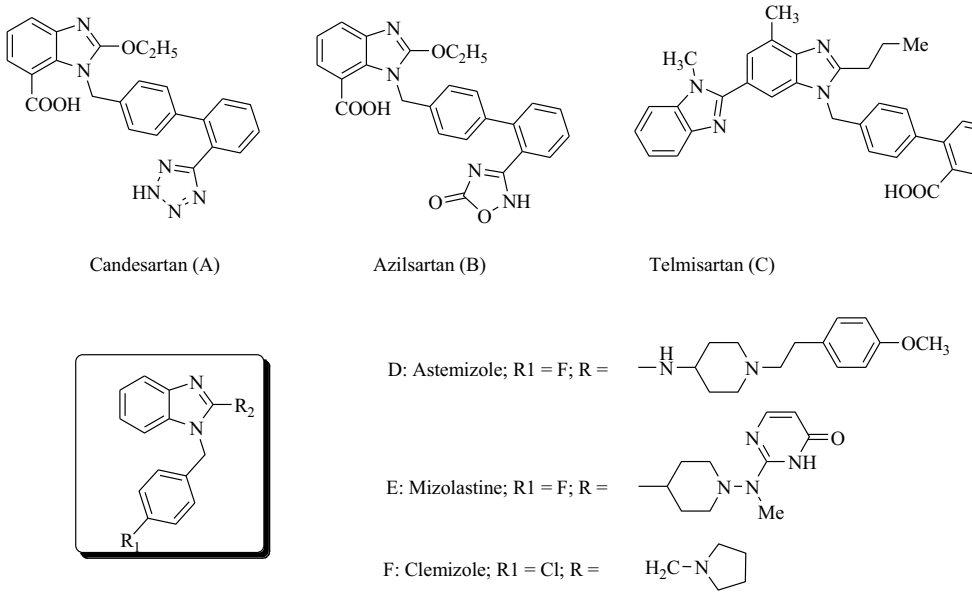
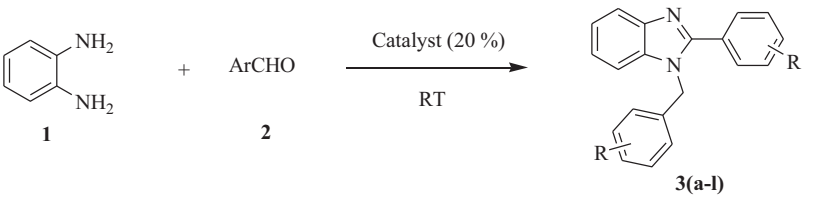


Figure 1. Some of the potentially active benzimidazole drugs.



Scheme 1. Synthesis of 1,2-disubstituted benzimidazoles.

Table 1. Optimization of catalyst concentration.

Entry	Catalyst concentration %(W/V)	Time (min)	Yield (%)[a]
1	10	270	89
2	20	180	97
3	30	130	95
4	40	130	95
5	50	80	91
6	–	600	NR[b]

[a]Isolated yield of **3a**.
[b]No reaction.

nanocrystals,[40] Indion 190 resin,[41] sodium dodecylsulfate–water,[42] nano-In_2O_3,[43] and alumina–sulfuric acid.[44]

Acacia concinna is commonly known as Shikakai which belongs to the family Leguminosae and found in tropical rainforests of southern Asia. The fruits of *Acacia concinna* are well known for its cleansing property and hence it is used as a traditional shampoo. The cleansing properties of *Acacia concinna* fruit are due to the presence of saponins, which are foaming agents. Saponins isolated from the plant fruits have been traditionally used as a detergent. In particular, these saponins produces leather when shaken in aqueous solutions due to presence of amphipathic glycosides composed of one or more hydrophilic glycoside moieties combined with a lipophilic triterpene cores. The fruit is known to have 10–11.5% saponins and their structure has been reported.[45,46] These saponins have surfactant properties similar to that of dodecyl benzene sulfonates.[47] The saponin 'acacic acid' was found in pods of *Acacia concinna*. Specifically, it is a trihydroxy monocarboxylic triterpenic acid of either tetracyclic or α-amyrin group. Hence, the aqueous extract of these pods of *Acacia concinna* shows acidic pH.[48,49] These fascinating properties of aqueous extract of *Acacia concinna* pods promoted us to use it as an efficient and eco-friendly acidic surfactant type catalytic medium for organic synthesis.

Result and discussion

In continuation of our ongoing research on development of novel synthetic method for biologically active compounds,[50–55] we have presented here a simple, cost-effective and green protocol for the synthesis of 1,2-disubstituted benzimidazole derivatives using aqueous extract of pods of *Acacia concinna* as a green and inexpensive reaction medium (Scheme 1). The present approach for the synthesis of benzimidazoles reduces the use of hazardous halogenated organic solvents, tedious reaction work-up, and drastic reaction conditions.

In order to check the efficiency of the catalyst, a reaction of o-phenylenediamine (**1**) (1 mmol) and benzaldehyde (**2a**) (2 mmol) in 5 mL aqueous extract of *Acacia concinna* pods (10% W/V) was performed at ambient temperature and we are fortunate to get an excellent yield of product **3a** (89%) after 270 min. Encouraged by the above outcome, the optimization of the reaction conditions was conducted by studying the same reaction in the presence of different concentrations aqueous extract of *Acacia concinna* pods. It was found that 20% of the catalyst was sufficient to

Table 2. Effect of surface tension of surfactant solution on rate of reaction.

Entry	Catalyst concentration %(W/V)	Surface tension, *T* (dyne/cm)	Time (min)
1	50	13.48	80
2	40	18.87	130
3	30	32.34	130
4	20	40.43	180
5	10	48.51	270
6	Distilled water	67.38	–

Table 3. Effect of surfactant for the formation of **3a**.

Entry	Surfactant[a]	Time (min)	Yield (%)[b]
1	None	600	NR[c]
2	SDS	120	60
3	DBSA	120	64
4	Triton X-100	120	51
5	CTAB	120	48
6	CPB	120	45
7	*Acacia concinna* extract 20% (W/V)	180	97

[a]Reaction condition: *o*-phenylenediamine (1 mmol), benzaldehyde (2 mmol), *Acacia concinna* extract (5 mL), room temperature.
[b]Isolated yield.
[c]No reaction.

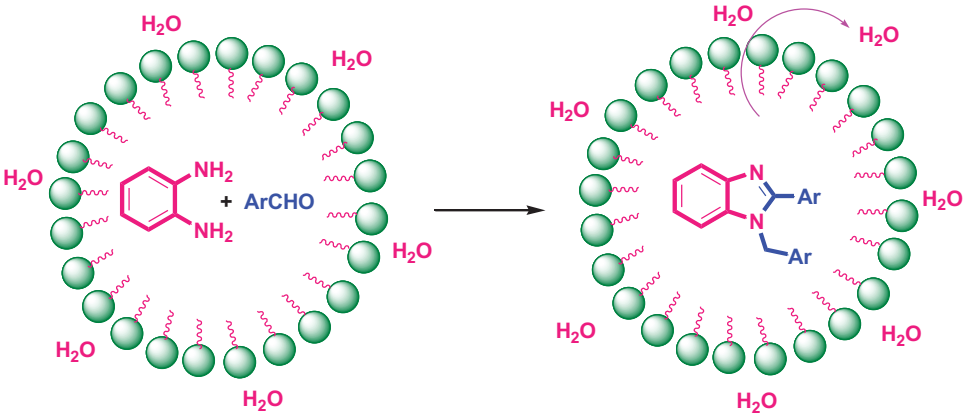


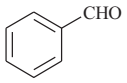
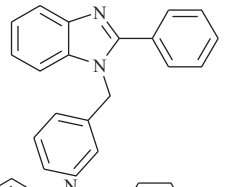
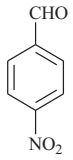
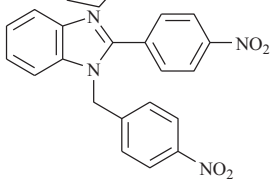
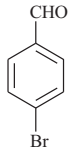
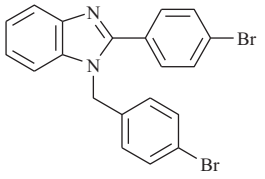
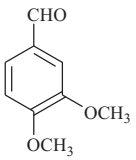
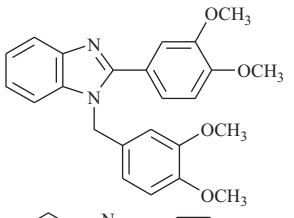
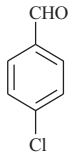
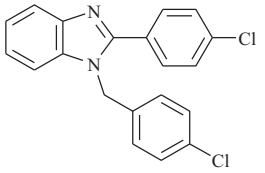
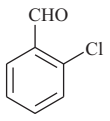
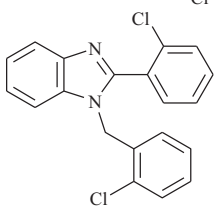
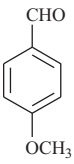
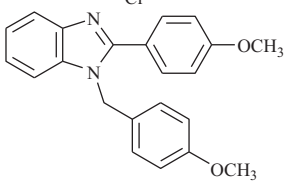
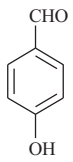
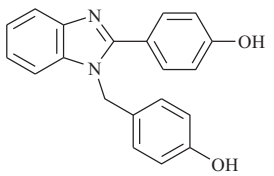
Figure 2. Micelle-promoted synthesis of 1,2-disubstituted benzimidazoles.

get highest yield of the product **3a** (97%) in short time (180 min). Increasing concentration of *Acacia concinna* pods (30%, 40%, and 50%) did not affect the yield of the final product. Therefore, 20% W/V aqueous extract of *Acacia concinna* pods and 5 mL volume was found to be the optimized amount of catalyst to push the reaction forward (Table 1).

As compared to distilled water aqueous solution of surfactant is found to reduce the surface tension of solution (Table 2) which increases the wetting and spreading properties. Surface tension and structure of surfactant governs the wetting and spreading characteristics.[56,57] A numerous reactions such as redox, photochemical, enzymatic, Diels-Alder, photochemical, etc. have altered the rate of reactions.[58] Micelle is collective of surfactant molecules in their aqueous solution. Hydrophilic groups of surfactant are sequestered in the micelle core.[59]

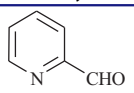
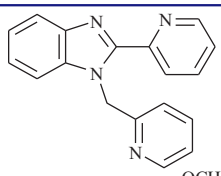
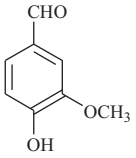
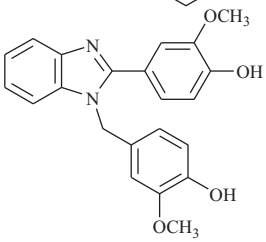
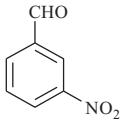
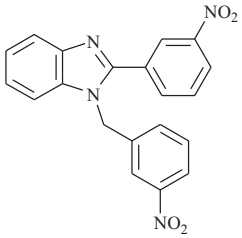
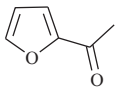
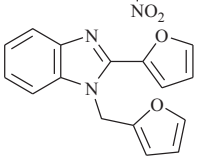
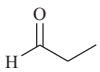
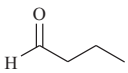
In order to evaluate the catalytic potency of the aqueous extract of the *Acacia concinna* pods, a model reaction of *o*-phenylenediamine (**1**) and two equivalents of benzaldehyde (**2**) was conducted in aqueous solutions of various cationic, anionic, and nonionic surfactants at room

Table 4. Synthesis of 1,2-disubstituted benzimidazole.

Entry	Aldehyde	Product		Time (min)	Yield (%)[a]	M.P. (°C)[b]
1.			**3a**	180	94	130–132[60]
2.			**3b**	175	98	302–304[60]
3.			**3c**	160	93	156–158[61]
4.			**3d**	158	94	170–173[61]
5.			**3e**	170	90	132–134[60]
6.			**3f**	185	88	160–163[61]
7.			**3g**	160	94	124–126[60]
8.			**3h**	155	98	124–126[60]

(*continued*)

Table 4. Continued.

Entry	Aldehyde	Product		Time (min)	Yield (%)[a]	M.P. (°C)[b]
9.			**3i**	180	96	129–130[62]
10.			**3j**	175	94	184–186
11.			**3k**	165	92	166–168[61]
12			**3l**	180	90	96–98[60]
13		[c]NR	–	–	–	–
14		[c]NR	–	–	–	–

[a]Isolated yields of the products.
[b]Ref, reference.
[c]NR, no reaction.

temperature (Table 3). The surfactants like SDS, triton X-100, CTAB and CPB were used to compare the efficacy of aqueous extract of the *Acacia concinna* pods. It has been found that aqueous extract of the *Acacia concinna* pods was superior surfactant medium for the synthesis of **3a**.

The aqueous solutions of surfactants under investigation were taken above their critical micellar concentrations (CMC). The reaction when conducted in the presence of dodecylbenzene sulfonic acid (DBSA) as acidic surfactant, the desired product **3a** was obtained in 64% yield (Table 3, entry 3). In the presence of sodium dodecyl sulfate (SDS) as anionic surfactant, the desired product **3a** was obtained in 60% yield (Table 3, entry 2). Other surfactants such as Triton X-100, cetyl pyridinium bromide (CPB), and cetyl trimethylammonium bromide (CTAB), afforded **3a** in low yields (Table 3, entries 3–6). However, in the presence of the aqueous extract of *Acacia concinna* pods, the desired product was obtained in 97% yield (Table 3, entry 7). The reaction when conducted in water in absence of surfactants, no product formation was observed after 600 min (Table 3, entry 1). Thus, the aqueous extract of *Acacia concinna* pods was found to be superior over all other surfactants. This fact promoted us for further exploration of the present method other aldehydes possessing wide range of substituents. The increased rate of reaction catalyzed by the aqueous extract of *Acacia concinna* pods might be attributed due to its surfactant property and acidic pH (pH = 4.1). The saponins, which are highly acidic, solubilize the reactant species

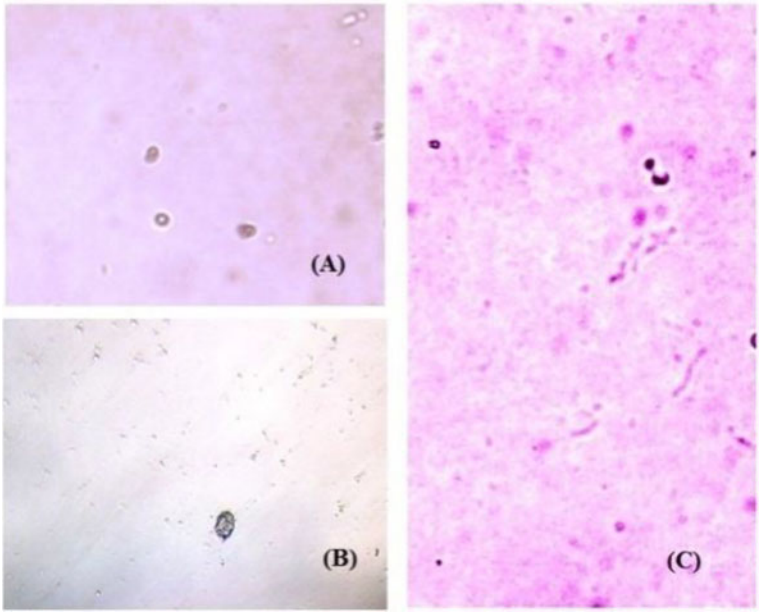
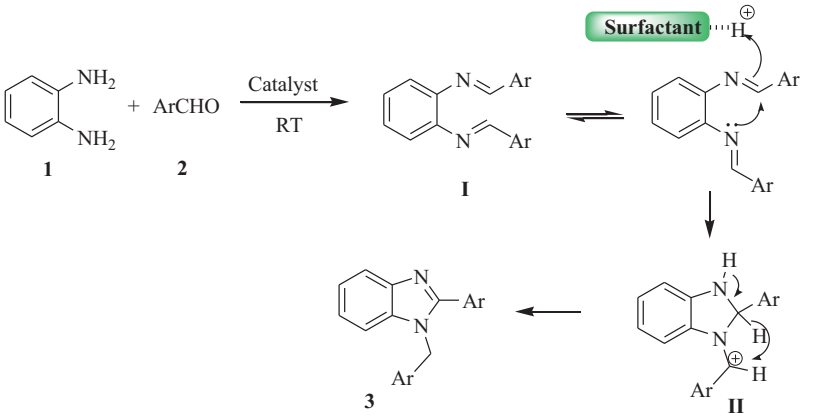


Figure 3. Photograph of micelle observed in reaction medium during formation of **3a**.



Scheme 2. Proposed mechanism for formation of 1,2-disubstituted benzimidazoles (**3**).

strongly by hydrogen bond formation in aqueous medium. This increases the number of favorable collisions between the reactant species. Further encapsulation of the reactants in micellar cages may drive the equilibrium toward the product side by expelling the water molecule out of its hydrophobic interior that increases the speed as well as the yields of products (Figure 2). This remarkable enhancement in reaction rate prompted us to explore the potential of this protocol for the synthesis of 1,2-disubstituted benzimidazole derivatives.

The synthetic utility of the present biocompatible approach was evaluated for the synthesis of wide range of 1,2-disubstituted benzimidazole derivatives using optimized reaction conditions. The results obtained are summarized in Table 4. The presence of electron donating or electron withdrawing groups and their position on the aromatic aldehyde did not show any noticeable effect on the yields of the 1,2-disubstituted benzimidazole derivatives (Figure 3).

The desired 1,2-disubstituted benzimidazoles were obtained in excellent yields with diversified functional groups. Chemically reactive substrates like furfuraldehyde and cinamaldehyde

underwent smooth to produce corresponding 1,2-disubstituted benzimidazole without any side product formation (Table 4, Entry 12 and 13). In general, all aromatic aldehyde undergo multi-component cyclocondensation afforded corresponding 1,2-disubstituted benzimidazoles. However, aliphatic aldehyde such as proanaldehyde and butyraldehyde unsuccessful to react under the present reaction conditions (Table 4, Entry 14 and 15).

The proposed mechanism for the synthesis of the 1,2-disubstituted benzimidazoles may involve the iminium-catalyzed formation of *N,N′*-dibenzylidene-o-phenylenediamine (**I**), activation by catalyst and ring closure giving a five-member ring (**II**) either in a sequential or a concerted manner (Scheme 2).[63]

Conclusion

In conclusion, we have described an efficient, economical, and environmental friendly catalyst for the synthesis of 1,2-disubstituted benzimidazole derivatives catalyzed by aqueous extract of *Acacia concinna* pods. The uses of water as reaction medium and biocompatible catalyst, short reaction time, high purity of the products, mild reaction conditions and a simple workup procedure are most the attractive features of the present method.

Experimental

General conditions

All chemicals were obtained from commercial suppliers and were used without further purification. The melting points were determined in open capillaries and were uncorrected. The solvents were dried and redistilled before use. Melting points were recorded on Digital Electro thermal Melting point apparatus (VEEGO, VMP-DS) and are uncorrected. Reaction monitoring was conducted using thin layer chromatography (TLC) using precoated silica gel $60F_{254}$ plates with layer thickness 0.25 nm purchased from Merck Ltd. TLC plates were visualized under ultraviolet light at 254 nm wavelength. IR spectra were recorded on KBr discs on Shimazdzu 470 IR spectrophotometer. ^{1}H-NMR was recorded on Varian-NMR mercury 300 MHz spectrometer in DMSO-d_6 using TMS as an internal standard. Chemical shifts values (δ) are expressed parts per million (ppm). Mass spectra were recorded on Varian MAT 311 A at 70 ev.

General procedure for the preparation of catalyst

A fine powder of *Acacia concinna* pods (20 g) in water (100 mL) was heated in a 250 mL conical flask at 100 °C for 20 min. The solid material was filtered and the aqueous extract was collected. The prepared extract has concentration 20% w/v.

General procedure for the synthesis of 1,2-disubstituted benzimidazole (3a–l)

A mixture of o-phenylenediamine (1 mmol) and aldehyde (2 mmol) in catalyst solution (20%, 5 mL) was stirred at room temperature for specified time (Table 3). After completion of the reaction (as indicated by TLC), a separated solid was filtered on Buchner funnel, washed with water and dried to obtain pure products[3] in excellent yields.

Spectral data

1-(4-Hydroxy-3-methoxybenzyl)-2-(4-hydroxy-3-methoxyphenyl)-1H-1,3-benzimidazole (3j)

M.P.: 184–186 °C;^{1}H-NMR (DMSO-d6, 300 MHz): δ 3.63 (3H, s, CH_3), 3.71 (3H, s, CH_3), 5.44 (2H, s, CH_2), 6.36–6.38 (1H, d,$J = 6$Hz, Ar-H), 6.64–6.69 (1H, d, $J = 6$Hz, Ar-H), 6.90–6.93 (1H, d, $J = 6$Hz, Ar-H), 7.18–7.25 (4H, m, Ar-H), 7.47 (1H, s, Ar-H), 7.76–7.77 (1H, d, $J = 3.9$ Hz Ar-H), 8.98 (1H, s, OH), 9.56 (1H, s, OH); LCMS (ESI): m/z 377 ($M + H^+$).

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An Expeditious Synthesis of 3-methyl-4-arylmethylene-isoxazole-5(4*H*)-ones Using Aqueous Extract of *Acacia concinna* Pods as a Natural Surfactant Catalyst

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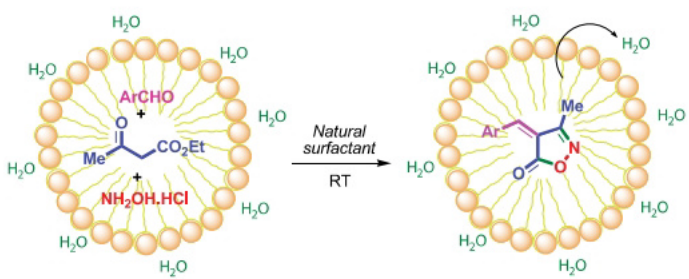
ABSTRACT An aqueous extract of *Acacia concinna* pods has been employed as a competent and effective natural surfactant type catalyst for the synthesis of 3-methyl-4-arylmethylene-isoxazole-5(4*H*)-one analogs through one-pot, three-component reaction of β-ketoester, aldehydes, and hydroxylamine hydrochloride. The present cyclocondensation reaction was performed in an environmentally benign catalytic system at room temperature and afforded the desired compounds in excellent yields. The advantages of this method are simple, economically viable, and biocompatible catalytic system suggested the possible utility of the present protocol for the large-scale construction of isoxazole cores.



KEYWORDS Natural surfactants, *Acacia concinna*, 3-methyl-4-arylmethylene-isoxazole-5(4*H*)-one, Green methodology, Multicomponent reaction.

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An expeditious synthesis of 1,3-oxazine and Betti bases catalyzed by aqueous extract of *Acacia concinna* pods as an efficient surfactant type catalyst

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Abstract: An efficient and simple procedure for the synthesis of 1,3-oxazines and Betti bases *via* Mannich type reaction was successfully carried out in aqueous extract of *Acacia concinna* pods as a green alternative. The present surfactant catalyst was found to be expeditious for in terms of economic viability, mild reaction conditions, good to excellent product yield and environment friendliness.

Keywords: Natural surfactants, *Acacia concinna,* Betti bases, 1,3-oxazines, green protocol.

INTRODUCTION

The identification and characterization of new catalysts isolated from natural resources has been enormously increasing to overcome various environmental constraints. These catalysts play an important role in acceleration of rate of the chemical reactions as well as ease of isolation of the final product. Nowadays, numerous natural and synthetic materials like supercritical solvent, ionic liquids, clays, enzymes and surfactants are extensively recognized as an alternative to the traditional expensive and toxic catalyst and reagents [1-3]. The surfactants isolated from natural sources are well known to have remarkable biological potential [4–6]. Moreover, the catalytic properties of these surfactants have been extensively studied. Specifically, the plant cell culture of *Daucus carota* root [7–12], soaked *Phaseolus Aureus* (green grams) [13], and coconut juice (*Cocos Nucifera*) [14] has been successfully utilized as biocatalysts for selective reduction of ketones. In the previous reports, aqueous extract of *Acacia concinna* has been utilized for the synthesis of 3-carboxycoumarins, cinnamic acids [15], acylation of amines [16] and synthesis of aryl-hydrazones [17].

Oxazine derivatives exhibits broad range of

bioactivities including anticancer (**A and B**), antibacterial (**C**), anticonversant, antitubular, non-nucleoside reverse transcriptase inhibitor (efavirenz) (**D**), drug (Ketazolam) (**E**) [18] (**Figure 1**), anti HIV-1 [19], anti-Parkinson's agents [20]. Due to broad range of bioactivities associated with these class of compounds, their synthesis is the major concern. Traditionally, 1,3-oxazine derivatives can be synthesised by using two step process from primary amines, aldehyde and phenols [21]. Although, several methods are reported so far for the synthesis of target compounds [22–24], only limited numbers of protocols are feasible on the basis of the multi component reactions (MCRs) [25].

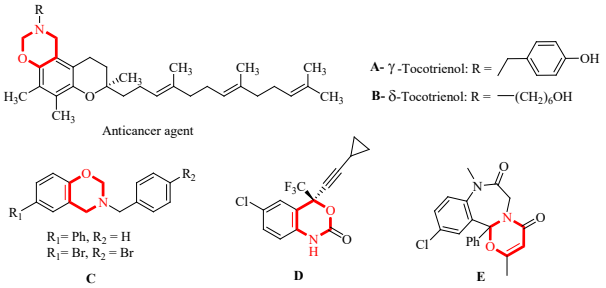


Figure 1.

Betti reaction is one of the most important C-C bond-forming reactions, which is typically a Mannich reaction [26]. Betti bases have associated with various synthetic and biological applications. They have exihibited various pharmacological properties like anti-bacterial, antipain and antihypertensive activities [27–30] **(Figure 2)**.

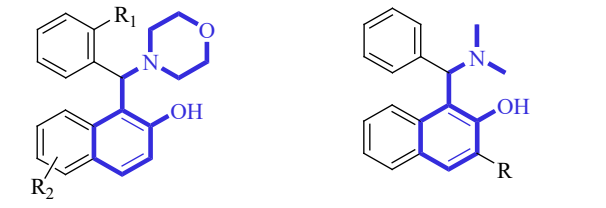


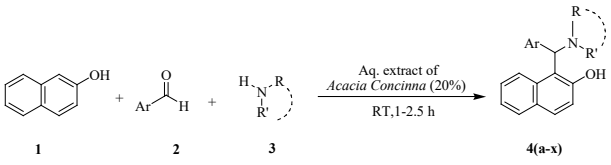
Figure 2. Biologically active Betti bases.

The classical Betti reaction involved the two step reaction of aldehyde, ammonia or urea and β-naphthol in an ethanolic solution of potassium hydroxide for 9–36 h [26,31]. Consequently, several recent reports on Betti reaction have been developed to overcome the drawbacks of the classical method. Therefore, the preferable route will be multicomponent reaction of aldehyde, amine and phenol [26,32,33]. Herein, we have reported the sustainable synthesis of Betti bases catalysed by aqueous extract of *Accacia concinna.*

Acacia concinna (commercially known as "Shikakai" in India) pods have surfactant properties since it contains saponins, which are foaming agents [34,35]. In addition, there is presence of acacic acid as one of the chemical constituent in the aqueous extract of pods of *Acacia concinna* [36]. In present protocol catalytic activity of the natural surfactant was studied for the synthesis of 1,3-oxazine and Betti bases.

Result and Discussion

In the present study, a simple, cost effective and green protocol for the synthesis of Betti bases and 1,3-oxazine derivatives using an aqueous extract of pods of *Acacia concinna* has been reported **(Scheme 1 and 2)**. The methodology presented here is in persistence of our ongoing research on construction of novel synthetic method for biologically active compounds [37].



Scheme 1. Synthesis of Betti Bases by using 2-naphthol

Initially, efficiency of the catalyst was studied by

conducting reaction of β-naphthol (**1**) (1mmol), benzaldehyde (**2a**) (1 mmol) and piperidine (1 mmol) using surfactant catalyst (20% w/v, 5 mL) aqueous extract of *Acacia concinna* pods at room temperature and we were pleased to get an admirable yield of product **4a** (94%) after 1 h. The above outcome encouraged us for the optimization the reaction conditions for the same reaction in presence of different concentrations aqueous extract of *Acacia concinna* pods. The results obtained suggested that 20% of the catalyst concentration was adequate to get maximum yield of the product. Further, increase in catalyst concentration as 30, 40 and 50% did not affected the yield of final product. The result obtained was summarised in **Table 1**. In order to estimate the catalytic strength of the present catalyst various surfactants like sodium dodecyl sulphate (SDS), triton X-100 and cetyl pyridinium bromide (CPB) were used. It has been observed that when the reaction was conducted in the presence of sodium dodecyl sulphate (SDS) as an anionic surfactant, the product '**4a**' was obtained in 64% yield (**Table 2**, entry 2). With other surfactants such as Triton X-100 and cetyl pyridinium bromide (CPB) did not showed appreciable results (**Table 2**, entries 3, 4). Therefore the present surfactant catalyst was found to be superior for the synthesis of structurally diversified Betti bases. Moreover the catalytic property of natural surfactant might be attributed due to the presence of saponins which solubilises the reactant molecules in aqueous surfactant. This may alters the number of favourable collisions among the reactant molecules. The surfactant property of extract leads to encapsulation of the reactants in micellar cages. This process of encapsulation drives the equilibrium toward product side by expelling the water molecule out of its hydrophobic interior (**Figure 3 and 4**) [15].

Table 1. Optimization of catalyst concentration for formation of '4a'

Entry	Catalyst concentration (%)	Time (h)	Yield(%)[a]
1.	10	1.25	89
2.	**20**	**1**	**94**
3.	30	1.50	93
4.	40	1.40	92
5.	50	1.35	92
6.	Catalyst free	12	--[b]

[a]*Isolated yield of the product,* [b]*No product formation was observed.*

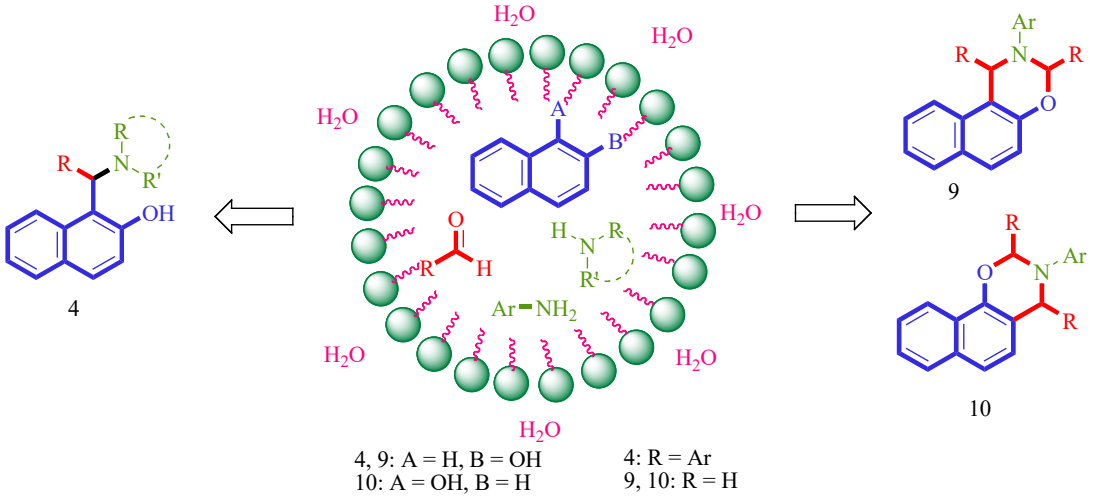


Figure 3. Micelle-promoted synthesis of Betti bases and oxazine derivatives

Table 2. Effect of surfactant for the formation of '4a'

Entry	Surfactant[a]	Time (h)	Yield (%)[b]
1.	None	12	--[c]
2.	SDS	2.25	64
3.	Triton X-100	2	56
4.	CPB	2.5	45
5.	***Acacia concinna* extract 20% (w/v)**	**1**	**94**

[a]*Reaction condition: 2-naphthol(**1**) (1mmol), benzaldehyde (**2**) (1 mmol) and piperidine* (**3**) (1 mmol)*, room temperature.* [b]*Isolated yield.* [c]*No reaction.*

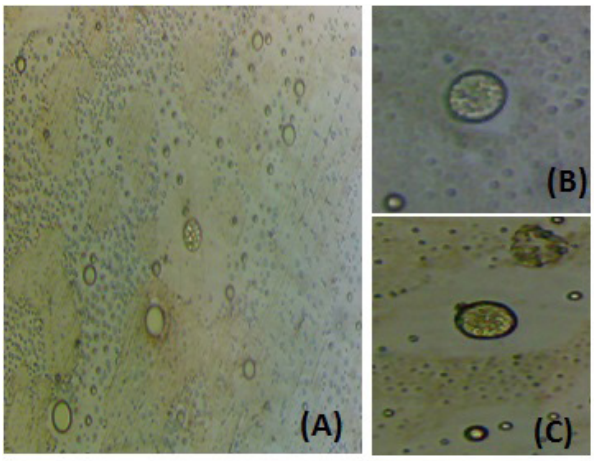


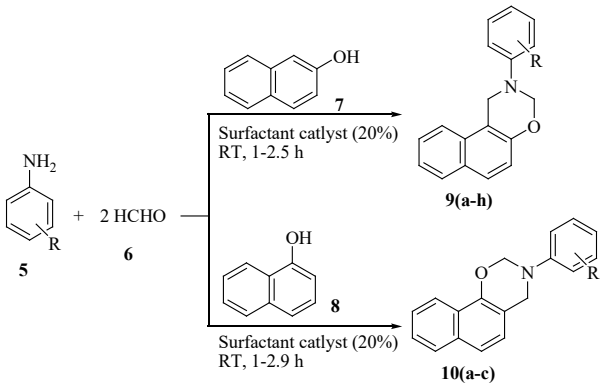
Figure 4. Photograph of micelle observed in reaction medium during formation of '4a'

Surfactant is found to decrease the surface tension of aqueous solution which increases wetting and spreading properties of water **(Table 3**) [38]. A several reactions such as redox, photochemical, enzymatic, Diels-Alder, photochemical etc are altered due to decrease the surface tension of medium [39].

Table 3. Effect of surface tension of surfactant solution on rate of reaction

Entry	Catalyst concentration %(w/v)	Time (h)	Surface Tension 'T' (dyne/cm)
1.	50	1.35	13.48
2.	40	1.40	18.87
3.	30	1.50	32.34
4.	**20**	**1**	**40.43**
5.	10	1.25	48.51
6.	Distilled Water	--	67.38

The desired Betti bases were obtained in admirable yields. Chemically reactive substrates like thiophene-2-aldehyde underwent smooth to produce corresponding Betti bases without any side product formation (**Table 4**, Entry-19). In general, all amines undergo multi-component condensation afforded corresponding Betti bases.



Scheme 2. Synthesis of oxazine derivatives

For further exposure of the synthetic potential of this aqueous methodology, we have successfully applied the method for synthesis of oxazine derivatives (**Scheme 2, Table 5**).

Table No. 4. Synthesis of 1(α-amino alkyl) 2-naphthol derivatives

Entry	Aldehydes	Amines	Product	Time(h)	Yield%	M.P.(°C)
1	C_6H_5CHO	Piperidine	**4a**	1	94	192-194[40]
2	C_6H_5CHO	$C_6H_5NH_2$	**4b**	1.25	91	132-133[40]
3	C_6H_5CHO	$4\text{-}NO_2C_6H_4NH_2$	**4c**	2.5	82	154-156[40]
4	C_6H_5CHO	Pyrrolidine	**4d**	1.8	94	176-177[40]
5	Vanillin	$4\text{-}NO_2C_6H_4NH_2$	**4e**	2.4	83	202-206[42]
6	3,4-dimethoxy-benzaldehyde	$C_6H_5NH_2$	**4f**	1.8	90	140-143[40]
7	$2\text{-}NO_2C_6H_4CHO$	$3\text{-}NO_2\ C_6H_4NH_2$	**4g**	2.8	86	192-194[43]
8	$3\text{-}NO_2C_6H_4CHO$	Pyrrolidine	**4h**	1.6	88	185-186[44]
9	$4\text{-}ClC_6H_4CHO$	$C_6H_5NH_2$	**4i**	1.4	91	121-123[40]
10	$4\text{-}\ NO_2C_6H_4CHO$	Morpholine	**4j**	1.8	86	178-179[45]
11	Pyridine-4-aldehyde	Piperidine	**4k**	1.2	90	185-187[45]
12	$4\text{-}\ NO_2C_6H_4CHO$	$C_6H_5NH_2$	**4l**	2.1	83	136-138[46]
13	$3\text{-}BrC_6H_4CHO$	$C_6H_5NH_2$	**4m**	1.8	88	139-141[46]
14	$3\text{-}ClC_6H_4CHO$	$C_6H_5NH_2$	**4n**	2.2	90	141-143[46]
15	$4\text{-}CH_3OC_6H_4CHO$	$C_6H_5NH_2$	**4o**	1.2	92	135-137[46]
16	$3\text{-}NO_2C_6H_4CHO$	Piperidine	**4p**	2.1	86	185-186[46]
17	$2\text{-}ClC_6H_4CHO$	$C_6H_5NH_2$	**4q**	1.6	88	150-152[40]
18	$3\text{-}ClC_6H_4CHO$	$3\text{-}ClC_6H_4NH_2$	**4r**	1.4	90	121-123[40]
19	C_6H_5CHO	Thiophene-2-aldehyde	**4s**	1.2	94	161-163[40]
20	C_6H_5CHO	Morpholine	**4t**	1.6	88	174-176[40]
21	$2\text{-}ClC_6H_4CHO$	Morpholine	**4u**	1.8	86	163-165[40]
22	$3\text{-}ClC_6H_4CHO$	Morpholine	**4v**	1.4	90	160-162[40]
23	$4\text{-}ClC_6H_4CHO$	Morpholine	**4w**	1.2	92	155-157[40]
24	$4\text{-}CH_3OC_6H_4CHO$	$3\text{-}NO_2C_6H_4NH_2$	**4x**	1.6	88	173-175[43]

** Reaction condition – Reaction mediated by 20 % aq. solution of Acacia Concinna and 2-nahphtol as phenol*

Table 5- Synthesis of 2,3-dihydro-2-phenyl-1H-naphtho[1,2-e][1,3] oxazine derivatives

Entry	Amine	Products	Time(h)	Yield (%)[a,b]	M.P.(°C) [ref]
1	$C_6H_5NH_2$	**9a**	2.1	90	46-48[47]
2	4-$CH_3C_6H_4NH_2$	**9b**	2	92	86-88[47]
3	3-$NO_2C_6H_4NH_2$	**9c**	2.8	82	132-134[47]
4	4-$NO_2C_6H_4NH_2$	**9d**	2.9	80	168-170[47]
5	2-$NO_2C_6H_4NH_2$	**9e**	2.4	86	109-110[47]
6	4-$ClC_6H_4NH_2$	**9f**	2.1	92	136-138[47]
7	4-$BrC_6H_4NH_2$	**9g**	2	90	118-119[41]
8	4-$CH_3OC_6H_4NH_2$	**9h**	2.1	94	75-77[41]
9	$C_6H_5NH_2$	**10a**	2	90	111-113[41]
10	4-$CH_3OC_6H_4NH_2$	**10b**	1.8	94	300(d) [41]
11	2,4,6-tri-$BrC_6H_2NH_2$	**10c**	1.8	94	76-77[41]

[a]Isolated yield of the product. [b]All the products are characterized by IR, ^{1}H NMR and Mass spectral data.

Conclusion

In conclusion, we have introduced environmental benign, efficient and economical catalyst as aqueous extract of *Acacia concinna* pods for the synthesis of Betti bases and oxazine derivatives. The striking features of current methodology are mild reaction conditions, high purity, short reaction time, high yield of products and a simple reaction workup procedure. Obtaining pure products by simply filtering makes possibility to approach for large scale production of Betti bases and oxazine derivatives.

EXPERIMENTAL SECTION

General

All chemicals were purchased from commercial suppliers and were used without further purification. Melting points were recorded on Digital Electro thermal Melting point apparatus (VEEGO, VMP-DS) and are uncorrected. The completion of reactions was confirmed with the help of Thin Layer Chromatography (TLC) using pre-coated Silica gel 60 F_{254} plates with layer thickness 0.25nm purchased from Merck Ltd. ^{1}H-NMR was recorded on Varian-NMR mercury 400 MHz spectrometer. Mass spectra were recorded on Varian MAT 311 A at 70 ev.

General procedure for the preparation of catalyst

A fine powder of *Acacia concinna* pods (20 g) in water (100 mL) was heated in a 250 mL conical flask at 100°C for 20 min. The mixture was filtered to remove all solid material and the aqueous extract was collected. The prepared extract has concentration 20% w/v.

General procedure for synthesis of 1-(α-amino alkyl) 2-naphthol derivatives (4a-x)

A mixture of 2-naphthol (1 mmol), aldehyde (1 mmol) and amine (1 mmol) in surfactant medium (20% w/v, 5 mL) was stirred at room temperature for specified time shown in Table 4. After completion of reaction (as indicated by TLC), reaction mixture was filtered using Whatmann No.1 filter paper. The product collected was recrystallized by using proper solvent and dried.

General procedure for synthesis of 2,3-dihydro-2-phenyl-1*H*-naphtho[1,2-e][1,3]oxazine derivatives (9a-h and 10a-c)

A mixture of 1-naphthol or 2-naphthol (1 mmol), amine (1 mmol) and formaldehyde (2 mmol) in surfactant medium (20% w/v, 5 mL) was

stirred at room temperature for specified time shown in Table 5. After completion of reaction (as indicated by TLC), reaction mixture was filtered using Whatmann No.1 filter paper. The product collected was recrystallized by using proper solvent and dried.

Spectroscopic data for representative compounds

1-(Phenyl(pipyridin-1-yl)methyl)naphthalen-2-ol (4a)

White solid; Yield 85 %; mp: 192–194 ^{0}C; 1H NMR (400MHz, $CDCl_3$,ppm): 13.81 (bs, 1H), 7.98-8.01 (d, *J* = 8.8 Hz, 1H), 7.67-7.74 (d, *J* =8.8Hz, 2H), 7.59-7.61 (m, 2H), 7.37-7.4 (t, *J* = 7.6 Hz, 1H), 7.19–7.35 (m, 5H), 7.06-7.09 (m, 1H), 5.28 (s, 1H), 2.35–2.50 (m, 4H), 1.45–1.55 (m, 6H). LCMS (ESI): m/z 318 ($M+H^+$)

1-[(3-nitrophenyl)(pyrrolidin-1-yl)methy] naphthalen-2-ol (4h)

White solid; Yield 94 %; mp:97-99◦C; 1H NMR (400MHz, $CDCl_3$,ppm): 8.53 (bs, 1H), 8.12-8.14(d, *J*=8 Hz, 1H), 8.07-8.09 (d, *J*=7.6 Hz, 1H), 7.72-7.76 (t, 2H), 7.59-7.63 (t, 1H), 7.40-7.44 (t, 1H), 7.23-7.26 (t, 1H), 7.11-7.13(m, 1H), 5.63 (s, 1H), 2.67 (m, 2H), 2.50 (m, 2H), 1.81 (m, 4H). LCMS (ESI): m/z 349 ($M+H^+$)

2-(4-chlorophenyl)-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazine (9f)

White solid; Yield 92 %; mp: 136-138◦C; 1H NMR (400MHz, $CDCl_3$,ppm): 7.83-7.89 (dd, 2H), 7.70-7.73 (d, *J*=8.8 Hz, 1H), 7.52-7.56 (t, 1H), 7.37-7.41 (t, 1H), 7.25-7.28 (t, 2H), 7.20-7.22 (d, *J*=9.2 Hz, 2H), 7.01-7.04 (d, *J*=8.8 Hz, 1H), 5.51 (s, 2H), 4.97 (s, 2H). LCMS (ESI): m/z 296 ($M+H^+$)

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N-butylpyridinium heptachlorodialuminate as a highly efficient catalyst for the synthesis of polyhydroquinolines under solvent-free ultrasound condition.

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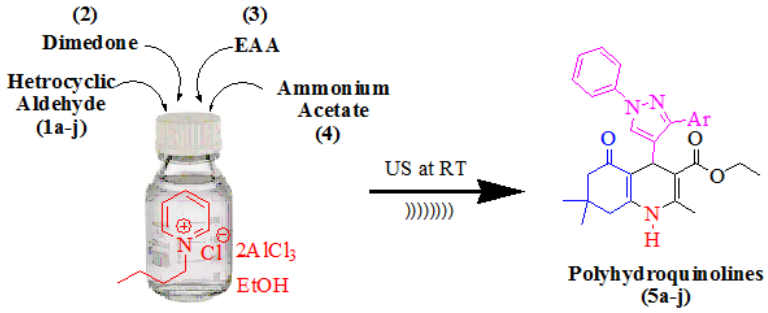
Abstract: A novel, simple and green protocol were adopted for the one pot synthesis of polyhydroquinoline derivatives from heterocyclic aldehydes, dimedone, ethyl acetoacetate and ammonium acetate by ultrasound irradiation at room temperature. The catalytic system is very effective for the bulkier aldehydes to give the corresponding polyhydroquinoline derivatives in excellent yield (80-92%) and easy for isolation of the product. This approach has the various benefits includes simple work-up procedure, excellent yields and environmentally benign path. The structure of synthesized compounds was confirmed by analytical techniques such as FTIR, 1HNMR, 13C NMR and Mass spectrometry.

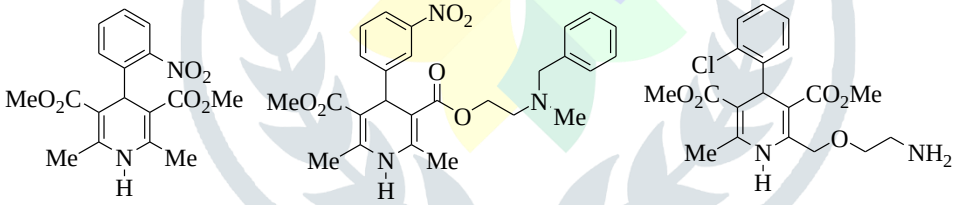


Keywords: 3-aryl-1-phenyl-1*H*-pyrazole-4-carboxaldehydes, *N*-butylpyridinium heptachlorodialuminate, Ultrasound Irradiation, polyhydroquinoline, multicomponent reaction.

1. Introduction

In recent years, Ionic liquids have been widely employed as green alternatives to those of conventional hazardous organic solvent. ILs has also been made significant growth in the catalytic processes. ILs has the potential to exhibit low human toxicities as well as eco-toxicities. It has been employed for various organic reactions include coupling reaction, hydrogenation, Diels-alder reaction, electrochemical reaction, esterification, friedal-Craft reaction, multicomponent reaction, etc. as a catalyst or solvent.[1-10]

Heterocycles are of enormous significance in the design and discovery of new compounds for biological applications.[11-12] The polyhydroquinoline scaffolds are also an important group of nitrogen containing heterocycle of extensive interest due to the significant structural design of the drugs for the treatment of cardiovascular diseases as well as hypertension.[13-14] They have also shows broad spectrum of biological activities such as antidiabetic, antiatherosclerotic, antitumor, bronchodilator, geroprotective, hepatoprotective, neuroprotectant, platelet anti-aggregratory activity, cerebral anti-ischemic activity in the treatment of Alzheimers disease and chemosensitizers in tumor therapy.[15-23] The some important drugs containing 1,4-dihyropyridine nucleus is given in below Figure 1.



1. Nifedipine **2.** Nicardipine **3.** Amlodipine

Cadiovascular agents effective in treatment of hypertension

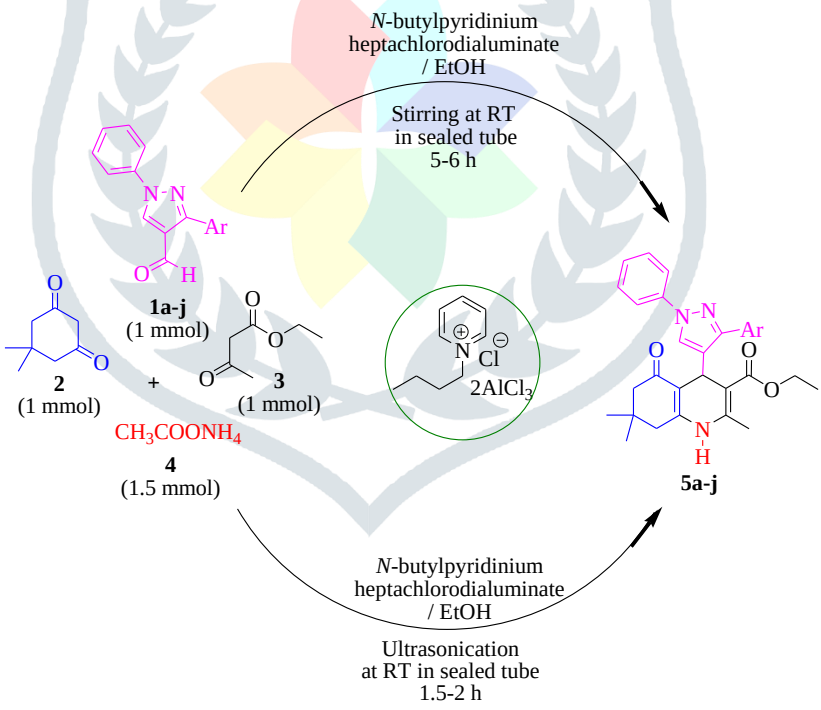
Figure 1. Illustrations of 1, 4-Dihydropyridine containing drugs

In 1882, the scientist Hantzsch and et al. firstly synthesized 1,4-DHPs by MCR of aldehyde, ethylacetoacetate and ammonia in AcOH under reflux condition in ethanol,[24] whereas polyhydroquinolines have been synthesized by using cyclic 1,3-dione instead of one mole ethyl acetoacetate. The various conventional and non-conventional methods has been employed for the synthesis of polyhydroquinoline derivatives in combination with different homogeneous as well as heterogeneous catalyst such as 5-pyrrolidin-2-yl-tetrazole,[25] Ni(0) nanoparticles,[26] La_2O_3/TFE,[27] cerium (IV) ammonium nitrate (CAN),[28] PPA-SiO_2,[29] TiO_2 NPs,[30] SnO_2,[31] SBA-15/SO_3H,[32] $HClO_4$-SiO_2,[33] $Gd(OTf)_3$,[34] (bzacen)MnCl,[35] $Cs_{2.5}H_{0.5}PW_{12}O_{40}$,[36] [1-Vinyl-3-ethyl imidazolium

iodide],[37] $[TBA]_2[W_6O_{19}]$,[38] bismuth(III) bromide,[39] Fe_3O_4@chitosan,[40] $[MSAIm]HSO_4$,[41] [2-MPyH]OTf,[42] DSIMHS,[43] [Pyridine-SO_3H]Cl,[44] $[hmim]BF_4$,[45] [SBA-IL],[46] molecular iodine[47] and Ni nanoparticle[48] etc.

In the last decades, ultrasound assisted synthesis is an important and well established technique, which were proceeds via the formation and adiabatic collapse of the transient cavitations bubble. It is used as an environmentally benign technique that is useful tool for achieving the green chemistry goals, helping to minimize the waste formation and reduce energy requirements. It also displays smooth and cleaner reactions by improving yields with homogeneous and heterogeneous processes.[49-52]

In present work instead of simple benzaldehyde derivatives, we have used 4-formyl pyrazole as a heterocyclic aldehyde for synthesis of polyhydroquinoline derivatives using *N*-butylpyridinium heptachlorodialuminate as a catalyst in ethanol under stirring condition and ultrasound irradiation for appropriate time. The syntheses of 3-aryl-1-phenyl-1*H*-pyrazole-4-carboxaldehydes were carried out by Vilsmeier-Haack reaction.[53]



Scheme 1. Synthesis of Polyhydroquinolene derivatives (5a-j)

2. Experimental

General procedure for the synthesis of polyhydroquinolene derivatives (5a-j)

2.1 Under stirring at room temperature

A 25 mL sealed tube was charged with 3-aryl-1-phenyl-1*H*-pyrazole-4-carboxaldehyde 1 (1 mmol), dimedone 2 (0.140 g, 1 mmol), ethyl acetoacetate 3 (0.130 g, 1 mmol), and NH_4OAc 4 (1.5 mmol) in 10 mL of ethanol. The sealed tube was placed in an ice bath to attain the temperature less than 10˚C. The catalytic amount of ionic liquid *N*-butylpyridinium heptachlorodialuminate was added. The sealed tube was capped and the reaction mixture was stirred for suitable time using a magnetic stirrer at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the content was poured into cold water; solid crude product thus obtained was separated by filtration. The product was dried and purified by recrystallization in n-hexane-ethyl acetate. The physical data of synthesized compounds are given in **Table 2**.

2.2 Under ultrasound irradiation at room temperature

A 25 mL sealed tube was charged with 3-aryl-1-phenyl-1*H*-pyrazole-4-carboxaldehyde 1 (1 mmol), dimedone 2 (0.140 g, 1 mmol), ethyl acetoacetate 3 (0.130 g, 1 mmol), and NH_4OAc 4 (1.5 mmol) in 10 mL of ethanol. The sealed tube was placed in an ice bath to attain the temperature less than 10˚C. The catalytic amount of *N*-butylpyridinium heptachloro-dialuminate was added. The sealed tube was capped and the reaction mixture was placed for ultra-sonication for suitable time at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the content was poured in cold water; solid crude product thus obtained was separated by filtration. The product was dried and purified by recrystallization in n-hexane-ethyl acetate. The physical data of synthesized compounds are given in **Table 2**.

3. Results and Discussion

Initially, we were interested in developing a facile protocol for the synthesis of polyhydroquinoline derivatives using ionic liquid *N*-butylpyridinium heptachlorodialuminate as catalyst. When 1-phenyl-3-*p*-tolyl-1*H*-pyrazole-4-carbaldehyde **1** was treated with dimedone **2**, ethylacetoacetate **3**, and NH_4OAc **4** by grinding and stirring in ethanol solvent without catalyst, formation of polyhydroquinoline was not observed. Also in the water and toluene the reaction did not proceed to any extent in the presence of a catalyst.

Table 1. Optimization of the reaction condition to synthesize ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-(1-phenyl-3-*p*-tolyl-1*H*-pyrazol-4-yl)quinoline-3-carboxylate (5a)

Entry	Catalyst/Solvent	Reaction Condition	Time	Isolated Yield (%)
1	No catalyst/SF	Grinding	1 h	NR
2	No catalyst/EtOH	Stirring at RT	12 h	NR
3	100 mg IL-kit/SF	Grinding	1 h	NR
4	50 mg IL-Kit/H_2O	Stirring at RT	5 h	NR
5	50 mg IL-Kit/EtOH	Stirring at RT	5 h	55
6	75 mg IL-Kit/EtOH	Stirring at RT	5 h	72
7	100 mg IL-Kit/EtOH	Stirring at RT	5 h	88
8	125 mg IL-Kit/EtOH	Stirring at RT	5 h	88
9	100 mg IL-Kit/Toluene	Stirring at RT	5 h	NR
10	100 mg IL-Kit/EtOH	US Irradiation at RT	1.5 h	90

Reaction condition: aldehyde **1** (1 mmol), Dimedone **2** (1 mmol), ethyl acetoacetate **3** (1 mmol), NH_4OAc **4** (1.5 mmol) and 0-125 mg IL-kit

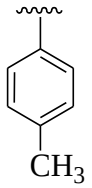
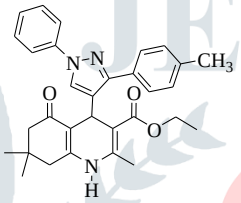
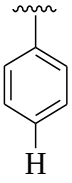
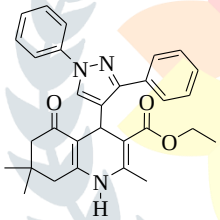
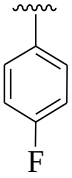
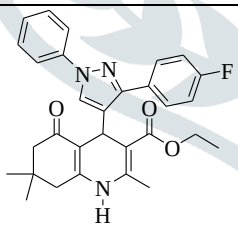
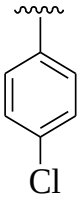
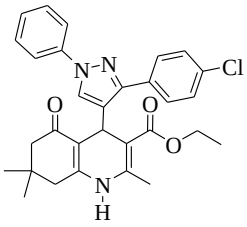
It was interesting to find that, the reaction was proceeding by simply stirring in ethanol at room temperature catalyzed by 50mg of *N*-butylpyridinium heptachlorodialuminate in low yield. However, by optimizing the amount of catalyst such as 50, 75, 100, 125 and optimum solvent quantity, it was possible to obtain polyhydroquinolines in good yields. Thus, the polyhydroquinoline derivative (**5a**) was obtained in excellent yield (88%) with high selectivity in the presence of 100 mg of ionic liquid by simply stirring at room temperature.

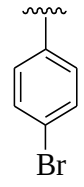
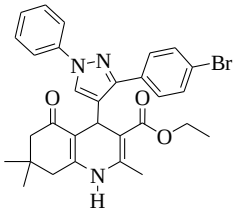
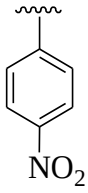
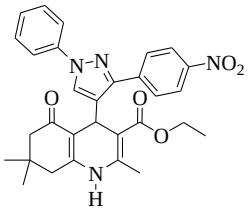
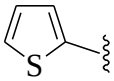
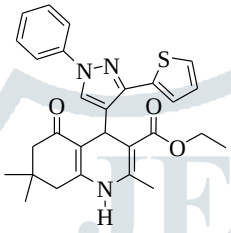
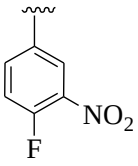
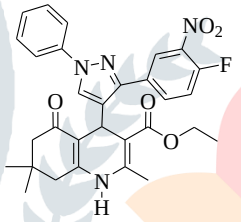
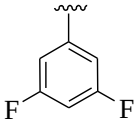
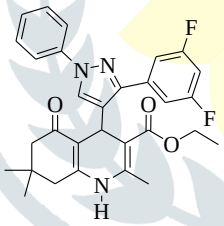
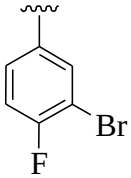
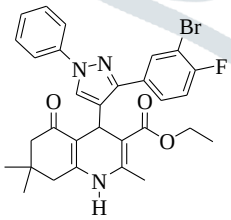
When the same model reaction was carried out under ultrasound irradiation at room temperature in the presence of *N*-butylpyridinium heptachloro-dialuminate in ethanol as solvent, the desired polyhydroquinoline (**5a**) was obtained in excellent yield (90%). Among all the systems studied, a combination of ionic liquid in ethanol was found to be the best preference, which was taken for synthesis of further derivatives.

To evaluate the efficiency and the applicability of the procedure, a variety of substituted heterocyclic aldehydes **1a-j** were used to give the corresponding polyhydroquinoline derivatives **5a-j** in good yields (80-92%) under optimized conditions.

The substrate with electron donating as well as electron withdrawing groups reacts smoothly to afford the product with excellent yield and selectivity. Also under the ultrasound irradiation yield of the product was increased with a reduction of reaction time than the stirring method. The data of synthesized polyhydroquinoline derivatives are given in **Table 2**.

Table 2. Synthesis of polyhydroquinoline derivatives (5a-j) using *N*-butylpyridinium heptachlorodialuminate.

Entry	Ar – Group	Product	Reaction Time (hrs)		Yield (%)		M.P. (˚C)
			Stirring at RT	US at RT	Stirring at RT	US at RT	
5a			5	1.5	88	90	224-226
5b			5	1.5	90	90	218
5c			5.5	1.5	84	84	206
5d			5.5	1.5	86	88	256-258

5e			6	2	88	92	262-264
5f			6	2	84	85	300<
5g			5.5	1.5	88	92	196-198
5h			6	2	82	82	300<
5i			6	2	82	84	300<
5j			5.5	1.5	82	86	226-228

Reaction condition: aldehyde **1** (1 mmol), dimedone **2** (1 mmol), ethyl acetoacetate **3** (1 mmol), NH_4OAc **4** (1.5 mmol) and 100 mg IL-kit in 10 mL ethanol.

4. Discussion of Spectral data of Synthesized Compounds

***ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-(1-phenyl-3-p-tolyl-1H-pyrazol-4-yl)quinoline-3-carboxylate* (Table 2, Entry 5a).**

The product was obtained as white solid: mp 224-226˚C; FT-IR (KBr) ν: 3273, 3199, 3071, 2957, 1737, 1686, 1598, 1488, 1449, 1390, 1212, 1169, 1025, 830, 740; ^{1}H NMR (DMSO-d_6, 400 MHz) δ= 0.69 (t, J=6.0

Hz, 3H, -CH_3), 0.99 (s, 3H, -CH_3), 1.05 (s, 3H, -CH_3), 2.09 (s, 2H, -CH_2-), 2.24 (s, 3H, -CH_3), 2.39 (s, 5H, -CH_2- & -CH_3), 3.74 (m, J=6.0 Hz, 2H, -CH_2-), 5.10 (s, 1H, -CH-), 7.24 (d, J=6.2 Hz, 3H, Ar-H), 7.44 (t, 2H, Ar-H), 7.72 (d, J=7.2 Hz, 2H, Ar-H), 7.93 (s, 1H, Ar-H, Pyrazole ring-H), 7.96 (d, J=7.0 Hz, 2H, Ar-H), 8.98 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 13.53, 18.07, 20.90, 26.16, 27.10, 28.77, 32.17, 50.41, 58.45, 105.06, 110.37, 117.84, 125.60, 127.06, 128.26, 128.35, 129.21, 129.26, 131.65, 136.25, 139.25, 143.49, 149.49, 150.05, 166.70, 194.62; MS(ESI m/z %): 518.25 $[M+Na]^+$.

***ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-(1,3-diphenyl-1H-pyrazol-4-yl)quinoline-3-carboxylate* (Table 2, Entry 5b)**.

The product was obtained as white solid: mp 218˚C; FT-IR (KBr) ν: 3275,3180, 3068, 2955, 1739, 1698, 1650, 1599, 1542, 1495, 1381, 1213, 1148, 1074, 959, 752; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.64 (t, J=5.6 Hz, 3H, -CH_3), 0.97 (s, 3H, -CH_3), 1.04 (s, 3H, -CH_3), 2.05 (s, 2H, -CH_2-), 2.08 (s, 3H, -CH_3), 2.31 (s, 2H, -CH_2-), 3.72 (q, J=5.6 Hz, 2H, -CH_2-), 5.10 (s, 1H, -CH-), 7.27 (t1H, Ar-H), 7.39 (t, 1H, Ar-H), 7.45-7.49 (m, 4H, Ar-H), 7.78 (m, 2H, Ar-H), 8.04 (s, 1H, Ar-H, Pyrazole ring-H), 8.08 (d, 2H, Ar-H), 9.05 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 14.14, 18.60, 26.65, 27.60, 29.22, 32.72, 50.85, 58.99, 105.26, 110.67, 118.47, 126.40, 127.80, 128.03, 128.37, 128.98, 129.93, 130.38, 135.01, 139.90, 144.28, 150.18, 150.50, 167.22, 195.28; MS(ESI m/z %): 504.32 $[M+Na]^+$.

***ethyl 4-(3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (Table 2, Entry 5c).**

The product was obtained as white solid: mp 206˚C; FT-IR (KBr) ν: 3269, 3204, 3074, 2958, 1687, 1645, 1628, 1599, 1526, 1486, 1377, 1211, 1079, 844, 741; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.75 (t, J=6.8 Hz, 3H, -CH_3), 0.92 (s, 3H, -CH_3), 1.02 (s, 3H, -CH_3), 2.17 (s, 2H, -CH_2-), 2.22 (s, 3H, Ar-CH_3), 2.41 (s, 2H, -CH_2-), 3.79 (q, J=6.8 Hz, 2H, -CH_2-), 5.09 (s, 1H, -CH-), 7.34 (m, 1H, Ar-H), 7.45 (m, 3H, Ar-H), 7.83 (m, 2H, Ar-H), 7.97 (m, 2H, Ar-H), 8.14 (m, 2H, Ar-H and Pyrazole ring-H), 9.13 (s, 1H, NH).

***ethyl 4-(3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (Table 2, Entry 5d).**

The product was obtained as white solid: mp 256-258˚C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.72 (t, 3H, -CH_3), 0.98 (s, 3H, -CH_3), 1.06 (s, 3H, -CH_3), 2.09 (s, 2H, -CH_2-), 2.22 (s, 3H, Ar-CH_3), 2.39 (s, 2H, -CH_2-), 3.77

(m, 2H, -CH_2-), 5.07 (s, 1H, -CH-), 7.25 (s, 1H, Ar-H), 7.45 (s, 4H, Ar-H), 7.73 (s, 2H, Ar-H), 7.95 (s, 1H, Pyrazole ring-H), 8.14 (d, J=7.2 Hz 2H, Ar-H), 9.02 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 13.54, 18.16, 26.21, 27.07, 28.75, 32.20, 50.35, 58.53, 110.36, 117.98, 125.81, 127.41, 127.71, 129.19, 129.96, 130.04, 132.21, 133.30, 139.32, 143.80, 148.72, 149.52, 166.59, 194.74; MS(ESI m/z %): 538.18 $[M+Na]^+$.

ethyl 4-(3-(4-bromophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate **(Table 2, Entry 5e).**

The product was obtained as white solid: mp 262-264˚C; FT-IR (KBr) ν: 3383, 3206, 3068, 2960, 1687, 1645, 1598, 1501, 1486, 1378, 1278, 1212, 1075, 961, 835; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.72 (t, J=6.0 Hz, 3H, -CH_3), 0.91 (s, 3H, -CH_3), 1.04 (s, 3H, -CH_3), 2.16 (s, 2H, -CH_2-), 2.23 (s, 3H, Ar-CH_3), 2.34 (m, 2H, -CH_2-), 3.81 (q, J=6.0 Hz, 2H, -CH_2-), 5.10 (s, 1H, -CH-), 7.32 (t, J=6.0 Hz, 1H, Ar-H), 7.47 (m, 2H, Ar-H), 7.73-7.82 (m, 3H, Ar-H), 7.99 (m, 2H, Ar-H), 8.19 (s, 1H, Ar-H, Pyrazole ring-H), 8.41 (m, 1H, Ar-H), 9.11 (s, 1H, NH).

ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-4-(3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)-5-oxoquinoline-3-carboxylate **(Table 2, Entry 5f).**

The product was obtained as white solid: mp 300˚C<; FT-IR (KBr) ν: 3267, 3199, 3073, 2980, 1691, 1646, 1599, 1521, 1487, 1379, 1342, 1212, 1065, 866; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.67 (t, J=5.6 Hz, 3H, -CH_3), 0.95 (s, 3H, -CH_3), 1.04 (s, 3H, -CH_3), 2.00 (s, 2H, -CH_2-), 2.24 (s, 3H, Ar-CH_3), 2.41 (s, 2H, -CH_2-), 3.73 (q, J=5.6 Hz, 2H, -CH_2-), 5.09 (s, 1H, -CH-), 7.33 (t, J=6.0 Hz, 1H, Ar-H), 7.49 (m, 2H, Ar-H), 7.83 (d, J=6.0 Hz, 2H, Ar-H), 8.17 (s, 1H, Ar-H, Pyrazole ring-H), 8.36 (d, J=7.2 Hz, 2H, Ar-H), 8.43(d, J=7.2 Hz, 2H, Ar-H), 9.14 (s, 1H, NH).

ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-(1-phenyl-3-(thiophen-2-yl)-1H-pyrazol-4-yl)quinoline-3-carboxylate **(Table 2, Entry 5g).**

The product was obtained as white solid: mp 196-198˚C; FT-IR (KBr) ν: 3273, 3180, 3069, 2954, 1698, 1642, 1599, 1494, 1381, 1309, 1278, 1212, 1148, 1074, 959, 749; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.75 (t, J=5.6 Hz, 3H, -CH_3), 0.92 (s, 3H, -CH_3), 1.03 (s, 3H, -CH_3), 2.10 (s, 2H, -CH_2-), 2.26 (s, 3H, Ar-CH_3), 2.40 (s, 2H, -CH_2-), 3.81 (q, J=5.6 Hz, 2H, -CH_2-), 5.14 (s, 1H, -CH-), 7.18 (m, 1H, Ar-H), 7.28 (t, 1H, Ar-H), 7.47 (m, 2H, Ar-H), 7.53 (m, 1H, Ar-H), 7.69 (d, 2H, Ar-H), 8.08 (s, 1H, Pyrazole ring-H), 8.13 (m, 1H, Ar-H), 9.09 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ:14.03, 18.72, 26.73, 27.33, 29.32, 32.71, 50.77, 59.28, 105.09,

110.85, 118.45, 125.59, 126.51, 127.11, 127.91, 128.57, 129.95, 130.49, 136.17, 139.63, 144.64, 145.00, 149.87, 167.28, 195.06; MS(ESI m/z %): 510.28 $[M+Na]^+$.

***ethyl 4-(3-(4-fluoro-3-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (Table 2, Entry 5h).**

The product was obtained as white solid: mp 300˚C<; FT-IR (KBr) ν: 3383, 2981, 1687, 1645, 1588, 1541, 1473, 1380, 1214, 1069, 960; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.72 (t, J=5.6 Hz, 3H, -CH_3), 0.95 (s, 3H, -CH_3), 1.04 (s, 3H, -CH_3), 2.19 (s, 2H, -CH_2-), 2.25 (s, 3H, Ar-CH_3), 2.40 (m, 2H, -CH_2-), 3.79 (q, J=5.6 Hz, 2H, -CH_2-), 5.01 (s, 1H, -CH-), 7.29 (m, 1H, Ar-H), 7.49 (m, 3H, Ar-H), 7.81 (m, 2H, Ar-H), 8.11 (m, 2H, Ar-H and Pyrazole ring-H), 8.50 (m, 1H, Ar-H), 9.11 (s, 1H, NH).

***ethyl 4-(3-(3,5-difluorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (Table 2, Entry 5i).**

The product was obtained as white solid: mp 300˚C<; FT-IR (KBr) ν: 3273, 3203, 3076, 2962, 1686, 1643, 1625, 1595, 1539, 1480, 1377, 1209, 1115, 985, 743; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.71 (t, J=5.6 Hz, 3H, -CH_3), 0.95 (s, 3H, -CH_3), 1.04 (s, 3H, -CH_3), 2.20 (s, 2H, -CH_2-),2.24 (s, 3H, Ar-CH_3), 2.42 (m, 2H, -CH_2-), 3.80 (q, J=5.6 Hz, 2H, -CH_2-), 5.03 (s, 1H, -CH-), 7.28-7.32 (m, 2H, Ar-H), 7.48 (t, 2H, Ar-H), 7.81 (d, 2H, Ar-H), 7.92 (m, 2H, Ar-H), 8.12 (s, 1H, Ar-H, Pyrazole ring-H), 9.17 (s, 1H, NH).

***ethyl 4-(3-(3-bromo-4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (Table 2, Entry 5j).**

The product was obtained as white solid: mp 224-226˚C; FT-IR (KBr) ν: 3282, 3228, 3084, 2962, 1696, 1633, 1601, 1541, 1487, 1439, 1376, 1209, 1066, 959, 750; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.73 (t, J=5.6 Hz, 3H, -CH_3), 0.94 (s, 3H, -CH_3), 1.03 (s, 3H, -CH_3), 2.19 (s, 2H, -CH_2-), 2.24 (s, 3H, Ar-CH_3), 2.38 (m, 2H, -CH_2-), 3.78 (q, J=5.6 Hz, 2H, -CH_2-), 5.01 (s, 1H, -CH-), 7.31 (t, J=6.0 Hz, 1H, Ar-H), 7.49 (m, J=6.0 and 4.8 Hz, 2H, Ar-H), 7.74-7.84 (m, 3H, Ar-H), 8.17 (s, 1H, Ar-H, Pyrazole ring-H), 8.54 (m, 1H, Ar-H), 8.92 (m, 1H, Ar-H), 9.14 (s, 1H, NH).

5. Conclusion

In conclusion, we have successfully demonstrated a novel method for the one pot synthesis of polyhydroquinoline derivatives from heterocyclic aldehydes, dimedone, ethyl acetoacetate and ammonium

acetate by simple stirring and ultrasound irradiation at room temperature. The catalytic system is very effective for the bulkier aldehydes to give the corresponding polyhydroquinoline derivatives in excellent yield (80-92%) and easy for isolation of the product. This approach has the various benefits includes simple work-up procedure, excellent yields and environmentally benign path.

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Ionic liquid catalyzed one pot green synthesis of isoxazolone derivatives *via* multicomponent reaction

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A series of 3-methyl-4-((3-aryl-1-phenyl-1*H*-pyrazol-4-yl)methylene)isoxazol-5(4*H*)-one derivatives have been efficiently synthesized by environmentally benign, one-pot three component condensation of substituted 1,3-diaryl-1*H*-pyrazole-4-carboxyaldehyde, β-keto ester and hydroxyl amine hydrochloride in the presence of ionic liquid [HNMP][HSO_4] as a catalyst in ethanol. These derivatives have been synthesized by conventional, ultrasound and microwave irradiation methods. The combination of ionic liquid with ultrasound as well as microwave irradiation makes the protocol fascinating and environmentally benign. In addition, it has several benefits such as simple work-up procedure, clean reaction profile, short reaction time and good yields.

Keywords: 1,3-Diaryl-1*H*-pyrazole-4-carboxyaldehyde, isoxazolone, ionic liquid, ultrasound, microwave

Recently ionic liquids (ILs) have grown interest in diverse areas of chemistry; because of considerable interest as eco-friendly reaction solvent and catalyst in the organic synthesis. They exhibit significant properties such as negligible vapor pressure, broad liquid range, non-flammability, adequate ionic conductivity, potentially recyclable properties and capacity to dissolve a variety of organic and inorganic solids. Acidic ionic liquids have been employed in divergent areas due to their fascinated physical and chemical properties. [HNMP][HSO_4] is also a brønsted acidic ILs has successfully used in various organic reactions such as cyclocondensations reactions, Oxa-Michael addition, Prins reaction and trans-esterification reactions[1-6].

Literature survey revealed that, the isoxazol-5(4*H*)-ones and their derivatives have vital importance in divergent areas such as organic synthesis, liquid crystalline materials, filter dyes in photographic films, light-conversion molecular devices, optical storage and nonlinear optical research[7-11]. The isoxazol-5(4*H*)-ones scaffold bearing both nitrogen and oxygen atoms are an important class of five member heterocycles, which display good pharmaceutical and biological activities[12, 13]. It is considered a major core in the discovery of protein kinase inhibitors, which is playing an important role in the growth of chemotherapeutic agents[14, 15]. They also show significant analgesic, antibacterial, anti-HIV, antifungal, anti-inflammatory, anti-mycobacterial, anticancer, antioxidant, antitumor, antiprotozoal, anti-tubercular, nematicidal and antiviral activities[16-28]. The some important illustrations of isoxazol-5(4*H*)-one nucleus containing agents are shown in Figure 1.

Several protocols have been studied in the literature for the synthesis of isoxazol-5(4*H*)-one and their analogues. Among them some illustrations are *N*-bromosuccinimide (NBS)[29], Ag/SiO_2[30], phthalimide-*N*-oxyl salts (POPINO and TBAPINO)[31], NaOAc/visible light[32], boric acid[33], catalyst free[34], citric acid[35], NaH_2PO_4[36], pyridine/reflux[37], sodium benzoate[38], sodium saccharin[39], pyridine/US[40], pottasium phthalimide[41], sodium sulfide[42], $H_3PW_{12}O_{40}$, clinoptilolite, nano Fe_2O_3[43], *etc*.

Ultrasound (US) and Microwave (MW) assisted transformations are well established class of synthetic organic chemistry. The significant benefit of MW and US irradiated organic synthesis is of rapidly synthesize library of organic compounds with improved yields and selectivities. The MW and US assisted multicomponent reaction with various green catalysts such as ionic liquids, nano-particles, vitamins and zeolites etc. makes protocol more interesting, fascinating and environmentally benign[44-54].

In view of biologial importance of isoxazolone nuclues as well as green approach of ILs in the multicomponent reaction and continution of our work in this field[55-59]; we have described the synthesis of isoxazolone derivatives by multi-component condensation of substituted 1,3-diphenyl-1*H*-pyrazole-4-carboxyaldehyde **(1)**, *β*-keto ester (**2**), hydroxylamine hydrochloride (**3)** and 100 mg of *N*-Methyl-2-Pyrrolidonium Hydrogen Sulphate [HNMP][HSO_4].

Results and Discussion

Initially, we examined the model reaction between 1-phenyl-3-*p*-tolyl-1*H*-pyrazole-4-carbaldehyde **1a,** ethyl acetoacetate **2**, hydroxyl amine hydrochloride **3** under different conditions. A literature study of solvents indicated that ethanol is the most suitable reaction medium for the synthesis of isoxazolone derivatives. When the reaction was conducted at room temperature with constant stirring, reaction did not proceed with and without catalyst. The reaction proceeds with good results under reflux condition. Additional experimental study revealed that the required catalyst amount was found to be 100 mg for better yield (Entry 7). The results obtained during optimization are summarized in Table I.

For comparison, reactions were also carried out under US and MW conditions. As expected, USI (Entry 10) and MWI (Entry 12) assisted synthesis required shorter reaction time and higher yield as compared to conventional heating.

After the determination of the optimized conditions, we twisted our consideration in the direction of studying the scope of the method. The isoxazolone derivatives with both electron-donating and electron-withdrawing substituent on the aromatic ring were tolerated and afforded high yields (Table II).

Experimental Section

The physical constants were recorded in an open capillary and are uncorrected. IR spectra were recorded on a Perkin-Elmer FTIR spectrophotometer. The ^{1}H NMR spectrums were recorded on a Brucker Avance II 400MHz in DMSO and ^{13}C NMR was recorded on 100MHz in DMSO. Mass spectra were recorded on a Finnigan Mass spectrometer. TLC was carried out on pre-coated silica gel Al-plates to check the purity of the compounds.

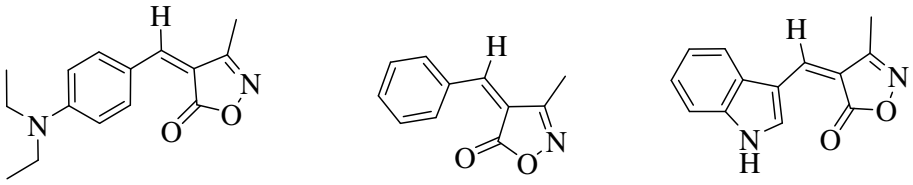


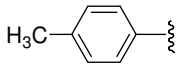
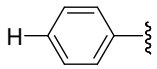
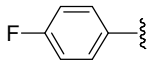
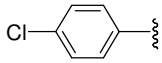
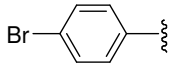
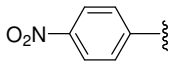
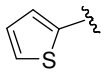
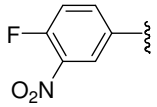
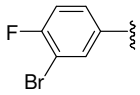
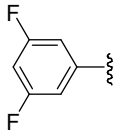
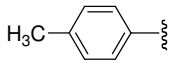
Figure 1 — Isoxazol-5(4*H*)-ones nucleus containing drugs

Table I — Optimization of reaction condition to synthesize isoxazolone derivative **4a**

Entry	Catalyst/ Solvent	Reaction Condition	Time	Yield (%)
1	No catalyst/ Solvent free	Stirring at RT	2 h	NR
2	No catalyst/ EtOH	Stirring at RT	2 h	NR
3	100 mg [HNMP][HSO_4]/ SF	Stirring at RT	2 h	NR
4	100 mg [HNMP][HSO_4]/ EtOH	Stirring at RT	2 h	NR
5	50 mg [HNMP][HSO_4]/ EtOH	Reflux	4 h	25
6	75 mg [HNMP][HSO_4]/ EtOH	Reflux	4 h	64
7	100 mg [HNMP][HSO_4]/ EtOH	Reflux	4 h	70
8	125 mg [HNMP][HSO_4]/ EtOH	Reflux	4 h	72
9	100 mg [HNMP][HSO_4]/ EtOH	USI at RT	30 min	Trace
10	100 mg [HNMP][HSO_4]/ EtOH	USI at 45°C	30 min	80
11	100 mg [HNMP][HSO_4]/ EtOH	MWI at 140 W	10 min	15
12	100 mg [HNMP][HSO_4]/ EtOH	MWI at 210 W	5 min	82

Reaction Conditions: 1-phenyl-3-*p*-tolyl-1*H*-pyrazole-4-carbaldehyde **1a** (1 mmol), Ethyl acetoacetate **2** (1 mmol), hydroxyl amine hydrochloride **3** (1 mmol) and 50-125 mg [HNMP][HSO_4]

Table II — Synthesis of isoxazolone derivatives **4a-k** using [HNMP][HSO_4] as a catalyst

Entry	Ar-Group	R-Group	Reaction Time (min.)			Yield (%)			m.p. in (^oC)
			Reflux	US	MW	Reflux	US	MW	
4a		-CH_3	240	30	5	70	80	82	210
4b		-CH_3	240	28	4	71	80	81	208
4c		-CH_3	270	34	6	68	78	80	204
4d		-CH_3	240	30	4	74	82	82	228
4e		-CH_3	240	30	5	72	80	80	234
4f		-CH_3	270	32	6	68	75	75	268
4g		-CH_3	240	28	4	74	82	84	192
4h		-CH_3	300	32	6	68	76	78	196
4i		-CH_3	300	30	6	70	80	82	226
4j		-CH_3	300	32	5	72	78	83	224
4k		-CF_3	240	30	4	72	80	80	160

Reaction Condition- Substituted 1,3-diphenyl-1*H*-pyrazole-4-carbaldehyde **1** (1 mmol), Ethyl acetoacetate **2** (1 mmol), hydroxyl amine hydrochloride **3** (1 mmol), 100 mg [HNMP][HSO_4] and 10 mL ethanol.

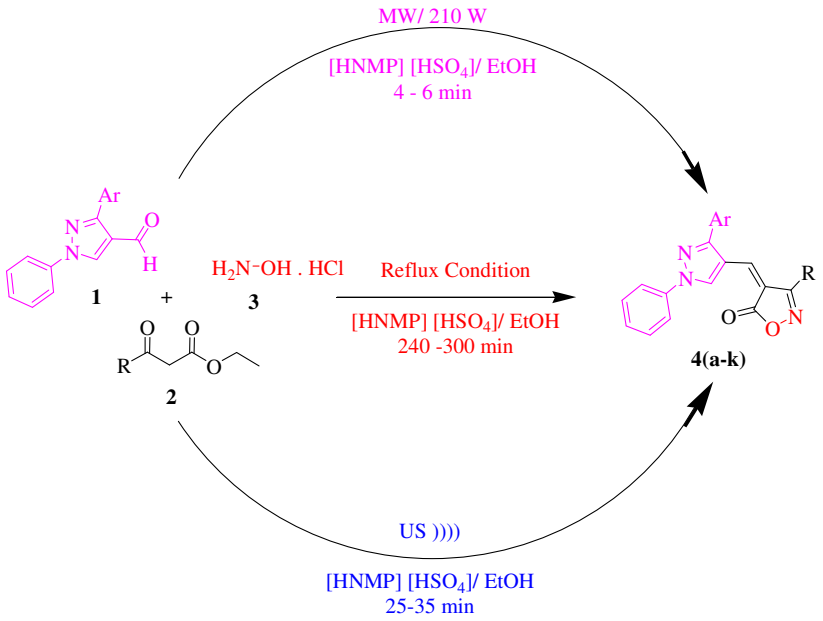
The precursor 1,3-diaryl-1*H*-pyrazole-4-carboxyaldehyde were synthesized by Vilsmeier Haack formylation reaction[60], whereas the catalyat [HNMP][HSO_4] was prepared and purified as reported by B. M. Bhanage and co-authors[4].

General Procedure for the Synthesis of Isoxazolone derivatives 4(a-k) Under Conventional Reflux Condition

A mixture equimolar quantities of 1,3-diaryl-1*H*-pyrazole-4-carboxyaldehyde 1 (1 mmol), *β*-keto ester 2 (1 mmol), hydroxyl amine hydrochloride 3 (1 mmol) and 100 mg of [HNMP][HSO_4] was placed in a 100 mL round bottom flask containing 10 mL of EtOH. Then the reaction mixture was refluxed for appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the content were cooled to room temperature, solid product thus obtained was separated by filtration. The crude product was washed by cold ethanol to get pure product (Scheme I).

Under Ultra Sound Irradiation

A mixture equimolar quantities of substituted 1,3-diphenyl-1*H*-pyrazole-4-carbaldehyde 1 (1 mmol), *β*-keto ester 2 (1 mmol), hydroxyl amine hydrochloride 3 (1 mmol) and 100 mg of Ionic liquid [HNMP][HSO_4] was taken in a 100 mL round bottom flask containing 10 mL of EtOH. The reaction mixture was placed for US irradiation at 45^oC for appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction,



Scheme I — Synthesis of isoxazolone derivatives

the content were cooled to room temperature, solid product thus obtained was separated by filtration. The crude product was washed with cold ethanol to get pure product (Scheme I).

Under Microwave Irradiation

A mixture equimolar quantities of substituted 1, 3-diphenyl-1*H*-pyrazole-4-carbaldehyde 1 (1mmol), *β*-keto ester 2 (1 mmol), hydroxyl amine hydrochloride 3 (1mmol) and 100 mg of Ionic liquid [HNMP][HSO_4] was taken in a 100 mL round bottom flask containing 10 mL of EtOH. The reaction mixture was subjected for MW irradiation at level 2 (210 W) for appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the content were cooled to room temperature, solid product thus obtained was separated by filtration. The crude product was washed with cold ethanol to get pure product (Scheme I).

Spectral Data of Synthesized Compounds

3-methyl-4-((1-phenyl-3-*p*-tolyl-1*H*-pyrazol-4-yl) methylene)isoxazol-5(4*H*)-one, 4a: Pale Yellow Solid; m.p. 210ºC; FT-IR (KBr) ν: 3145, 2980, 1735, 1612, 1599, 1532, 1507, 1454, 1231, 1122, 996, 873, 757; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.24 (s, 3H, -CH_3), 2.42 (s, 3H, -CH_3), 7.41 (d, 2H, Ar-H), 7.49 (t, 1H, Ar-H), 7.61-7.68 (m, 5H, Ar-H), 7.92 (s, 1H, Pyrazole ring-H), 7.94 (d, 1H, Ar-H), 9.87 (s, 1H, vinylic proton); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 10.89, 20.89, 114.73, 115.09. 116.62, 127.61, 128.24, 129.11, 129.66, 129.97, 133.48, 138.37, 139.18, 139.95, 149.25, 161.70, 168.93; MS: *m/z* = 344.39 $[M+1]^+$.

3-methyl-4-((1,3-diphenyl-1*H*-pyrazol-4-yl) methylene)isoxazol-5(4*H*)-one, 4b: Pale Yellow Solid; m.p. 208ºC; FT-IR (KBr) ν: 3148, 3057, 2982, 1735, 1613, 1599, 1517, 1502, 1447, 1335, 1222, 1128, 994, 872, 704; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.24 (s, 3H, -CH_3), 7.44 (t, 1H, Ar-H), 7.52-7.61 (m, 6H, Ar-H), 7.67 (m, 2H, Ar-H), 7.92 (m, 2H, Ar-H and Pyrazole ring-H), 10.03 (s, 1H, vinylic proton); MS: *m/z* = 330.53 $[M+1]^+$.

4-((3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)-3-methylisoxazol-5(4*H*)-one, 4c: Pale Yellow Solid; m.p. 204ºC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.243 (s, 3H, -CH_3), 7.29 (t, 2H, Ar-H), 7.44 (t, 2H, Ar-H), 7.49-7.69 (m, 4H, Ar-H), 7.90 (m, 2H, Ar-H and Pyrazole ring-H), 10.01 (s, 1H, vinylic proton); MS: *m/z* = 348.34 $[M+1]^+$.

4-((3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)-3-methylisoxazol-5(4*H*)-one, 4d: Pale Yellow Solid; m.p. 228ºC; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.31 (s, 3H, -CH_3), 7.26 (t, 2H, Ar-H), 7.42-7.45 (m, 2H, Ar-H), 7.53-7.57 (m, 5H, Ar-H), 7.89 (s,

1H, Pyrazole ring-H), 9.98 (s, 1H, vinylic proton); MS: *m/z* = 364.27 $[M+1]^+$.

4-((3-(4-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)-3-methylisoxazol-5(4*H*)-one, 4e: Pale Yellow Solid; m.p. 234ºC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.25 (s, 3H, -CH_3), 7.46 (t, 2H, Ar-H), 7.55 (m, 4H, Ar-H), 7.72 (m, 2H, Ar-H), 7.89 (m, 2H, Ar-H and Pyrazole ring-H), 10.04 (s, 1H, vinylic proton).

3-methyl-4-((3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)isoxazol-5(4*H*)-one, 4f: Pale Yellow Solid; m.p. 268ºC; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.27 (s, 3H, -CH_3), 7.47 (t, 2H, Ar-H), 7.49-7.56 (m, 3H, Ar-H), 7.78 (dd, *J* = 4.0 Hz, 2H, Ar-H), 8.04 (s, 1H, Pyrazole ring-H), 8.26 (dd, *J* = 4.0 Hz, 2H, Ar-H), 9.97 (s, 1H, vinylic proton); MS: *m/z* = 375.19 $[M+1]^+$.

3-methyl-4-((1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazol-4-yl)methylene)isoxazol-5(4*H*)-one, 4g: Pale Yellow Solid; m.p. 192ºC; FT-IR (KBr) ν: 3145, 3109, 2982, 1744, 1613, 1530, 1498, 1460, 1221, 1128; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.31 (s, 3H, -CH_3), 7.28 (m, 1H, Ar-H), 7.48 (m, 1H, Ar-H), 7.61 (m, 2H, Ar-H), 7.68 (m, 1H, Ar-H), 7.77 (m, 1H, Ar-H), 7.81 (s, 1H, Pyrazole ring-H), 7.88 (m, 2H, Ar-H), 9.86 (s, 1H, vinylic proton); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 10.94, 114.85, 115.24. 119.41, 128.17, 128.39, 128.46, 128.70, 129.80, 131.84, 133.53, 138.10, 138.66, 150.33, 161.42, 168.79; MS: *m/z* = 336.35 $[M+1]^+$.

4-((3-(4-fluoro-3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)-3-methylisoxazol-5(4*H*)-one, 4h: Pale Yellow Solid; m.p. 196ºC; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.28 (s, 3H, -CH_3), 7.40 (s, 1H, Ar-H), 7.47 (t, 1H, Ar-H), 7.53-7.59 (m, 3H, Ar-H), 7.89 (d, *J* = 4.0 Hz, 2H, Ar-H), 8.00 (s, 1H, Pyrazole ring-H), 8.39 (dd, *J* = 4.0 Hz, 1H, Ar-H), 10.03 (s, 1H, vinylic proton).

4-((3-(3-bromo-4-fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)-3-methylisoxazol-5(4*H*)-one, 4i: Pale Yellow Solid; m.p. 226ºC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.26 (s, 3H, -CH_3), 7.34 (t, 1H, Ar-H), 7.40 (d, 1H, Ar-H), 7.46 (t, 1H, Ar-H), 7.57 (m, 3H, Ar-H), 7.90 (m, 3H, Ar-H and Pyrazole ring-H), 10.00 (s, 1H, vinylic proton).

4-((3-(3,5-difluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl) methylene)-3-methylisoxazol-5(4*H*)-one, 4j: Pale Yellow Solid; m.p. 224ºC; FT-IR (KBr) ν: 3148, 3077, 2977, 1729, 1605, 1505, 1434, 1338, 1229, 1125, 992, 860, 794; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.28 (s, 3H, -CH_3), 7.02 (m, 1H, Ar-H), 7.21 (m, 2H, Ar-H), 7.46 (m, 2H, Ar-H), 7.57 (t, 2H, Ar-H), 7.89 (m, 2H, Ar-H and Pyrazole ring-H), 10.01 (s, 1H, vinylic proton); MS: *m/z* = 366.30 $[M+1]^+$.

Conclusion

We have developed a green protocol for the one-pot synthesis of isoxazolone derivatives using [HNMP][HSO_4] as an efficient catalyst. The series of isoxazolone **4(a-k)** derivatives was synthesized from various 1,3-diaryl-1*H*-pyrazole-4-carboxyaldehyde, aceto-acetic ester and hydroxyl amine hydrochloride in ethanol by conventional reflux condition, US, and MW irradiation for suitable time. It was found that, the US and MW assisted reaction in [HNMP][HSO_4] provides several benefits as compared with the conventional method. This fascinating US and MW assisted protocol was offered the simple work-up procedure, short reaction time, excellent yield with the environmentally benign approach and a significant contribution in green technology.

Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/60.

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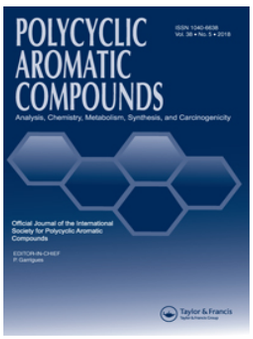

Polycyclic Aromatic Compounds

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Additive Free Greener Synthesis of 1,2-Disubstituted Benzimidazoles Using Aqueous Extract of *Acacia concinna* Pods as an Efficient Surfactant Type Catalyst

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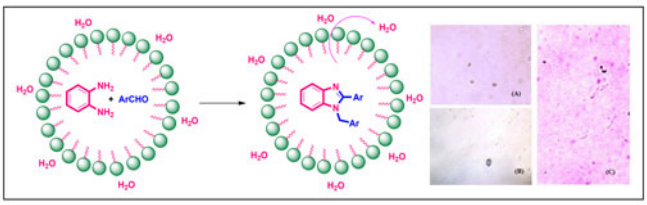
ABSTRACT

An efficient environmentally benign method for the synthesis of 1,2-disubstituted benzimidazole derivatives via one-pot multicomponent has been reported using aqueous extract of *Acacia concinna* pods as a naturally occurring surfactant type catalyst. The present surfactant medium was found superior and additive free for the condensation of o-phenylene diamine and two equivalent of aldehyde to yield 1,2-disubstituted benzimidazole derivatives in excellent yields under mild conditions. A simple, economically viable and biocompatible catalytic system suggested the possible utility of the present protocol for the large scale construction of benzimidazole derivatives.



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Acacia concinna; 12-disubstituted benzimidazoles; green methodology; multi-component reaction; natural surfactants

Introduction

The development of new catalytic systems originated from renewable sources has been enormously increasing to minimize environmental disturbance generated by the field of medicinal chemistry and production of fine chemicals. Moreover, new and efficient catalytic protocols are necessary to construct the promising classes of organic compounds for molecular and biomedical research. Nowadays, numerous natural and synthetic materials like supercritical solvent, ionic liquids, clays, enzymes and surfactants are extensively recognized as practical substitute to traditional synthetic procedures. These materials are found to be convenient to solve certain incredible synthetic problems concerning environmental aspects to some extent. In order to overcome the problems associated with existing catalysts such as environmental hazards, expensiveness, use of halogenated organic solvents, handling problems, use elevated temperature to get desired yield

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of the required organic compound etc., natural sources are found to be the best remedy. Nature offers an incredible array of biochemicals providing unique class of potential biocatalysts useful for the reactions of various organic substrates.[1–3] The synthetic utility of these materials are biodegradable and generate less waste than the conventional methods. In addition, the emphasis of Green Chemistry is towards development of designing of chemical products and processes through pollution free and eco-friendly protocols.[4] In this context, the plant cell culture of *Daucus carota* root,[5–10] soaked *Phaseolus aureus* (green grams),[11] and coconut juice (*Cocos nucifera*)[12] has been successfully utilized as biocatalysts for selective reduction of ketones. In the previous reports, aqueous extract of *Acacia concinna* has been utilized for the synthesis of 3-carboxycoumarins and Cinnamic acids via Knoevenagel condensation,[13] acylation of amines,[14] and synthesis of aryl-hydrazones.[15]

In the field of medicinal chemistry, the benzimidazole core is one of the privileged substructures for drug design due to its affinity towards the broad range of enzymes and proteins.[16] It has been displayed remarkable potential against HIV, herpes (HSV-1), RNA, influenza, and human cytomegalovirus (HCMV) viruses.[17–21] Various benzimidazole derivatives are known to have topoisomerase, smooth muscle cell proliferation and angiotensin II inhibiting properties, selective neuropeptide YY1 receptor antagonists, 5-HT3 antagonists, antitumor, antimicrobial agents.[22–27] Some of the potentially active benzimidazole derivatives such as candesartan (**A**) plays an important role in AT1 receptors binding exhibiting stronger blood pressure lowering effect, azilsartan (**B**), is as AT1 receptor antagonist for the treatment of hypertension,[24] telmisartan (**C**) is an orally active potent AT1-selective antagonist discovered by Boehringer Ingelheim in 1991[28] astemizole (**D**), is a second-generation H1-receptor antagonist discovered by Janssen Pharmaceutica in 1977,[29] mizolastine (**E**) is a non-sedating antihistaminic drug[30] and clemizole (**F**) is first-generation antihistamine drug used against itching and allergic reactions[31] (Figure 1).

The traditional synthesis of benzimidazoles involves the reaction between an *o*-phenylenediamine and a carboxylic acid or its derivatives (nitriles, amidates, orthoesters) under harsh dehydrating conditions.[32] Very recently, a literature survey revealed several methods for synthesis of benzimidazole and its derivatives using L-proline,[33] glyoxalic acid,[34] $SiO_2/ZnCl_2$,[35] $Fe(ClO_4)_3$,[36] trimethylsilyl chloride,[37] silica sulfuric acid,[38] oxalic acid,[39] mesoporous metal oxide

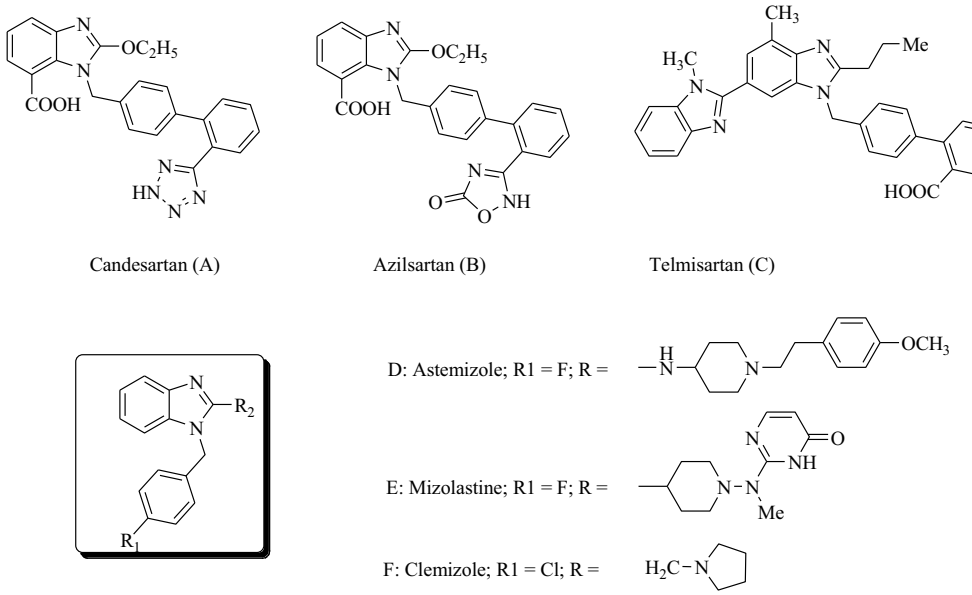
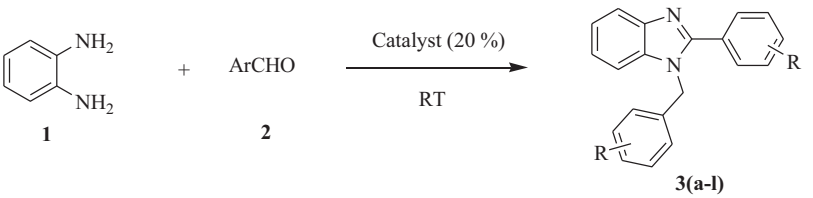


Figure 1. Some of the potentially active benzimidazole drugs.



Scheme 1. Synthesis of 1,2-disubstituted benzimidazoles.

Table 1. Optimization of catalyst concentration.

Entry	Catalyst concentration %(W/V)	Time (min)	Yield (%)[a]
1	10	270	89
2	20	180	97
3	30	130	95
4	40	130	95
5	50	80	91
6	–	600	NR[b]

[a]Isolated yield of **3a**.
[b]No reaction.

nanocrystals,[40] Indion 190 resin,[41] sodium dodecylsulfate–water,[42] nano-In_2O_3,[43] and alumina–sulfuric acid.[44]

Acacia concinna is commonly known as Shikakai which belongs to the family Leguminosae and found in tropical rainforests of southern Asia. The fruits of *Acacia concinna* are well known for its cleansing property and hence it is used as a traditional shampoo. The cleansing properties of *Acacia concinna* fruit are due to the presence of saponins, which are foaming agents. Saponins isolated from the plant fruits have been traditionally used as a detergent. In particular, these saponins produces leather when shaken in aqueous solutions due to presence of amphipathic glycosides composed of one or more hydrophilic glycoside moieties combined with a lipophilic triterpene cores. The fruit is known to have 10–11.5% saponins and their structure has been reported.[45,46] These saponins have surfactant properties similar to that of dodecyl benzene sulfonates.[47] The saponin 'acacic acid' was found in pods of *Acacia concinna*. Specifically, it is a trihydroxy monocarboxylic triterpenic acid of either tetracyclic or α-amyrin group. Hence, the aqueous extract of these pods of *Acacia concinna* shows acidic pH.[48,49] These fascinating properties of aqueous extract of *Acacia concinna* pods promoted us to use it as an efficient and eco-friendly acidic surfactant type catalytic medium for organic synthesis.

Result and discussion

In continuation of our ongoing research on development of novel synthetic method for biologically active compounds,[50–55] we have presented here a simple, cost-effective and green protocol for the synthesis of 1,2-disubstituted benzimidazole derivatives using aqueous extract of pods of *Acacia concinna* as a green and inexpensive reaction medium (Scheme 1). The present approach for the synthesis of benzimidazoles reduces the use of hazardous halogenated organic solvents, tedious reaction work-up, and drastic reaction conditions.

In order to check the efficiency of the catalyst, a reaction of o-phenylenediamine (**1**) (1 mmol) and benzaldehyde (**2a**) (2 mmol) in 5 mL aqueous extract of *Acacia concinna* pods (10% W/V) was performed at ambient temperature and we are fortunate to get an excellent yield of product **3a** (89%) after 270 min. Encouraged by the above outcome, the optimization of the reaction conditions was conducted by studying the same reaction in the presence of different concentrations aqueous extract of *Acacia concinna* pods. It was found that 20% of the catalyst was sufficient to

Table 2. Effect of surface tension of surfactant solution on rate of reaction.

Entry	Catalyst concentration %(W/V)	Surface tension, *T* (dyne/cm)	Time (min)
1	50	13.48	80
2	40	18.87	130
3	30	32.34	130
4	20	40.43	180
5	10	48.51	270
6	Distilled water	67.38	–

Table 3. Effect of surfactant for the formation of **3a**.

Entry	Surfactant[a]	Time (min)	Yield (%)[b]
1	None	600	NR[c]
2	SDS	120	60
3	DBSA	120	64
4	Triton X-100	120	51
5	CTAB	120	48
6	CPB	120	45
7	*Acacia concinna* extract 20% (W/V)	180	97

[a]Reaction condition: *o*-phenylenediamine (1 mmol), benzaldehyde (2 mmol), *Acacia concinna* extract (5 mL), room temperature.
[b]Isolated yield.
[c]No reaction.

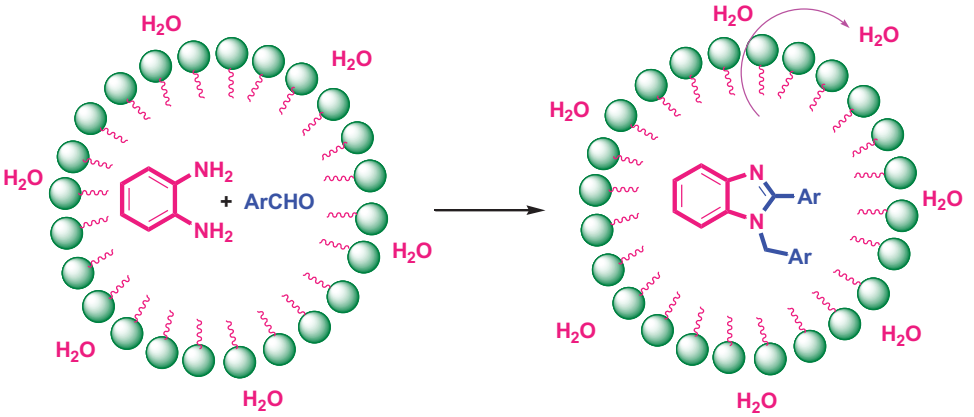


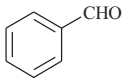
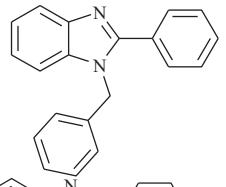
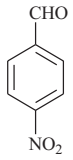
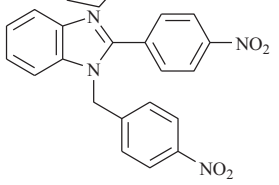
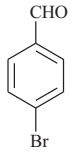
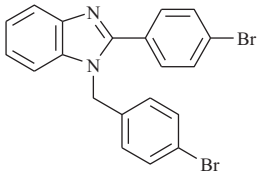
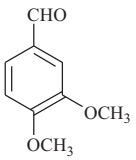
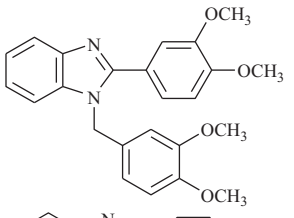
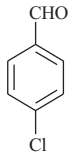
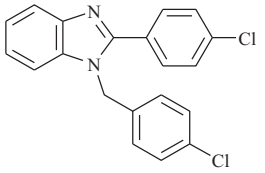
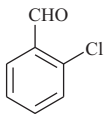
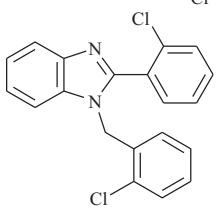
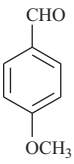
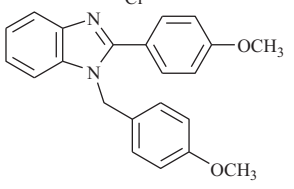
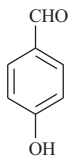
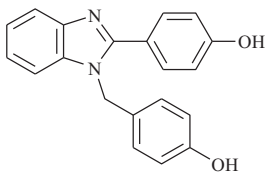
Figure 2. Micelle-promoted synthesis of 1,2-disubstituted benzimidazoles.

get highest yield of the product **3a** (97%) in short time (180 min). Increasing concentration of *Acacia concinna* pods (30%, 40%, and 50%) did not affect the yield of the final product. Therefore, 20% W/V aqueous extract of *Acacia concinna* pods and 5 mL volume was found to be the optimized amount of catalyst to push the reaction forward (Table 1).

As compared to distilled water aqueous solution of surfactant is found to reduce the surface tension of solution (Table 2) which increases the wetting and spreading properties. Surface tension and structure of surfactant governs the wetting and spreading characteristics.[56,57] A numerous reactions such as redox, photochemical, enzymatic, Diels-Alder, photochemical, etc. have altered the rate of reactions.[58] Micelle is collective of surfactant molecules in their aqueous solution. Hydrophilic groups of surfactant are sequestered in the micelle core.[59]

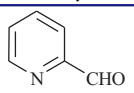
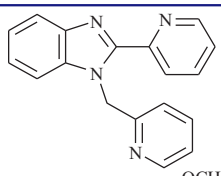
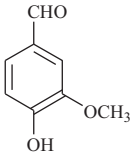
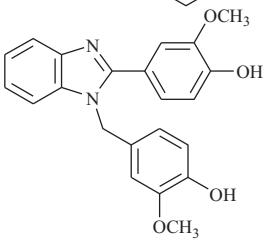
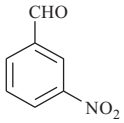
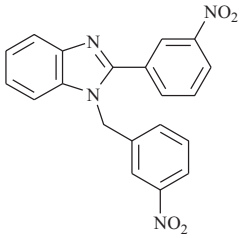
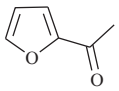
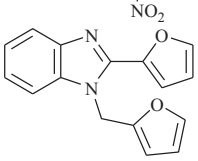
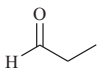
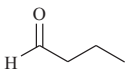
In order to evaluate the catalytic potency of the aqueous extract of the *Acacia concinna* pods, a model reaction of *o*-phenylenediamine (**1**) and two equivalents of benzaldehyde (**2**) was conducted in aqueous solutions of various cationic, anionic, and nonionic surfactants at room

Table 4. Synthesis of 1,2-disubstituted benzimidazole.

Entry	Aldehyde	Product		Time (min)	Yield (%)[a]	M.P. (°C)[b]
1.			**3a**	180	94	130–132[60]
2.			**3b**	175	98	302–304[60]
3.			**3c**	160	93	156–158[61]
4.			**3d**	158	94	170–173[61]
5.			**3e**	170	90	132–134[60]
6.			**3f**	185	88	160–163[61]
7.			**3g**	160	94	124–126[60]
8.			**3h**	155	98	124–126[60]

(*continued*)

Table 4. Continued.

Entry	Aldehyde	Product		Time (min)	Yield (%)[a]	M.P. (°C)[b]
9.			**3i**	180	96	129–130[62]
10.			**3j**	175	94	184–186
11.			**3k**	165	92	166–168[61]
12			**3l**	180	90	96–98[60]
13		[c]NR	–	–	–	–
14		[c]NR	–	–	–	–

[a]Isolated yields of the products.
[b]Ref, reference.
[c]NR, no reaction.

temperature (Table 3). The surfactants like SDS, triton X-100, CTAB and CPB were used to compare the efficacy of aqueous extract of the *Acacia concinna* pods. It has been found that aqueous extract of the *Acacia concinna* pods was superior surfactant medium for the synthesis of **3a**.

The aqueous solutions of surfactants under investigation were taken above their critical micellar concentrations (CMC). The reaction when conducted in the presence of dodecylbenzene sulfonic acid (DBSA) as acidic surfactant, the desired product **3a** was obtained in 64% yield (Table 3, entry 3). In the presence of sodium dodecyl sulfate (SDS) as anionic surfactant, the desired product **3a** was obtained in 60% yield (Table 3, entry 2). Other surfactants such as Triton X-100, cetyl pyridinium bromide (CPB), and cetyl trimethylammonium bromide (CTAB), afforded **3a** in low yields (Table 3, entries 3–6). However, in the presence of the aqueous extract of *Acacia concinna* pods, the desired product was obtained in 97% yield (Table 3, entry 7). The reaction when conducted in water in absence of surfactants, no product formation was observed after 600 min (Table 3, entry 1). Thus, the aqueous extract of *Acacia concinna* pods was found to be superior over all other surfactants. This fact promoted us for further exploration of the present method other aldehydes possessing wide range of substituents. The increased rate of reaction catalyzed by the aqueous extract of *Acacia concinna* pods might be attributed due to its surfactant property and acidic pH (pH = 4.1). The saponins, which are highly acidic, solubilize the reactant species

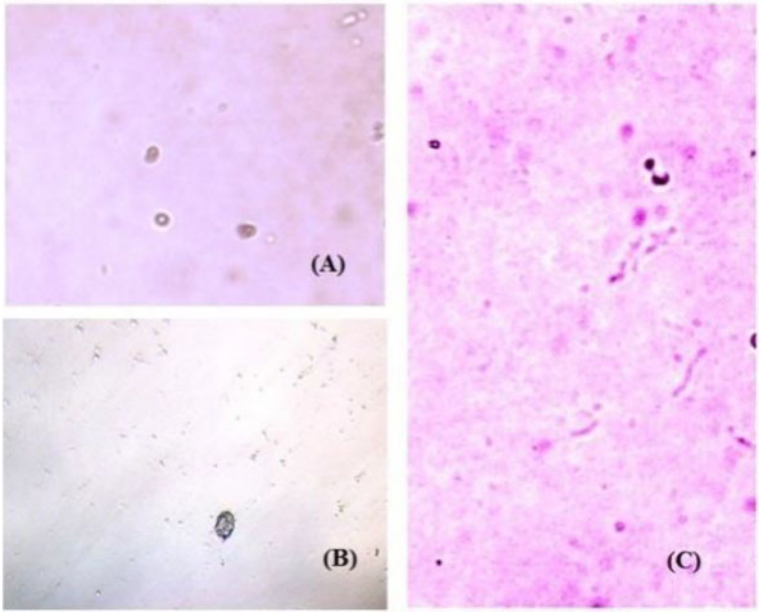
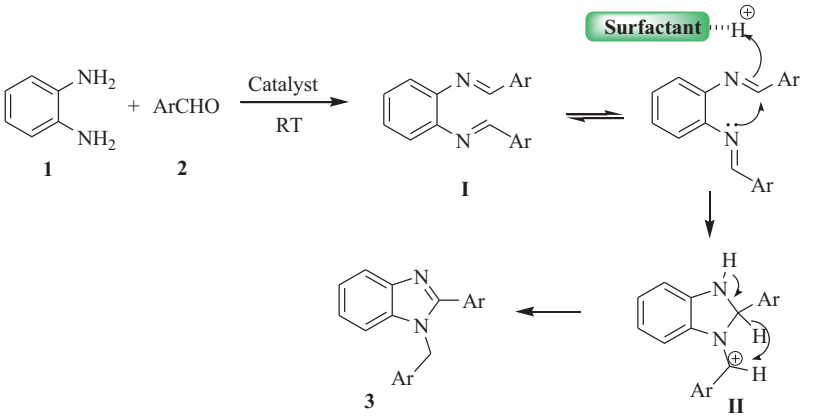


Figure 3. Photograph of micelle observed in reaction medium during formation of **3a**.



Scheme 2. Proposed mechanism for formation of 1,2-disubstituted benzimidazoles (**3**).

strongly by hydrogen bond formation in aqueous medium. This increases the number of favorable collisions between the reactant species. Further encapsulation of the reactants in micellar cages may drive the equilibrium toward the product side by expelling the water molecule out of its hydrophobic interior that increases the speed as well as the yields of products (Figure 2). This remarkable enhancement in reaction rate prompted us to explore the potential of this protocol for the synthesis of 1,2-disubstituted benzimidazole derivatives.

The synthetic utility of the present biocompatible approach was evaluated for the synthesis of wide range of 1,2-disubstituted benzimidazole derivatives using optimized reaction conditions. The results obtained are summarized in Table 4. The presence of electron donating or electron withdrawing groups and their position on the aromatic aldehyde did not show any noticeable effect on the yields of the 1,2-disubstituted benzimidazole derivatives (Figure 3).

The desired 1,2-disubstituted benzimidazoles were obtained in excellent yields with diversified functional groups. Chemically reactive substrates like furfuraldehyde and cinamaldehyde

underwent smooth to produce corresponding 1,2-disubstituted benzimidazole without any side product formation (Table 4, Entry 12 and 13). In general, all aromatic aldehyde undergo multi-component cyclocondensation afforded corresponding 1,2-disubstituted benzimidazoles. However, aliphatic aldehyde such as proanaldehyde and butyraldehyde unsuccessful to react under the present reaction conditions (Table 4, Entry 14 and 15).

The proposed mechanism for the synthesis of the 1,2-disubstituted benzimidazoles may involve the iminium-catalyzed formation of *N,N′*-dibenzylidene-o-phenylenediamine (**I**), activation by catalyst and ring closure giving a five-member ring (**II**) either in a sequential or a concerted manner (Scheme 2).[63]

Conclusion

In conclusion, we have described an efficient, economical, and environmental friendly catalyst for the synthesis of 1,2-disubstituted benzimidazole derivatives catalyzed by aqueous extract of *Acacia concinna* pods. The uses of water as reaction medium and biocompatible catalyst, short reaction time, high purity of the products, mild reaction conditions and a simple workup procedure are most the attractive features of the present method.

Experimental

General conditions

All chemicals were obtained from commercial suppliers and were used without further purification. The melting points were determined in open capillaries and were uncorrected. The solvents were dried and redistilled before use. Melting points were recorded on Digital Electro thermal Melting point apparatus (VEEGO, VMP-DS) and are uncorrected. Reaction monitoring was conducted using thin layer chromatography (TLC) using precoated silica gel $60F_{254}$ plates with layer thickness 0.25 nm purchased from Merck Ltd. TLC plates were visualized under ultraviolet light at 254 nm wavelength. IR spectra were recorded on KBr discs on Shimazdzu 470 IR spectrophotometer. ^{1}H-NMR was recorded on Varian-NMR mercury 300 MHz spectrometer in DMSO-d_6 using TMS as an internal standard. Chemical shifts values (δ) are expressed parts per million (ppm). Mass spectra were recorded on Varian MAT 311 A at 70 ev.

General procedure for the preparation of catalyst

A fine powder of *Acacia concinna* pods (20 g) in water (100 mL) was heated in a 250 mL conical flask at 100 °C for 20 min. The solid material was filtered and the aqueous extract was collected. The prepared extract has concentration 20% w/v.

General procedure for the synthesis of 1,2-disubstituted benzimidazole (3a–l)

A mixture of o-phenylenediamine (1 mmol) and aldehyde (2 mmol) in catalyst solution (20%, 5 mL) was stirred at room temperature for specified time (Table 3). After completion of the reaction (as indicated by TLC), a separated solid was filtered on Buchner funnel, washed with water and dried to obtain pure products[3] in excellent yields.

Spectral data

1-(4-Hydroxy-3-methoxybenzyl)-2-(4-hydroxy-3-methoxyphenyl)-1H-1,3-benzimidazole (3j)

M.P.: 184–186 °C;^{1}H-NMR (DMSO-d6, 300 MHz): δ 3.63 (3H, s, CH_3), 3.71 (3H, s, CH_3), 5.44 (2H, s, CH_2), 6.36–6.38 (1H, d,$J = 6$Hz, Ar-H), 6.64–6.69 (1H, d, $J = 6$Hz, Ar-H), 6.90–6.93 (1H, d, $J = 6$Hz, Ar-H), 7.18–7.25 (4H, m, Ar-H), 7.47 (1H, s, Ar-H), 7.76–7.77 (1H, d, $J = 3.9$ Hz Ar-H), 8.98 (1H, s, OH), 9.56 (1H, s, OH); LCMS (ESI): m/z 377 ($M + H^+$).

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An Expeditious Synthesis of 3-methyl-4-arylmethylene-isoxazole-5(4*H*)-ones Using Aqueous Extract of *Acacia concinna* Pods as a Natural Surfactant Catalyst

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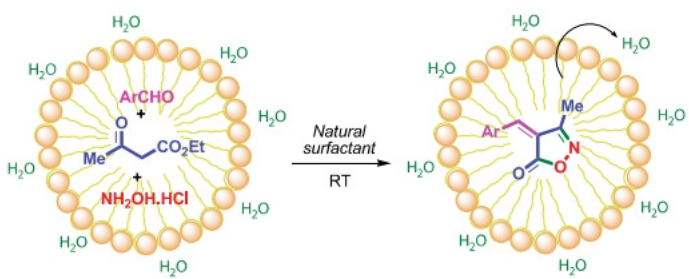
ABSTRACT An aqueous extract of *Acacia concinna* pods has been employed as a competent and effective natural surfactant type catalyst for the synthesis of 3-methyl-4-arylmethylene-isoxazole-5(4*H*)-one analogs through one-pot, three-component reaction of β-ketoester, aldehydes, and hydroxylamine hydrochloride. The present cyclocondensation reaction was performed in an environmentally benign catalytic system at room temperature and afforded the desired compounds in excellent yields. The advantages of this method are simple, economically viable, and biocompatible catalytic system suggested the possible utility of the present protocol for the large-scale construction of isoxazole cores.



KEYWORDS Natural surfactants, *Acacia concinna*, 3-methyl-4-arylmethylene-isoxazole-5(4*H*)-one, Green methodology, Multicomponent reaction.

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An expeditious synthesis of 1,3-oxazine and Betti bases catalyzed by aqueous extract of *Acacia concinna* pods as an efficient surfactant type catalyst

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Abstract: An efficient and simple procedure for the synthesis of 1,3-oxazines and Betti bases *via* Mannich type reaction was successfully carried out in aqueous extract of *Acacia concinna* pods as a green alternative. The present surfactant catalyst was found to be expeditious for in terms of economic viability, mild reaction conditions, good to excellent product yield and environment friendliness.

Keywords: Natural surfactants, *Acacia concinna,* Betti bases, 1,3-oxazines, green protocol.

INTRODUCTION

The identification and characterization of new catalysts isolated from natural resources has been enormously increasing to overcome various environmental constraints. These catalysts play an important role in acceleration of rate of the chemical reactions as well as ease of isolation of the final product. Nowadays, numerous natural and synthetic materials like supercritical solvent, ionic liquids, clays, enzymes and surfactants are extensively recognized as an alternative to the traditional expensive and toxic catalyst and reagents [1-3]. The surfactants isolated from natural sources are well known to have remarkable biological potential [4–6]. Moreover, the catalytic properties of these surfactants have been extensively studied. Specifically, the plant cell culture of *Daucus carota* root [7–12], soaked *Phaseolus Aureus* (green grams) [13], and coconut juice (*Cocos Nucifera*) [14] has been successfully utilized as biocatalysts for selective reduction of ketones. In the previous reports, aqueous extract of *Acacia concinna* has been utilized for the synthesis of 3-carboxycoumarins, cinnamic acids [15], acylation of amines [16] and synthesis of aryl-hydrazones [17].

Oxazine derivatives exhibits broad range of

bioactivities including anticancer (**A and B**), antibacterial (**C**), anticonversant, antitubular, non-nucleoside reverse transcriptase inhibitor (efavirenz) (**D**), drug (Ketazolam) (**E**) [18] (**Figure 1**), anti HIV-1 [19], anti-Parkinson's agents [20]. Due to broad range of bioactivities associated with these class of compounds, their synthesis is the major concern. Traditionally, 1,3-oxazine derivatives can be synthesised by using two step process from primary amines, aldehyde and phenols [21]. Although, several methods are reported so far for the synthesis of target compounds [22–24], only limited numbers of protocols are feasible on the basis of the multi component reactions (MCRs) [25].

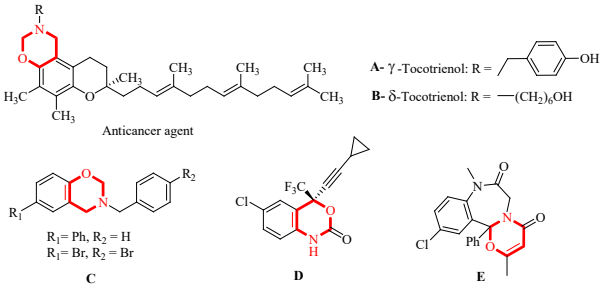


Figure 1.

Betti reaction is one of the most important C-C bond-forming reactions, which is typically a Mannich reaction [26]. Betti bases have associated with various synthetic and biological applications. They have exihibited various pharmacological properties like anti-bacterial, antipain and antihypertensive activities [27–30] **(Figure 2)**.

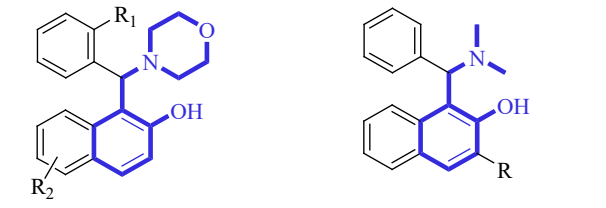


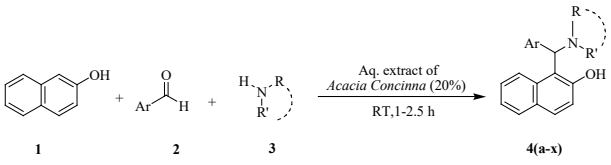
Figure 2. Biologically active Betti bases.

The classical Betti reaction involved the two step reaction of aldehyde, ammonia or urea and β-naphthol in an ethanolic solution of potassium hydroxide for 9–36 h [26,31]. Consequently, several recent reports on Betti reaction have been developed to overcome the drawbacks of the classical method. Therefore, the preferable route will be multicomponent reaction of aldehyde, amine and phenol [26,32,33]. Herein, we have reported the sustainable synthesis of Betti bases catalysed by aqueous extract of *Accacia concinna.*

Acacia concinna (commercially known as "Shikakai" in India) pods have surfactant properties since it contains saponins, which are foaming agents [34,35]. In addition, there is presence of acacic acid as one of the chemical constituent in the aqueous extract of pods of *Acacia concinna* [36]. In present protocol catalytic activity of the natural surfactant was studied for the synthesis of 1,3-oxazine and Betti bases.

Result and Discussion

In the present study, a simple, cost effective and green protocol for the synthesis of Betti bases and 1,3-oxazine derivatives using an aqueous extract of pods of *Acacia concinna* has been reported **(Scheme 1 and 2)**. The methodology presented here is in persistence of our ongoing research on construction of novel synthetic method for biologically active compounds [37].



Scheme 1. Synthesis of Betti Bases by using 2-naphthol

Initially, efficiency of the catalyst was studied by

conducting reaction of β-naphthol (**1**) (1mmol), benzaldehyde (**2a**) (1 mmol) and piperidine (1 mmol) using surfactant catalyst (20% w/v, 5 mL) aqueous extract of *Acacia concinna* pods at room temperature and we were pleased to get an admirable yield of product **4a** (94%) after 1 h. The above outcome encouraged us for the optimization the reaction conditions for the same reaction in presence of different concentrations aqueous extract of *Acacia concinna* pods. The results obtained suggested that 20% of the catalyst concentration was adequate to get maximum yield of the product. Further, increase in catalyst concentration as 30, 40 and 50% did not affected the yield of final product. The result obtained was summarised in **Table 1**. In order to estimate the catalytic strength of the present catalyst various surfactants like sodium dodecyl sulphate (SDS), triton X-100 and cetyl pyridinium bromide (CPB) were used. It has been observed that when the reaction was conducted in the presence of sodium dodecyl sulphate (SDS) as an anionic surfactant, the product '**4a**' was obtained in 64% yield (**Table 2**, entry 2). With other surfactants such as Triton X-100 and cetyl pyridinium bromide (CPB) did not showed appreciable results (**Table 2**, entries 3, 4). Therefore the present surfactant catalyst was found to be superior for the synthesis of structurally diversified Betti bases. Moreover the catalytic property of natural surfactant might be attributed due to the presence of saponins which solubilises the reactant molecules in aqueous surfactant. This may alters the number of favourable collisions among the reactant molecules. The surfactant property of extract leads to encapsulation of the reactants in micellar cages. This process of encapsulation drives the equilibrium toward product side by expelling the water molecule out of its hydrophobic interior (**Figure 3 and 4**) [15].

Table 1. Optimization of catalyst concentration for formation of '4a'

Entry	Catalyst concentration (%)	Time (h)	Yield(%)[a]
1.	10	1.25	89
2.	**20**	**1**	**94**
3.	30	1.50	93
4.	40	1.40	92
5.	50	1.35	92
6.	Catalyst free	12	--[b]

[a]*Isolated yield of the product,* [b]*No product formation was observed.*

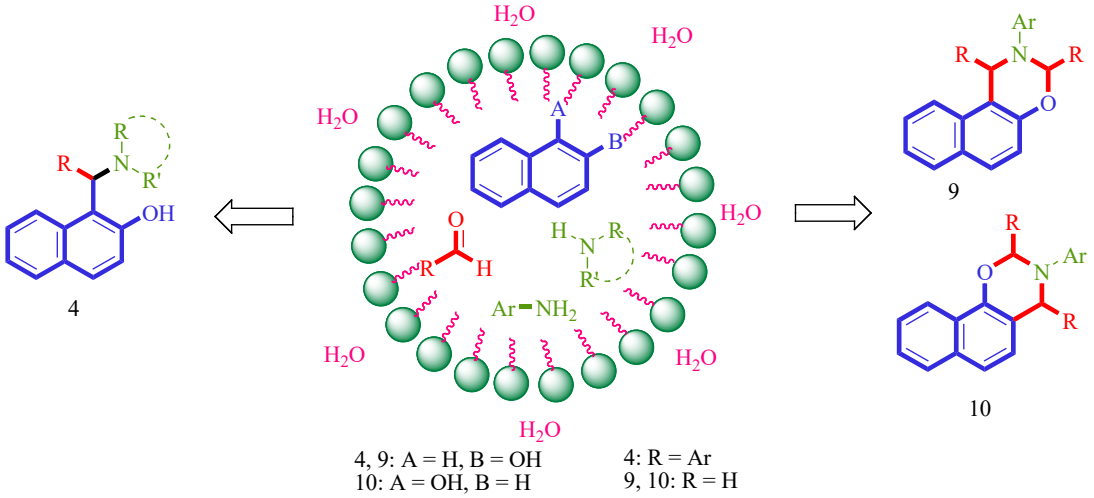


Figure 3. Micelle-promoted synthesis of Betti bases and oxazine derivatives

Table 2. Effect of surfactant for the formation of '4a'

Entry	Surfactant[a]	Time (h)	Yield (%)[b]
1.	None	12	--[c]
2.	SDS	2.25	64
3.	Triton X-100	2	56
4.	CPB	2.5	45
5.	***Acacia concinna* extract 20% (w/v)**	**1**	**94**

[a]*Reaction condition: 2-naphthol(**1**) (1mmol), benzaldehyde (**2**) (1 mmol) and piperidine* (**3**) (1 mmol)*, room temperature.* [b]*Isolated yield.* [c]*No reaction.*

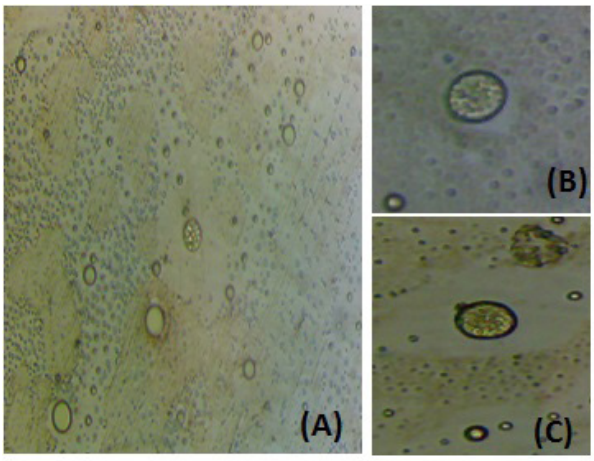


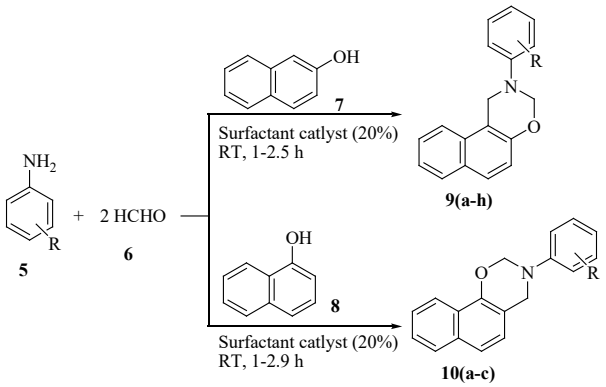
Figure 4. Photograph of micelle observed in reaction medium during formation of '4a'

Surfactant is found to decrease the surface tension of aqueous solution which increases wetting and spreading properties of water **(Table 3**) [38]. A several reactions such as redox, photochemical, enzymatic, Diels-Alder, photochemical etc are altered due to decrease the surface tension of medium [39].

Table 3. Effect of surface tension of surfactant solution on rate of reaction

Entry	Catalyst concentration %(w/v)	Time (h)	Surface Tension 'T' (dyne/cm)
1.	50	1.35	13.48
2.	40	1.40	18.87
3.	30	1.50	32.34
4.	**20**	**1**	**40.43**
5.	10	1.25	48.51
6.	Distilled Water	--	67.38

The desired Betti bases were obtained in admirable yields. Chemically reactive substrates like thiophene-2-aldehyde underwent smooth to produce corresponding Betti bases without any side product formation (**Table 4**, Entry-19). In general, all amines undergo multi-component condensation afforded corresponding Betti bases.



Scheme 2. Synthesis of oxazine derivatives

For further exposure of the synthetic potential of this aqueous methodology, we have successfully applied the method for synthesis of oxazine derivatives (**Scheme 2, Table 5**).

Table No. 4. Synthesis of 1(α-amino alkyl) 2-naphthol derivatives

Entry	Aldehydes	Amines	Product	Time(h)	Yield%	M.P.(°C)
1	C_6H_5CHO	Piperidine	**4a**	1	94	192-194[40]
2	C_6H_5CHO	$C_6H_5NH_2$	**4b**	1.25	91	132-133[40]
3	C_6H_5CHO	$4\text{-}NO_2C_6H_4NH_2$	**4c**	2.5	82	154-156[40]
4	C_6H_5CHO	Pyrrolidine	**4d**	1.8	94	176-177[40]
5	Vanillin	$4\text{-}NO_2C_6H_4NH_2$	**4e**	2.4	83	202-206[42]
6	3,4-dimethoxy-benzaldehyde	$C_6H_5NH_2$	**4f**	1.8	90	140-143[40]
7	$2\text{-}NO_2C_6H_4CHO$	$3\text{-}NO_2\ C_6H_4NH_2$	**4g**	2.8	86	192-194[43]
8	$3\text{-}NO_2C_6H_4CHO$	Pyrrolidine	**4h**	1.6	88	185-186[44]
9	$4\text{-}ClC_6H_4CHO$	$C_6H_5NH_2$	**4i**	1.4	91	121-123[40]
10	$4\text{-}\ NO_2C_6H_4CHO$	Morpholine	**4j**	1.8	86	178-179[45]
11	Pyridine-4-aldehyde	Piperidine	**4k**	1.2	90	185-187[45]
12	$4\text{-}\ NO_2C_6H_4CHO$	$C_6H_5NH_2$	**4l**	2.1	83	136-138[46]
13	$3\text{-}BrC_6H_4CHO$	$C_6H_5NH_2$	**4m**	1.8	88	139-141[46]
14	$3\text{-}ClC_6H_4CHO$	$C_6H_5NH_2$	**4n**	2.2	90	141-143[46]
15	$4\text{-}CH_3OC_6H_4CHO$	$C_6H_5NH_2$	**4o**	1.2	92	135-137[46]
16	$3\text{-}NO_2C_6H_4CHO$	Piperidine	**4p**	2.1	86	185-186[46]
17	$2\text{-}ClC_6H_4CHO$	$C_6H_5NH_2$	**4q**	1.6	88	150-152[40]
18	$3\text{-}ClC_6H_4CHO$	$3\text{-}ClC_6H_4NH_2$	**4r**	1.4	90	121-123[40]
19	C_6H_5CHO	Thiophene-2-aldehyde	**4s**	1.2	94	161-163[40]
20	C_6H_5CHO	Morpholine	**4t**	1.6	88	174-176[40]
21	$2\text{-}ClC_6H_4CHO$	Morpholine	**4u**	1.8	86	163-165[40]
22	$3\text{-}ClC_6H_4CHO$	Morpholine	**4v**	1.4	90	160-162[40]
23	$4\text{-}ClC_6H_4CHO$	Morpholine	**4w**	1.2	92	155-157[40]
24	$4\text{-}CH_3OC_6H_4CHO$	$3\text{-}NO_2C_6H_4NH_2$	**4x**	1.6	88	173-175[43]

** Reaction condition – Reaction mediated by 20 % aq. solution of Acacia Concinna and 2-nahphtol as phenol*

Table 5- Synthesis of 2,3-dihydro-2-phenyl-1H-naphtho[1,2-e][1,3] oxazine derivatives

Entry	Amine	Products	Time(h)	Yield (%)[a,b]	M.P.(°C) [ref]
1	$C_6H_5NH_2$	**9a**	2.1	90	46-48[47]
2	4-$CH_3C_6H_4NH_2$	**9b**	2	92	86-88[47]
3	3-$NO_2C_6H_4NH_2$	**9c**	2.8	82	132-134[47]
4	4-$NO_2C_6H_4NH_2$	**9d**	2.9	80	168-170[47]
5	2-$NO_2C_6H_4NH_2$	**9e**	2.4	86	109-110[47]
6	4-$ClC_6H_4NH_2$	**9f**	2.1	92	136-138[47]
7	4-$BrC_6H_4NH_2$	**9g**	2	90	118-119[41]
8	4-$CH_3OC_6H_4NH_2$	**9h**	2.1	94	75-77[41]
9	$C_6H_5NH_2$	**10a**	2	90	111-113[41]
10	4-$CH_3OC_6H_4NH_2$	**10b**	1.8	94	300(d) [41]
11	2,4,6-tri-$BrC_6H_2NH_2$	**10c**	1.8	94	76-77[41]

[a]Isolated yield of the product. [b]All the products are characterized by IR, ^{1}H NMR and Mass spectral data.

Conclusion

In conclusion, we have introduced environmental benign, efficient and economical catalyst as aqueous extract of *Acacia concinna* pods for the synthesis of Betti bases and oxazine derivatives. The striking features of current methodology are mild reaction conditions, high purity, short reaction time, high yield of products and a simple reaction workup procedure. Obtaining pure products by simply filtering makes possibility to approach for large scale production of Betti bases and oxazine derivatives.

EXPERIMENTAL SECTION

General

All chemicals were purchased from commercial suppliers and were used without further purification. Melting points were recorded on Digital Electro thermal Melting point apparatus (VEEGO, VMP-DS) and are uncorrected. The completion of reactions was confirmed with the help of Thin Layer Chromatography (TLC) using pre-coated Silica gel 60 F_{254} plates with layer thickness 0.25nm purchased from Merck Ltd. ^{1}H-NMR was recorded on Varian-NMR mercury 400 MHz spectrometer. Mass spectra were recorded on Varian MAT 311 A at 70 ev.

General procedure for the preparation of catalyst

A fine powder of *Acacia concinna* pods (20 g) in water (100 mL) was heated in a 250 mL conical flask at 100°C for 20 min. The mixture was filtered to remove all solid material and the aqueous extract was collected. The prepared extract has concentration 20% w/v.

General procedure for synthesis of 1-(α-amino alkyl) 2-naphthol derivatives (4a-x)

A mixture of 2-naphthol (1 mmol), aldehyde (1 mmol) and amine (1 mmol) in surfactant medium (20% w/v, 5 mL) was stirred at room temperature for specified time shown in Table 4. After completion of reaction (as indicated by TLC), reaction mixture was filtered using Whatmann No.1 filter paper. The product collected was recrystallized by using proper solvent and dried.

General procedure for synthesis of 2,3-dihydro-2-phenyl-1*H*-naphtho[1,2-e][1,3]oxazine derivatives (9a-h and 10a-c)

A mixture of 1-naphthol or 2-naphthol (1 mmol), amine (1 mmol) and formaldehyde (2 mmol) in surfactant medium (20% w/v, 5 mL) was

stirred at room temperature for specified time shown in Table 5. After completion of reaction (as indicated by TLC), reaction mixture was filtered using Whatmann No.1 filter paper. The product collected was recrystallized by using proper solvent and dried.

Spectroscopic data for representative compounds

1-(Phenyl(pipyridin-1-yl)methyl)naphthalen-2-ol (4a)

White solid; Yield 85 %; mp: 192–194 ^{0}C; 1H NMR (400MHz, $CDCl_3$,ppm): 13.81 (bs, 1H), 7.98-8.01 (d, *J* = 8.8 Hz, 1H), 7.67-7.74 (d, *J* =8.8Hz, 2H), 7.59-7.61 (m, 2H), 7.37-7.4 (t, *J* = 7.6 Hz, 1H), 7.19–7.35 (m, 5H), 7.06-7.09 (m, 1H), 5.28 (s, 1H), 2.35–2.50 (m, 4H), 1.45–1.55 (m, 6H). LCMS (ESI): m/z 318 ($M+H^+$)

1-[(3-nitrophenyl)(pyrrolidin-1-yl)methy] naphthalen-2-ol (4h)

White solid; Yield 94 %; mp:97-99◦C; 1H NMR (400MHz, $CDCl_3$,ppm): 8.53 (bs, 1H), 8.12-8.14(d, *J*=8 Hz, 1H), 8.07-8.09 (d, *J*=7.6 Hz, 1H), 7.72-7.76 (t, 2H), 7.59-7.63 (t, 1H), 7.40-7.44 (t, 1H), 7.23-7.26 (t, 1H), 7.11-7.13(m, 1H), 5.63 (s, 1H), 2.67 (m, 2H), 2.50 (m, 2H), 1.81 (m, 4H). LCMS (ESI): m/z 349 ($M+H^+$)

2-(4-chlorophenyl)-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazine (9f)

White solid; Yield 92 %; mp: 136-138◦C; 1H NMR (400MHz, $CDCl_3$,ppm): 7.83-7.89 (dd, 2H), 7.70-7.73 (d, *J*=8.8 Hz, 1H), 7.52-7.56 (t, 1H), 7.37-7.41 (t, 1H), 7.25-7.28 (t, 2H), 7.20-7.22 (d, *J*=9.2 Hz, 2H), 7.01-7.04 (d, *J*=8.8 Hz, 1H), 5.51 (s, 2H), 4.97 (s, 2H). LCMS (ESI): m/z 296 ($M+H^+$)

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N-butylpyridinium heptachlorodialuminate as a highly efficient catalyst for the synthesis of polyhydroquinolines under solvent-free ultrasound condition.

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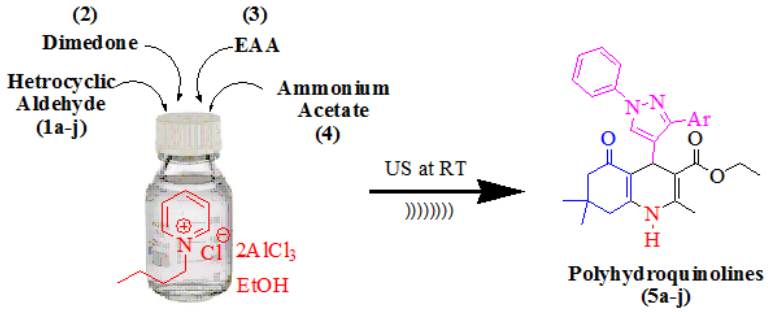
Abstract: A novel, simple and green protocol were adopted for the one pot synthesis of polyhydroquinoline derivatives from heterocyclic aldehydes, dimedone, ethyl acetoacetate and ammonium acetate by ultrasound irradiation at room temperature. The catalytic system is very effective for the bulkier aldehydes to give the corresponding polyhydroquinoline derivatives in excellent yield (80-92%) and easy for isolation of the product. This approach has the various benefits includes simple work-up procedure, excellent yields and environmentally benign path. The structure of synthesized compounds was confirmed by analytical techniques such as FTIR, 1HNMR, 13C NMR and Mass spectrometry.

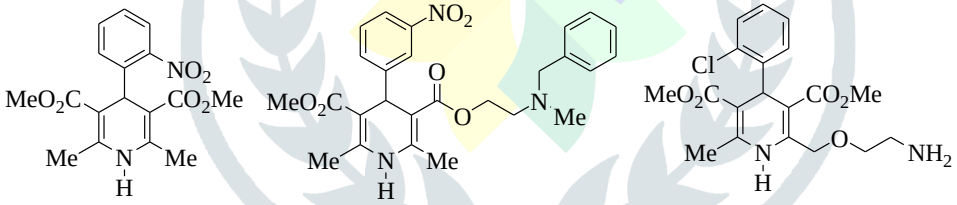


Keywords: 3-aryl-1-phenyl-1*H*-pyrazole-4-carboxaldehydes, *N*-butylpyridinium heptachlorodialuminate, Ultrasound Irradiation, polyhydroquinoline, multicomponent reaction.

1. Introduction

In recent years, Ionic liquids have been widely employed as green alternatives to those of conventional hazardous organic solvent. ILs has also been made significant growth in the catalytic processes. ILs has the potential to exhibit low human toxicities as well as eco-toxicities. It has been employed for various organic reactions include coupling reaction, hydrogenation, Diels-alder reaction, electrochemical reaction, esterification, friedal-Craft reaction, multicomponent reaction, etc. as a catalyst or solvent.[1-10]

Heterocycles are of enormous significance in the design and discovery of new compounds for biological applications.[11-12] The polyhydroquinoline scaffolds are also an important group of nitrogen containing heterocycle of extensive interest due to the significant structural design of the drugs for the treatment of cardiovascular diseases as well as hypertension.[13-14] They have also shows broad spectrum of biological activities such as antidiabetic, antiatherosclerotic, antitumor, bronchodilator, geroprotective, hepatoprotective, neuroprotectant, platelet anti-aggregratory activity, cerebral anti-ischemic activity in the treatment of Alzheimers disease and chemosensitizers in tumor therapy.[15-23] The some important drugs containing 1,4-dihyropyridine nucleus is given in below Figure 1.



1. Nifedipine **2.** Nicardipine **3.** Amlodipine

Cadiovascular agents effective in treatment of hypertension

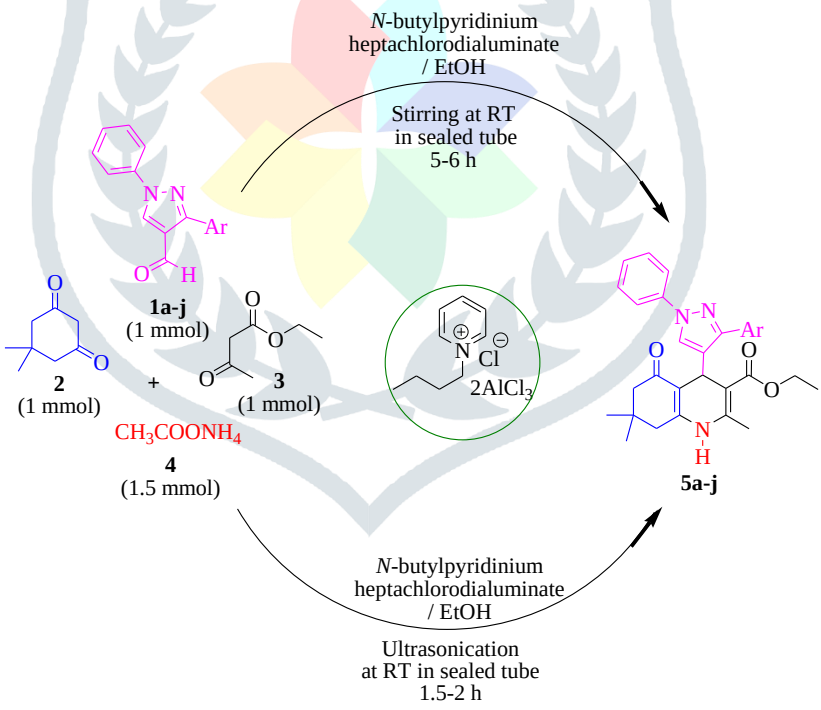
Figure 1. Illustrations of 1, 4-Dihydropyridine containing drugs

In 1882, the scientist Hantzsch and et al. firstly synthesized 1,4-DHPs by MCR of aldehyde, ethylacetoacetate and ammonia in AcOH under reflux condition in ethanol,[24] whereas polyhydroquinolines have been synthesized by using cyclic 1,3-dione instead of one mole ethyl acetoacetate. The various conventional and non-conventional methods has been employed for the synthesis of polyhydroquinoline derivatives in combination with different homogeneous as well as heterogeneous catalyst such as 5-pyrrolidin-2-yl-tetrazole,[25] Ni(0) nanoparticles,[26] La_2O_3/TFE,[27] cerium (IV) ammonium nitrate (CAN),[28] PPA-SiO_2,[29] TiO_2 NPs,[30] SnO_2,[31] SBA-15/SO_3H,[32] $HClO_4$-SiO_2,[33] $Gd(OTf)_3$,[34] (bzacen)MnCl,[35] $Cs_{2.5}H_{0.5}PW_{12}O_{40}$,[36] [1-Vinyl-3-ethyl imidazolium

iodide],[37] $[TBA]_2[W_6O_{19}]$,[38] bismuth(III) bromide,[39] Fe_3O_4@chitosan,[40] $[MSAIm]HSO_4$,[41] [2-MPyH]OTf,[42] DSIMHS,[43] [Pyridine-SO_3H]Cl,[44] $[hmim]BF_4$,[45] [SBA-IL],[46] molecular iodine[47] and Ni nanoparticle[48] etc.

In the last decades, ultrasound assisted synthesis is an important and well established technique, which were proceeds via the formation and adiabatic collapse of the transient cavitations bubble. It is used as an environmentally benign technique that is useful tool for achieving the green chemistry goals, helping to minimize the waste formation and reduce energy requirements. It also displays smooth and cleaner reactions by improving yields with homogeneous and heterogeneous processes.[49-52]

In present work instead of simple benzaldehyde derivatives, we have used 4-formyl pyrazole as a heterocyclic aldehyde for synthesis of polyhydroquinoline derivatives using *N*-butylpyridinium heptachlorodialuminate as a catalyst in ethanol under stirring condition and ultrasound irradiation for appropriate time. The syntheses of 3-aryl-1-phenyl-1*H*-pyrazole-4-carboxaldehydes were carried out by Vilsmeier-Haack reaction.[53]



Scheme 1. Synthesis of Polyhydroquinolene derivatives (5a-j)

2. Experimental

General procedure for the synthesis of polyhydroquinolene derivatives (5a-j)

2.1 Under stirring at room temperature

A 25 mL sealed tube was charged with 3-aryl-1-phenyl-1*H*-pyrazole-4-carboxaldehyde 1 (1 mmol), dimedone 2 (0.140 g, 1 mmol), ethyl acetoacetate 3 (0.130 g, 1 mmol), and NH_4OAc 4 (1.5 mmol) in 10 mL of ethanol. The sealed tube was placed in an ice bath to attain the temperature less than 10˚C. The catalytic amount of ionic liquid *N*-butylpyridinium heptachlorodialuminate was added. The sealed tube was capped and the reaction mixture was stirred for suitable time using a magnetic stirrer at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the content was poured into cold water; solid crude product thus obtained was separated by filtration. The product was dried and purified by recrystallization in n-hexane-ethyl acetate. The physical data of synthesized compounds are given in **Table 2**.

2.2 Under ultrasound irradiation at room temperature

A 25 mL sealed tube was charged with 3-aryl-1-phenyl-1*H*-pyrazole-4-carboxaldehyde 1 (1 mmol), dimedone 2 (0.140 g, 1 mmol), ethyl acetoacetate 3 (0.130 g, 1 mmol), and NH_4OAc 4 (1.5 mmol) in 10 mL of ethanol. The sealed tube was placed in an ice bath to attain the temperature less than 10˚C. The catalytic amount of *N*-butylpyridinium heptachloro-dialuminate was added. The sealed tube was capped and the reaction mixture was placed for ultra-sonication for suitable time at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the content was poured in cold water; solid crude product thus obtained was separated by filtration. The product was dried and purified by recrystallization in n-hexane-ethyl acetate. The physical data of synthesized compounds are given in **Table 2**.

3. Results and Discussion

Initially, we were interested in developing a facile protocol for the synthesis of polyhydroquinoline derivatives using ionic liquid *N*-butylpyridinium heptachlorodialuminate as catalyst. When 1-phenyl-3-*p*-tolyl-1*H*-pyrazole-4-carbaldehyde **1** was treated with dimedone **2**, ethylacetoacetate **3**, and NH_4OAc **4** by grinding and stirring in ethanol solvent without catalyst, formation of polyhydroquinoline was not observed. Also in the water and toluene the reaction did not proceed to any extent in the presence of a catalyst.

Table 1. Optimization of the reaction condition to synthesize ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-(1-phenyl-3-*p*-tolyl-1*H*-pyrazol-4-yl)quinoline-3-carboxylate (5a)

Entry	Catalyst/Solvent	Reaction Condition	Time	Isolated Yield (%)
1	No catalyst/SF	Grinding	1 h	NR
2	No catalyst/EtOH	Stirring at RT	12 h	NR
3	100 mg IL-kit/SF	Grinding	1 h	NR
4	50 mg IL-Kit/H_2O	Stirring at RT	5 h	NR
5	50 mg IL-Kit/EtOH	Stirring at RT	5 h	55
6	75 mg IL-Kit/EtOH	Stirring at RT	5 h	72
7	100 mg IL-Kit/EtOH	Stirring at RT	5 h	88
8	125 mg IL-Kit/EtOH	Stirring at RT	5 h	88
9	100 mg IL-Kit/Toluene	Stirring at RT	5 h	NR
10	100 mg IL-Kit/EtOH	US Irradiation at RT	1.5 h	90

Reaction condition: aldehyde **1** (1 mmol), Dimedone **2** (1 mmol), ethyl acetoacetate **3** (1 mmol), NH_4OAc **4** (1.5 mmol) and 0-125 mg IL-kit

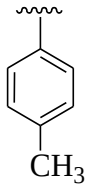
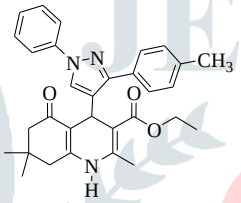
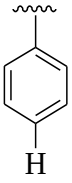
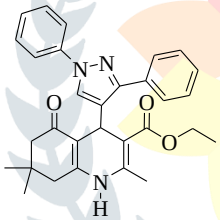
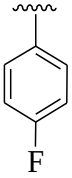
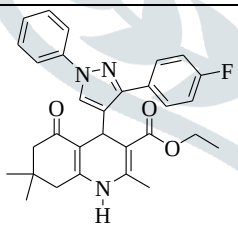
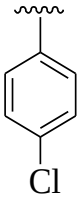
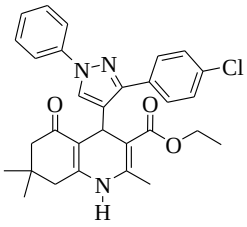
It was interesting to find that, the reaction was proceeding by simply stirring in ethanol at room temperature catalyzed by 50mg of *N*-butylpyridinium heptachlorodialuminate in low yield. However, by optimizing the amount of catalyst such as 50, 75, 100, 125 and optimum solvent quantity, it was possible to obtain polyhydroquinolines in good yields. Thus, the polyhydroquinoline derivative (**5a**) was obtained in excellent yield (88%) with high selectivity in the presence of 100 mg of ionic liquid by simply stirring at room temperature.

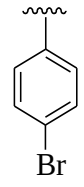
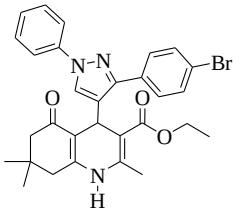
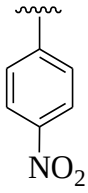
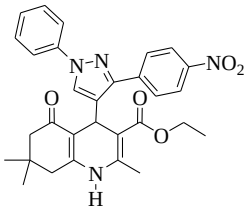
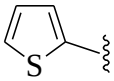
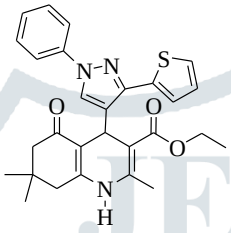
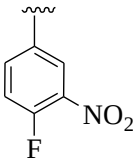
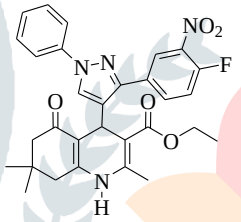
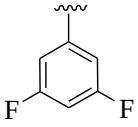
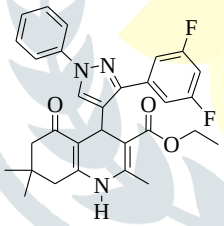
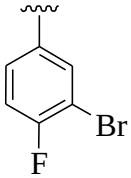
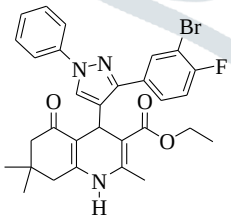
When the same model reaction was carried out under ultrasound irradiation at room temperature in the presence of *N*-butylpyridinium heptachloro-dialuminate in ethanol as solvent, the desired polyhydroquinoline (**5a**) was obtained in excellent yield (90%). Among all the systems studied, a combination of ionic liquid in ethanol was found to be the best preference, which was taken for synthesis of further derivatives.

To evaluate the efficiency and the applicability of the procedure, a variety of substituted heterocyclic aldehydes **1a-j** were used to give the corresponding polyhydroquinoline derivatives **5a-j** in good yields (80-92%) under optimized conditions.

The substrate with electron donating as well as electron withdrawing groups reacts smoothly to afford the product with excellent yield and selectivity. Also under the ultrasound irradiation yield of the product was increased with a reduction of reaction time than the stirring method. The data of synthesized polyhydroquinoline derivatives are given in **Table 2**.

Table 2. Synthesis of polyhydroquinoline derivatives (5a-j) using *N*-butylpyridinium heptachlorodialuminate.

Entry	Ar – Group	Product	Reaction Time (hrs)		Yield (%)		M.P. (˚C)
			Stirring at RT	US at RT	Stirring at RT	US at RT	
5a			5	1.5	88	90	224-226
5b			5	1.5	90	90	218
5c			5.5	1.5	84	84	206
5d			5.5	1.5	86	88	256-258

5e			6	2	88	92	262-264
5f			6	2	84	85	300<
5g			5.5	1.5	88	92	196-198
5h			6	2	82	82	300<
5i			6	2	82	84	300<
5j			5.5	1.5	82	86	226-228

Reaction condition: aldehyde **1** (1 mmol), dimedone **2** (1 mmol), ethyl acetoacetate **3** (1 mmol), NH_4OAc **4** (1.5 mmol) and 100 mg IL-kit in 10 mL ethanol.

4. Discussion of Spectral data of Synthesized Compounds

***ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-(1-phenyl-3-p-tolyl-1H-pyrazol-4-yl)quinoline-3-carboxylate* (Table 2, Entry 5a).**

The product was obtained as white solid: mp 224-226˚C; FT-IR (KBr) ν: 3273, 3199, 3071, 2957, 1737, 1686, 1598, 1488, 1449, 1390, 1212, 1169, 1025, 830, 740; ^{1}H NMR (DMSO-d_6, 400 MHz) δ= 0.69 (t, J=6.0

Hz, 3H, -CH_3), 0.99 (s, 3H, -CH_3), 1.05 (s, 3H, -CH_3), 2.09 (s, 2H, -CH_2-), 2.24 (s, 3H, -CH_3), 2.39 (s, 5H, -CH_2- & -CH_3), 3.74 (m, J=6.0 Hz, 2H, -CH_2-), 5.10 (s, 1H, -CH-), 7.24 (d, J=6.2 Hz, 3H, Ar-H), 7.44 (t, 2H, Ar-H), 7.72 (d, J=7.2 Hz, 2H, Ar-H), 7.93 (s, 1H, Ar-H, Pyrazole ring-H), 7.96 (d, J=7.0 Hz, 2H, Ar-H), 8.98 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 13.53, 18.07, 20.90, 26.16, 27.10, 28.77, 32.17, 50.41, 58.45, 105.06, 110.37, 117.84, 125.60, 127.06, 128.26, 128.35, 129.21, 129.26, 131.65, 136.25, 139.25, 143.49, 149.49, 150.05, 166.70, 194.62; MS(ESI m/z %): 518.25 $[M+Na]^+$.

***ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-(1,3-diphenyl-1H-pyrazol-4-yl)quinoline-3-carboxylate* (Table 2, Entry 5b)**.

The product was obtained as white solid: mp 218˚C; FT-IR (KBr) ν: 3275,3180, 3068, 2955, 1739, 1698, 1650, 1599, 1542, 1495, 1381, 1213, 1148, 1074, 959, 752; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.64 (t, J=5.6 Hz, 3H, -CH_3), 0.97 (s, 3H, -CH_3), 1.04 (s, 3H, -CH_3), 2.05 (s, 2H, -CH_2-), 2.08 (s, 3H, -CH_3), 2.31 (s, 2H, -CH_2-), 3.72 (q, J=5.6 Hz, 2H, -CH_2-), 5.10 (s, 1H, -CH-), 7.27 (t1H, Ar-H), 7.39 (t, 1H, Ar-H), 7.45-7.49 (m, 4H, Ar-H), 7.78 (m, 2H, Ar-H), 8.04 (s, 1H, Ar-H, Pyrazole ring-H), 8.08 (d, 2H, Ar-H), 9.05 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 14.14, 18.60, 26.65, 27.60, 29.22, 32.72, 50.85, 58.99, 105.26, 110.67, 118.47, 126.40, 127.80, 128.03, 128.37, 128.98, 129.93, 130.38, 135.01, 139.90, 144.28, 150.18, 150.50, 167.22, 195.28; MS(ESI m/z %): 504.32 $[M+Na]^+$.

***ethyl 4-(3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (Table 2, Entry 5c).**

The product was obtained as white solid: mp 206˚C; FT-IR (KBr) ν: 3269, 3204, 3074, 2958, 1687, 1645, 1628, 1599, 1526, 1486, 1377, 1211, 1079, 844, 741; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.75 (t, J=6.8 Hz, 3H, -CH_3), 0.92 (s, 3H, -CH_3), 1.02 (s, 3H, -CH_3), 2.17 (s, 2H, -CH_2-), 2.22 (s, 3H, Ar-CH_3), 2.41 (s, 2H, -CH_2-), 3.79 (q, J=6.8 Hz, 2H, -CH_2-), 5.09 (s, 1H, -CH-), 7.34 (m, 1H, Ar-H), 7.45 (m, 3H, Ar-H), 7.83 (m, 2H, Ar-H), 7.97 (m, 2H, Ar-H), 8.14 (m, 2H, Ar-H and Pyrazole ring-H), 9.13 (s, 1H, NH).

***ethyl 4-(3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (Table 2, Entry 5d).**

The product was obtained as white solid: mp 256-258˚C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.72 (t, 3H, -CH_3), 0.98 (s, 3H, -CH_3), 1.06 (s, 3H, -CH_3), 2.09 (s, 2H, -CH_2-), 2.22 (s, 3H, Ar-CH_3), 2.39 (s, 2H, -CH_2-), 3.77

(m, 2H, -CH_2-), 5.07 (s, 1H, -CH-), 7.25 (s, 1H, Ar-H), 7.45 (s, 4H, Ar-H), 7.73 (s, 2H, Ar-H), 7.95 (s, 1H, Pyrazole ring-H), 8.14 (d, J=7.2 Hz 2H, Ar-H), 9.02 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 13.54, 18.16, 26.21, 27.07, 28.75, 32.20, 50.35, 58.53, 110.36, 117.98, 125.81, 127.41, 127.71, 129.19, 129.96, 130.04, 132.21, 133.30, 139.32, 143.80, 148.72, 149.52, 166.59, 194.74; MS(ESI m/z %): 538.18 $[M+Na]^+$.

ethyl 4-(3-(4-bromophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate **(Table 2, Entry 5e).**

The product was obtained as white solid: mp 262-264˚C; FT-IR (KBr) ν: 3383, 3206, 3068, 2960, 1687, 1645, 1598, 1501, 1486, 1378, 1278, 1212, 1075, 961, 835; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.72 (t, J=6.0 Hz, 3H, -CH_3), 0.91 (s, 3H, -CH_3), 1.04 (s, 3H, -CH_3), 2.16 (s, 2H, -CH_2-), 2.23 (s, 3H, Ar-CH_3), 2.34 (m, 2H, -CH_2-), 3.81 (q, J=6.0 Hz, 2H, -CH_2-), 5.10 (s, 1H, -CH-), 7.32 (t, J=6.0 Hz, 1H, Ar-H), 7.47 (m, 2H, Ar-H), 7.73-7.82 (m, 3H, Ar-H), 7.99 (m, 2H, Ar-H), 8.19 (s, 1H, Ar-H, Pyrazole ring-H), 8.41 (m, 1H, Ar-H), 9.11 (s, 1H, NH).

ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-4-(3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)-5-oxoquinoline-3-carboxylate **(Table 2, Entry 5f).**

The product was obtained as white solid: mp 300˚C<; FT-IR (KBr) ν: 3267, 3199, 3073, 2980, 1691, 1646, 1599, 1521, 1487, 1379, 1342, 1212, 1065, 866; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.67 (t, J=5.6 Hz, 3H, -CH_3), 0.95 (s, 3H, -CH_3), 1.04 (s, 3H, -CH_3), 2.00 (s, 2H, -CH_2-), 2.24 (s, 3H, Ar-CH_3), 2.41 (s, 2H, -CH_2-), 3.73 (q, J=5.6 Hz, 2H, -CH_2-), 5.09 (s, 1H, -CH-), 7.33 (t, J=6.0 Hz, 1H, Ar-H), 7.49 (m, 2H, Ar-H), 7.83 (d, J=6.0 Hz, 2H, Ar-H), 8.17 (s, 1H, Ar-H, Pyrazole ring-H), 8.36 (d, J=7.2 Hz, 2H, Ar-H), 8.43(d, J=7.2 Hz, 2H, Ar-H), 9.14 (s, 1H, NH).

ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-(1-phenyl-3-(thiophen-2-yl)-1H-pyrazol-4-yl)quinoline-3-carboxylate **(Table 2, Entry 5g).**

The product was obtained as white solid: mp 196-198˚C; FT-IR (KBr) ν: 3273, 3180, 3069, 2954, 1698, 1642, 1599, 1494, 1381, 1309, 1278, 1212, 1148, 1074, 959, 749; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.75 (t, J=5.6 Hz, 3H, -CH_3), 0.92 (s, 3H, -CH_3), 1.03 (s, 3H, -CH_3), 2.10 (s, 2H, -CH_2-), 2.26 (s, 3H, Ar-CH_3), 2.40 (s, 2H, -CH_2-), 3.81 (q, J=5.6 Hz, 2H, -CH_2-), 5.14 (s, 1H, -CH-), 7.18 (m, 1H, Ar-H), 7.28 (t, 1H, Ar-H), 7.47 (m, 2H, Ar-H), 7.53 (m, 1H, Ar-H), 7.69 (d, 2H, Ar-H), 8.08 (s, 1H, Pyrazole ring-H), 8.13 (m, 1H, Ar-H), 9.09 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ:14.03, 18.72, 26.73, 27.33, 29.32, 32.71, 50.77, 59.28, 105.09,

110.85, 118.45, 125.59, 126.51, 127.11, 127.91, 128.57, 129.95, 130.49, 136.17, 139.63, 144.64, 145.00, 149.87, 167.28, 195.06; MS(ESI m/z %): 510.28 $[M+Na]^+$.

***ethyl 4-(3-(4-fluoro-3-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (Table 2, Entry 5h).**

The product was obtained as white solid: mp 300˚C<; FT-IR (KBr) ν: 3383, 2981, 1687, 1645, 1588, 1541, 1473, 1380, 1214, 1069, 960; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.72 (t, J=5.6 Hz, 3H, -CH_3), 0.95 (s, 3H, -CH_3), 1.04 (s, 3H, -CH_3), 2.19 (s, 2H, -CH_2-), 2.25 (s, 3H, Ar-CH_3), 2.40 (m, 2H, -CH_2-), 3.79 (q, J=5.6 Hz, 2H, -CH_2-), 5.01 (s, 1H, -CH-), 7.29 (m, 1H, Ar-H), 7.49 (m, 3H, Ar-H), 7.81 (m, 2H, Ar-H), 8.11 (m, 2H, Ar-H and Pyrazole ring-H), 8.50 (m, 1H, Ar-H), 9.11 (s, 1H, NH).

***ethyl 4-(3-(3,5-difluorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (Table 2, Entry 5i).**

The product was obtained as white solid: mp 300˚C<; FT-IR (KBr) ν: 3273, 3203, 3076, 2962, 1686, 1643, 1625, 1595, 1539, 1480, 1377, 1209, 1115, 985, 743; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.71 (t, J=5.6 Hz, 3H, -CH_3), 0.95 (s, 3H, -CH_3), 1.04 (s, 3H, -CH_3), 2.20 (s, 2H, -CH_2-),2.24 (s, 3H, Ar-CH_3), 2.42 (m, 2H, -CH_2-), 3.80 (q, J=5.6 Hz, 2H, -CH_2-), 5.03 (s, 1H, -CH-), 7.28-7.32 (m, 2H, Ar-H), 7.48 (t, 2H, Ar-H), 7.81 (d, 2H, Ar-H), 7.92 (m, 2H, Ar-H), 8.12 (s, 1H, Ar-H, Pyrazole ring-H), 9.17 (s, 1H, NH).

***ethyl 4-(3-(3-bromo-4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (Table 2, Entry 5j).**

The product was obtained as white solid: mp 224-226˚C; FT-IR (KBr) ν: 3282, 3228, 3084, 2962, 1696, 1633, 1601, 1541, 1487, 1439, 1376, 1209, 1066, 959, 750; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.73 (t, J=5.6 Hz, 3H, -CH_3), 0.94 (s, 3H, -CH_3), 1.03 (s, 3H, -CH_3), 2.19 (s, 2H, -CH_2-), 2.24 (s, 3H, Ar-CH_3), 2.38 (m, 2H, -CH_2-), 3.78 (q, J=5.6 Hz, 2H, -CH_2-), 5.01 (s, 1H, -CH-), 7.31 (t, J=6.0 Hz, 1H, Ar-H), 7.49 (m, J=6.0 and 4.8 Hz, 2H, Ar-H), 7.74-7.84 (m, 3H, Ar-H), 8.17 (s, 1H, Ar-H, Pyrazole ring-H), 8.54 (m, 1H, Ar-H), 8.92 (m, 1H, Ar-H), 9.14 (s, 1H, NH).

5. Conclusion

In conclusion, we have successfully demonstrated a novel method for the one pot synthesis of polyhydroquinoline derivatives from heterocyclic aldehydes, dimedone, ethyl acetoacetate and ammonium

acetate by simple stirring and ultrasound irradiation at room temperature. The catalytic system is very effective for the bulkier aldehydes to give the corresponding polyhydroquinoline derivatives in excellent yield (80-92%) and easy for isolation of the product. This approach has the various benefits includes simple work-up procedure, excellent yields and environmentally benign path.

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Ionic liquid catalyzed one pot green synthesis of isoxazolone derivatives *via* multicomponent reaction

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A series of 3-methyl-4-((3-aryl-1-phenyl-1*H*-pyrazol-4-yl)methylene)isoxazol-5(4*H*)-one derivatives have been efficiently synthesized by environmentally benign, one-pot three component condensation of substituted 1,3-diaryl-1*H*-pyrazole-4-carboxyaldehyde, β-keto ester and hydroxyl amine hydrochloride in the presence of ionic liquid [HNMP][HSO_4] as a catalyst in ethanol. These derivatives have been synthesized by conventional, ultrasound and microwave irradiation methods. The combination of ionic liquid with ultrasound as well as microwave irradiation makes the protocol fascinating and environmentally benign. In addition, it has several benefits such as simple work-up procedure, clean reaction profile, short reaction time and good yields.

Keywords: 1,3-Diaryl-1*H*-pyrazole-4-carboxyaldehyde, isoxazolone, ionic liquid, ultrasound, microwave

Recently ionic liquids (ILs) have grown interest in diverse areas of chemistry; because of considerable interest as eco-friendly reaction solvent and catalyst in the organic synthesis. They exhibit significant properties such as negligible vapor pressure, broad liquid range, non-flammability, adequate ionic conductivity, potentially recyclable properties and capacity to dissolve a variety of organic and inorganic solids. Acidic ionic liquids have been employed in divergent areas due to their fascinated physical and chemical properties. [HNMP][HSO_4] is also a brønsted acidic ILs has successfully used in various organic reactions such as cyclocondensations reactions, Oxa-Michael addition, Prins reaction and trans-esterification reactions[1-6].

Literature survey revealed that, the isoxazol-5(4*H*)-ones and their derivatives have vital importance in divergent areas such as organic synthesis, liquid crystalline materials, filter dyes in photographic films, light-conversion molecular devices, optical storage and nonlinear optical research[7-11]. The isoxazol-5(4*H*)-ones scaffold bearing both nitrogen and oxygen atoms are an important class of five member heterocycles, which display good pharmaceutical and biological activities[12, 13]. It is considered a major core in the discovery of protein kinase inhibitors, which is playing an important role in the growth of chemotherapeutic agents[14, 15]. They also show significant analgesic, antibacterial, anti-HIV, antifungal, anti-inflammatory, anti-mycobacterial, anticancer, antioxidant, antitumor, antiprotozoal, anti-tubercular, nematicidal and antiviral activities[16-28]. The some important illustrations of isoxazol-5(4*H*)-one nucleus containing agents are shown in Figure 1.

Several protocols have been studied in the literature for the synthesis of isoxazol-5(4*H*)-one and their analogues. Among them some illustrations are *N*-bromosuccinimide (NBS)[29], Ag/SiO_2[30], phthalimide-*N*-oxyl salts (POPINO and TBAPINO)[31], NaOAc/visible light[32], boric acid[33], catalyst free[34], citric acid[35], NaH_2PO_4[36], pyridine/reflux[37], sodium benzoate[38], sodium saccharin[39], pyridine/US[40], pottasium phthalimide[41], sodium sulfide[42], $H_3PW_{12}O_{40}$, clinoptilolite, nano Fe_2O_3[43], *etc*.

Ultrasound (US) and Microwave (MW) assisted transformations are well established class of synthetic organic chemistry. The significant benefit of MW and US irradiated organic synthesis is of rapidly synthesize library of organic compounds with improved yields and selectivities. The MW and US assisted multicomponent reaction with various green catalysts such as ionic liquids, nano-particles, vitamins and zeolites etc. makes protocol more interesting, fascinating and environmentally benign[44-54].

In view of biologial importance of isoxazolone nuclues as well as green approach of ILs in the multicomponent reaction and continution of our work in this field[55-59]; we have described the synthesis of isoxazolone derivatives by multi-component condensation of substituted 1,3-diphenyl-1*H*-pyrazole-4-carboxyaldehyde **(1)**, *β*-keto ester (**2**), hydroxylamine hydrochloride (**3)** and 100 mg of *N*-Methyl-2-Pyrrolidonium Hydrogen Sulphate [HNMP][HSO_4].

Results and Discussion

Initially, we examined the model reaction between 1-phenyl-3-*p*-tolyl-1*H*-pyrazole-4-carbaldehyde **1a,** ethyl acetoacetate **2**, hydroxyl amine hydrochloride **3** under different conditions. A literature study of solvents indicated that ethanol is the most suitable reaction medium for the synthesis of isoxazolone derivatives. When the reaction was conducted at room temperature with constant stirring, reaction did not proceed with and without catalyst. The reaction proceeds with good results under reflux condition. Additional experimental study revealed that the required catalyst amount was found to be 100 mg for better yield (Entry 7). The results obtained during optimization are summarized in Table I.

For comparison, reactions were also carried out under US and MW conditions. As expected, USI (Entry 10) and MWI (Entry 12) assisted synthesis required shorter reaction time and higher yield as compared to conventional heating.

After the determination of the optimized conditions, we twisted our consideration in the direction of studying the scope of the method. The isoxazolone derivatives with both electron-donating and electron-withdrawing substituent on the aromatic ring were tolerated and afforded high yields (Table II).

Experimental Section

The physical constants were recorded in an open capillary and are uncorrected. IR spectra were recorded on a Perkin-Elmer FTIR spectrophotometer. The ^{1}H NMR spectrums were recorded on a Brucker Avance II 400MHz in DMSO and ^{13}C NMR was recorded on 100MHz in DMSO. Mass spectra were recorded on a Finnigan Mass spectrometer. TLC was carried out on pre-coated silica gel Al-plates to check the purity of the compounds.

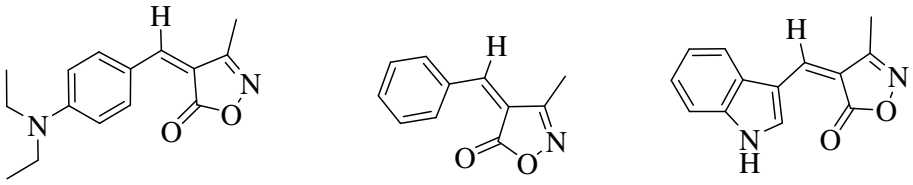


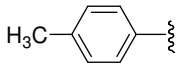
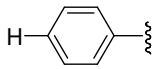
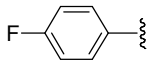
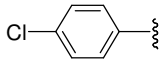
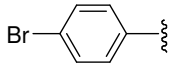
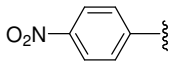
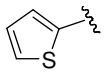
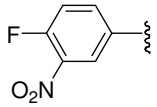
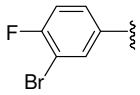
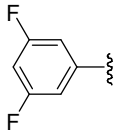
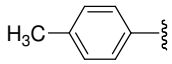
Figure 1 — Isoxazol-5(4*H*)-ones nucleus containing drugs

Table I — Optimization of reaction condition to synthesize isoxazolone derivative **4a**

Entry	Catalyst/ Solvent	Reaction Condition	Time	Yield (%)
1	No catalyst/ Solvent free	Stirring at RT	2 h	NR
2	No catalyst/ EtOH	Stirring at RT	2 h	NR
3	100 mg [HNMP][HSO_4]/ SF	Stirring at RT	2 h	NR
4	100 mg [HNMP][HSO_4]/ EtOH	Stirring at RT	2 h	NR
5	50 mg [HNMP][HSO_4]/ EtOH	Reflux	4 h	25
6	75 mg [HNMP][HSO_4]/ EtOH	Reflux	4 h	64
7	100 mg [HNMP][HSO_4]/ EtOH	Reflux	4 h	70
8	125 mg [HNMP][HSO_4]/ EtOH	Reflux	4 h	72
9	100 mg [HNMP][HSO_4]/ EtOH	USI at RT	30 min	Trace
10	100 mg [HNMP][HSO_4]/ EtOH	USI at 45°C	30 min	80
11	100 mg [HNMP][HSO_4]/ EtOH	MWI at 140 W	10 min	15
12	100 mg [HNMP][HSO_4]/ EtOH	MWI at 210 W	5 min	82

Reaction Conditions: 1-phenyl-3-*p*-tolyl-1*H*-pyrazole-4-carbaldehyde **1a** (1 mmol), Ethyl acetoacetate **2** (1 mmol), hydroxyl amine hydrochloride **3** (1 mmol) and 50-125 mg [HNMP][HSO_4]

Table II — Synthesis of isoxazolone derivatives **4a-k** using [HNMP][HSO_4] as a catalyst

Entry	Ar-Group	R-Group	Reaction Time (min.)			Yield (%)			m.p. in (^oC)
			Reflux	US	MW	Reflux	US	MW	
4a		-CH_3	240	30	5	70	80	82	210
4b		-CH_3	240	28	4	71	80	81	208
4c		-CH_3	270	34	6	68	78	80	204
4d		-CH_3	240	30	4	74	82	82	228
4e		-CH_3	240	30	5	72	80	80	234
4f		-CH_3	270	32	6	68	75	75	268
4g		-CH_3	240	28	4	74	82	84	192
4h		-CH_3	300	32	6	68	76	78	196
4i		-CH_3	300	30	6	70	80	82	226
4j		-CH_3	300	32	5	72	78	83	224
4k		-CF_3	240	30	4	72	80	80	160

Reaction Condition- Substituted 1,3-diphenyl-1*H*-pyrazole-4-carbaldehyde **1** (1 mmol), Ethyl acetoacetate **2** (1 mmol), hydroxyl amine hydrochloride **3** (1 mmol), 100 mg [HNMP][HSO_4] and 10 mL ethanol.

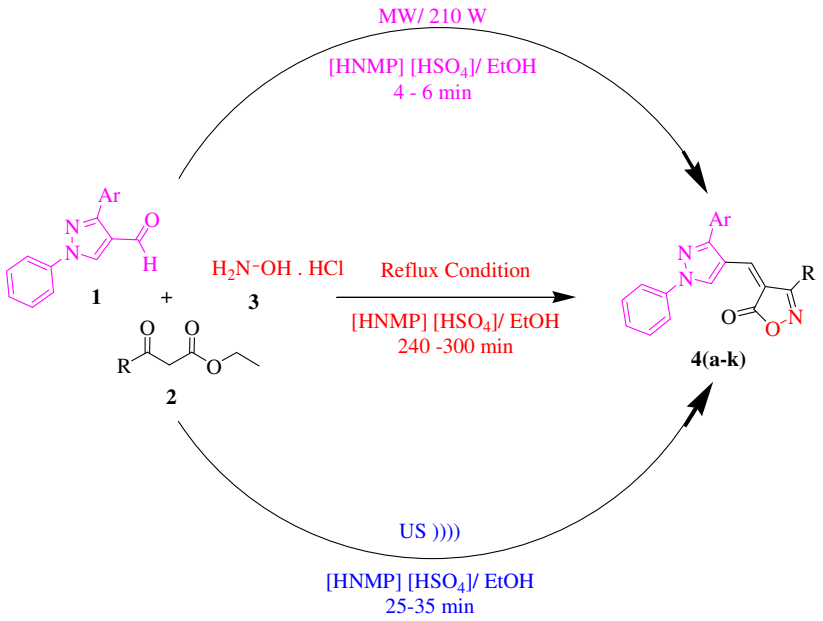
The precursor 1,3-diaryl-1*H*-pyrazole-4-carboxyaldehyde were synthesized by Vilsmeier Haack formylation reaction[60], whereas the catalyat [HNMP][HSO_4] was prepared and purified as reported by B. M. Bhanage and co-authors[4].

General Procedure for the Synthesis of Isoxazolone derivatives 4(a-k) Under Conventional Reflux Condition

A mixture equimolar quantities of 1,3-diaryl-1*H*-pyrazole-4-carboxyaldehyde 1 (1 mmol), *β*-keto ester 2 (1 mmol), hydroxyl amine hydrochloride 3 (1 mmol) and 100 mg of [HNMP][HSO_4] was placed in a 100 mL round bottom flask containing 10 mL of EtOH. Then the reaction mixture was refluxed for appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the content were cooled to room temperature, solid product thus obtained was separated by filtration. The crude product was washed by cold ethanol to get pure product (Scheme I).

Under Ultra Sound Irradiation

A mixture equimolar quantities of substituted 1,3-diphenyl-1*H*-pyrazole-4-carbaldehyde 1 (1 mmol), *β*-keto ester 2 (1 mmol), hydroxyl amine hydrochloride 3 (1 mmol) and 100 mg of Ionic liquid [HNMP][HSO_4] was taken in a 100 mL round bottom flask containing 10 mL of EtOH. The reaction mixture was placed for US irradiation at 45^oC for appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction,



Scheme I — Synthesis of isoxazolone derivatives

the content were cooled to room temperature, solid product thus obtained was separated by filtration. The crude product was washed with cold ethanol to get pure product (Scheme I).

Under Microwave Irradiation

A mixture equimolar quantities of substituted 1, 3-diphenyl-1*H*-pyrazole-4-carbaldehyde 1 (1mmol), *β*-keto ester 2 (1 mmol), hydroxyl amine hydrochloride 3 (1mmol) and 100 mg of Ionic liquid [HNMP][HSO_4] was taken in a 100 mL round bottom flask containing 10 mL of EtOH. The reaction mixture was subjected for MW irradiation at level 2 (210 W) for appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the content were cooled to room temperature, solid product thus obtained was separated by filtration. The crude product was washed with cold ethanol to get pure product (Scheme I).

Spectral Data of Synthesized Compounds

3-methyl-4-((1-phenyl-3-*p*-tolyl-1*H*-pyrazol-4-yl) methylene)isoxazol-5(4*H*)-one, 4a: Pale Yellow Solid; m.p. 210ºC; FT-IR (KBr) ν: 3145, 2980, 1735, 1612, 1599, 1532, 1507, 1454, 1231, 1122, 996, 873, 757; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.24 (s, 3H, -CH_3), 2.42 (s, 3H, -CH_3), 7.41 (d, 2H, Ar-H), 7.49 (t, 1H, Ar-H), 7.61-7.68 (m, 5H, Ar-H), 7.92 (s, 1H, Pyrazole ring-H), 7.94 (d, 1H, Ar-H), 9.87 (s, 1H, vinylic proton); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 10.89, 20.89, 114.73, 115.09. 116.62, 127.61, 128.24, 129.11, 129.66, 129.97, 133.48, 138.37, 139.18, 139.95, 149.25, 161.70, 168.93; MS: *m/z* = 344.39 $[M+1]^+$.

3-methyl-4-((1,3-diphenyl-1*H*-pyrazol-4-yl) methylene)isoxazol-5(4*H*)-one, 4b: Pale Yellow Solid; m.p. 208ºC; FT-IR (KBr) ν: 3148, 3057, 2982, 1735, 1613, 1599, 1517, 1502, 1447, 1335, 1222, 1128, 994, 872, 704; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.24 (s, 3H, -CH_3), 7.44 (t, 1H, Ar-H), 7.52-7.61 (m, 6H, Ar-H), 7.67 (m, 2H, Ar-H), 7.92 (m, 2H, Ar-H and Pyrazole ring-H), 10.03 (s, 1H, vinylic proton); MS: *m/z* = 330.53 $[M+1]^+$.

4-((3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)-3-methylisoxazol-5(4*H*)-one, 4c: Pale Yellow Solid; m.p. 204ºC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.243 (s, 3H, -CH_3), 7.29 (t, 2H, Ar-H), 7.44 (t, 2H, Ar-H), 7.49-7.69 (m, 4H, Ar-H), 7.90 (m, 2H, Ar-H and Pyrazole ring-H), 10.01 (s, 1H, vinylic proton); MS: *m/z* = 348.34 $[M+1]^+$.

4-((3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)-3-methylisoxazol-5(4*H*)-one, 4d: Pale Yellow Solid; m.p. 228ºC; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.31 (s, 3H, -CH_3), 7.26 (t, 2H, Ar-H), 7.42-7.45 (m, 2H, Ar-H), 7.53-7.57 (m, 5H, Ar-H), 7.89 (s,

1H, Pyrazole ring-H), 9.98 (s, 1H, vinylic proton); MS: *m/z* = 364.27 $[M+1]^+$.

4-((3-(4-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)-3-methylisoxazol-5(4*H*)-one, 4e: Pale Yellow Solid; m.p. 234ºC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.25 (s, 3H, -CH_3), 7.46 (t, 2H, Ar-H), 7.55 (m, 4H, Ar-H), 7.72 (m, 2H, Ar-H), 7.89 (m, 2H, Ar-H and Pyrazole ring-H), 10.04 (s, 1H, vinylic proton).

3-methyl-4-((3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)isoxazol-5(4*H*)-one, 4f: Pale Yellow Solid; m.p. 268ºC; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.27 (s, 3H, -CH_3), 7.47 (t, 2H, Ar-H), 7.49-7.56 (m, 3H, Ar-H), 7.78 (dd, *J* = 4.0 Hz, 2H, Ar-H), 8.04 (s, 1H, Pyrazole ring-H), 8.26 (dd, *J* = 4.0 Hz, 2H, Ar-H), 9.97 (s, 1H, vinylic proton); MS: *m/z* = 375.19 $[M+1]^+$.

3-methyl-4-((1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazol-4-yl)methylene)isoxazol-5(4*H*)-one, 4g: Pale Yellow Solid; m.p. 192ºC; FT-IR (KBr) ν: 3145, 3109, 2982, 1744, 1613, 1530, 1498, 1460, 1221, 1128; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.31 (s, 3H, -CH_3), 7.28 (m, 1H, Ar-H), 7.48 (m, 1H, Ar-H), 7.61 (m, 2H, Ar-H), 7.68 (m, 1H, Ar-H), 7.77 (m, 1H, Ar-H), 7.81 (s, 1H, Pyrazole ring-H), 7.88 (m, 2H, Ar-H), 9.86 (s, 1H, vinylic proton); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 10.94, 114.85, 115.24. 119.41, 128.17, 128.39, 128.46, 128.70, 129.80, 131.84, 133.53, 138.10, 138.66, 150.33, 161.42, 168.79; MS: *m/z* = 336.35 $[M+1]^+$.

4-((3-(4-fluoro-3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)-3-methylisoxazol-5(4*H*)-one, 4h: Pale Yellow Solid; m.p. 196ºC; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.28 (s, 3H, -CH_3), 7.40 (s, 1H, Ar-H), 7.47 (t, 1H, Ar-H), 7.53-7.59 (m, 3H, Ar-H), 7.89 (d, *J* = 4.0 Hz, 2H, Ar-H), 8.00 (s, 1H, Pyrazole ring-H), 8.39 (dd, *J* = 4.0 Hz, 1H, Ar-H), 10.03 (s, 1H, vinylic proton).

4-((3-(3-bromo-4-fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)-3-methylisoxazol-5(4*H*)-one, 4i: Pale Yellow Solid; m.p. 226ºC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.26 (s, 3H, -CH_3), 7.34 (t, 1H, Ar-H), 7.40 (d, 1H, Ar-H), 7.46 (t, 1H, Ar-H), 7.57 (m, 3H, Ar-H), 7.90 (m, 3H, Ar-H and Pyrazole ring-H), 10.00 (s, 1H, vinylic proton).

4-((3-(3,5-difluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl) methylene)-3-methylisoxazol-5(4*H*)-one, 4j: Pale Yellow Solid; m.p. 224ºC; FT-IR (KBr) ν: 3148, 3077, 2977, 1729, 1605, 1505, 1434, 1338, 1229, 1125, 992, 860, 794; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.28 (s, 3H, -CH_3), 7.02 (m, 1H, Ar-H), 7.21 (m, 2H, Ar-H), 7.46 (m, 2H, Ar-H), 7.57 (t, 2H, Ar-H), 7.89 (m, 2H, Ar-H and Pyrazole ring-H), 10.01 (s, 1H, vinylic proton); MS: *m/z* = 366.30 $[M+1]^+$.

Conclusion

We have developed a green protocol for the one-pot synthesis of isoxazolone derivatives using [HNMP][HSO_4] as an efficient catalyst. The series of isoxazolone **4(a-k)** derivatives was synthesized from various 1,3-diaryl-1*H*-pyrazole-4-carboxyaldehyde, aceto-acetic ester and hydroxyl amine hydrochloride in ethanol by conventional reflux condition, US, and MW irradiation for suitable time. It was found that, the US and MW assisted reaction in [HNMP][HSO_4] provides several benefits as compared with the conventional method. This fascinating US and MW assisted protocol was offered the simple work-up procedure, short reaction time, excellent yield with the environmentally benign approach and a significant contribution in green technology.

Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/60.

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One Pot Synthesis of Lead Sulphide Thin Films

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Abstract- The Lead Sulphide (PbS) nanoparticles are creating interests among the scientific community because of its applications as tuneable infrared detectors, bulk hybrid solar cells, solid state laser, biological sensing application etc. Various synthesis techniques are utilized to synthesize Lead Sulphide material which requires hazardous chemicals, cumbersome vacuum techniques and large instrumentation. In the current work, the simple chemical bath deposition technique is used. The as synthesized and annealed PbS films were characterized using X-ray diffraction, UV-visible spectroscopy. The J-V characteristic of annealed films are showing better Schottky behaviour under IR illumination and hence suitable IR detector application.

Keywords-PbS, XRD, UV-Visible, Chemical Bath Deposition, J-V characteristics

Introduction:

The semiconductor thin film has been studied by the researchers because of their uses in photo catalysis, nonlinear optics, optoelectronics, energy conversion, and microelectronics industries [1-3]. PbS is direct band gap of 0.41 eV [4] and belongs to the group IV-VI, with its exciton Bohr radius of 18 nm at room temperature. PbS is used in Sensors [5], photography [6], IR detector [7] (due to absorption Near IR region), Solar absorber [8] etc.

PbS also have application as a photo resistance and diode lasers. The thin films of PbS shows good photovoltaic [9,10] properties as compared to its bulk counterpart. The NO_2 gas at low ppm [11,12] is also detected by PbS thin film. Quantum dot solar cells sensitized with PbS quantum dots are fabricated by using different photoanode [13,14]. The simple and facile technique of synthesis QDs [15] is also adopted for its application in solar cell. The synthesis techniques for PbS nanomaterial are adopted as per applicability and significant properties [16-20]. The chemical bath deposition (CBD) [7,8,15,21,22] technique is preferred to its simplicity, low cost. This technique

used to control thickness and crystallinity and also for multilayer deposition in counter electrode for solar cell application [23].

In the current work, the PbS thin films were fabricated by CBD and annealed at 400 ^{0}C for 30 min. These as prepared thin films are useful in IR sensors application.

Material and Methods:

Lead acetate $(CH_3COO)_2Pb.3H_2O$, Triethanolamine-TEA ($C_6H_{15}NO_3$), Sodium Hydroxide (NaOH) and Thiourea (CH_4N_2S) were AR grade and used as received. 0.01 M Lead Acetate and TEA were added in a pot contains 50 ml double distilled water (DDW). TEA acts as a complexing agent was added in to the solution, which avoids the formation of bulk PbS. The pH of the solution was adjusted by adding the NaOH to 11. Clean and dry glass substrate was inserted in to the solution. At the final stage 0.1 M thiourea was added into the solution which serves as a sulphur source. During the complete process the solution was stirred continuously and heated up to 80 ^{0}C. The film was deposited in 1hr; the film was ultrasonically cleaned in DDW to remove the unreacted part. The film was then annealed in air ambient at 400 ^{0}C for 30 minutes and further characterized by using X-ray diffraction technique to obtain the information of composition, phase and crystallite orientations of the material, the absorption of the material as well as bandgap is studied by UV-Vis absorption spectroscopy and 150 W IR source was used to study the I-V characteristic of the material in dark and light mode.

Result and Discussion:

a) X-ray diffraction-

The as synthesized and annealed PbS thin films were characterized by X-ray diffraction technique (D8 ADVANCED Bruker). Figure1 shows the XRD patterns, all the diffraction peaks (111), (200), (220), (311), (222) are exactly matches to standard JCPDF file no. 05-0592. This confirms the formation of cubic PbS structure on the on glass substrate.

The average crystallites size was found to be 28.56 nm and 42.75 nm for both as-deposited and annealed films respectively using Scherer's formula. After annealing it is observed that the crystallinity of the film increases.

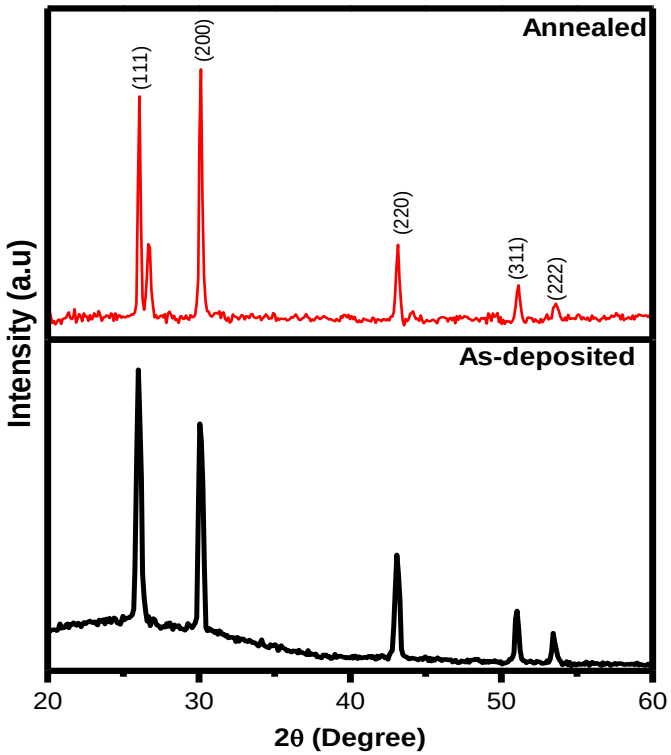

Figure1. XRD pattern of as-deposited and annealed PbS thin films

b) Optical Absorption Spectroscopy-

The optical properties were studied by using UV-VIS absorption spectrophotometer (JASCO-UV-VIS-NIR Spectrophotometer; model V-670). The spectra of the films were recorded in the wavelength range 500-2500 nm. Figure 2. a) shows optical absorption spectra of as-deposited and annealed PbS thin film. Absorption spectra shows that for annealed films the absorption edge is red shifted as compare to as-deposited sample, which is due to increase in particle size after annealing. Figure 2. b) shows tauc plot, the band-gap values as calculated are 1.23 eV and 1.03 eV for as-deposited and annealed PbS thin films. The decrease in band gap values for annealed PbS thin films as compare to as-deposited can be attributed to increase in particle size.

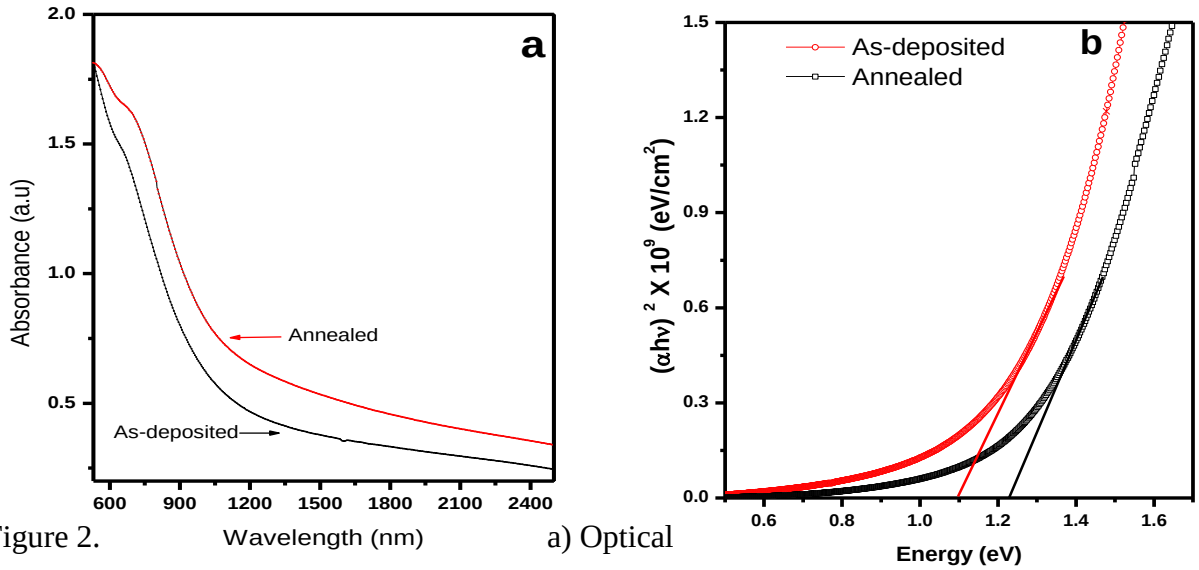

Figure 2. a) Optical spectra and b) Tauc plot of as-deposited and annealed PbS thin films

c) Current-Voltage characteristics under dark and IR illumination-

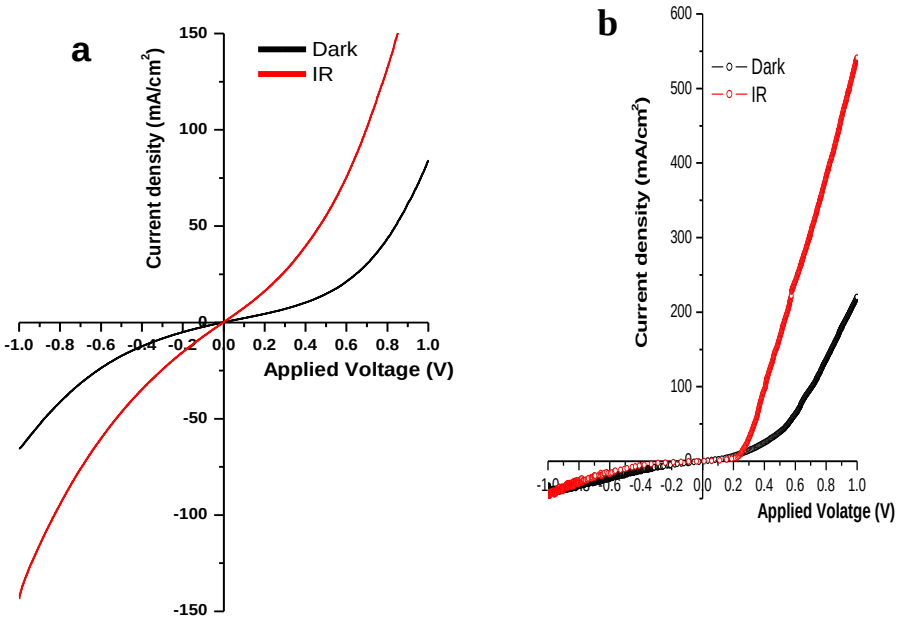

Figure 3. J-V curves for a) as-deposited b) annealed PbS films under dark and IR illumination

Figure 3. shows the Current density (J)-Voltage (V) curves for a) as-deposited films and b) annealed PbS thin films. Both the film shows Schottky behaviour under dark and under IR

illumination. It is also observed that after IR illumination the current density increases and as compared to as- deposited films, the annealed film shows significant enhancement in the current density.

Conclusion:

PbS thin films can be successfully deposited by chemical bath deposition method. The cubic phase of the PbS is confirmed from the X-ray diffraction. The PbS films are having absorption in the IR region and the band gap values are found to be 1.3 eV and 1.03 eV for both as-deposited and annealed PbS films respectively. Both PbS thin film shows Schottky behaviour under dark and IR illumination. The annealed film shows enhancement in current density as compare to as-deposited sample as crystallinity increases with annealing. Hence, the prepared PbS thin films from chemical bath deposition are suitable for application in IR detector.

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VARIATIONAL ITERATION TECHNIQUE FOR NONLINEAR BOUNDARY VALUE PROBLEMS

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Abstract

In this Paper, Variational iteration technique(VIT)is used to solve various boundary value problems(BVP). For better choice of initial approximation in the VIT gives solution closed to exact solution of nonlinear partial differential equation (PD)only by taking at most two iterations. This technique is easily applied to the BVPs.Numerical examples are selected to demonstrate solution of two point BVPs, singular BVPs and singular perturbation BVPs. The VIT is not only used to solve BVPs but system of BVPs also. Some illustrations of System of nonlinear BVPs are given here. Also nonlinear system of second and fourth order BVPs are illustrated numerically. The analytical results are in terms of convergent series which is easily computable. Numerical result shows that VIT gives high accuracy. Also this technique is reliable and efficient for solving wide class of nonlinear BVPs.

Keywords: *Nonlinear problems, Singular perturbation, Boundary value problem, Variational iteration technique (VIT).*

1.Introduction:

In recent years, techniques like Adomian decomposition method(ADM) [1], homotopy perturbation methods (HPM) and others have been proposed for finding exact and analytical approximation solutions for nonlinear problems. For investigating approximate or exact solutions of nonlinear ordinary and partial differential (PD)equations, variational iteration techniques(VIT) is powerful. General Lagrange multiplier method is proposed by Inokuti et.al [8].in 1978.which is then modified by the Chinese mathematician Ji-Huan He in 1999 and developed VIT [2]. This technique does not require that nonlinearities to be differentiable with respective to dependent variable and derivative of it. This method gives rapidly convergent successive approximations of the exact solution if such solution exists, otherwise a few approximations can be used for numerical purpose. VIT solves large class of nonlinear problems easily, effectively and accurately.

In this paper, application of VIT is discuss for solving some nonlinear BVPs like two point [4], singular, system of second order nonlinear BVP and nonlinear fourth order BVPs [7].

The Paper has been organized as follows. In section 2, He's VIM is introduced. Section 3 deals with numerical solution BVPs by using VIT and its comparison is also given graphically. In Conclusion are presented in the last section.

2.Analysis of the Variational Iteration Technique:

Consider general nonlinear partial differential equation as

$$Lv + Nv = g(t) \qquad (1)$$

where L and N are linear and nonlinear operators respectively, and $g(t)$ is the source inhomogeneous term. Construct the correction functional for Equation (1) in the form,

$$v_{n+1}(t) = v_n(t) + \int_0^t \lambda(s)\big(Lv_n(s) + N\tilde{v}_n(s) - g(s)\big)ds, \; n \geq 0 \qquad (2)$$

26. Solution of Homogeneous Nonlinear Advection Equation by using Variational Iteration Technique

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Abstract

In this Paper, Variational iteration technique(VIT) is used to solve various nonlinear partial differential Advection equations(NPDA).For better choice of initial approximation in the VIT gives solution closed to exact solution of nonlinear partial differential equation (PD)only by taking at most two iterations. This technique is easily applied to the NPDA equations. Numerical examples are selected to demonstrate solution of homogeneous NPDA equations. The analytical results are in terms of convergent series which is easily computable. Numerical result shows that VIT gives high accuracy. Also this technique is reliable and efficient for solving wide class of nonlinear NPDA equations.

Keywords: Nonlinear problems, homogeneous advection equation, nonlinear Partial differential equation, Variational iteration technique (VIT).

1. Introduction

Recently, methods like Adomian decomposition method (ADM) [5], Homotopy perturbation methods (HPM) and others have been proposed for finding exact and analytical approximation solutions for nonlinear problems. For investigating approximate or exact solutions of nonlinear ordinary and partial differential (PD)equations, variational iteration techniques(VIT) is powerful. General Lagrange multiplier method is proposed by Inokuti et.al [8].in 1978.which is then modified by the Chinese mathematician Ji-Huan He in 1999 and developed VIT [2]. This technique does not require that nonlinearities to be differentiable with respective to dependent variable and derivative of it. This method gives rapidly convergent successive approximations of the exact solution if such solution exists, otherwise a few approximations can be used for numerical purpose.VIT solves large class of nonlinear problems easily, effectively and accurately.

SEASONAL VARIATION OF MONIEZIA (B) HIRCUSAE IN CAPRA HIRCUS AT SANGAMNER REGION, AHMEDNAGAR DISTRICT.

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ABSTRACT:

*The present statistical communication deals with the study of seasonal variation of cestodes **Moniezia (B) hircusae** along with incidence and intensity of the parasites according to the seasons in the year oct2008 to sept2009 at Sangamner region, district Ahmednagar. The seasonal variation of gastro-intestinal cestodes infection show the high Incidence in rainy season (62.35%) and low in winter season (8.33%). And high Intensity in summer season (6.5) and low in winter season (2.00). Because of easy dispersal of parasite resulting is increased contact with the host.*

Key words: Cestode, Incidence, Capra hircus, Intensity, Season.

Introduction

About 82% of population of Sangamner region in rural and depends directly on agriculture and animal husbandry. Parasitic infection affects the gastro-intestinal track of *Capra hircus*. Often without clinical manifestation is major cause of production loss. The incidence of cestode infection varies with age, sex, season and agro-climatic conditions.

The effect of climatic factors on helminthes are studied by the workers like Lawrence (1970),Crofton (1971). Many authors worked considerably on the population dynamics of the cestode parasites from different hosts. Dogiel et.al.(1958,1964),Hopkins (1959),Pennyuick(1971a) ,Anderaon(1976), Susheela (1987) have clearly shown the seasonal effect on the geographical distribution of the cestode parasites.

Material and Method

For the study of parasites, the intestine of *Capra hircus* was collected from different region of Sangamner, from Oct 2008 to Sept 2009. The parasites were collected, flattened, stained and identified, also record of infected and non infected host and number of parasites for further study. Data was collected month wise and the incidence and intensity of parasites calculated seasonally.

Result and discussion

After closer observation the collected parasites were found belonging to genus *Moniezia* (Blanchard,1891)From the recorded data, Table I-a) shows that, the incidence of infection for October 2008 to January 2009 (winter) was 8.33 %, I- b) for Feb 2009 to May2009 (summer) . was 23.37 %, I-c) for June 2009 to September 2009 was 62.35 %.

*Incidence of infection = (Bx100)/A *Intensity of infection = C/B

Where A stands for number of host examined, B stands for number of host infected and C stands for number of parasites collected

Table II shows that, the intensity of infection was 02 in winter, 6.5 in summer and 5.16 rainy season.

Table I- Seasonal incidence of *Moniezia hircusae* in *Capra hircus* during different season.

I-a) Winter (Oct 2008 to Jan 2009)

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8. Agri-Tourism - An Upcoming Trends in Tourism and Advancements in Agricultural Research (An Overview 'Agri-tourism')

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Abstract

Innovation change that unlocks new value. It is a saying that a need is pre-requisite of innovation. Now-a-days a need is originated by the biggest force called competition. Competition left you no choice other than going for innovation. It may be any form like product strategy, marketing strategy or may be in any business operation. Innovation can easily quantifiable in product or manufacturing industry, it is proving it by giving modified product, new versions of basic model or altogether new concept. Product innovation goes hand in hand with technology. Service sector has good scope to bring innovation in practice, but the real challenge is to maintain it for long time and even not imitable. In tourism, innovation can be translated into two broad categories; one can find new places or re-positioning of the old one. But in tourism the new wave is by the farmers. Here farmers have played the role of innovators. They have not found new places, not even re-positioned any monument or historical place.

The recent improvements in agriculture are way more advanced. These advancements along with the increase in urbanization are major drivers for the evolution of agricultural research. Recent trends in the area of Agricultural Research comprise of Eco-Agro-tourism, Big Data Analytics, Climate Smart Agriculture, Advanced Marketing Linkages, Integrated Farming System, etc. These trends are important not only from the research context but also from the policy point of view towards ambitious goal of doubling farmers' income by 2022. In today's' era technology plays a very important role in encouraging farmers to take up entrepreneurial ventures and agro-based industries.

Keywords: innovation, competition, eco-agro-tourism, big data analytics, climate smart agriculture, advanced marketing linkages, integrated farming system, direct seeded rice.

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A Study of Role Regional Rural Bank in The Rural Development of Maharashtra

Abhilasha R. Dhokate
Dr. R.N. Wakchaure

Introduction :-

Maharashtra state is [illegible]ltural based state, Maximum population of this state stays in rural area. These rural areas are [illegible] weak and poor for development, so there is need to develop those areas. Considering need of [illegible]pment of rural sector RRBs were established to provide financial support to those sector[illegible]is Regional Rural Bank plays an important role in agricultural financing. This bank were [illegible]ablished under the RRBs Act 1976 with an objectives of to ensure sufficient institutional [illegible] for rural and agriculture sectors. These banks also providing other facilities for development purpose to developing those needed sectors. The main beneficiaries of RRBs are small and marginal farmers, agricultural labourers, various artisans, retail traders and other weaker sections of rural areas. RRBs also meet the credit need of the rural poor people by providing them credit facility.

The establishment of RRBs was Start under the provision of an ordinance promulgated on the September 26, 1975 and the RRBs Act 1976. During the period from 1976 to 2006 the banking industries had gone through various changes and the RRBs were no exception. As per the changing economic scenario there is need for structural change in RRBs. By the notification dated March 25, 2008 two RRBs were amalgamated i.e. Aurangabad Jalna Gramin Bank and Thane Gramin Bank into a single RRB named as 'Maharashtra Godavari Gramin Bank'. After the notification issued by government of India, Ministry of Finance and Department of Financial Services 'Maharashtra Gramin Bank' came into existence by amalgamation of Maharashtra Godavari Gramin Bank and Marathwada Gramin Bank. RRBs are jointly owned by government of India.

Literature Review :-

Ram, J.K., Subudhi, R.N. (2014) given in his research that the Regional Rural Banks (RRBs), are now playing an important role in the development of rural areas and financial inclusion. It means financial support is very important for the development.

Jindal, A.K., Sharma, K., Shamim, A. (2014) Regional Rural Banks, from the beginning have become an inseparable part of the rural credit structure of India. After The five year, since the existence Of the RRB became a matter of concern. A number of reform committees have raised an issue of the RRBs possible restructuring and financial viability. The present study follows a deductive approach, in finding and analysing the extent of the problem of the loss making RRBs, if it is limited to some particular sponsor banks or States, the probable factors that influence the performance of the RRBs have been studied.

Devi, N.S. (2014) explain in report Regional Rural Banks plays an important role in the agriculture and rural development of India, the success of rural credit largely depends on the financial strength of these RRBs, as they are the key financing institution at the rural level which meets credit needs of agricultural labourers in rural areas, but at present, these Regional Rural Banks are facing challenges of overdue, recovery of non-performing assets

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Financial Analysis of Women's Co-Operative Credit Societies in Ahmednagar District

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Sangamner.

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Abstract

The ethical principles of dignity and confidentiality, autonomy, beneficence, and justice concerning the rights and welfare of the research subjects for undertaking research are acknowledged to be of the utmost importance to the whole process of this research. There were three types of ethical issues involved in this research : Access to the research sites and research participants, the relationship between data collection and the setting routine, and publication of research findings. The researcher access to the subject and participants was built upon the informed consent forms, which stated clearly the aim of research project and consent statement However, differences were revealed in research participant's awareness of ethics and research settings.

Key words: NPV, Financial Statement particulars, Dividend policy, Working and Management of WNCCS.

Introduction

The research can start from the identification of a research topic of the researcher's interest or related experiences and identifies 'five important questions' in the process of defining research questions : (1) the perspective about and the nature of WNCCS; (2) the epistemological position (3) broad research topic question, what topic is the research concerned with: (4) what is the intellectual puzzle; and (5) what exactly are the research questions included in the questionnaire. The importance of defining research questions has been considered as the key to determine for research topic, data collection methods and data analysis.

The ethical principles of dignity and confidentiality, autonomy, beneficence, and justice concerning the rights and welfare of the research subjects for undertaking research are acknowledged to be of the utmost importance to the whole process of this research. There were three types of ethical issues involved in this research . Access to the research sites and research participants, the relationship between data collection and the setting routine, and publication of research findings. The researcher access to the subject and participants was built upon the informed consent forms, which stated clearly the aim of research project and

Importance of Rural Entreprenevrship

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Abstract :

India is a country of villages with agriculture as its backbone. More than 70% of the population of India lives rural areas out of which more than 75% is still dependent on agriculture and allied activities for earning th livelihood. But the fact remains that land is limited to absorb this increasing population in agriculture.

Rural entrepreneur plays an important role in the overall development of economy of country specially in case countries like India. Therefore it is necessary to create and develop more and more rural entrepreneurs. This pa makes an attempt to find out the strengths of rural entrepreneurs so that more and more entrepreneurs can be develo as well as their weakness so that needed steps can be taken to remove or at least minimize them. All attempts is a made to know the opportunities that can be converted into more and more rural industries and threats and problems t can be solved to keep the rural entrepreneurs motivated.

Keywords : Importance of Rural Entrepreneur.

Introduction :

An entrepreneur can be defined as an individual who, rather than working as an employee, runs a small business and assumes all the risk and reward of a given business venture, idea or good or service offered for sale. The entrepreneur is commonly seen as a business leader and innovator of new ideas and business processes. He is a person who sets up a business or businesses, taking on financial risks role in any economy. These are the peoples who have the skills and initiative necessary to take good new ideas to market and make the right decisions to make the idea profitable.

Entrepreneurship is he capacity and willingness to develop, organize and manage a business venture along with any of it's risks in order to make a profit. In economics, entrepreneurship, combined with land, labour, natural resources and capital can produce profit. Entrepreneurial spirit is characterized by innovation and risk- taking and is an essential part of a nation's ability to succeed in an ever changing and increasingly competitive global marketplace.

Objective of the Study :

1. To analyze the importance of rural entrepreneurship in economic development of the country.
2. To understand the concept of rural entrepreneurship

Rural Entrepreneurship :

The Indian agricultural practices are economies, scattered traditional and unchanging. When all these characteristics are combine to be added in econo development, it is nothing but rural entrepreneurship.

India is a country of villages and agriculture is backbone. Even after 60 years of independence industrialization, a large amount of population is ur poverty line. More than 70% of India's population lives in villages and agriculture continues to be backbone of the rural society. More than 75% of rural population is dependent on agriculture and al activities and the fact is that the population continuously increasing. Being the limited availab of land, it is really difficult to absorb this increa population in agriculture. This excess of population be absorbed in industries which are based on agricul and allied activities known popularly as rural indust

According to KVIC (Khadi and Village Indu Commission), "Village or rural industry means industry located in rural areas, population of which not exceed 10000 or such other figure which prod any goods or renders any services with or without of power and in which the fixed capital investmen head of an artisan or a worker does not exce thousand rupees. This process of establishing indus in rural areas is known as rural entrepreneurship.

Types of Rural Industries :

1. **Forest Based Industries** : Covering wo products, bamboo products, making eati plates form the leaves of plants, bor collecting, coir industry etc.
2. **Agro Based Industries:** Covering su industries, oil processing from oil see

8. A Review of Cashless Policy in India

Dr. Pulate S. K.
SSRI, ACS College, Rahata.

Introduction

Our current Prime Minister, Shri Narendra Modi, took the whole world by surprise when he announced on 8 November 2016 that the currency notes of denominations Rs.1,000 & Rs.500 were no longer legal tender.

What was seen as a move towards checking the menace of black money in the country, soon paved the way for India's push to becoming a cashless economy.

"Paperless, Cashless" is one of the goals of Digital India. Numerous benefits have been associated with transforming India into a cashless society. Some of the major advantages include:

- Brings transparency into the system.
- Helps to fight against corruption.
- Will increase the tax base.
- Reduces costs incurred on the minting of coins & printing paper notes.
- Cashless transactions are faster & secure.
- Lower transaction costs.
- A boost to the country's Economic Growth.
- The biggest advantage of cashless India is in the promotion of Financial Inclusion of the people.

If implemented properly, a cashless India can really become a reality rather than just a distant dream. However, it remains to be seen if our country is actually ready to go cashless.

Designating or of financial transactions handled as by means of credit cards, bank transfers, & checks, with no bills or coins handed from person to person: some say we are headed toward a *cashless* society

Example

Credit card processing blink cards is an innovation designed to make **cashless** consumer purchases faster, unique & fun to do while boosting sales for retailers.

- The game is truly coming to grips with our seemingly **cashless** society that we have adapted to.

"HUMAN RESOURCE: ROLE OF MANAGEMENT AS ON INDUSTRY"

Dr. Suresh Kashinath Pulate,
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Abstract

In the modern times the organization could only by ensuring a competitive edge vis-à-vis other. Apart from other steps, an objective and balanced HRD policy is the most essential requirement preferably in its entirety. At the micro level apart from conductive environment, job satisfaction, role clarity and job effectiveness are important contributors to the excellence in working of any industry.

As India is going through aftermath of her integration with global economy after exploding the nuclear devices, the one area, which is receiving greater attention, in industry is "Managing the men" for the simple reason that the entry of multinationals and their state of art technologies coupled with economic crisis are causing turmoil amongst the worker as well as managers in the corporate world productivity, quality, competencies are the key words all over the world now.

Human resources is the division of a business, corporation or organization that manages all aspects related to its personal, including recruiting employees, training and career development, overseeing compensation packing, manging benefits plans and other duties that serve to maximize a company business and its employee's satisfaction with the job. Simply, the function of the human resources industry is to produce competent personal and to keep employees productive. More than 8,00,000 people work in human resources and related fields.

Introduction :

Have a look at the world of human resource beings is a rewarding experience. Contrasts & similarities can be observed in this world e.g. industriousness with laziness, mercy with cruelty, health with disease etc. though the machineries have cornered the most of the today's corporate worlds, one thing is certain-it is the people who make to the organization a success or allow it to be handle over to the Board for Industrial and Financial Reconstruction (BIFR).

Simply, the function of the human resources industry is to produce competent personnel and to keep employees productive. More than 800,000 people work in human resources and related fields today any organization with many employees, whether a bank, oil company of fast food restaurant need personnel specialists.

As an increasingly large portion to the U.S. economy has come to depend on service industries business in which the man product is not an item sold in a store but rather is a set of actions performed for a client by the business employees the growth of the human resources industry has increased proportionally.

Key Facts :

- Human resources is the umbrella term used to describe the management and development of employees.
- Human resources today plays a significant role in developing positive business culture and improving employee.
- The HR Industry is fast gaining ground. They are no longer a small and slow dept. but crucial member in the major business decision making processes in various companies.
- Top three countries – Norway (0-949 score), Australia (0.939) and Switzerland (0.939).
- India related facts India's Human Development Index Value increased from 0.428 in 1990 to 2018 increase in 0.640. India rank 130 on 2018 Human Development Index.

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"Economic and Marketing Problems of Women Entrepreneurs in Rural Area" A Case Study of Ahmednagar District in Maharashtra

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Abstract:

The entrepreneurship is the usefull path to increase women's contribution in economic development. Women should take an important part in production activates. But very few numbers of women entrepreneurs have been seen in business area. Woman education in India plays important role in the development of the country. After the independence the government has taken various measures to provide education to all Indian woman. As a result woman literacy rate has grown up. As a result women's literacy rate has grown up. As education has spread woman, started to go to out of home for wage employment or entrepreneurship career.Woman are seeking increasing opportunity as an entrepreneurship. The research paper highlights the problems faced by women entrepreneurs with reference to Ahmednagar district of Maharashtra.

Keywords : Women, Entrepreneurship, Development.

1.1 Introduction :

In the emerging economic scenario of liberalization, the contribution of woman towords the gross domestic product is important. The entrepreneurship is the use full path to increase women's contribution in economic development. "Women in Business" is considered a recent phenomenon in India. In India, the female population is 48.46%of the country's total population as per the census 2011. It indicates that women should take part in production activates. According to 2011 census there are 940 females behind every 1000 males are working in informal sector. But very few numbers of women entrepreneurs have been seen in business area.

Woman education in India plays important role in the development of the country. After the independence the government has taken various measures to provide education to all Indian woman. As a result woman literacy rate has grown up. As a result women's literacy rate has grown up. As education has spread woman, started to go to out of home for wage employment or entrepreneurship career.Woman are seeking increasing opportunity as an entrepreneurship.

The Central and State government have been working in implementing various schemes to enable more women to undertake entrepreneurial activities in order to improve income level of urban and rural women's. Now a days Indian women are coming out kitchen and taking up entrepreneurial activities on a per with men. Women are making all efforts to upgrade their standard of living by increasing their income and saving. Their is no field today where women are not approaching. Women plough field, harvest crops, sells food, make handicrafts, work as an entrepreneurs.

1.2 Entrepreneurs :

'The word entrepreneur originate from the French word 'Entreprendre' which means 'to undertake' in business context, It means to start business'[1]

The entrepreneur is commonly known as a business leader who promotes the unit, establish the factors of production and manage the affairs of the business. Management skill and strong team building abilities are needed to become successful entrepreneur. The entrepreneur is define in following approach. 1. 'Entrepreneur' is a business leader an innovator of new ideas in the business process'.[2]

2. According to business Dictionary, 'The capacity and willingness to develop, organize and manage the business venture along with any of its risks in order to make a profit. The most noticeable example of entrepreneur is the starting a new business.

In Economics, entrepreneurship combined with land, labour, natural resource and capital to produce profit.'[3]

As per the researcher, 'Entrepreneur is the person who takes decision and decides what, how and how much of a good will be produced.'

1.3 Literature Review:

Dhameja S.K. (2002) studied the "women entrepreneur's opportunities performance problems." According to the study, 'In Canada, one third of small business is owned by women and in France it is One

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APPLICATIONS OF GIS TECHNIQUES FOR ANALYZING SPREAD OF COVID- 19 DISEASE IN INDIA

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Abstract:

The outbreak of the 2019 novel coronavirus disease (COVID-19) has caused more than 50,00,000 people infected with the virus and more than 333,000 of deaths as of 24th May, 2020 (World Health Organization (WHO) as of 24th May, 2020) across the world . At present, the number of infections and casualtiesis increasing rapidly throughout the world. COVID-19 seriously hovers human health, social functioning, and international relations. In the fight against COVID-19, Geographic Information Systems (GIS) has played a prominent role in many ways, including the rapid combination of various data, visualization of pandemic information, spatial tracking of infections, prediction of regional transmission, spatial segmentation of the pandemic risk and prevention, management of the supply and demand of material resources, and social-emotional guidance, which provided concrete spatial information support for decision-making, measures formulation, and effectiveness assessment of COVID-19 prevention and control. GIS technology has developed and matured relatively faster and has a complete technological way for data preparation, platform construction, model construction, and map production. However, for the struggle against the widespread pandemic, the main challenge is finding strategies to adjust technical methods and improve the speed and accuracy of information provided for social management. In this article methods like Spatial Interpolation, Quantities etc are used to show spatial distribution of covid-19 cases in the states and union territories of India.

Keywords: GIS, COVID-19, Geospatial, IDW, Interpolation

Introduction

In today's world data no longer come mainly from the government but are collected from more diverse enterprises. As a result, the use of GIS faces difficulties in data acquisition and the integration of heterogeneous data, which requires governments, businesses, and academic institutions to jointly promote the formulation of relevant policies. The development of GIS

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Detection of Land-use/Land-cover Changesby Using RS and GISTechniques:A Case Study of ShrigondaTahsil, Maharashtra State, India

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Abstract

Land-use/land-cover change detection study plays a key role in a study endeavored for development and planning purposes. With timely satellite data, these studies are carried out with good accuracy. Throughout the world, the emphasis has been given on such studies because of the increasing demand for land as its limited availability. The present study attempts to focus on land use/land cover changes at the tahsil/block level. By using satellite images for the year 2000 and 2015the land-use/ land-cover was extracted in the study area with a supervised classification method. Appropriate training sites were taken for each LULC categories to achieve good accuracy in the classification. Accuracy assessment was performed after classification for finding the accuracy of the classification based on KAPPA analysis. The change detection of these classes for two images was computed. The most dominant category in terms of change was barren land. The study indicates that the study area has undergone substantial changes in land-use and land-cover particularly in the case of barren land and agriculture land use categories.

Keywords

Land-use/Land-cover,RemoteSensing,GIS,Change Detection,Kappa coefficient.

Introduction

The history of mankind has been closely related to natural resources. The land is one of the important components on which physical, economic, and social development depends. Land provides food and a variety of minerals and therefore, it needs judicious use of land. The land resource has very often been left in past entirely applications of traditional and primitive methods resulting in basic resources gradually deteriorated (Siddiqi, 1971). With the growing pressure of population on limited land resources, man has to use optimum usage of every acre of land. This necessitates the determination of the optimum use of every piece of land. There is a consequent need for a system of land utilization (Stamp, 1960). The importance of land classification is on the basis of the quality and intensity of Land-use (Mohammad, 1978).

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COLLABORATIVE TEACHING STRATEGIES: FOSTERING STUDENT ENGAGEMENT AND ACADEMIC SUCCESS

❒ **Dr. Rohini D. Kasar***

ABSTRACT

Collaborative teaching has gained increasing attention as an effective pedagogical approach to enhance student learning outcomes. This research article explores various collaborative teaching strategies and their impact on student engagement, academic achievement, and the development of essential skills. Drawing upon a review of existing literature and empirical studies, this research aims to provide insights into the benefits and challenges of collaborative teaching, offering practical recommendations for educators seeking to implement these strategies in diverse educational settings.

Keywords: Collaborative teaching, Pedagogical approach, Educators seeking

Introduction

Collaborative teaching is a dynamic approach that emphasizes active student participation, shared responsibility, and cooperative learning. This section provides an overview of the importance of collaborative teaching in fostering a positive learning environment and introduces the key objectives of the research. Collaborative teaching-learning, also known as collaborative learning or cooperative learning is an educational approach that emphasizes the active participation of students in group activities and projects. The key idea is to promote learning through collaboration, where students work together to achieve common goals, share knowledge, and contribute to each other's understanding.

Literature Review

This section examines the theoretical foundations of collaborative learning, drawing on prominent educational theories such as constructivism and social learning. Additionally, it reviews empirical studies that have investigated the impact of collaborative teaching on student outcomes, including academic achievement, critical thinking, and interpersonal skills.

Theoretical Framework

Collaborative teaching strategies find their roots in educational theories that emphasize active learning, social constructivism, and the importance of peer interaction in the learning process. Scholars such as Vygotsky and Dewey have underscored the significance of social environments in shaping cognitive development. Collaborative teaching, aligned with these theories, aims to create a dynamic, interactive learning space that goes beyond traditional didactic methods.

Social Learning and Constructivism

Social learning theories posit that individuals learn by observing, imitating, and interacting with others. Collaborative teaching aligns with this framework, fostering a community of learners where knowledge is co-constructed through shared experiences. Constructivism emphasizes the role of learners as active participants in building their

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understanding of the world. The literature supports the idea that collaborative teaching provides a conducive environment for the construction of knowledge through meaningful interaction and shared exploration.

Empirical Studies on Collaborative Teaching

Numerous empirical studies have investigated the impact of collaborative teaching strategies on various aspects of student learning. Smith and Johnson (2006) conducted a meta-analysis of cooperative learning and found a positive correlation between collaborative approaches and academic achievement. Additionally, research by Anderson et al. (2018) explored the role of collaborative projects in enhancing critical thinking skills, revealing a positive association between group work and higher-order cognitive skills.

Student Engagement and Motivation

Collaborative teaching has been consistently linked to increased student engagement and motivation. Hämäläinen and Vähäsantanen (2011) observed higher levels of enthusiasm and participation in classes that incorporated collaborative activities. The literature suggests that the social nature of collaborative learning fosters a sense of community and shared responsibility, positively influencing students' attitudes toward the learning process.

Challenges in Collaborative Teaching

While the benefits of collaborative teaching are well-documented, it is essential to acknowledge the challenges associated with its implementation. Unequal participation, conflicts within groups, and the need for effective facilitation have been identified as potential obstacles (Johnson et al., 2014). Understanding and addressing these challenges are crucial for creating a positive collaborative learning environment.

Technology and Collaborative Learning

In the digital age, technology plays a significant role in collaborative teaching. Online platforms, collaborative software, and virtual collaboration tools have expanded the possibilities for interactive learning beyond physical classrooms. Research by Wang and Woo (2017) explores the integration of technology in collaborative teaching, highlighting its potential to enhance communication, resource-sharing, and collaborative project management.

Conclusion of the Literature Review

In summary, the literature review establishes the theoretical foundations of collaborative teaching, emphasizing its alignment with social learning and constructivist theories. Empirical studies demonstrate the positive impact of collaborative teaching on academic achievement and critical thinking skills. While challenges exist, addressing them can contribute to creating a more effective and inclusive learning environment. Moreover, the integration of technology opens new avenues for collaborative learning in contemporary educational settings. The literature review sets the stage for the present research, highlighting gaps and providing a context for the exploration of collaborative teaching strategies in fostering student engagement and academic success.

Key Collaborative Teaching Strategies

Collaborative teaching-learning, also known as collaborative learning or cooperative learning is an educational approach that emphasizes the active participation of students in group activities and projects. The key idea is to promote learning through collaboration, where students work together to achieve common goals, share knowledge, and contribute to each other's understanding.

Here are some key features and principles of collaborative teaching-learning:

1. Group Work: Students are organized into small groups to work on tasks, projects, or assignments. These groups may be formed based on diverse criteria, such as skill levels, interests, or a mix of abilities.
2. Interdependence: Collaborative learning emphasizes interdependence among group members. Each student's success is linked to the success of the group, fostering a sense of shared responsibility.
3. Communication: Effective communication is crucial in collaborative learning. Students discuss ideas, ask questions, and provide explanations to their peers. This verbal interaction helps reinforce

learning and deepen understanding.

4. Active Engagement: Students are actively engaged in the learning process, as they contribute their thoughts, skills, and perspectives. This active involvement promotes a deeper understanding of the subject matter.

5. Social Skills: Collaborative learning enhances social skills such as communication, teamwork, and conflict resolution. Students learn to work effectively with others, improving their interpersonal skills.

6. Peer Teaching: Collaborative learning often involves students teaching and explaining concepts to their peers. This process of peer teaching reinforces understanding and helps identify gaps in knowledge.

7. Diverse Perspectives: Group work allows students to benefit from diverse perspectives and experiences. This can lead to a richer learning experience and a more comprehensive understanding of the topic.

8. Problem-solving: Collaborative learning often involves problem-solving activities. Students tackle challenges together, encouraging critical thinking and creative problem-solving skills.

9. Teacher Facilitation: While students take an active role in the learning process, the teacher serves as a facilitator, guiding discussions, providing support, and ensuring that the learning objectives are met.

Collaborative teaching-learning is widely recognized for its effectiveness in promoting a positive learning environment, enhancing student engagement, and developing both academic and interpersonal skills. This approach aligns with constructivist theories of learning, emphasizing the social construction of knowledge through interaction and collaboration.

Benefits of Collaborative Teaching

Collaborative teaching offers a range of benefits that positively impact both students and educators. Understanding these advantages is crucial for educators looking to enhance the learning experience. Here are the key benefits of collaborative teaching:

1.Increased Student Engagement: Collaborative teaching fosters active participation and engagement among students. Working together on projects, discussions, or activities keeps students involved in the learning process, making it more dynamic and meaningful.

2.Enhanced Academic Performance: Numerous studies have shown a positive correlation between collaborative learning and improved academic achievement. When students collaborate, they can gain diverse perspectives, clarify concepts, and reinforce their understanding through discussions and shared problem-solving.

3.Development of Social Skills: Collaborative teaching provides opportunities for students to interact with their peers, promoting the development of crucial social skills. Communication, teamwork, and conflict resolution are integral components of collaborative learning, preparing students for real-world interactions.

4. Promotion of Critical Thinking: Through collaboration, students are exposed to different viewpoints and approaches to problem-solving. This diversity stimulates critical thinking skills as students evaluate and analyze various perspectives, leading to more robust and well-rounded conclusions.

5. Preparation for the Workforce: The collaborative skills acquired through group work mirror the teamwork and collaboration expected in many professional settings. Students who experience collaborative teaching are better equipped for future careers that require effective communication, cooperation, and the ability to work in diverse teams.

6. Increased Motivation and Confidence: Working collaboratively allows students to share their strengths and learn from their peers. This positive interdependence contributes to increased motivation as students feel a sense of accomplishment through collective success. Additionally, collaborative learning can boost confidence, particularly in students who may be hesitant to express their ideas individually.

7. Fostering a Positive Learning Environment: Collaborative teaching creates a supportive and inclusive atmosphere within the classroom. Students often feel a sense of belonging and community, leading to a positive learning environment where individuals are more likely to take risks, share ideas,

and learn from each other.

8. Diversity of Perspectives: Collaborative teaching encourages the exchange of diverse perspectives and experiences. This diversity enriches the learning experience, exposing students to a variety of ideas and approaches that they might not encounter in a traditional, individual learning setting.

9. Efficient Use of Resources: Educators can leverage collaborative teaching to make efficient use of resources. Group projects and activities allow students to pool their knowledge and skills, creating a more resourceful learning environment.

10. Professional Development for Educators: Collaborative teaching is not only beneficial for students but also for educators. Teachers can share insights, strategies, and resources, leading to professional development opportunities. Collaborating with colleagues allows educators to continuously refine their teaching methods and stay current with best practices.

Challenges and Considerations

While collaborative teaching offers numerous benefits, it also presents various challenges that educators must navigate. Understanding these challenges is crucial for effective implementation. Here are key challenges and considerations associated with collaborative teaching:

1. Unequal Participation:

Challenge: In group settings, there may be variations in the level of engagement among students. Some may contribute more actively, while others may be less involved.

Consideration: Establish clear expectations for individual contributions and encourage equitable participation. Implementing strategies such as peer evaluations can help address this challenge.

2. Group Dynamics and Conflict:

Challenge: Collaborative learning environments can sometimes lead to interpersonal conflicts or challenges in managing group dynamics.

Consideration: Provide guidelines for effective communication and conflict resolution. Educators should be prepared to address conflicts promptly and guide students in navigating disagreements constructively.

3. Assessment Issues:

Challenge: Assessing individual contributions in a group setting can be challenging. Determining each student's level of understanding and participation can be complex.

Consideration: Implement a combination of individual and group assessments. Communicate assessment criteria and encourage self-reflection to help students recognize their contributions.

4. Varied Learning Styles:

Challenge: Students have diverse learning styles, and what works well for some may not be as effective for others in a collaborative setting.

Consideration: Provide a mix of collaborative and individual activities to cater to diverse learning preferences. Encourage students to reflect on their preferred learning styles and adapt to different approaches.

5. Time Management:

Challenge: Collaborative projects may require careful planning and time management. Coordinating schedules for group meetings and ensuring that all members contribute can be challenging.

Consideration: Incorporate time management skills into the collaborative learning process. Encourage students to establish timelines, set goals, and regularly assess their progress.

6. Preparation and Facilitation:

Challenge: Effective collaborative teaching requires thorough preparation and facilitation. Educators need to guide discussions, ensure learning objectives are met, and manage the overall learning experience.

Consideration: Provide training and support for educators in collaborative teaching methods. Foster a continuous feedback loop to refine facilitation skills and adapt teaching strategies based on student needs.

7. Technology Integration:

Challenge: Integrating technology for collaborative purposes may present challenges related to access, technical difficulties, or a learning curve for both students and educators.

Consideration: Ensure that all students have equal access to necessary technology. Provide training and support for both students and educators to navigate technological tools effectively.

8. Balancing Collaboration and Individual Accountability:

Challenge: Striking the right balance between collaborative activities and individual accountability can be challenging. Overemphasis on group work may lead to the neglect of individual learning needs.

Consideration: Design activities that allow both collaborative and individual components. Communicate the expectations for individual accountability within the group context.

9. Resistance to Change:

Challenge: Students or educators may resist collaborative teaching due to unfamiliarity or a preference for traditional teaching methods.

Consideration: Implement a gradual transition to collaborative teaching methods. Provide rationale and evidence for the benefits of collaboration to build understanding and acceptance.

10. Inclusive Practices:

Challenge: Ensuring that collaborative activities are inclusive and accommodate diverse backgrounds, abilities, and learning needs can be challenging.

Consideration: Implement inclusive teaching practices by providing options for diverse participation styles, accommodating different learning needs, and promoting a culture of respect and understanding.

While collaborative teaching brings numerous benefits, addressing these challenges through thoughtful planning, clear communication, and continuous adaptation is essential for creating a successful and inclusive collaborative learning environment.

Case Studies and Exemplars

The researcher has experimented with collaborative teaching-learning in the classes of undergraduate i.e. FYBA-Compulsory English, SYBA-Special English, and TYBA-Compulsory English. The students were 45, 15 and 37 respectively for the three classes. One common thread for all the classes was that she asked them to learn a poem on their own. Of course, all the instructions regarding the experiment were given to the students beforehand. She appealed to the students to participate actively and even told the benefits of the activity to them. She took the same activity twice as the students took time to get acquainted with the collaborative teaching. But the output was amazing and students enjoyed the activity. The teacher also learnt a lot from the experiment.

The poems selected for collaborative teaching were as follows: 'The Felling of the Banyan Tree' by Dilip Chitre to FYBA, 'London' by William Blake to SYBA, and 'Charge of the Light Brigade' by Lord Alfred Tennyson to TYBA. The classes were divided into groups of 4-5 students. Each group was given a stanza of the poem and they were advised to interfere with the stanza in their discussion with each other. They were given freedom to use a dictionary and they could even discuss their difficulties with the teacher.

The outcomes of the activity are as follows:

1. Students started thinking on their own.
2. They learnt the value of team spirit and mutual understanding.
3. They come up with the best meaning of the poem, sometimes giving up one's ideas for the whole.
4. It created an interest among them for facilitated self-learning.
5. Leadership qualities, time management, writing, and reading skills improved.
6. Fear about English language learning was removed to a large extent.

Conclusion

In conclusion, collaborative teaching offers a multifaceted approach to education, contributing to the holistic development of students and providing a platform for a more interactive and engaging learning experience. Collaborative teaching should be considered as one of the modern and useful teaching strategies to engage students in the present era. The use of modern technology and the internet would enhance the quality of such teaching provided students avoid copying from these sources. It is certainly a student-centric approach and the involvement of students makes it lively. Practicing teachers and research scholars should experiment with collaborative teaching to make it an effective pedagogical tool.

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Research Paper-Hindi

"अजय शुक्ला के नाटक 'ताजमहल का टेंडर' में व्यंग्य"

डॉ. दादासाहेब नारायण डांगे
सहायक प्राध्यापक, हिंदी विभाग, कला, विज्ञान एवं वाणिज्य महाविद्यालय, राहाता जिला– अहमदनगर, महाराष्ट्र

स्वतंत्रता के उपरांत हमारे देश में जनतंत्र की स्थापना हुईप् जिससे मनुष्य का राजनीति से सीधा संपर्क हुआप् इस स्वतंत्रता ने प्रत्येक व्यक्ति को अपने कर्तव्यों एवं अधिकारों के प्रति सचेत किया। प्रत्येक व्यक्ति अपने आपको मुक्त पाकर स्वच्छंद रूप से जीवन जीने का सपना देखने लगा। उसे यह विश्वास होने लगा कि, अब उसे भरपेट खाना मिल जाएगा। अपना दुख, अपनी समस्याएं कम हो जाएगी। परंतु कुछ ही समय बाद उसे यह महसूस हुआ कि, इनमें से कुछ भी नहीं हुआ। सबकुछ पहले जैसा ही चलता रहा। विपरित उसके सामान्य व्यक्ति का जीवन जीना दुष्कर हुआ। एक प्रकार से समूचे राष्ट्र में आजादी के बाद मोह भंग की स्थिति उत्पन्न हुई। मनुष्य की आशाओं पर पानी फिर गया। अब वह क्या करेगा? कहा जाएगा? उसके पास कोई विकल्प नहीं बचा।

जनतंत्र की स्थापना के बाद देश की सत्ता कुछ खास गिने–चुने लोगों के हाथ में चली गयी। वें ही आज हमारे देश को चला रहें हैंप् जनता के लिए वें लोग ही आज भगवान बन गए हैं। परंतु जब शासक ही भक्षक बन जाएगा, तो सामान्य जनता का क्या होगा? यही एक सवाल अब सवाल बनकर रह गया है। जिसका उत्तर शायद ही कभी मिल जाए। देश का सामाजिक एवं राजनीतिक परिवेश पूरी तरह से भ्रष्टाचार में लिप्त है। जिन्हें जनता ने अपने कल्याण के लिए चुना है, वहीं आज सामान्य जनता का शोषण कर रहें हैं और केवल अपना स्वार्थ सिद्ध करने में जी–जान से लगे हुए हैं। ऐसे में उन तथाकथित भ्रष्टाचारियों से अच्छे दिनों की अपेक्षा करना व्यर्थ है।

वर्तमान युग की इसी विडंबना को सच्चाई के साथ प्रस्तुत करने का महत्वपूर्ण काम समकालीन नाटककारों ने किया है। समाज के हर क्षेत्र में व्याप्त स्वार्थता, भ्रष्टाचार, अवसरवाद, दमननीति, शोषण एवं अपराध जैसी प्रवृत्तियों को समकालीन नाटककारों ने अपने नाटकों में प्रस्तुत किया है। साथ ही इन भ्रष्टाचारियों की प्रवृत्ति पर व्यंग्य के माध्यम से तिखा प्रहार किया है। अजय शुक्ला समकालीन युग के ऐसे ही नाटककार है, जिन्होंने अपने नाटक 'ताजमहल का टेंडर' में भ्रष्ट व्यवस्था पर व्यंग्य के हथियार से प्रहार किया है। प्रस्तुत शोध आलेख में हम 'ताजमहल का टेंडर' नाटक के माध्यम से तत्कालीन भ्रष्ट व्यवस्था पर किए गए व्यंग्य को दिखाने की कोशिश कर रहे हैं।

अजय शुक्ला समकालीन युग के एक सशक्त नाटककार है। उनका 'ताजमहल का टेंडर' नाटक कथ्य एवं शिल्प की दृष्टि से बहुत ही सशक्त एवं सफल नाटक रहा है। यह एक व्यंग्य नाटक है, जिसमें उन्होंने राजनीतिक व्यंग्य को पूरी सच्चाई के साथ पेश किया है। नाटक की बुनावट हास्य विनोदपूर्ण शैली में की गयी है। देखते समय दर्शकों को हँसी आती है। उन्हें कथावस्तु की दृष्टि से यह नाटक मजेदार प्रतीत होता है। परंतु उसमें वर्तमान समय की भ्रष्ट व्यवस्था पर करारा व्यंग्य किया गया है।

इस दृष्टि से यह एक अत्यंत गंभीर नाटक है। सामाजिक एवं राजनीतिक क्षेत्र में रक्तबीज के समान फैले भ्रष्टाचार का पर्दापाश करना ही इस नाटक का मूल उद्देश्य है। अजय शुक्ला उनके इस उद्देश्य में सफल हुए हैं, क्योंकि उनके पास व्यंग्य का धारदार हथियार है। जिसका उन्होंने समय–समय पर उचित उपयोग किया है और देश की जनता का भ्रष्टाचार के इस भयावह रूप से परिचय करवाया है। आज देश का एक भी क्षेत्र ऐसा नहीं है, जिसमें भ्रष्टाचार नहीं होता हो। सभी प्रशासनिक, सरकारी, गैर–सरकारी विभाग भ्रष्टाचार में लिप्त हैं।

नाटक के उक्त संवाद इस बात को बखुबी स्पष्ट करते हैं– "आप ही देख लीजिए क्या हाल है? कभी यहाँ जावों चढ़ावा देने? कभी उधार जावो। बीच में तो एक बाबू ने कहा कि फाईल ही खो गयी है। पुरा केस फिर से शुरू करना पड़ेगा। ढ़ाई महिने बिल क्लर्क दबाए बैठा रहा। क्या बताऊँ गुप्त जी, चपरासियों तक ने नहीं छोड़ा। सभी को पता था करोडों का मामला है"।[1] किसप्रकार सरकारी अधिकारी, न्यायपालिका, पुलिस अफसर, बिल्डर, ठेकेदार, नेता आदि सभी मिलकर भ्रष्टाचार करते हैं, उनकी पोल खोलने का काम इस नाटक ने किया है।

इस नाटक के शिर्षक में ही हमें व्यंग्यात्मकता दिखायी देती है। 'ताजमहल का टेंडर' निकाला जाना ही

व्यवस्था पर किया गया एक करारा व्यंग्य है नाटककार की कल्पना ही इस नाटक की सफलता की कुंजी है। जो मुगल सम्राट को आज की अर्थहीन एवं भ्रष्ट व्यवस्था में लाकर खडा करते है। वैसे यह संभव नहीं हो सकता और नहीं अर्थपूर्ण लगता है। परंतु फिर भी दर्शक उसे स्वीकार करते हैं। इस नाटक में नाटककार ने एक कल्पना की है कि, शाहजहाँ अपनी बेगम मुमताज के लिए ताजमहल बनवाने का सपना देख रहें हैं। जो कि, आज की परिस्थिति में मुमकिन नहीं है। वर्तमानयुगीन भ्रष्ट शासन व्यवस्था के चलते शाहजहाँ का ताजमहल बनवाने का यह सपना कैसे पूरा होगा। यही हमारे देश की विडंबना हैप् हमारी इसी विडंबना को यह नाटक यथार्थ रूप में प्रस्तुत करता है।

आज हम देख रहें, सामाजिक जीवन से नैतिक मूल्यों एवं मान्यताओं का कैसे ऱ्हास हो रहा है। सभी स्वार्थता एवं भ्रष्टता में लिप्त है। अपने स्वार्थ के लिए किसी भी हद तक जाने के लिए तैयार हैं। ऐसे में उनकी नैतिकता पर प्रश्नचिन्ह लगता हैप् इस नाटक ने बादशाह शाहजहाँ को आज के स्वार्थी, सत्ता–पिपासू एवं रिश्वतखोरों के बीच लाकर खड़ा कर दिया है।

इस संबंध में नाटककार भूमिका में लिखते हैं– "अतीत को वर्तमान या वर्तमान को अतीत में स्थापित करने की यह कल्पना हमें एक ऐसे दुष्च्क्र के रू–ब–रू जा खड़ा करती है। जिसमें फँसकर आदमी तो क्या, एक सर्व सत्ता संपन्न सम्राट का हुक्म और ख्वाब तक रिश्वत और फाईलों के चक्रव्यूह में दम तोड देते हैं"।[2] इस कथन से यह स्पष्ट रूप से पता चलता है कि, हमारी व्यवस्था में व्याप्त भ्रष्टाचार का रूप कितना भयावह है। जिसके चंगुल से आम आदमी तो क्या, मुगल सम्राट भी नहीं छूट सकता।

'ताजमहल का टेंडर' नाटक में नाटककार ने हास्य–विनोद के माध्यम से तत्कालीन भ्रष्ट एवं निरंकुश व्यवस्था पर व्यंग्य किया है। इस नाटक में शाहजहाँ मुमताज के लिए ताजमहल बनवाने का सपना देखते हैं। वही शासक होने के कारण वें तुरंत अपने राज्य के मुख्य इंजिनिअर गुप्ता को सात दिनों में ताजमहल का काम शुरू करने का आदेश देते है। यही से ताजमहल बनवाने का असली नाटक शुरू हो जाता है, जो अत्यंत मजेदार है। अब इस काम के लिए टेंडर निकालना है। गुप्ता अपने ठेकेदार भैय्या जी के साथ बैठकर ताजमहल का प्लान बनवाना शुरू करता है।

ताजमहल निर्माण करने का काम करोडों रूपयों का है। सभी को लगता है कि, इसमें बहुत पैसा खाने को मिला सकता है। इसीलिए सब एकसाथ मिलकर ताजमहल के नाम पर करोडों का भ्रष्टाचार करने लगते हैं। इसमें न्यायपालिका, पुलिस, इंजिनिअर, ठेकेदार, नेता, सभी विभाग के सरकारी अधिकारी आदि शामिल हैं। सभी अपना–अपना स्वार्थ सिद्ध करने में जूट जाते हैं। शाहजहाँ के लिए ताजमहल बनवाने का काम दिन–रात चलता है। परंतु पच्चीस साल बीत जाने पर भी ताजमहल पूर्ण नहीं होता। हाँ! इस बीच गुप्ता का घर, होटल, फार्म हाउस सब तैयार हो जाता है। अन्य सभी को अपना–अपना हिस्सा मिल जाता है। परन्तु राजा का सपना मरते दम तक पूरा नहीं होता। आखिर ताजमहल को देखने का अपना सपना साथ लिए शाहजहाँ की मृत्यु हो जाती है।

एक राजा की यह हालत हो जाती है, तो आम आदमी का इस भ्रष्ट व्यवस्था के बीच क्या होगा। यह देखकर दर्शक सोचने पर मजबूर हो जाते हैं कि, इस भ्रष्ट व्यवस्था का कोई निदान नहीं है। 'ताजमहल का टेंडर' नाटक सामाजिक, राजनीतिक एवं प्रशासनिक व्यवस्था की इसी बिमारी को यथार्थ रूप में प्रस्तुत करता है। नाटक का उक्त संवाद हमारी इसी भ्रष्ट व्यवस्था को सच्चाई के साथ उद्घाटित करता हैं– "ईमानदार आदमी का तो यहाजीना ही मुश्किल है"।[3]

नाटककार ने इस संवाद का बार–बार जिक्र किया है। यह संवाद एक ओर हमारी भ्रष्ट व्यवस्था का नग्न चित्र उतारता है, तो दूसरी ओर भ्रष्टाचारियों की भ्रष्ट प्रवृत्ति पर व्यंग्य के माध्यम से प्रहार भी करता है। नाटककार कहते हैं आज भ्रष्टाचारियों का ही भविष्य उज्वल है। उन्हें भ्रष्टाचार की बिमारी ने जकड़ा हुआ है। उनकी इसी बिमारी का नाटककार निदान करना चाहते है। जिसके लिए वे व्यंग्य का हथियार इस्तेमाल करते हैं। भ्रष्टाचार ने हमारे देश को पूरी तरह खोकला कर दिया है। उससे मुक्त हो पाना अब असंभव लगता है।

भ्रष्टाचार के इस रूप को हम निम्न संवाद में देख सकते हैं। "अब आप ही देखिए सर, मैं इतने सालों से आपका पी–ए हूँ, कभी मैने किसी से कुछ माँगा? जो कुछ मिला ईमानदारी से वो चुपचाप रख लिया। है न सर? और वो, कोई काम धाम, एक झुग्गी मारने का आधा परसेंट, हे भगवान क्या जमाना आ गया है"।[4]

यहाँ भ्रष्टाचार एवं स्वार्थ में पूरी तरह से लिप्त चरित्रहीन व्यक्ति की प्रवृत्ति को उजागर किया गया है।

इस नाटक में चित्रित दो पात्र, नेता एक और नेता दोन की प्रवृत्ति आज के भ्रष्ट नेताओं के समान ही भ्रष्ट है। जो अपने आपको जनता का सेवक बताते हैं और गरीब भोली–भाली जनता का शोषण करते हैं। उनके भोलेपन का फायदा उठाकर अपना स्वार्थ सिद्ध करना ही उनके जीवन का लक्ष्य बन गया है। नेता चाहे किसी भी समय के हो, रिश्वत देने में और लेने में ही विश्वास करते है। नाटक में प्रस्तुत यह संवाद नेताओं की भ्रष्ट प्रवृत्ति को समाज के सामने लाते हैंप् नेता गुप्ता से कहता है– "आप चाहेंगे तो सब हो जाएगा और भरोसा रखें, मैं भी आपकी पूरी तरह सेवा करूँगा। जितना भैय्या जी ने दिया उससे दो पैसे उपर ही दूँगा, कम नहीं। आखिर जनता का सेवक हूँ"[5] 'ताजमहल का टेंडर' तत्कालीन भ्रष्ट

व्यवस्था पर व्यंग्य करता है। नेता, पुलिस, प्रशासनिक एवं सरकारी अधिकारी सरकारी विविध प्रलोभन दिखाकर जनता की भावनाओं के साथ खिलवाड करते हैं। जैसे इस नाटक में ठेकेदार भैय्या अपने नीजि स्वार्थ के लिए शाहजहाँ की भावनाओं से खेलता है।

आज की तारीख में कोई सरकारी योजना समय पर पूरी हो जाए, तो सरकारी अफसरों की प्रतिष्ठा खंडित होती है। अजय शुक्ला जी ने नाटक में इसी सत्य को व्यंग्य के माध्यम से उजागर करने का प्रयास किया है। सत्ता हाथ में होकर भी शाहजहाँ की यह हालत होती है, तो सामान्य व्यक्ति की क्या दशा होगी। इसकी कल्पना मात्र से दिल दहल जाता है यहाँ राजा होकर भी उनकी आज्ञा का कोई मूल्य नहीं है। इस नाटक में नाटककार ने गुप्ता एवं भैय्या जैसे भ्रष्ट एवं स्वार्थी अधिकारी एवं ठेकेदारों की मूल्यहीनता को सूक्ष्मता से मुखरित किया हैं।

इस संबंध में नाटक का उक्त संवाद बहुत ही उचित एवं असरदार है– "आजकल चपरासी से चाय लाने को कहो तो सात दिनों में चाय भी नहीं आती। साल–भर में तो फाईल पुटअप होती है और बादशाह सलामत चाहते हैं कि, सात दिनों में काम शुरू हो जाए।"[6] अर्थात् इस कथन से यह स्पष्ट हो जाता है कि, इन लोगों को काम करना ही नहीं है। केवल अपना स्वार्थ सिद्ध करना है। मूल्यहीनता का इससे अच्छा दुसरा उदाहरण हो ही नहीं सकता। हमारा पुरा देश भ्रष्टाचार के रोग से ग्रस्त हुआ है। भविष्य में भी इस रोग का निवारण संभव नहीं लगता। हम निरंतर इसी प्रकार भ्रष्ट व्यवस्था की ओर से छलते रहेंगे।

समाज में व्याप्त भ्रष्टाचार को पूरी सच्चाई के साथ उजागर करने में अजय शुक्ला जी का यह नाटक सफल है। नाटक के अंत में उन्होंने अपना आशावादी दृष्टिकोन समाज के सम्मुख रखा है। वें दर्शकों को अंत में सोचने पर मजबूर करते हैं। पाठकों एवं दर्शकों के दिमाग को झकझोरते हैं। उन्हें अपनी लाचारी एवं बेबसी पर सोचने की क्षमता प्रदान करते हैं। नाटक में शाहजहाँ की मृत्यु के बाद सुधीर फाईल के बेकार होने की बात करता है, तब गुप्ता जी उसे इस सत्य से अवगत कराते हैं कि, ताजमहल का सपना देखनेवाले कभी खत्म नहीं हो सकते।

गुप्ता कहते हैं– "वक्त गया बात गयी पर हम नहीं जाएँगे। फिर कोई ताज का ख्वाब देखेगा, तब हम फिर बुलाये जाएँगे, तब ये फाईल फिर काम आएगी।"[7] यहाँ नाटककार के आशावाद में भी हमें व्यंग्य की झलक देखने को मिलती है। निष्कर्ष रूप में कह सकते हैं कि, 'ताजमहल का टेंडर' नाटक स्वार्थता में आकंठ डुबे भ्रष्ट नेताओं, रिश्वतखोर अधिकारियों तथा दमनकारी अफसरों की सच्चाई को दर्शकों के सम्मुख लाता है। राज्य का सम्राट भी जो सर्व शक्तिमान एवं सत्ता प्रमुख है, वह भी इन भ्रष्ट एवं स्वार्थियों के चंगुल से नहीं बच सकता। बेबस और लाचार हो जाता है, तो साधारण मनुष्य की क्या हालत होती होगी। एक प्रकार से इस नाटक में अजय शुक्ला जी ने हमें सचेत करने का प्रयास किया है। समाज में फैले भ्रष्टाचार की ओर हमारा ध्यान खींचने का सार्थक प्रयास किया है।

सामाजिक एवं राजनीतिक क्षेत्र में व्याप्त भ्रष्टाचार का पर्दापाश करने के लिए नाटककार ने बहुत ही सुंदर कल्पना की है। इस भ्रष्टाचार का आगे बादशाह भी हार जाता है। यही हमारे समाज की विडम्बना है। नाटककार ने हमारी इसी विडम्बना को व्यंग्य के माध्यम से प्रस्तुत किया है। नाटककार के व्यंग्य की धार अत्यंत तीक्ष्ण है। इस दृष्टि से 'ताजमहल का टेंडर' नाटक बहुत ही सशक्त एवं सफल है।

संदर्भ सूचीः

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मुख्य सम्पादक – डॉ. कृष्णबीर सिंह का मानद पद कार्य पूर्णतः अवैतनिक है।
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Research Paper -Hindi

"वर्तमान परिप्रेक्ष्य में विवाह का बदलता स्वरूप"

डॉ. दादासाहेब एन. डांगे

सहायक प्राध्यापक, हिंदी विभाग कला, विज्ञान व वाणिज्य महाविद्यालय तहसिल– राहाता, जिला– अहमदनगर,महाराष्ट्र

प्राचीन काल से विवाह एक पवित्र बंधन माना जाता हैप् विवाह हमेशा–से दो परिवारों के बीच बहुमूल्य संबंध स्थापित करता आ रहा है। परंतु वर्तमान समय में जिंदगी की तेज रफ्तार में यह बहुत ही कमजोर साबित हो रहा है। उसका वह मूल्य कम हो रहा है, जो पहले था। आज नयी पीढी विवाह में 'लिव ईन रिलेशनशिप' को बेझिजक स्वीकार रही हैप् उन्हें विवाह गले में गुलामी का पट्टा लग रहा है। विवाह को लेकर अब उनकी सोच बदल रही हैप्अब वें छोटे–छोटे कारणों से भी एक–दुसरे से अलग होने की बात करने लगे हैं। इसमें लडकियां लडकों से भी अधिक स्वतंत्र हुई हैं।

इसका मतलब यही है कि, आज की पीढी विवाह को, विवाह की पवित्रता को समझनानहीं चाहती या समझने में नाकाम है। प्राचीन और नयी शादियों में आज काफी अंतर दिखायी देता है। पहले माता–पिता और परिवार–जनों की सहमति से शादियां होती थी। उसमें कई परिवार, रिश्तेदार, मित्र–परिवार शामिल होकर विवाह के साक्षी बनते थे। ऐसे में जब कभी रिश्तों में दरार उत्पन्न होती, तो उसे बचाने में सभी एकसाथ जूट जाते। परंतु विपरित उसके, आज विवाह कुछ खास गिने–चुने लोगों के सहयोग से तय होते हैं और असमय टूट भी जाते हैं।

सामाजिक प्रतिष्ठा का आज किसी को भय नहीं रहा है। पहले यही सामाजिक प्रतिष्ठा रिश्तों को बचाती थीप् आज उसे कोई महत्व नहीं दे रहा है। आज सभी आत्मनिर्भर हैंप् सभी अकेले–अकेले जीवन जीने की कोशिश कर रहें हैं और जीवन जीने की इसी पद्धति ने विवाह जैसी पवित्र संस्था को खोखला कर दिया है। यह मानव जीवन एवं संस्कृति के लिए एक दिन घातक सिद्ध हो सकता है।

विवाह हमेशा जोडने का काम करते आया है। वह दो व्यक्तियों को ही नहीं बल्कि दो परिवारों और उनसे जुडें अन्य सभी सगे–संबंधियों तथा दो भिन्न–भिन्न स्थानों को भी प्रत्यक्ष अप्रत्यक्ष रूप से जोडने का काम करता है। प्रारंभिक काल में समाज में विवाह को लेकर अलग–अलग मान्यताएं थी। लोगों को जीवन–यापन की विभिन्न समस्याओं से टकराना पडता था। खराब आर्थिक स्थिति के चलते उन्हें बच्चों की आवश्यकता महसूस होती थी।क्योंकि बच्चें उनके काम में उन्हें सहयोग देते थे और उनके बुढापें का सहारा भी बनते थे। बावजुद इसके, विवाह में प्रेम और सहयोग की भावना दिखायी देती थी। दो परिवारों के बीच परस्पर संबंध हो जाने से उन्हें आर्थिक एवं मानसिक आधार प्राप्त हो जाता था। वें अपने आप को सुरक्षित महसूस करते थे।

इसीलिए उस समय घर के बडें–बुजुर्ग लडकें–लडकियों को देखकर नहीं, उनका परिवार, उनकी आर्थिक स्थिति, समाज में उनकी प्रतिष्ठा, उनकी जाति, कुण्डलि तथा लेन–देन आदि को देखकर रिश्ता तय करते थे। लडकें–लडकियों की सहमति–असहमति का कोई महत्व नहीं था। उन्हें अपना जीवन साथी चुनने का कोई अधिकार

नहीं दिया जाता था। जबतक रिश्ता तय नहीं हो जाता, लडका–लडकी एक–दुसरे को देख भी नहीं सकते थे परंतु फिर भी इसप्रकार के रिश्तें चिरकाल तक टिकते थें। इसके विपरित वर्तमान समय में विवाह परंपराओं में बहुत ही जादा बदलाव आया है।

आज विवाह दो परिवारों में नहीं बल्कि दो व्यक्तियों में हो रहें हैं और उन्हें तय करने के लिए किसी की अनुमति या सहमति का होना भी जरूरी नहीं समझा जाता है। केवल व्यक्ति के अकेलेपन को दूर करना तथा अपनी यौन इच्छाओं को पूर्ण करना ही आज विवाह का उद्देश्य माना जा रहा है। ऐसे में हमारी प्राचीन विवाह संस्कृति को धक्का पहुंचना कोई विशेष बात नहीं है। यही चिंता का विषय है।

परिवर्तन प्रकृति का नियम है। मानव जीवन इससे अलग नहीं है। मानव समाज में भी निरंतर परिवर्तन होते रहते हैं। समाज में हमेशा नयी पीढि अपनी वर्तमान इच्छा–अपेक्षाओं को पूर्ण करने के लिए पुरानी परंपराओं तथा मान्यताओं को अपर्याप्त एवं बाधक मानती है और नवीन मूल्यों की खोज करना चाहती है। नयी पीढी की इस आधुनिक सोच के कारण कुछ नये मुल्यों का विकास तो होता है, परंतु उससे हमारे परंपरागत सांस्कृतिक मूल्यों की भी हानि हो सकती है। इस बारे में वे नहीं सोचते। आज समाज के हर क्षेत्र में चाहे वह सामाजिक हो या सांस्कृतिक, आर्थिक हो या धार्मिक क्रांतिकारी परिवर्तन हो रहें हैं। च्युंकि विवाह भी समाज की एक प्रमुख संस्था है, तो वह कैसे इन परिवर्तनों से अछुति रह सकती है।

सामाजिक परिवर्तन में शिक्षा, औद्योगिकरण, शहरीकरण, यातायात एवं संचार के क्षेत्र में हुई क्रांति का महत्वपूर्ण योगदान दिखायी देता है। जागतिकिकरण, संचार माध्यमों के प्रभाव एवं पाश्यात्य सभ्यता के बढते प्रभाव के कारण लोगों की मानसिकता में तीव्र गति से बदलाव आया है। इन विभिन्न साधनों ने विवाह रूपी संस्था को काफी हदतक प्रभावित किया है। आज की विवाह पद्धति उसका मूर्त उदाहरण है प्राचीन विवाह पद्धति और आज की विवाह पद्धति में काफी अंतर आया है। हम तो यहां तक कह सकते हैं कि, पहले विवाह रिश्तों को जोडने का काम करते थे और आज के विवाह रिश्तों को तोडने का काम कर रहें हैं।

वर्तमान समय में विवाह पद्धति में एक अलग ही मोड आया हुआ हम देख रहें हैं। विवाह अब झूठी सामाजिक प्रतिष्ठा का विषय बन गया है। आज हर कोई विवाह के जरिए दुसरों के सामने अपनी झूठी प्रतिष्ठा एवं अहं का प्रदर्शन कर रहा है। चाहे उसके लिए उसे किसी भी हदतक न जाना पडे। पहले आर्थिक विपन्नता के कारण लोग शादी करने के लिए तैयार नहीं होते थे।

दहेज न दे सकने के कारण एक तो विवाह नहीं होते थे या फिर विवाह टूट जाते थे। परंतु आज परिस्थिति चाहे कितनी भी खराब हो, विवाह में खर्च करना प्रतिष्ठा का विषय माना जा रहा है। ऐसे लग रहा है, जैसे लोगों में होड लगी हुई। परंतु आज की इसी फैशन–परस्ति तथा प्रतिष्ठा की होड ने विवाह की पवित्रता को नष्ट किया है। उसकी मौलिकता को खो दिया है आज विवाह में लोगों को वर–वधू को आशिर्वाद देने के लिए नहीं, बल्कि विवाह का ताम–झाम दिखाने के लिए आमंत्रित किया जाता है। लोग भी विवाह में आते हैं, भोजन करते हैं और तुरंत चले जाते हैं। वर–वधू को आशिर्वाद देने के लिए भी उनके पास समय नहीं है। यह हमारे समाज की विडम्बना है।

विवाह के रूप में की जानेवाली इस स्पर्धा ने कई लोगों के घर उजाड डाले हैं। आम आदमी का जीवन पूरी तरह से बरबाद हुआ है। वह दुसरों की बराबरी करना चाहता है। अमीर लोगों के समान विवाह में खर्चा करना चाहता है, परंतु कर नहीं पाता। इसी बीच वह अपना सबकुछ दांव पर लगाता है और कर्ज निकालकर विवाह करता है। परंतु कर्ज के ब्याज से वर्षों तक उबर नहीं पाता। यह सब विवाह की झूठी प्रतिष्ठा का ही तो नतीजा है। हमें आम आदमी के मनोविज्ञान को समझना होगा। उसकी भी अपने बच्चों को लेकर कुछ इच्छाएं हैं। उसे भी लगता है, अपने लडकी का विवाह भी अन्य की तरह बडे धूमधाम से हो। आज के समय में जब कोई आम इंसान विवाह को लेकर एक ऐसा सपना देखता है, जो की वह कभी पुरा नहीं कर सकता, तब उसके मन पर क्या बीतती होगी। क्या इसका अंदाजा हम लगा सकते है? यह सोचनेवाली बात है।

आज के विवाह में कहीं भी नैतिकता दिखायी नहीं देती। सभी ने मुल्यों को जैसे खो दिया है। आज का विवाह ऐसे लगता है, जैसे कोई मेला लगा हो। जिसमें रंग–बिरंगी किंमती वस्त्रों, आभूषणों तथा सौंदर्य–प्रसादनों का बाजार लगा हुआ है। विभिन्न प्रकार के व्यंजनों का प्रदर्शन हो रहा है। चारों ओर फटाकों की आतिशबाजी हो रही है। अलग–अलग प्रकार की साज–सज्जा, रूप सज्जा, मंच सज्जा आदि की व्यवस्था की गयी है, जैसे किसी नाटक के लिए रंगमंच पर की जाती है।

एक बहुत ही शानदार आयोजन किया जाता है, परंतु उसमें प्राचीन विवाह की पवित्रता की गंध लेशमात्र भी नहीं है। जिस विवाह में इसप्रकार का बढिया आयोजन किया हो, वही विवाह सबसे अच्छा यही आज के विवाह का मापदंड है। विवाह में लडके–लडकी को कोई नहीं देखता। सभी शादी का ताम–झाम और भोजन देखते हैं और यही एक अच्छी शादी होने का प्रमाणपत्र है, जो अतिथियों की ओर से पिता को दिया जाता है। जिसे पाने की होड आजकल समाज के सभी पिताओं में लगी हुई है।

पहले विवाह के लिए शुभ मुहरत देखा जाता था। अगर शुभ मुहरत नहीं निकलता तो विवाह नहीं किया जाता था। क्योंकि लोगों का यह मानंना था कि, अशुभ मुहरत में विवाह करने से विवाह में बाधा उत्पन्न होती है। परंतु आज बिना मुहरत के विवाह हो रहें हैं। विवाह के अनुरूप मुहरत को बनाया जा रहा है। अब इस बात को उठाकर हम अंधश्रद्धा को बढावा नहीं दे रहें हैं, बल्कि विवाह की पवित्रता एवं गंभीरता को टिकाए रखते हुए उसकी वास्तविकता की ओर सबका ध्यान खींचना चाहते है।

वर्तमान पीढी की सोच में काफी बदलाव आया है। उन्हें परंपरागत मूल्यों की कोई अहमियत नहीं रही है। विवाह उनके लिए केवल एक व्यवहार बनकर रह गया है। जिसमें कोई प्रेम, संवेदना नहीं है। इसीलिए आज के विवाह की बुनियाद मजबूत नहीं दिखायी देती। वह छोटे–छोटे कारणों से भी बहुत जल्द हिल जाती है। पहले जिन रिश्तों को निभाते–निभाते पूरी जिंदगी निकल जाती थी, आज उन्हीं रिश्तों को बडी आसानी से नजरन्दाज किया जा रहा है, जो की अपने हैं और बेहद किंमती हैं। एक शब्द में कहें तो आज का विवाह केवल आत्मा विहिन शरीर है। अब इसमें सुधार की आवश्यकता है। विवाह की पवित्रता तथा सांस्कृतिक मूल्यों को बचाए रखने के लिए अपनी सोच में बदलाव लाना जरूरी है। बदलते सामाजिक मूल्यों के दौर में हमारी परंपरागत विवाह पद्धति पर संदेह किया जाने लगा है।

युवाओं का प्रेम विवाह पर या उससे भी आगे 'लिव ईन रिलेशनशिप' की ओर आकर्षण बढता जा रहा है। समाज के बंधन काफी हदतक ढीले हो रहें हैं। लडकियां स्वतंत्र होने से उनकी सोच में परिवर्तन आया है। उन्हें विवाह अब बंधन लगने लगा है। वे अब इस बंधन में नहीं बंधे रहना चाहती। वे अपनी मर्जी से जीना चाहती है। नयी पीढी पर पाश्यात्य संस्कृति का प्रभाव पड रहा है। ऐसे में परंपरागत विवाह पद्धति को धक्का पहुंच रहा है। रिश्तों में दरारें उत्पन्न हो रही हैं।

विवाह की मान्यताओं को लेकर नयी–पुरानी पीढियों में वैचारिक मतभेद हो रहा है। अब इस स्थिति में नये मूल्यों की स्थापना के साथ–साथ स्थापित मूल्यों की रक्षा के लिए हमें नये कदम उठानें की आवश्यकता है। उसमें कोई मध्य निकालकर, दोनों में तालमेल बिठाकर आज की विवाह पद्धति के कारण होनेवाले दुष्परिणामों से बचना होगा। अब सवाल यह है कि विवाह का स्वरूप कैसे होना चाहिए।

अगर परंपरा से हटकर विवाह को युवाओं पर छोड दिया जाए तो, समाज के लिए यह हानिकारक सिध्द हो सकता है। दूसरी ओर युवाओं की सहमति–असहमति, उनकी इच्छाओं को दरकिनार करना भी उचित नहीं होगा। इसीलिए दोनों के बीच मध्य निकालकर उनके विचारों में मेल करना ही ठीक होगा। तभी परंपरागत विवाह पद्धति को बचाया जा सकता है और हमारे सांस्कृतिक मूल्यों की भी रक्षा की जा सकती है। निष्कर्ष रूप में कह सकते है कि, वर्तमान समय में विवाह का स्वरूप बदल रहा है। शिक्षा के बढते प्रभाव एवं औद्योगिक क्रांति के कारण युवा पीढी आत्मनिर्भर बन रही है। यही वजह है कि विवाह का परंपरागत स्वरूप बदल रहा है।

अब सुखमय जीवन व्यतित करने की लिए विवाह एकमात्र साधन नहीं है, जैसे पहले था। परंतु फिर भी वंशवृद्धि, दाम्पत्य प्रेम तथा सुख प्राप्ति विवाह के अलावा किसी अन्य साधन से संभव नहीं है। विवाह समाज को जोडने का काम करता है और आगे भी करता रहेगा, इसमें कोई संदेह नहीं। भले ही उसमें समय–समय पर कुछ परिवर्तन होते रहें। आज की विवाह प्रणाली पर सोच–विचार कर उसमें बदलाव लाने की आवश्यकता है। परिवर्तन के नाम पर समाज में जो उछुंखलता आयी है, उसे कम करना होगा। विवाह के नाम पर किया जानेवाला प्रतिष्ठा का झूठा व्यापार अब बंद करना होगा। नवीनता का स्वीकार करना अच्छी बात है, परंतु उसके नाम पर परंपरागत मूल्यों को तोडना ठीक नहीं है। इस बात पर अमल करना आवश्यक है।

विवाह के कारण होनेवाली निरर्थक वित्तहानि को कम करना होगा, जिससे हमारी अर्थ व्यवस्था को मजबूत किया जा सके। विलासिता एवं प्रतिष्ठा की इस अंधि दौड में आम आदमी भीतर से पूरी तरह टूट गया है। आर्थिक विपन्नता के कारण वह इस स्पर्धा में टिक नहीं पाता और घुटन भरी जिंदगी जीने पर मजबूर हो जाता है। उसकी इस मानसिक कुंठा एवं घुटन को समझना आवश्यक है। कभी–कभी इसप्रकार की स्थिति उत्पन्न हो जाती है कि, सामान्य व्यक्ति इस त्रासदी को सहन न कर सकने के कारण खुद्खुशी भी करता है। इस समस्या का निवारण करना है, तो आज की विवाह पद्धति में सामाजिक एवं सांस्कृतिक स्तर पर कुछ बदलाव करने जरूरी है। आज की विवाह पद्धति में नवीनता को अपनाते हुए परंपरागत सांस्कृतिक मूल्यों की, जो कि आज भी समाज के लिए हितकारक हैं, रक्षा करना आवश्यक है।

अतः वर्तमान परिप्रेक्ष्य में विवाह के बदलते स्वरूप को लेकर हमारी सोच बदलनी चाहिए, जिससे समाज में संतुलन बना रहें और समाज विकास की ओर अग्रसर हो जाए। यह हम सब की जिम्मेदारी है।

4. Library Automation

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Abstract

Library automation and the changing scenario of library management. The impact of ICT has changed the library operation and its functionality in to a fast to faster mode. Clients need not to visit shelf to shelf to find out a document. They just get their documents sitting in front of a desktop. Automation has reduced the man power. This article will discuss about the concept of automation, its requirement and various components helps to automate library. Some software package has given which are available for automation purposes.

Introduction

Automation is a process of using machinery for easily working and saving human power and time. The main purpose of library automation is to free the librarians and library staff and to allow them to contribute more meaningfully to the spread of knowledge and information. In Library Science automation is 'the technology concerned with the design and development of the process and system that minimizes the necessity of human intervention in their operation.'

Beginning in the 1960s with the development of the machine-readable catalog record (MARC), the process of automation has expanded to include the core functions of acquisitions, cataloging and authority control, serials control, circulation and inventory, and interlibrary loan and document delivery.

Definition of Library Automation

ALA Glossary of Library and Information Science defines automation as "the performance of an operation, a series of operation or a process by self-activating, self-controlling, or automatic means. Automation implies use of automatic data processing equipment such as a computer or other labour saving devices". Although, the term automation was first introduced by D. S. Harder in 1936, the word library automation is being used in literature for the last five decades.

According to Encyclopedia of Library and Information Sciences (Kent, 1977) "Library Automation is the use of automatic and semiautomatic data processing machines to perform such

11. Open Source Library Management Software

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Abstract

Open source software are those which permit execution, copy, read, distribution and improvement of the software without any restrictions. Library Management Software (LMS), is an enterprise resource planning system for a library, used to track items owned, orders made, bills paid, and patrons who have borrowed. Commercial library management software are very expensive. Therefore, open source library management system can be appropriate alternatives for automatic library systems. This paper discusses features of open source library management software, criteria of selection of best open source library management software, their, advantages and limitations. Open source library management software is a solution to reduce that cost. The paper describes in brief about the feature of some of the open source library management software like Koha, NewGenlib, Evergreen,

Introduction

There are many commercial library software are in use in the different libraries, but open source library management software has generated lot of interest among the library professionals over the past years. Library automation starts with the adoption of library management software in the library. The software should have the maximum facilities to automate the library into computerized systems. Library automation is the general term for information and communication technologies that are used to replace manual systems in the library. The key functions of the library, which may be automated are acquisition, cataloguing, circulation, serials control, and reference service. Libraries do not have huge funds to experiment, and they don't usually purchase additional resources. The need for library management software, its installation, training and the lack of financial resources have forced many libraries to stand for themselves when it comes to staying up to date with the latest technology. Unless, of course, they adopt the open source movement and use a few of them available to overcome these problems.

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Massive Open Online Courses (MOOC): an overview of recent perspective

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Abstract

Massive open online courses (MOOCs) are one of the most prominent trends in higher education in recent years. The term 'MOOCs' represents open access, global, free, video-based instructional content, videos, problem sets and forums released through an online platform to high volume participants aiming to take a course or to be educated. With time and place flexibility, MOOCs gathers scholars and 'like-minded fellow learners around the globe'. Although it has a great prominence in its implementation, there is a lack of research studies and critical papers examining its current situation around the world.

Keywords:MOOC, Massive Open Online Courses, edX, Coursera, Udacity

Introduction

A massive open online course (MOOC) is a model for delivering learning content online to any person who wants to take a course, with no limit on attendance MOOC stands for Massive Open Online Course. They are distance -learning courses run online by many universities worldwide. Usually, they are open to anyone who registers. One single course may admit even thousands of students. It is possible to study almost any subject through this method, and dozens of famous universities worldwide are now offering MOOCs. They can be treated as a standalone study for individuals interested in a particular subject matter.MOOCs give students the option of studying a subject in depth without the constraints of a traditional university course. They can be anywhere in the world as the resources are all online and they do not require previous qualifications. They are open to anyone, regardless of whether or not they have studied before.

Students can simply follow the course at their own pace, taking as much time as they need. However, most MOOCs are available for a limited amount of time so in most cases, the online lectures and webinars won't be available for more than one year.

MOOCs usually have no end-of-course assessment or exams that need to be passed. Instead, there are often weekly online quizzes or peer-assessed assignments, but mostly optional. However, they are a good opportunity to test your knowledge and see how much of what you learned and studied you managed to acquire.

Benefit of MOOC

1. Importing access to higher Education
2. Providing an affordable alternative to formal Education
3. Sustainable Development Goals
4. Offers a Flexible Learning Schedule
5. Online Collaboration
6. To Connect Students from around the world

Challenges of MOOC

1. Relying on user-generated content can create a chaotic learning environments
2. Digital Literacy to make use of the online materials
3. The Term and effort required from participant may exceed what students are willing to commit to a free online courses.
4. Once the course is released, content will be reshaped and reinterpreted by the massive student body, making the course strategy difficult for instructor to control.

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1. RFID

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Abstract

RFID provides a solution to such a problem, by reducing the amount of time required to perform circulation operations. The paper covers the components and technical features of a modern RFID library system, its advantages and issues related to use of RFID in libraries. It's grouped under the broad category of automatic identification technologies. RFID is increasingly used with biometric technologies for security. Information and Communication Technology has transformed the format of information and work culture of libraries. Still libraries are trying to address various problems like qualitative information management, speedy acquisition and dissemination of information and security of information products.

Introduction

RFID stands for Radio Frequency Identification. It is an electronic technology whereby digital data encoded in an RFID Tag is retrieved utilizing a reader. In contrast to bar code technology RFID systems do not require line-of-sight access to the tag in order to retrieve the tag's data, and they are well suited to harsh environments. The RFID reader is typically a microcontroller-based radio transceiver that powers the tag with a time-varying electromagnetic radio frequency (RF) field. When the RF field passes through the tag's antenna, AC voltage is generated in the antenna and rectified to supply power to the once powered; the tag can receive commands from the reader Radio Frequency Identification (RFID) is a next generation of Auto Identification and Data Collection (AIDC) technology which helps to automate business processes in an Open environment with security. This automation can provide accurate and timely information without any human intervention. The new method for data collection and auto identification is called radio frequency identification of RFID that enable to automate the process of business.

RFID in Libraries

Librarians are always known as early adopters of technology, as seen in case of Computer and later in case of Bar-codes. Later have seen standards like MARC and OCLC