KURIAKOSE GREGORIOS COLLEGE PAMPADY

3.3.1 RESEARCH PAPERS PUBLISHED

2020-21

SL NO	PUBLICATION	NAME OF AUTHOR	SUBJECT
1	Malayalam Ke Sresht Kavi Sreekumaran Thampi Ke Kavithavom Ka Anuvadh	Dr A Priya	Hindi
2	"Ram Ke Atmasangharsh Ki Thulana - Sarayu Ki Aur Owr Samshay Ki Ek Rath Ke Vishesh Sandarbh Mein"	Dr A Priya	Hindi
3	"Phaneeswarnath Renu Ki Kahaniyom Mein Gavu Ke Chithru"	Dr A Priya	Hindi
4	"Adhurepan Ki Dasthaan : Sisakthi Dastan Ke Sandarbh Mein"	Dr A Priya	Hindi
5	"Hindi Kavitha Aur Gandhiji Ki Vaichariki"	Dr A Priya	Hindi
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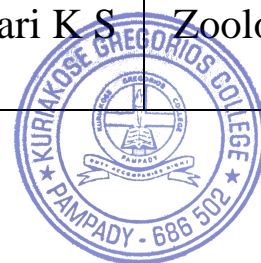
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(1)   मैंने फूलो को उछाला

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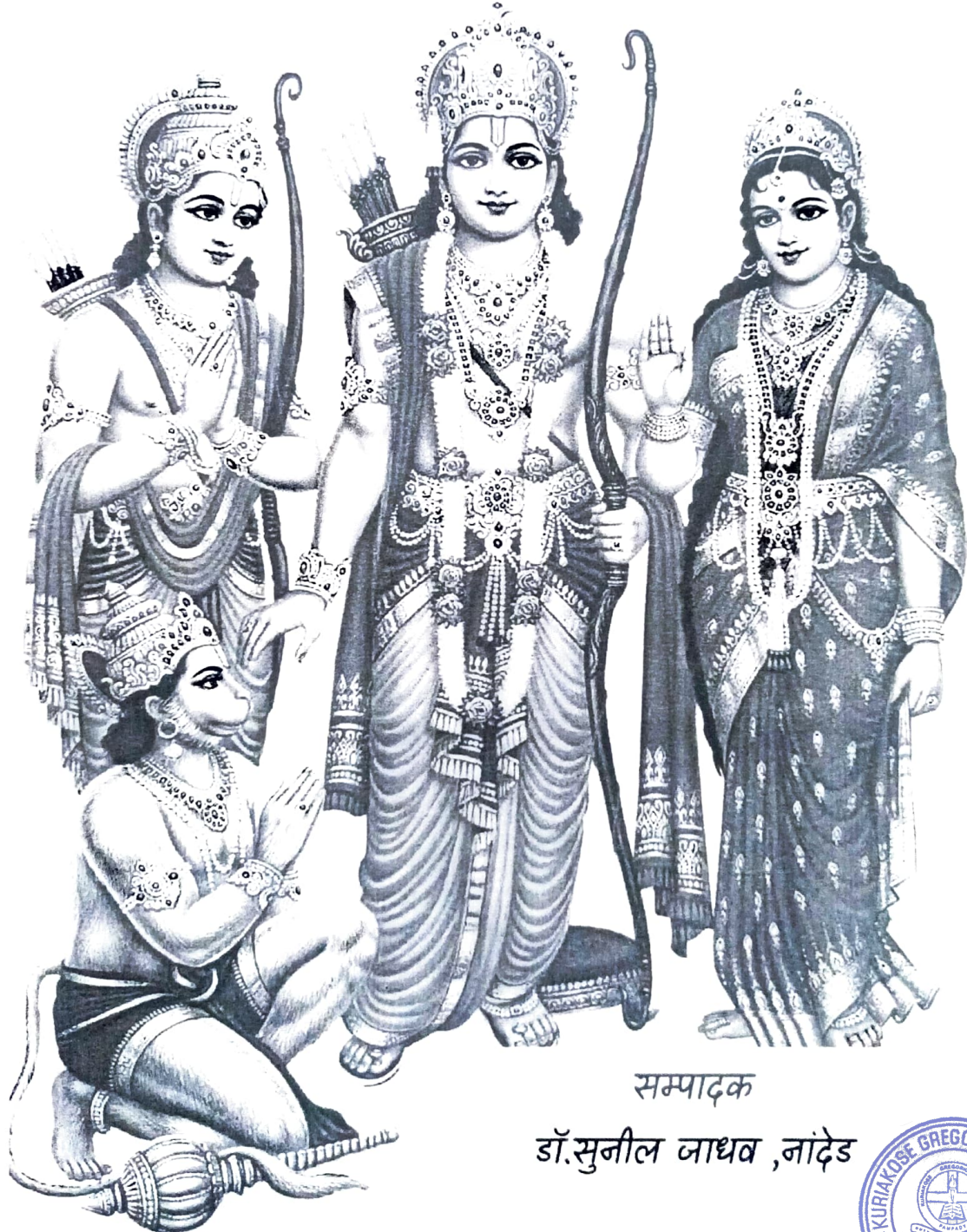निराशा ने तुम को खुट से ही अंकन किया

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सम्पादक

डॉ.सुनील जाधव ,नांदेड

17.राम के आत्म संघर्ष की तुलना–सरयू की ओर और संशय की एक रात के विशेष संदर्भ में

डॉ. प्रिया ए.

असिस्टेंट प्रोफेसर,हिंदी विभाग, के.जी. कॉलेज
पाम्पाडी, कोट्टयम, केरल

मलयालम काव्य साहित्य को समग्र योगदान के लिए सन 2007 में मलयालम के प्रिय कवि ओ.एन.वी. कुरुप को ज्ञानपीठ पुरस्कार से सम्मानित किया गया था। मलयालम साहित्य एवं साँस्कृतिक कार्यों के लिए उन्होंने अपना जीवन समर्पित किया। कविता के प्रति उनकी विशेष रुचि थी। उनकी 1988 से 89 तक की कविताओं को मृगया (शिकार) नामक संकलन में समाहित किया है। इस संकलन की एक लंबी कविता है – सरयू की ओर। राम के मन की शोक भावना एवं उससे उत्पन्न आत्मसंघर्ष को प्रस्तुत कविता दर्ज करती है। समकालीनता के परिवेश में कविता के कथ्य को प्रबन्धात्मक शिल्प के सहारे संप्रेषित करना इस कविता का प्रयास है। राम को एक मिथक बनाकर उनके सहारे वर्तमान आधुनिक बोध को उभारा है। पौराणिक कथा में नवीन दृष्टि लाने एवं उसके माध्यम से युग की जटिल स्थितियों को परिभाषित करने का उपक्रम इस कविता का ध्येय है। इससंशय की एक रातर हिंदी के कवि नरेश मेहता द्वारा लिखा गया पौराणिक गीतिनाट्य है। राम–रावण युद्ध का निश्चय। साँझ संशय का प्रतीक और बालूतट विचार विश्रृंखलता, जीवन की निस्सहायता एवं असफलता का प्रतीक है। पौराणिक प्राकृतिक, वैज्ञानिक और जनजीवन से संबद्ध प्रतीकों का प्रयोग इसमें किया है।

संशय की एक रात में कवि ने राम के भीतर युद्ध के प्रति संशय पैदा कर एक आधुनिक मनुष्य की चिन्ता प्रकट की है। राम के चरित्र की पुनर्रचना की है। राम सनातन प्रज्ञा पुरुष है। नरेश मेहता ने एक अभूतपूर्व संकट राम के सामने उपस्थित किए हैं, जो न वाल्मीकि के राम के सामने था, न तुलसी या अन्य कवि के राम के सम्मुख। राम के सामने संशय

यही था कि सीता के लिए युद्ध करना सार्वजनिक है या व्यक्तिगत? संशय राम का है। युगजीवन की अनेक विडंबनापूर्ण स्थितियों के बीच से गुजरता हुआ अपनी अस्मिता की बेचौनी भरी खोज का मार्मिक चित्रण किया है। युग की जटिल स्थितियों को परिभाषित करने का उपक्रम किया है। परिस्थितियों की विषमता से आक्रांत होने के कारण अपने अस्तित्व को ही निर्थक मानने लगता है।

राम का मानसिक संकट मूलतः उत्तरदायित्व का संकट है। राम की अपनी विडंबना युग जीवन की विडंबना का स्वरूप बनती है। राम की मन:स्थिति उनकी दुर्बलताओं का परिचायक नहीं। मानवीय मूल्यों और सत्यों के स्थापन और संरक्षण, शांतिमय और अहिंसक उपायों की खोज और उनके समर्थन की बौखलाहट है। उनके संशय के मूल में व्यक्तिगत हानि सहकर भी नर–संहारकारी युद्ध से बचने की लोक संग्रहीय संवेदना सन्निहित है। यह संशय किसी असमर्थ, अविवेकी को नहीं व्यापक जनहित और जन–रक्षा के उदात्त लक्ष्य के प्रति समर्पित एक समर्थ और विवेक व्यक्ति का है।

मर्यादा पुरुषोत्तम राम के अन्य संघर्षपूर्ण जीवन की अनेक विडंबनापूर्ण स्थितियों से पाठक अवगत होता है। हर एक आधुनिक मानव की आत्म स्थितियों को पहचानना और अपनी अस्मिता की बेचौनी भरी खोज का मार्मिक चित्रण इसमें लक्षित है। राम परिस्थितियों की विषमता से आक्रांत होने के कारण अपने अस्तित्व को ही निर्थक मानने लगते हैं। मानसिक संघर्ष की पीडा के कारण राम सरयू नदी को ओर प्रस्थान करते हैं।

सरयू की ओर नामक कविता की पहली पंक्तियाँ राम और सरयू नदी के बीच के अंत:संबंध को स्पष्ट करती हैं। रावण के सीताहरण के बाद समाज के एक वर्ण में संदेह उत्पन्न हो चला कि माँ सीता पहले की तरह ही पवित्र और सति है। भारतीय समाज में सीता को परम पवित्र और आदर्श नारी का दर्जा प्राप्त है। पर समाज में यह धारणा भी प्रचलित है कि माता सीता को भगवान राम ने समाज द्वारा सवाल उठाए जाने पर अपनी प्रतिष्ठा बचाने छोड़ दिया था।

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अधूरेपन की दास्तान : 'सिसकती दास्तान' के संदर्भ में

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हिजड़ा समुदाय व थर्ड जेंडर का इतिहास काफी पुराना है। जबसे मनुष्य जाति धरती पर है, तभी से हिजड़ों का इतिहास है। महाभारत और रामायण के पन्नों में ही इनका इतिहास लिखा हुआ है। थर्ड जेंडर शब्द बहुत ही सामान्य रूप से प्राचीन भारतीय समाज में प्रचलित रहा। विशेष शारीरिक संरचना, व्यवहार तथा मनोविज्ञान के अनुसार थर्ड जेंडर पर वैदिक साहित्य में उनकी उत्पत्ति के कारण, विविध प्रकार, व्यवहार, समस्याएँ आदि पर विचार किया गया है। वर्तमान समय में हिन्दी साहित्य के आईने में हिजड़ा विमर्श का प्रतिफलन देख सकते हैं। साहित्य में हिजड़ों की मानसिक स्थिति का पूर्ण संवेदनाओं के साथ चित्रण किया जा रहा है। जन्मतः जननाँग की विकृति के कारण ये न तो स्त्री होते हैं और न पुरुष। इन्हें तृतीय लिंगी या हिजड़ा या थर्ड जेंडर कहा जाता है। मानव समाज के अंग होने पर भी मुख्यधारा समाज इन्हें घृणा की दृष्टि से ही देखता है। इनकी जटिल सामाजिक संरचना के विभिन्न आयामों को डॉ. लता अग्रवाल अपने काव्यसंग्रह 'सिसकती दास्तान' के माध्यम से प्रस्तुत करती है। उन्होंने हिजड़ा समुदाय की मानसिक हालत को अत्यंत गहरे हृदयस्पर्शी ढंग से इस संकलन में दर्ज किया है।

दुनिया के सबसे बड़े लोकतंत्र में समाज के हाशिए पर जीनेवाले लैंगिक विकलाँगों की यौन अस्मिता और उनकी समाजार्थिक स्थितियों का मुद्दा अक्सर उठता रहा है। 'हिजड़ा' शब्द जेहन में आते ही हमारे मन में एक खास तरह की भाव-भंगिमा, आचार-व्यवहार, रहन-सहन, एवं चाल-ढाल वाले इन्सानों का रूप आ जाता है। मुख्यधारा के समाज से बहिष्कृत, व्यंग्य, घृणा, तिरस्कार आदि सहने को अभिशप्त इस श्रेणी के इन्सानों की यौनस्थिति के

आधार पर कई नामों में पुकारा जाता है; जैसे - किन्नर उभयलिंगी, शिखंडी आदि। लैंगिक विकलाँगों के प्रति समाज के नकारात्मक व्यवहार को 'नासूर' नामक कविता दर्शाती है - "घर से कर बेदखल/छीनकर दुनिया/मोहब्बत भरी/धकेल दिया था उस रोज/अँधेरे कुएँ में/जहाँ विचरते है/विष भरे साँप, बिच्छु/जो खुरचकर नाखून से/घावों को/कर देते हैं गहरा/रिसता है जिनसे मवाद/मवाद की ठसक/देती है पीड़ा।"१

पैदाईश से लेकर जीवन के हर मोड़ पर इनको कई प्रकार के संघर्षों से जूझना पड़ता है। माता-पिता से लेकर बन्धु-मित्र जन तक इनकी अवमानना करते हैं। अपनों से मिलनेवाले इस व्यथा के भार से यह वर्ग घर-परिवार को छोड़कर दूसरी दुनिया की ओर जाने के लिए विवश होते हैं। समाज से जो तिरस्कार सहना पड़ा, वह नासूर के समान निष्ठुर हो जाता है। मन में व्याप्त दर्द की गहराई को प्रकट करने के लिए उनकी मानसिक पीड़ा को नासूर की पीड़ा से तुलना की है।

शास्त्रानुसार गणेश पुराण के अनुरूप भाद्रपद शुक्ल चतुर्थी के दिन चन्द्रमा देख लेने पर कलंक अवश्य लगता है। ऐसा गणेश जी का वचन है। भारतीय शास्त्रों में गणेश चतुर्थी के दिन चंद्र दर्शन को निषेध माना गया है। हिजड़ा समुदाय के प्रति भारतीय समाज की अवमानना एवं तंग मानसिकता को 'अभिशप्त चाँद' नामक कविता व्यक्त कर रही है - "जीवन हमारा/चाँद/गणेश चतुर्थी सा/आधा अधूरा अभिशप्त/जिसे देखने भर से/लग जाता दोष/मिटाने दोष अपना/करते पत्थर वार लोग/काश !/कभी देखे जाते/करवा चौथ के/चाँद से/पूजे जाते/हम भी/प्रियतम के/प्यार से।"२

अपनी जीवन की अभिशप्तता का उल्लेख करने के साथ-साथ दुनिया की वास्तविकता की चर्चा भी इन पंक्तियों में देखने को मिलती है। साँस्कृतिक पृष्ठभूमि के आधार पर दो प्रकार के प्रसंगों का उल्लेख भी यहाँ किया गया है।

दरअसल समाज में रहते हुए भी समाज से पृथक ऐसी इकाई के रूप में उनकी जो पहचान होती है, वह वास्तविकताओं के बजाय पूर्वाग्रहों, मान्यताओं और अफवाहों पर ही आधारित होती है। समाज उनकी लिंगीय सच्चाई एवं संघर्ष की मानसिकता से अनभिज्ञ रहता है। मानसिक रूप की अस्त-व्यस्तता को 'बीच के' नामक कविता शब्दबद्ध करती है - "माना दिन-दिन होता/रात होती रात/दोनों का अस्तित्व अपने में सम्पूर्ण/मगर... मगर... इन दोनों के बीच/जो होती/उसका भी अपना अस्तित्व होता/साँझ बेला कह/अंगीकार करते सब/पावन भाव से/देहली पर घर दीप/

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हिन्दी कविता और गाँधीजी की वैचारिकी

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साहित्य और समाज का संबन्ध गहरा और अटूट है। गाँधीजी के विचारों का प्रभाव समाज और साहित्य पर दृष्टिगत था, अब भी दृष्टिगत है। स्वातंत्र्योत्तर साहित्य में गाँधीजी के दर्शन को आत्मसात करके साहित्यकारों ने समाज को दिशा निर्देश करने की कोशिश की थी। प्रेम, सत्य, अहिंसा और सद्भाव को महत्व देकर भारत के धरोहर रूपी गाँधीजी के विचारों का सही संप्रेषण किया था। मैथिलीशरण गुप्त, रामधारी सिंह दिनकर, माखनलाल चतुर्वेदी, सोहनलाल द्विवेदी, गिरिजाकुमार माथुर, हरिवंशराय बच्चन, नरेश मेहता, सुमित्रानंदन पंत, जयशंकर प्रसाद, भवानीप्रसाद मिश्र, सुभद्राकुमारी चौहान जैसे स्वातंत्र्योत्तर समय के कवियों ने गाँधीवादी दर्शन से प्रभावित होकर अपनी सृजन धर्मिता को निभाया है।

सोहनलाल द्विवेदी हिन्दी के प्रमुख राष्ट्रीय कवि के रूप में प्रसिद्ध हैं। राष्ट्रपिता महात्मा गाँधी के महान व्यक्तित्व का परिचय उन्होंने अपनी कविता 'युगावतार गाँधी' में यों किया है - "चल पड़े जिधर दो डगमग पग, बढ़ चले कोटि पग उसी ओर / पड़ गई जिधर भी एक दृष्टि / गड़ गए कोटि दृग उसी ओर / जिसके सिर पर निज धरा हाथ / उसके चिर रक्षक कोटि हाथ / जिस पर निज मस्तक झुका दिया / झुक गए उसी पर कोटि माथ।"[1]

इन पंक्तियों द्वारा कवि ने गाँधीजी को युग का अवतार पुरुष माना है। युग-पुरुष का लक्षण यह है कि वह देश और समाज का नेतृत्व करें, जनता उसके विचारों का और कार्यों का अनुवर्तन करें। गाँधीजी इन विशेषताओं से युक्त युग-पुरुष थे।

'सत्य' गाँधी दर्शन का प्राणतत्व है। गाँधीजी ने सत्य को ही ईश्वर और ईश्वर को ही सत्य माना है। उनके अनुसार सत्य के द्वारा ही शिवम् अर्थात मंगल और सौंदर्य का दर्शन होता है। सत्य की महिमा को राष्ट्रकवि रामधारी सिंह दिनकर यों शब्दबद्ध करते हैं - "दमन करो मत कभी सत्य, मुख के बाहर आने दो / भय के भीषण अंधकार में, ज्योति उसे फैलाने दो।"[2] इन पंक्तियों द्वारा असत्य पर सत्य की विजय, अन्याय पर न्याय की विजय, बुराई की कालिमा पर अच्छाई के प्रकाश की विजय की महत्ता का आह्वान किया है।

सत्यं शिवम सुन्दरम की विराट कल्पना को, जो समाज के हित के लिए ज़रूरी है; इस तत्व को अपनी रचना द्वारा गिरिजाकुमार माथुर ने यों प्रस्तुत किया है - "विश्व में जब कुटिलता है, त्रास है / सत्य शिव का सब हमें विश्वास है।"[3]

वर्तमान समय की सबसे विडंबनात्मक सच्चाई है त्रास एवं भय का माहौल। इस विकल - विद्रूपात्मक समय में भी सत्य-न्याय-धर्म का पक्षधर बनकर हर एक नागरिक को अपनी सामाजिक प्रतिबद्धता जतानी होगी। इस कविता के तहत इसी लक्ष्य की पूर्तिकरण का आह्वान दिया है।

गाँधी दर्शन का दूसरा मुख्य तत्व है - अहिंसा। अहिंसा की आत्मिक शक्ति द्वारा ही महात्मा गाँधीजी ने संसार की प्रबल शक्ति से लोहा लेने का साहस किया था। उनकी नीति में छल, कपट या कूटनीति के लिए कोई स्थान नहीं था। उनकी राय में हिंसा मनुष्य को कायर बनाती है और अहिंसा साहसी। हमारी संस्कृति की आधार शिला अहिंसा ही है। अहिंसात्मक मार्ग को अपनाने पर मानवीय मूल्यों की वृद्धि भी होती है। इन सभी तत्वों को सन्निवेशित करके भारतीयता का हमारे देश भारत का गुणगान सुमित्रानंदन पंत यों करते हैं - "भू के समृद्ध देशों को, भारत से शक्ति तपोज्वल, दिव्यास्त्र अहिंसा - दे करती

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मानवीय संवेदना की कविताई

डॉ. प्रिया ए.*

इक्कीसवीं सदी की हिन्दी कविता मानवीय संवेदनाओं की कुतुबनुमा बनकर जिन्दादिली से अपनी उपस्थिति दर्ज करती है। संवेदनशील कवि जब अपने आस-पास बदलते हुए जीवन और उसके मूल्यों को देखता है तो वह चुप नहीं रहता है। अपने विचारों को शब्दबद्ध करके संवेदनाओं की कौंध से कविता को सजाता है। समकालीन कविता के केन्द्र में मनुष्य को ही प्रमुख स्थान दिया जाता है। उत्तराधुनिक मानवविरोधी समय की सच्चाई को समकालीन हिन्दी कविता अंकित करती है। वर्तमान समय के मानव जीवन के तनावों, कुंठाओं, विसंगतियों को इक्कीसवीं सदी की कविता ने आत्मसात किया है। मूल्य संक्रमण के इस प्रौद्योगिक दौर में साहित्य सिकुड़ रहा है। मानवीय संवेदनाएं भी घट रही है। पर साहित्य बृहत आकार धारण करके मानवीय संवेदनाओं को पुनः स्थापित करने का प्रयास करता है।

इक्कीसवीं सदी में सामाजिक, राजनीतिक, आर्थिक परिस्थितियों में तीव्रता के साथ परिवर्तन हुआ था। इस द्रुतगामी परिवर्तन के फलस्वरूप एक तरफ सांस्कृतिक अवमूल्यन दिखाई दिया और दूसरी तरफ विश्व संस्कृति का विस्तार भूमंडलीकरण और पूँजीवाद पर केंद्रित नव साम्राज्यवादी ताकतों के विरुद्ध समकालीन हिन्दी कविता की नयी भूमिका एवं नया आयाम सराहनीय ही है। अपने समय के संत्रस्त एवं हताश जनता की पीड़ा को समकालीन कवि अपनी रचनाओं में पनाह देते है।

इक्कीसवीं सदी की कविता सियासी - समाजी हादसों, अन्यायों और दुःखों की गहरी शिनाख्त है। सत्ता और शक्ति की विभिन्न आक्रामक संरचनाओं के विरुद्ध चीखते रहने की कवि नियति का सहर्ष स्वीकार इसमें विद्यमान है। समकालीन कवि चन्द्रकांत देवताले की 'खुद पर निगरानी का वक्त' नामक कविता सामाजिक अन्याय के प्रति जनता को आगाह करती है, "हाँफ रही कविता / कितनी कर सकती है छातीकुट्टा / कह रही बार-बार निगरानी रखो / जैसी दुश्मन पर वैसी ही खुद पर / विश्वासघात न हो जाए / अपनी भाषा, धरती और लोगों के साथ।"[1]

मानवीय संकट के विकल समय में कवि अपनी रचनाधर्मिता को निभाते हुए कहते हैं कि जनता की भाषा; जो उनका स्वत्व है, अस्मिता है - उसे सुरक्षित रखने का आह्वान करते हैं।

इक्कीसवीं सदी के जन विरोधी समय ने किसानी संस्कृति पर कुठाराघात किया है। किसान वर्ग व किसानी चेतना को हाशिए पर धकेल दिया है। ऐसी विडंबनात्मक सच्चाई को प्रस्तुत करती है उमा शंकर चौधरी जी की कविता 'किसान की आत्महत्या भी मृत्यु है "इतिहास में यह समय / जितना विकास के लिए दर्ज होगा / उससे अधिक होगा अपनी विडंबनाओं के लिए / और जब बारी उन विडंबनाओं की पड़ताल की आएगी / तब जो सब से ऊपर आएगा / उसमें होगा / अख़बार में छपी किसानों की आत्महत्या की खबर।"[2]

इस कविता के द्वारा कवि किसानी संस्कृति की आवश्यकता एवं आर्थिक विपन्नता के कारण किसान की आत्महत्या की अधिकता की

पड़ताल करते हैं। ऐसे विद्रूपात्मक हालत से किसानी संस्कृति को उबारने की कोशिश कविता में लक्षित है।

भूमंडलीय पूँजीवादी ताकतों का शिकंजा जीवन के हर क्षेत्र को जकड़ रहा है। प्राकृतिक संपदाओं का शोषण भी एक विडंबनात्मक सच्चाई है। प्रकृति की सभी संपदाएं — नदियां, पेड़-पौधे,

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डॉ० रामकेश्वर तिवारी

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इक्कीसवीं सदी में हिंदी भाषा का वैश्विक विस्तार

डॉ. प्रिया ए. *

वर्तमान समय में वैश्वीकरण या भूमंडलीकरण मानव जीवन के प्रत्येक क्षेत्र को प्रभावित कर रहा है। अतः भूमंडलीकरण एक बहुआयामी खुली प्रक्रिया के रूप में हमारे सामने उपस्थित है। ऐसी प्रक्रिया के तहत पूरा विश्व अपनी भाषा, संस्कृति और व्यापार को एक दूसरे से साझा करके अपने विकास की ओर बढ़ रहा है। इसके फलस्वरूप सूचना और संचार क्रांति ने तकनीकी रूप से लोगों को आपस में जोड़ कर वैश्विक लोकतंत्र की व्यापक अवधारणा को संभव कर दिखाया है। सूचना और संचार क्रांति के रूप में सब डिजिटल बन गया है। हमारा देश भारत भी 'डिजिटल इंडिया' हो गया। हिंदी भारत की राष्ट्रभाषा एवं राजभाषा है। आज भूमंडलीकरण के युग में हिंदी की तरफ लोगों का ध्यान बढ़ रहा है। भारत में ही नहीं विदेशों में भी हिंदी भाषा का प्रचार-प्रसार हो रहा है।

आज मीडिया का युग है। हमारे जीवन का प्रत्येक क्षेत्र प्रत्यक्ष या परोक्ष रूप में मीडिया जगत से प्रभावित हो रहा है। जनसंचार का उद्देश्य जानकारी या विचारों को समाज के तमाम लोगों तक सम्प्रेषित करना है। वर्तमान समय में हर एक क्षेत्र में यह प्रासंगिक भी बन गया है। "हिंदी को वैश्विक सन्दर्भ देने में उपग्रह चैनलों, विज्ञापन एजेन्सियों, बहुराष्ट्रीय निगमों तथा यांत्रिक सुविधाओं का विशेष योगदान है। वैश्वीकरण के आगमन के बाद हिंदी भाषा की विकास प्रक्रिया में अनेक अवसर भी प्राप्त हो रहे हैं।"[1] हिंदी भाषा को बोलने, जानने तथा चाहने वाले लोगों की संख्या बढ़ रही है। हिंदी भाषा में साहित्य सृजन की प्रदीर्घ परंपरा भी रही है। वर्तमान समय में भूमंडलीकरण की विकास प्रक्रिया के कारण साहित्य भी इंटरनेट और वेबसाइट से जुड़कर व्यापक हो गया है। हिंदी के विकास में मुद्रित और विद्युतिकी जनसंचार माध्यम का महत्व अनुदिन बढ़ रहा है। नए जनसंचार माध्यमों में सर्वाधिक शक्तिशाली है 'इंटरनेट'। संचार माध्यमों में प्रचार-प्रसार की क्षमता दूसरे माध्यमों से अधिक है। साहित्य का ज़्यादा प्रचार-प्रसार भी इन जनसंचार माध्यमों के द्वारा ही हो रहा है।

इक्कीसवीं सदी में सोशल मीडिया सही मायने में अभिव्यक्ति का सशक्त माध्यम बन गया है। इसके कारण हमारी अपनी हिंदी भाषा एवं साहित्य का फैलाव भी हो रहा है। साहित्य के क्षेत्र में सोशल मीडिया ने एक नया आयाम खोल दिया है। फेसबुक, व्हाट्सअप के आगमन से आदि काल के साहित्य से लेकर समकालीन साहित्य तक का अध्ययन करने का बड़ा सौभाग्य हमें प्राप्त होता है। नए रचनाकारों को एक अच्छा प्लेटफॉर्म मिलता है। साहित्यिक संवाद एवं विमर्श के लिए एक बेहतरीन मंच समाज के सामने खुलता है। सोशल मीडिया का धरातल कागज़ और कलम की भूमिका को अपदस्थ कर एक नई पृष्ठभूमि तैयार करता है। "सोशल मीडिया लेखक को सीधे पाठक वर्ग से जोड़ देती है।"[2] पाठक रचनाओं को पढ़कर आलोचक का दायित्व तुरंत ही बखूबी निभा सकता है।

हिंदी जनसंचार माध्यमों की सबसे प्रिय एवं अनुकूल भाषा बनकर निखरी है। जनसंचार संसाधनों में आई तकनीकी समृद्धि का प्रभाव हिंदी भाषा पर पड़ा है। रेडियो, टी.वी, कंप्यूटर, इंटरनेट और पत्रकारिता के अत्याधुनिक तकनीकों से हिंदी भाषा आज जुड़ी हुई है। हिंदी हमारी

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विजय कुमार संदेश के यात्रा-वृतांत में प्रकृति एवं संस्कृति का अनोखा संगम

मनुष्य प्रकृति व सौंदर्य का प्रेमी होता है। यात्रा करना मनुष्य की नैसर्गिक प्रवृति है। मनुष्य के विकास की गाथा में यायावरी का महत्त्वपूर्ण योगदान है। हर आदमी अपने जीवन काल में कभी न कभी, कोई न कोई यात्रा अवश्य करता है। पर सृजनात्मक प्रतिभा के धनी अपने यात्रा अनुभवों को पाठकों के सम्मुख प्रस्तुत कर यात्रा-साहित्य की रचना करने में सक्षम हो पाते हैं। यात्रा साहित्य के माध्यम से लेखक के यात्रा अनुभवों को पाठकों के साथ बाँटना और पाठकों को भी उन स्थानों की यात्रा के लिए प्रेरित करना संभव है। इन स्थानों की प्राकृतिक विशिष्टता, सामाजिक संरचना, भाषा एवं संस्कृति की जानकारी भी इस साहित्य से प्राप्त होती है। लेखक प्रकृति प्रेम, प्रकृति सौंदर्य, भाषा, स्मृति आदि को अपने शुद्ध मनोभावों से प्रकट करता है। जो साहित्य में समाहित होकर एक नई विधा का रूप ले लेता है। ऐसी साहित्य विधा को यात्रावृतांत कहते हैं।

वर्तमान समय के विख्यात लेखक के रूप में विजय कुमार सन्देश का नाम उल्लेखनीय है। वे कवि, कहानीकार, आलोचक होने के साथ-साथ यायावर भी हैं। उन्होंने ग्यारह यात्रा संस्मरण भी लिखे हैं। यात्रा में विशेष रूचि रखने के कारण उन्होंने मॉरीशस, अमरीका, श्रीलंका, उज्बेकिस्तान, अंडमान, अबुदाबी और दुबई जैसे विदेशी राज्यों की यात्रा की है। भारत में हिमाचल प्रदेश, राजस्थान, झारखंड, कश्मीर आदि जगहों पर भी उन्होंने यात्रा की है। इन सभी जगहों के बारे में उन्होंने यात्रा सस्मरण भी लिखे हैं, जिससे पाठक भी भाव विभोर होकर यात्री का अनुभव कर सकते हैं। यात्रा साहित्य में लेखक अपने यात्रा के प्रत्येक स्थान और क्षेत्रों का संयोजन करता है, जिनको वह अद्भुत सत्य के रूप में ग्रहण करता है। अपने हृदय में उमड़नेवाली भावनाओं को सशक्त रूप में अभिव्यक्त भी करता है। विजय कुमार संदेश ने अपने यात्रा सस्मरणों में एक जिज्ञासु की तरह समाज, संस्कृति, प्रकृति और परिवेश को देखने-परखने का प्रयास किया है।

'हिमाच्छादित उतुंग शिखर और धुली हरियाली' नामक यात्रा वृतांत में लेखक ने कश्मीर के सोनमर्ग, गुलमर्ग और पीर की गली की सुन्दरता का वर्णन किया है। संसार के सुन्दरतम स्थलों में कश्मीर का अपना विशेष महत्व है। इसी कारण से कवियों, लेखकों और पर्यटकों ने इसे 'धरती का स्वर्ग' कहा है। कश्मीर की वादियाँ हिमाच्छादित पर्वत शिखरों के लिए ख्यात है और अद्भुत हरियाली के लिए भी प्रसिद्ध हैं। चीड़, बाँज और देवदार वृक्ष की शोभा का वर्णन भी लेखक ने किया है। उन्होंने लिखा है "कश्मीर के हिमाच्छादित उतुंग शिखर और धुली हरियाली को देखना और उसे आत्मसात करना किसी भी पर्यटक के लिए सुखद सपने जैसा होता है।"[1]

जम्मू-कश्मीर की राजधानी श्रीनगर में (सितंबर 2014 को) प्राकृतिक कहर के साथ बड़ी विपदा आयी। झेलम नदी का उफनता हुआ पानी श्रीनगर शहर में प्रवेश कर गया और कई जगह पूरी तरह पानी में डूब गए थे। इस घटना के बाद लेखक ने अपने ग्यारह साथियों के साथ श्रीनगर की यात्रा की। उस समय श्रीनगर की श्रीहीन हालत को लेखक इस प्रकार लिखते हैं - "दुनिया का स्वर्ग कहलानेवाला श्रीनगर प्राकृतिक कहर की मार से इतना टूट चुका था कि चतुर्दिक जलते दूधिया बल्बों की रोशनी में भी यह पहली नज़र में हमें श्रीहीन दिखलाई पड़ा, जो अपनी बेबसी और लाचारी की कहानी मूक वाणी में बयां कर रहा था।"[2] श्रीनगर के आजू-बाजू में प्रसिद्ध पर्यटन स्थल और हिल स्टेशन सोनमर्ग और गुलमर्ग स्थित है।

सोनमर्ग की दूरी श्रीनगर से लगभग 90 किलोमीटर की है। जाने की राह में कल-कल, छल-छल करती हुई सिंधु नदी साफ़-स्वच्छ धारा में बहती है। सिंधु नदी कश्मीर से निकलकर वाया पाकिस्तान अरब सागर में जा मिलती है। इसके बाद बाबा अमरनाथ की गुफा के निकट 'बल-टाल' नामक जगह है। इसको देखने के बाद सोनमर्ग के 'ज़ीरो प्वाइंट' है। वहाँ तक पहुँचने के लिए लगभग डेढ़ घंटे की पहाड़ी चढ़ाई करनी है। पहाड़ जड़ से
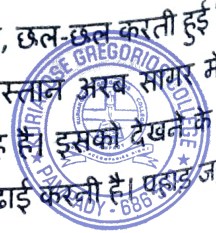
विजय कुमार संदेश ने अपने यात्रावृत्तांत के द्वारा यात्रा साहित्य के लिए अद्वितीय योगदान दिया है। लेखक ने प्रकृति का वर्णन सौंदर्यबोध की दृष्टि से प्रस्तुत किया है। जिससे पाठक के मन में उस विशेष स्थान के प्रति उल्लास के साथ-साथ अवबोध भी जागरित होता है। कश्मीर एवं हिमालय की प्रकृति वर्णना, अत्यंत सजीवता के साथ की गयी हैं। सांस्कृतिक महत्व का उल्लेख भी किया गया है। अत्यंत काव्यमयी भाषा में, प्रवाहमयी शैली में लेखक ने इस यात्रा संस्मरण को उज्ज्वल बनाया है। यात्रा करते हुए प्रकृति सौंदर्य ने लेखक के मन को जितना प्रभावित किया था, उतना ही प्रभाव पाठक मन में भी रचना के अध्ययन करने पर होता है। भारत की प्रकृति एवं संस्कृति का अनोखा सामंजस्य इन रचनाओं में लक्षित होता है।

संदर्भ

1. विजय कुमार संदेश - हिमाच्छादित उत्तुंग शिखर और धुली हरियाली (साहित्य दर्पण) - पृ. 23

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6. विजय कुमार संदेश - कोहरे के चादर में लिपटी चाँदनी (संग्रथन) - पृ. 29

प्रस्तुतकर्ता

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असिस्टेंट प्रोफेसर

हिन्दी विभाग, के.जी. कॉलेज

पाम्पाड़ी, कोट्टयम, केरल

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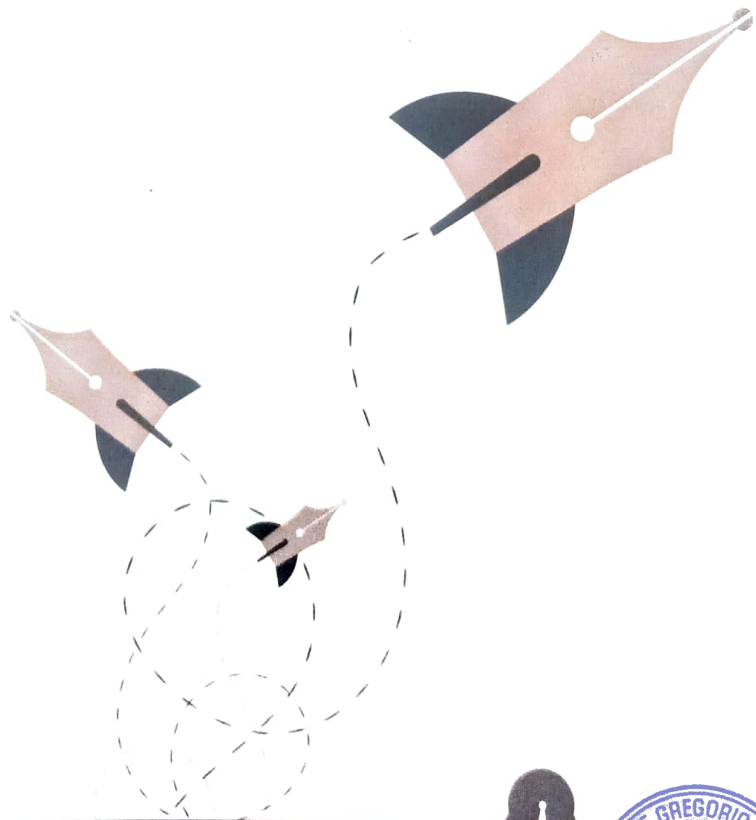
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ज़हीर कुरेशी के ग़ज़लों में मानवबोध

❑ डॉ. प्रिया ए.*

शोध सारांश

गजल का सर्वसाधारण अर्थ है – माशूक से बातचीत का माध्यम। ग़जल शेरों से बनती हैं। हर शेर में दो पंक्तियाँ होती हैं। शेर की हर पंक्ति को 'मिसरा' कहते हैं। ग़ज़ल की खास बात यह है कि उसका प्रत्येक शेर अपने आप में एक संपूर्ण कविता होती है। इसका संबन्ध ग़ज़ल में आनेवाले अगले–पिछले अथवा अन्य शेरों से नहीं होता है। अतः हम कह सकते हैं कि जितने शेर हो उतनी ही स्वतंत्र कविताएँ हैं।पहलेपहल 'ग़ज़ल' में केवल प्रेम पूर्ण भाव ही निहित थे। पर वर्तमान समय में 'ग़ज़ल' को एक नया मोड़ मिल गया है। समकालीन समय के संकटों को, समस्याओं को ग़ज़ल में स्थान मिलता है। समकालीन हिन्दी कविता भूमंडलीकरण के इस वर्चस्ववादी समय को जिस प्रकार शब्दबद्ध करती है, उसी गहराई के साथ हिन्दी के ग़ज़लकार ज़हीर कुरेशी अपने ग़ज़लों में मानवीय संकटों के त्रस्त परिवेश में मूल्यों की आवश्यकता प्रस्तुत करते हैं। 2017 में प्रकाशित उनका एक नया ग़ज़ल संग्रह है – रास्तों से रास्ते निकले। प्रस्तुत संग्रह में उन्होंने समकालीन समाज की समस्याओं को दर्ज किया है। आजकल अपसांस्कृतिक बोलबाले के कारण मानवीय मूल्यों का क्षरण हो रहा है। इस विद्रूपात्मक परिवेश को वे अपनी रचना में व्यक्त करते हैं।

Keywords : प्रेम पूर्ण भाव, विद्रूपात्मक परिवेश ,वैश्वीकृत परिवेश, समाज की पक्षधरता

'ग़ज़ल' नामक साहित्यिक विधा पर्शियन और अरबी भाषाओं से उर्दू में आयी। ग़ज़ल का सर्वसाधारण अर्थ है – माशूक से बातचीत का माध्यम। ग़ज़ल शेरों से बनती हैं। हर शेर में दो पंक्तियाँ होती हैं। शेर की हर पंक्ति को 'मिसरा' कहते हैं। ग़ज़ल की खास बात यह है कि उसका प्रत्येक शेर अपने आप में एक संपूर्ण कविता होती है। इसका संबन्ध ग़ज़ल में आने वाले अगले–पिछले अथवा अन्य शेरों से नहीं होता है। अतः हम कह सकते हैं कि जितने शेर हो उतनी ही स्वतंत्र कविताऐं हैं।

पहलेपहल 'ग़ज़ल' में केवल प्रेम पूर्ण भाव ही निहित थे। पर वर्तमान समय में 'ग़ज़ल' को एक नया मोड़ मिल गया है। समकालीन समय के संकटों को, समस्याओं को ग़ज़ल में स्थान मिलता है। समकालीन हिन्दी कविता भूमंडलीकरण के इस वर्चस्ववादी समय को जिस प्रकार शब्दबद्ध करती है। उसी गहराई के साथ हिन्दी के ग़ज़लकार ज़हीर कुरेशी अपने ग़ज़लों में मानवीय संकटों के त्रस्त परिवेश में मूल्यों की आवश्यकता प्रस्तुत करते हैं। 2017 में प्रकाशित उनका एक नया ग़ज़ल संग्रह है – रास्तों से रास्ते निकले। प्रस्तुत संग्रह में उन्होंने समकालीन समाज की समस्याओं को दर्ज किया है। आजकल अपसांस्कृतिक बोलबाले के कारण मानवीय मूल्यों का क्षरण हो रहा है। इस विद्रूपात्मक परिवेश को वे अपनी रचना में व्यक्त करते हैं।

वैश्वीकृत परिवेश में साहित्य अपनी बहुस्वरता से मनुष्य की, समाज की पक्षधरता को दर्ज करता है। भूमंडलीकरण से उपजी अपसंस्कृति की पदचाप सब कहीं विद्यमान है। जैसे – बाज़ारवाद, उपभोग संस्कृति, नगरीकरण, औद्योगिकीकरण की सभ्यता ने सामाजिक संरचना के आकार को पलट दिया है। ऐसे अपसांस्कृतिक माहौल में मानवीय मूल्यों की गिरावट हो रही हैं। समाज को ऐसी विद्रूपात्मक परिवेश के प्रति आगाह करना एवं मूल्यों के संरक्षण के द्वारा समाज को सही दिशा प्रदान करना प्रतिबद्ध साहित्यकार का लक्ष्य बनता है।

अवाम को नज़रंदाज़ करके शासन करने वाले सत्ताधारी शासकों की सुविधा भोगी ज़िन्दगी को जनता पहचानती है। पर आम मनुष्य की समस्या को पहचाननेवाला, देखने वाला समाज में कोई नहीं है। आम जनता की परेशानियों को सत्ताधारी वर्ग अनदेखा करते हैं। ऐसी हालत को ग़ज़लकार ने यों व्यक्त किया है–

"सत्ताधीशों को 'खास' याद रहे
हैं करोड़ों में आम, भूल गए।"1

अक्सर समाज में जनता का ध्यान ताज़ी खबर की ओर खींचता चला जाता है। हाशिएकृत वर्ग की पीड़ा को, समस्याओं को कोई भी समझने के लिए तैयार नहीं होता। समय की ऐसी हकीकत को बयान करती है – ये पंक्तियाँ–
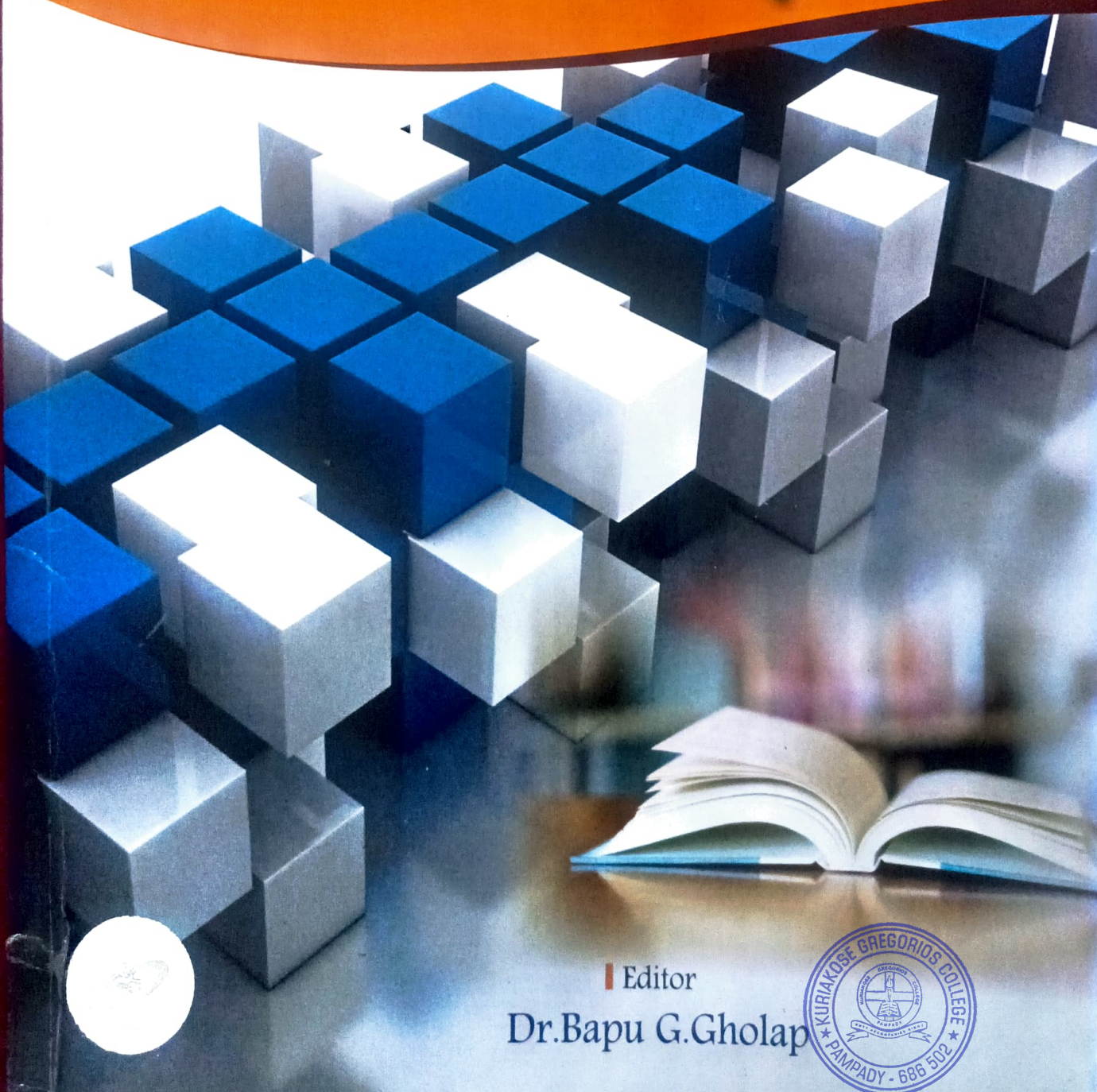
"ताज़ा खबर ने खींचा हमेशा सभी का ध्यान

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विद्यावार्ता ®

Editor

Dr.Bapu G.Gholap

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प्रवासी हिन्दी कविता में भारतीयता का परिदृश्य

डॉ. प्रिया ए.

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प्रवासी साहित्य, हिन्दी साहित्य की ही एक शाखा है, जो अपनी रचनाओं के द्वारा प्रवास की संस्कृति, संस्कार एवं वहाँ के भू-भाग से जुड़े लोगों की स्थितियों से अवगत करने का कार्य कर रही है। प्रवासी हिन्दी साहित्य हिन्दी साहित्य से जुड़ी हुई एक नवीन विधा एवं चेतना है जो प्रवासियों के मनोविज्ञान से जुड़ी है। प्रवासी साहित्य द्वारा साहित्यकार अपनी मातृभूमि से जुड़ा रहता है। भारत से दूर अन्य देशों में बसे भारतीयों के अथक प्रयासों से ही वर्तमान समय में प्रवासी साहित्य समृद्ध और सशक्त बना हुआ है।

प्रवास में रहनेवाले भारतीयों ने अपनी संवेदनाओं को वाणी दी तो वह प्रवासी साहित्य बन गया। वैश्वीकरण, बाज़ारीकरण एवं प्रौद्योगिकी के इस उत्तराधुनिक युग में प्रवासी साहित्य की अनभूत संवेदनाओं के बहुआयामी परिदृश्य को हम देख सकते हैं; जैसे कि - हिन्दी भाषा के प्रति प्रेम, मातृभूमि के प्रति प्रेम, पाश्चात्य और भारतीय संस्कृति का द्वन्द्व-गृहातुरता, भारतीय संस्कृति की गरिमा, सामाजिक-राजनीतिक समस्याएँ एवं स्वत्वबोध की चिंता। 'मेरे पासपोर्ट का रंग' नामक कविता में तेजेन्द्र शर्मा मातृभूमि के प्रति अपने मन का श्रद्धा भाव प्रकट करते हैं। 'पासपोर्ट' या पारपत्र किसी राष्ट्रीय सरकार द्वारा जारी दस्तावेज़ है, जो अंतर्राष्ट्रीय यात्रा के लिए उसके धारक की पहचान और राष्ट्रीयता को प्रमाणित करता है। भारत में पासपोर्ट का रंग नीला होता है। पर ब्रिटेन में इसका रंग लाल होता है। जब कवि विदेश गए तो उनका पासपोर्ट भी नीले रंग से लाल हो गया। विदेशी राज्य के नागरिक होने पर भी उसके मन में भारतीय राष्ट्रगान की गूँज इस प्रकार छायी रहती है-
मेरा पासपोर्ट नीले से लाल हो गया है।
मेरे व्यक्तित्व का एक हिस्सा
कहीं खो गया है।

मेरी चमड़ी का रंग आज भी वही है
मेरे सीने में वही दिल धड़कता है
जन गण मन की आवाज़; आज भी
कर देती है मुझे सावधान।"[1]

भारतीय नागरिक से विदेशी नागरिक होने पर भी अपनी अस्मिता की पहचान के लिए वे देश, राष्ट्रगान एवं भारतीय संस्कृति से जुड़े रहना चाहते हैं।

'हिन्दी को संयुक्त राष्ट्र की भाषा बनानी है' नामक कविता में तेजेन्द्र शर्मा दो बातों की ओर जनता को आगाह करते हैं। विदेश में रहकर विदेशी भाषा ज़रूर पढ़नी चाहिए, वहाँ के त्योहारों का मनाना भी चाहिए। पर दूसरी ओर अपनी राष्ट्रभाषा का उत्थान भी हर नागरिक का कर्तव्य बनता है। इस उत्थान को कामना करते हुए वे लिखते हैं-

"भारत का प्रवासी दिवस अंग्रेज़ी में मनाना है
लेकिन हिन्दी को संयुक्त राष्ट्र की भाषा बनाना है।
तीज लोहड़ी दशहरा भला कैसे मनाएँ
हम संत वैलेण्टाइन से फुरसत भी तो पाएँ
त्योहार हर विदेशी, सभी को मनाना है
लेकिन हिन्दी को संयुक्त राष्ट्र की भाषा बनाना है।"[2]

भाषाई संस्कृति को सुरक्षित रखने के दायित्व को यहाँ अभिव्यक्त किया है। हिन्दी को संयुक्त राष्ट्र की भाषा घोषित करने का आह्वान भी किया गया है।

पद्मेश गुप्त की कविताओं में प्रवासी जीवन के अनेक पहलुओं का समग्र चित्र आकलित किया गया है। उनकी राय में प्रवासी नागरिक दोहरी नागरिकता को स्वीकार करता है। अपनी कर्मभूमि ब्रिटेन में रहकर भी उन्होंने भारतीय मूल के लोगों को भारत से जुड़े रहने का आह्वान किया है। इस तथ्य का सशक्त दस्तावेज़ बनी हुई है 'दोहरी नागरिकता' शीर्षक कविता-
"एक नये स्वप्न में जी रहे हैं
आजकल कृष्ण,
किसी ने उनसे कहा है
कि वे अब
दोनों के साथ रह सकते हैं,
यशोदा के भी और देवकी के भी !
नहीं देना पड़ेगा
अब उन्हें तौल कर
इस प्रश्न का उत्तर
कि वे किससे अधिक प्रेम करते हैं

केरल : महामारी से उत्पन्न लोक परम्पराएँ

डॉ. प्रिया ए.

भारत का प्रत्येक अंचल महामारी की त्रासदी से गुजरा है। संकटों के उस दौर में मनुष्य की अदम्य जिजीविषा ने उसे इन महामारियों में संघर्ष करके उबरने की ऊर्जा प्रदान की। अतीत के ये साक्ष्य हमारी लोक परम्परा में स्रोत के रूप में अंकित हैं। लोक परम्परा में जीवन शैली, पारिस्थितिकी, पहचान के सांस्कृतिक आयाम सब निहित है। किसी विशेष क्षेत्र में निवास करने वाले लोगों के पारम्परिक धर्म, त्योहार, पर्व, रीति-रिवाज़ एवं कला को लोक संस्कृति का नाम दिया जाता है। महामारी से उत्पन्न केरल की लोक परम्पराओं का उल्लेख लोकजीवन के कुछ मुद्दों के माध्यम से प्रस्तुत करना चाहती हूँ।

कलाएँ समय के दर्पण होती हैं। इस मायने में लोककलाएँ अतीत के साक्ष्य को प्रस्तुत करने में सक्षम सिद्ध होती हैं। केरल की लोककलाओं के अंतर्गत पडयणी, कलमेषुत्तु, कल्मपाट्टु, मुडियेट्टु, सर्पम तुल्लल, तिरयाट्टम और तेय्यम आते हैं।

पडयणी

केरल की प्राचीन लोक संस्कृति का प्रतीक है पडयणी। भगवती के मंदिरों में इस अनुष्ठान कलारूप का आयोजन होता है। गाँवों में फसल की कटाई के समय इसका आयोजन होता है। 'चेचक' की महामारी से पूरे गाँव की जनता की रक्षा के लिए पडयणी कला का आयोजन होता था। आज के समय में भी पडयणी का आयोजन इसी उद्देश्य की पूर्ति के लिए किया जाता है। तप्पु (एक प्रकार का बाजा), कैमणी (छोटी घंटी), चेंड़ा (वाद्योपकरण) जैसे वाद्योपकरण को बजाकर, पडयणी की वेश-भूषा के लिए पश्पर्णं (सुपारी के पेड़ के फूलों के गुच्छे का आवरण) को निश्चित आकार में काट-छाँट कर हल्दी, कोयला और लाल पत्थर के साथ ... रंग वेश-भूषा को पहनकर (कोलम) मशाल की रोशनी में पडयणी का आयोजन होता है। यह केरल के मध्य ... है।

Polycarbonate nanocomposite fibres and thin films with versatile morphological, optical and thermal properties

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ARTICLE INFO

ABSTRACT

Polymer nanocomposites are versatile materials with wide variety of applications. The present contribution elaborately discussed about the preparation and characterization of polycarbonate (PC) nanocomposites incorporated with oleic acid (OA) capped cadmium sulphide (CdS) nanoparticles. The variation in properties based on the surface area of polymer composites was studied by the preparation of both nanofibres and thin films. It was observed that the properties are in close relation with the surface morphology of the prepared composite materials. The composites exhibit absorption in the ultraviolet as well as in the visible region of the spectrum. Quenching of emission in the ultraviolet region with a simultaneous increase of emission in the visible region by the addition of filler content was observed. The thermal stability gradually increased with increase of nanofiller content. The glass transition temperatures of PC nanocomposite fibres and thin films were also increased by the increase of CdS nanoparticles.
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1. Introduction

The properties associated with nanomaterials are outstanding compared to the bulk counterparts due to large surface area to volume ratio [1]. A polymer nanocomposite is a combination of a polymer matrix and a filler in which any one of the component must be nano in size [2,3]. Large number of polymers were utilized to prepare nanocomposites with innumerable properties. Polycarbonate (PC) is a thermoplastic material with a range of excellent utilities that covers household to advanced aerospace applications. The main reasons for the wide applications are its superior optical properties, transparency, impact strength, temperature resistant properties, toughness and other mechanical properties [4,5]. One of the major advantages of polycarbonate is the ability to mould into suitable size and shape.

Electrospinning and spin coating are the most simple and widely accepted methods to prepare nanofibres and thin films respectively [6,7]. The electric potential applied on the polymer jet should be sufficient to overcome the surface tension force developed during electrospinning. The splitting and splaying of the polymer jet finally lead to the deposition of fibres on the target

with opposite polarity. Solution parameters (concentration, viscosity and conductivity), process parameters (applied potential, working distance and flow rate) and ambient parameters (temperature and humidity) are the factors affecting surface morphology and average diameter of the electrospun fibres [8]. Polymer films are widely used in sensors, solar cells, filtration scaffolds, nanocatalysis and various optoelectronic applications. To reduce the film thickness as far as possible is the major challenge during thin film preparation by spin coating method. Formation of a thin film depends on various material properties like surface tension, viscosity, drying rate, boiling point and vapour pressure. It also depends on various spinning parameters like acceleration, deposition time and rotational speed [9].

A suitable preparation method is essential to ensure the qualities of a nanomaterial as a suitable filler for a polymer nanocomposite. Cadmium sulphide (CdS) nanoparticle is a well-known semiconductor material blessed with many attractive properties. Homogeneous distribution of nanoparticles in the polymer matrix is essential for the formation of a useful nanocomposite. This can be improved by preventing the agglomeration tendency of nanoparticles by surface protection using suitable capping agents. Oleic acid (OA) was proved to be a highly efficient capping agent as it effectively reduces segregation of nanoparticles [10,11].
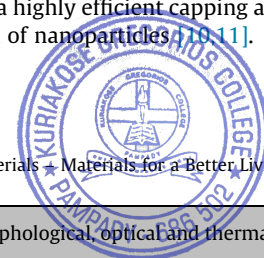
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The present work discussed about the preparation of OA capped CdS nanoparticles by a chemical precipitation method. This also explains the preparation of CdS nanoparticles dispersed PC-CdS nanocomposite fibres by electrospinning and thin films by spin coating methods. The properties associated with the nanofibres and thin films were compared with the help of various characterization techniques.

2. Materials and methods

Poly (Bisphenol A carbonate) (PC) pellets with average molecular weight of 45,000 g/mol was purchased from Sigma-Aldrich USA. Cadmium chloride ($CdCl_2$), Sodium sulphide (Na_2S), Oleic acid (OA), Dichloromethane (DCM) and N, N dimethyl formamide (DMF) were procured from Merck India Ltd.

0.1 M $CdCl_2$ solution in ethanol was taken, added OA which was 1% of the total volume and stirred well. 0.1 M solution of Na_2S was then added slowly and again stirred for further 1 h. The precipitated CdS nanoparticles were filtered, washed and dried. 14 w/v% of PC solutions in 1:1 DCM-DMF mixture were prepared in three different conical flasks. 2, 4 and 6 w/w% of CdS nanoparticles were added to the PC solutions separately, sonicated and stirred for 24 h. Nanocomposite fibres were prepared by electrospinning with a flow rate of 0.5 mL/h, working distance of 15 cm and an applied voltage of 20 kV. Thin films were prepared by spin coating method by a 10 min reset programme with an initial rotational speed below 1000 rpm and accelerated up to 3000 rpm.

The prepared nanofibres and thin films were characterized by methods like scanning electron microscopy (SEM), Transmission electron microscopy (TEM), UV–Visible spectroscopy, Photoluminescence (PL) spectroscopy, Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC).

3. Results and discussion

3.1. Surface morphology of nanofibres and thin films

The surface morphological characters of nanocomposite fibres and thin films were carried out by SEM and TEM investigations.

SEM analysis was done using TESCAU VEGA 3 SBH scanning electron microscope and the images were shown in Fig. 1. A 14 w/v% of PC solution in 1:1 DCM-DMF mixture upon electrospinning was produced beadless nanofibres of average diameter 90 nm (Fig. 1(a)). Formation of almost uniform fibres can be observed from the histogram of PC nanofibres provided (Fig. 2(a)). The average diameter of the fibres increased with increase of nanofiller content in the composite (Fig. 1(b-d)). PC nanocomposite fibres with 2 w/w% CdS nanoparticles, the average diameter becomes 106 nm (Fig. 1(b)). The average diameter becomes 122 nm by the addition of 4 w/w% of the nanofiller into the PC matrix (Fig. 2(c)). For 6 w/w% of the CdS nanoparticles in the PC composite fibres the average diameter becomes 127 nm (Fig. 1(d)).

A small variation of fibre uniformity is vivid from the histograms provided in Fig. 2. The histograms of the PC-CdS nanocomposite fibres show that the fibre uniformity gradually decreased with the increase of CdS nanoparticles (Fig. 2).

The standard deviation values of plane PC and that of PC-CdS nanocomposite fibres were measured using Image J software. The average diameter and the corresponding standard deviation (S.D) values are provided in Table 1.

The gradual increase of standard deviation with the increase of average diameter is an indication of decrease in fiber uniformity. 14 w/v% PC in 1:1 DCM-DMF mixture has a solution viscosity of 52.3 cP. The solution viscosity becomes 55.8, 58.1 and 60.4 cP for 2, 4 and 6 w/w% of CdS nanoparticles respectively. The gradual increase in the viscosity of the polymer solution by the addition of nanofiller caused extensive polymer entanglement. This was subsequently instigated an increase in fiber average diameter [12].

Table 1
Average diameter and standard deviation (S.D) of plane PC and PC-CdS nanocomposite fibres.

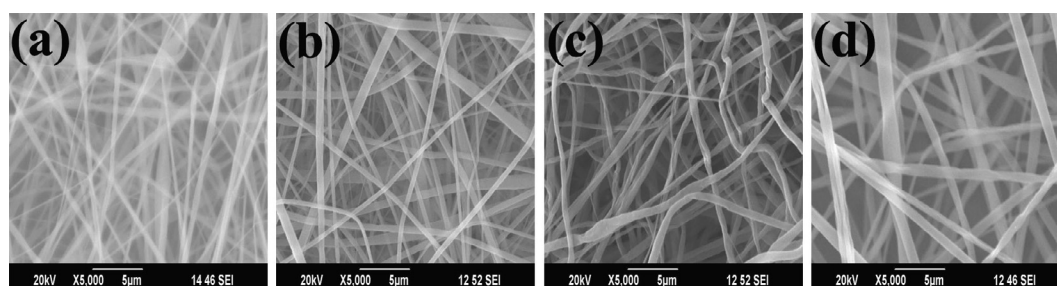| Fibre sample	Average diameter (nm)	S.D (nm)
Plane PC	90	12.242
PC-CdS 2 w/w%	106	19.912
PC-CdS 4 w/w%	122	26.748
PC-CdS 6 w/w%	127	31.024

Fig. 1. SEM images nanofibres of: (a) Plane PC; (b) PC-CdS 2 w/w%; (c) PC-CdS 4 w/w%; (d) PC-CdS 6 w/w%.
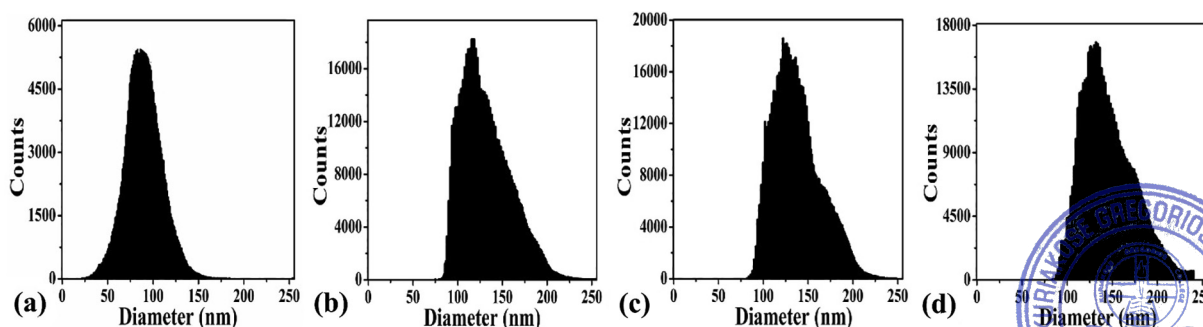

Fig. 2. Histograms of nanofibres of: (a) Plane PC; (b) PC-CdS 2 w/w%; (c) PC-CdS 4 w/w%; (d) PC-CdS 6 w/w%.

Surface morphology analysis of PC-CdS nanocomposite thin films was carried out using Zigma TM series field emission scanning electron microscope (FE-SEM) and the images are shown in Fig. 3.

Plane PC thin film exhibits a porous surface morphology as shown in Fig. 3(a). The porous surface morphology was found to be reduced very much by the addition of CdS nanoparticles. The nanoparticles effectively interacted with the polymer matrix and distributed uniformly all over the film surface. Homogeneous distribution of nanoparticles in the polymer matrix is necessary to develop uniform thin films during spin coating.

Morphology of OA capped CdS nanoparticles and its uniform distribution in the PC composite fibres can be observed from the TEM images shown in Fig. 4. The TEM investigations were done with the help of JEOL JEM 2100 Transmission electron microscope.

TEM image of surface capped CdS nanoparticles reveals reduced agglomeration of particles (Fig. 4(a)). OA as a capping agent has helped to minimize the surface energy and thereby the segregation of nanoparticles. Electrospinning of PC solutions with different nanofiller concentration has generated defect free fibres with uniform dispersion of CdS nanoparticles (Fig. 4(c)).

3.2. Investigation of optical properties

The absorption properties of PC-CdS nanocomposite fibres and thin films were examined with the help of Agilent Technologie
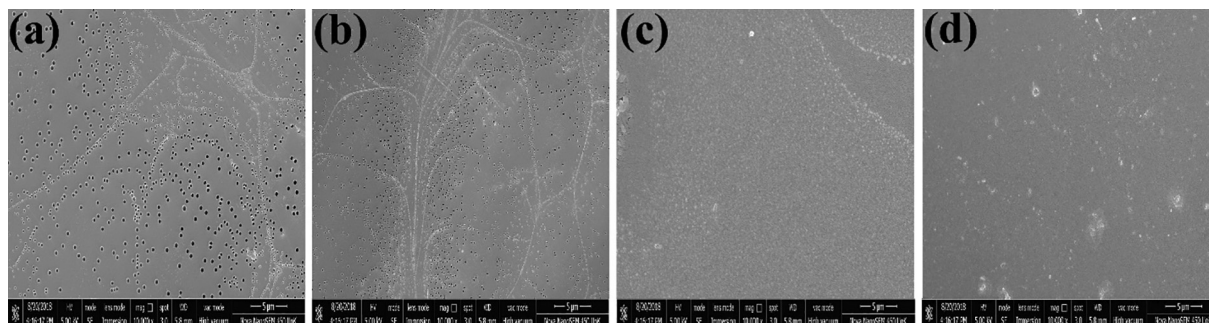

Fig. 3. FE-SEM images of thin films of: (a) Plane PC; (b) PC-CdS 2 w/w%; (c) PC-CdS 4 w/w%; (d) PC-CdS 6 w/w%.
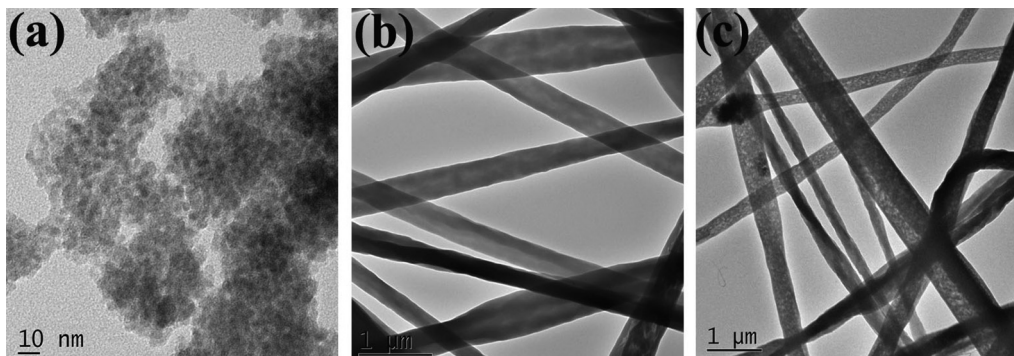

Fig. 4. TEM images of (a) OA capped CdS nanoparticles; (b) Plane PC nanofibres; (c) PC-CdS nanocomposite fibres.
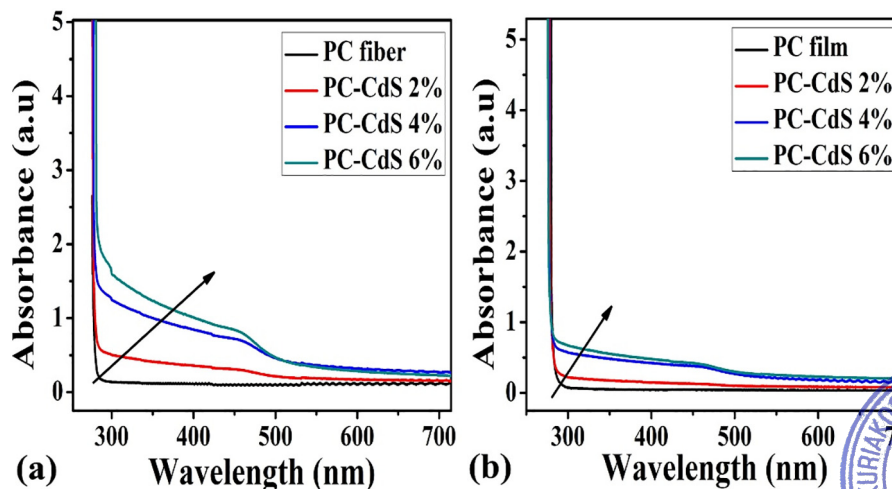

Fig. 5. The UV–Vis spectra of (a) plane PC and nanocomposite fibres; (b) Plane PC and nanocomposite thin films.

Carry 5000 UV–Visible spectrophotometer. Fig. 5 shows the absorption spectra of plane PC fibres, PC-CdS nanocomposite fibres, plane PC thin film and that of the corresponding thin film composites. Plane PC fibres and thin films exhibit excellent ultraviolet absorption capability. From the absorption spectra, PC fibres absorb sharply at a wavelength of 277 nm and that of the thin films at a wavelength of 279 nm. Absorption in the UV region corresponds to the chemical structure of PC with repeating phenyl groups in the polymer chain [13]. The unsaturated multiple bonds in PC causes n-π* electronic transitions from the carbonyl group and is the reason for the corresponding absorption band in the molecule [14]. Ultraviolet absorption property of PC and its application as a UV blocking agent were reported earlier [15].

In the case of PC-CdS nanocomposite fibres absorption start from the higher wavelength region of the visible spectrum. This is then gradually increased to the lower wavelength region. The intensity of absorption in the visible region was found to increase with increase of the amount of CdS nanoparticles in the composite.
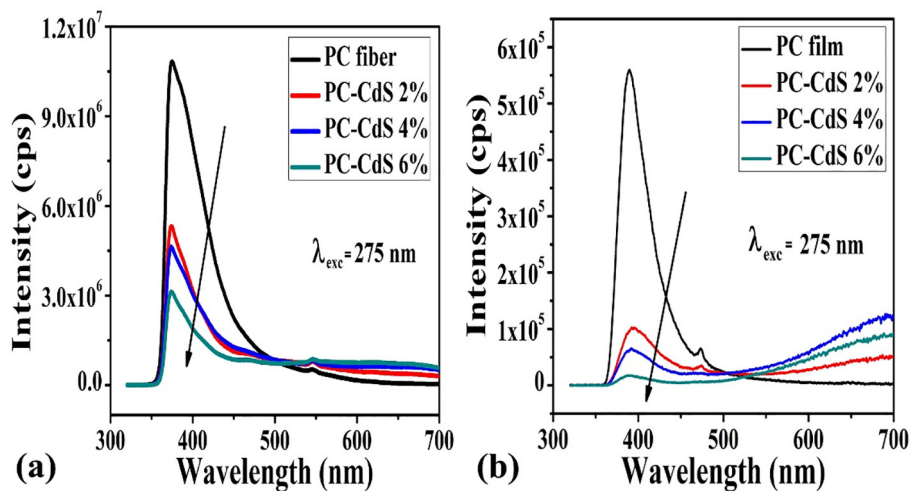

Fig. 6. PL spectra of (a) PC fibres and PC-CdS nanocomposite fibres; (b) PC thin film and PC-CdS nanocomposite thin films.
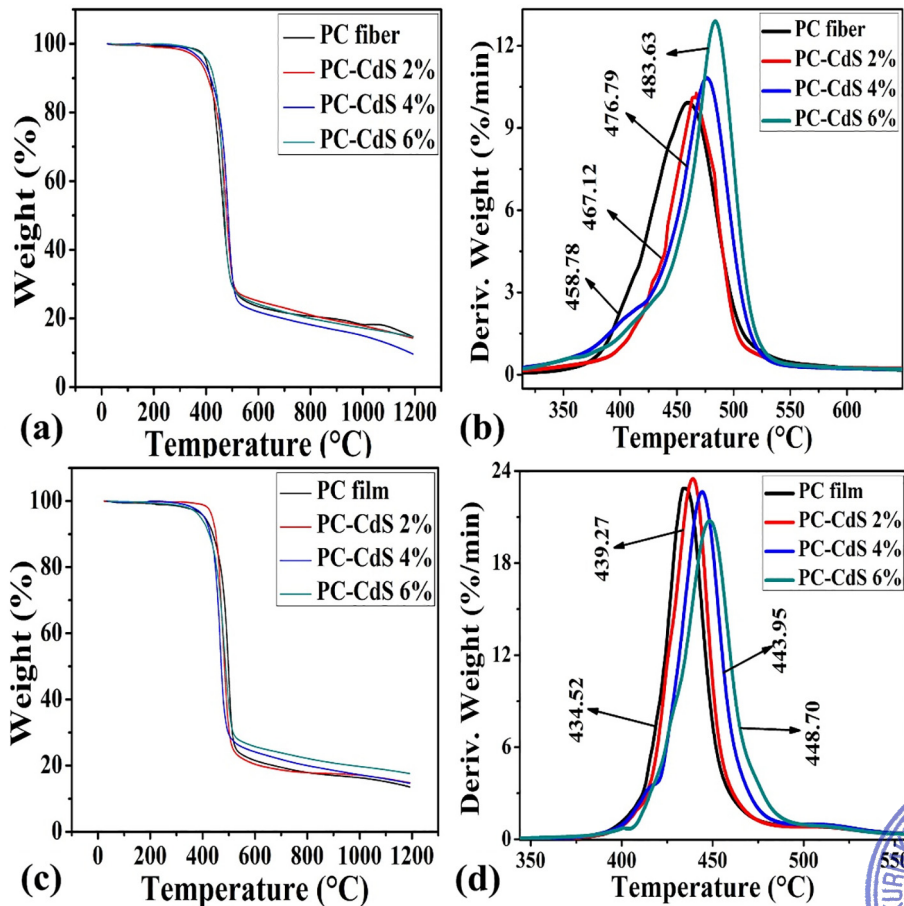

Fig. 7. Thermal studies of PC-CdS nanocomposites: (a) TGA plots of fibres; (b) dTG plots of fibres; (c) TGA plots of thin films; (d) dTG plots of thin films.
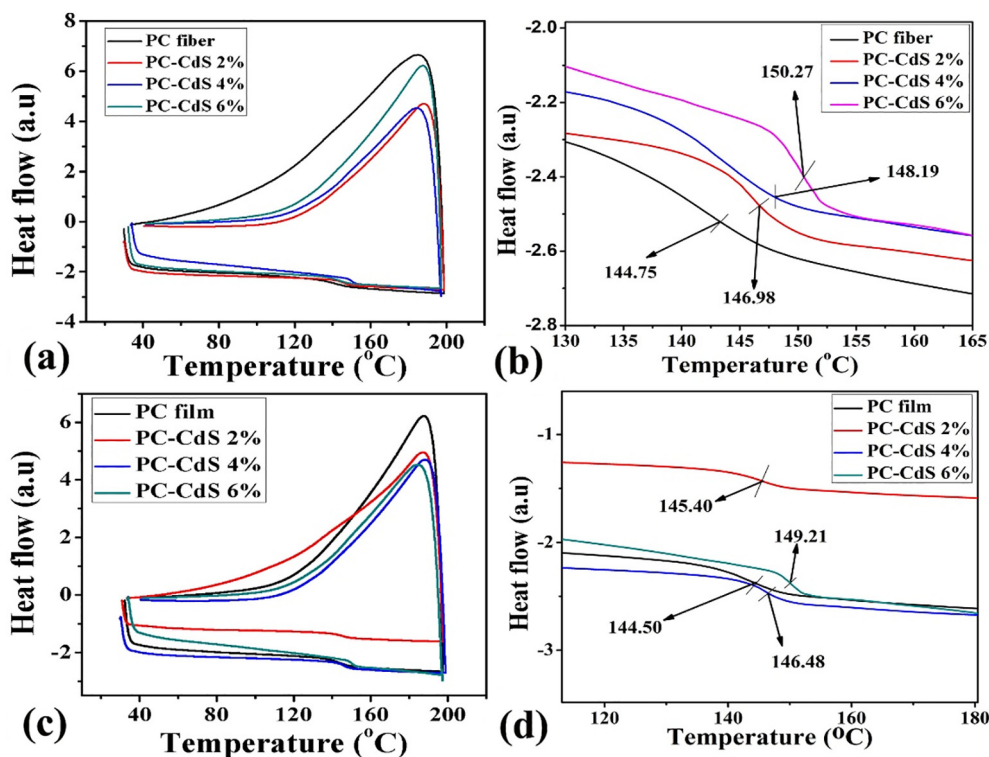
Fig. 8. DSC plots with magnified images of PC-CdS nanocomposites: (a) & (b) Fibres; (c) & (d) Thin films.

But for PC composite thin films, the intensity of absorption in the visible region was less compared to the composite fibres. Nanocomposite formation leads to the appearance of new energy levels due to excess crosslinking in the system. This was the reason for the observed shift in absorption edge. The absorption in the visible region of the spectrum and its enhancement by increasing the amount of nanoparticles can be attributed to the formation of extended system of conjugated bonds and decrease in the forbidden band width [16,17]. The comparatively higher absorption intensity observed in nanocomposite fibres than in thin films can be attributed to the more feasible electronic transitions due to the larger surface area.

PC-CdS nanocomposite fibres and thin films were investigated for their photoluminescence properties. The study was done with the help of Flourolog 3 TCSPC photoluminescence spectrophotometer. The PL spectra of plane PC fibre, thin film, nanocomposite fibres and nanocomposite thin films were investigated in detail and provided in Fig. 6.

At an excitation wavelength of 275 nm, plane PC fibres and thin film exhibit sharp emission at 373 nm in the ultraviolet region. But for PC-CdS nanocomposite fibres and thin films the emission intensity decreased very much with nanofiller loading. At the same time, the nanocomposite fibres and thin films undergo an emission in the visible region of the spectrum. The intensity of emission at the visible region found to increase with increase of CdS concentration in the composite. Uniform distribution of nanoparticles has strong interaction with the PC matrix that effectively quenched the emission at the UV region.

3.3. Thermal studies

The thermo gravimetric analysis (TGA) of the composites was done with the help of Perkin Elmer STA 6000 instrument. The TGA thermogram with the corresponding dTG curves of the nanofibres and that of the thin films are shown in Fig. 7.

The dTG curves established an increase in thermal stability of the nanocomposite fibres and thin films by the addition of nanofiller content. Uniform distribution of CdS nanoparticles has created high degree of fibre entanglement that subsequently caused increased stability. PC nanocomposite fibres show higher stability than the corresponding thin films. This can be attributed to the surface morphological properties of the fibres with more active surface area.

One of the most important property of an amorphous polymer, the glass transition temperature (T_g) was measured by differential scanning calorimetry (DSC) analysis with the help of TA instrument DSC Q20, Germany. Various DSC plots showing T_g values of the plane PC fibre, plane PC thin film, PC-CdS nanocomposite fibres and PC-CdS nanocomposite thin films are given in Fig. 8.

It was observed that the T_g gradually increased by the increase of nanofiller content in the polymer matrix. The variation was in almost similar pattern for the nanofibres and thin films. A slight increase can be observed for nanocomposite fibres. The restricted mobility of the polymer chain by the addition of nanofillers is the reason for the increase in T_g.

4. Conclusion

The nanofibres prepared by electrospinning and thin films by spin coating methods have noticeable morphological, optical and thermal properties. OA capped CdS nanoparticles were proved to be suitable candidates for the fabrication of nanocomposites of polymers with tunable size dependent properties. Uniform distribution of nanoparticles in the polymer matrix was possible by the reduction in agglomeration due to efficient surface capping. PC-CdS nanocomposites exhibit absorption in the ultraviolet as well as in the visible region. The absorption in the visible region was found to increase with increase in the amount of nanoparticles in the polymer matrix. Nanocomposite fibres exhibit higher intensity of absorption in the visible region compared to the thin film

composites. The PC nanocomposites exhibit quenching of emission in the ultraviolet region along with emergence of a broad emission in the visible region compared to plane PC fibre and thin film. The intensity of emission in thin films was less compared to that of nanocomposite fibres. Thermal stability of polymer nanocomposites increased gradually with the increase in the nanofiller content. There was a slight increase in the thermal stability of the nanocomposite fibres in comparison with the corresponding polymer thin film composites. The glass transition temperature (T_g) of the composite shows an increasing trend with increase in the percentage of CdS nanoparticles. Here also slight variation was observed for the fibres and thin film composites. This work demonstrates the ability of polymer composite materials to acquire tunable size dependent properties by moulding them into nanofibres and thin films.

Declaration of Competing Interest

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

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ORIGINAL PAPER

A facile approach for the preparation of polycarbonate nanofiber mat with filtration capability

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Abstract

The present day environmental issues demand a lot from scientists and engineers to keep the planet earth safe for its habitats. There were lot of attempts for developing efficient air and liquid filters as the demand increases with an utmost concern of present environmental situations. Thanks to its large surface area to volume ratio, polymer nanofibers and composites are found to be good substitute for conventional filters. As per the research and analysis data, filtration efficiency increases proportional to the reduction of the average diameter of the fibers. In this study, the most efficient electrospinning technology was adopted to prepare polycarbonate (PC) nanofiber mat which yields a very fine surface morphology. There are earlier researches and associated data available about the preparation of PC nanofibers but with average fiber diameter above 1000 nm. In this study, a systematic methodology was instigated to generate PC nanofibers with least average diameter of 90 nm without using any surfactants or salts. The most suitable solvents, solvent proportion, polymer concentration and electrospinning conditions for the formation of the fiber mat are discussed elaborately. PC fiber mat of least average diameter was proved to be highly efficient for particulate matter adsorption using a dust sampling analyzer.

Keywords Electrospinning · Taylor cone · Beaded fiber · Particulate matter · Fiber mat

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Introduction

Air pollution is considered as a great curse of twenty-first century as a result of modernization of all levels of present day life. The air quality of New Delhi, India in November 2019 has been created an emergency situation with thousands of people under threat (Fig. 1). The central pollution control board (CPCB) estimated the national capital's average air quality index (AQI) on 3rd Sunday 4.00 pm as 494. The World Health Organization (WHO) perceived air pollution as a dangerous situation that causes premature deaths around seven million every year worldwide. Out of this 2.6 million premature deaths were reported to be of indoor air pollution. Particulate matter in air is the major reason for indoor air pollution and sources include households, agriculture, industry, automobiles, burning of waste and power plants [1–3]. The victims of indoor air pollution are generally children and women. The ramifications and deaths were attributed to be a result of diseases like stroke, pneumonia, pulmonary diseases, lung cancer and heart disease. It was estimated that more than 80% of the world population are not in a position to access modern technologies. They are still in a situation to depend on inefficient energy sources which again worsen the burning situation.

To use nanofibrous mat as filters for bio-aerosols is a serious concern among scientists particularly during the present outbreak of Covid-19 virus. The potential pandemic has created an emergency situation particularly in the global health care sector. According to WHO the total number of infected COVID 19 cases as on 27th April 2020 were 28,83,603 and killed 1,98,842 people. The Chinese center for disease control and prevention reported that the size of Covid-19 virus is approximately 100 nm. Various types of face masks used for precaution against the virus cannot assure complete protection. WHO has recently given an interim guidance on the use of face masks which emphasized on the standard test methods to ensure the filtration efficiency, fluid penetration resistance and breathability. Virus, allergens, pollens, bacteria and fungus are biological aerosols that result adverse health effects in humans [4]. In this worst scenario, various remediation strategies and measures were being adopted to control air pollution. Microorganisms like viruses usually possess electronegative surface due to the presence of phosphate and carboxyl groups [5]. Most of the nanofibers possess positive charge and that facilitate the effective filtration of viruses and other bio-aerosols [6, 7]. There were various reports on the

Fig. 1 Some of the air polluted regions of Delhi in 2019 November (**a**–**c**)

preparation of nanofiber filter masks and different filters with improved capacity to filter microbiological objects like viruses [8]. Thinner nanofiber membranes with small pores were made to improve the bacterial retention capacity of sterilizing grade filters [9].

Aerosol filters are the most commonly used technique for purifying and sampling of air. There is a growing demand for innovative and efficient scavenging system for the immediate removal of pollutants contaminated in air. Fibrous filters were found to be highly promising and more efficient than conventional air filters [10–12]. The depth filtration capability of fibrous filters is the resultant of diffusion, inertial impaction, interception and electrostatic interaction [13].

Superior filtration efficiency of ultrafine polymer fiber membranes has been recapitulated as a result of high surface-to-volume ratio, high porosity, microscale interstitial space and interconnectivity [14, 15]. In filtration field the term nanofiber is attributed to fibers of average diameter well below 500 nm [16]. There were numerous reports on the diverse applications of nanofiber filter media mainly focused on contaminants and environment. The effective size exclusion nanofibrous mats are well suited for air and water particulate matter removal [17, 18].

Most accepted and well-known method for generating nanofibrous scaffolds for filtration applications is electrospinning. The wide acceptance of this approach is due to its simplicity, cost-effectiveness and the narrow distribution of fiber diameter by which the filtration can be properly controlled [19–21]. Suitable polymer concentration, solvent system, solvent ratio and other spinning parameters are essential for fabricating fibers with least average diameter. The polymer solution taken in the spinneret ejected out of the needle tip by the application of a high electric potential. Both electrical and mechanical forces make use for the ejection of polymer jet from the needle tip. The electrically charged drop at the needle tip assumes a cone shape which is called Taylor cone. This phenomenon is observed when the force due to electric field outweigh the force of surface tension. At this critical electric voltage, the polymer jet starts ejected from the Taylor cone tip. This then undergoes a bending instability and the main jet splits into number of mini jets. Solvent evaporation occurs from the polymer jets during the flight towards the oppositely charged collector [22]. During the movement towards the collector the mini-jets suffer strong competition between different instabilities. This include the whipping instability, Rayleigh instability and axisymmetric conducting mode instability. These instabilities vary depending on the electrospinning and fluid parameters. So optimizing the solution properties and other spinning parameters are crucial for the final morphology of the fibers [23, 24].

The flow of polymer jet from the nozzle tip to the collector undergoes variation in current under an applied voltage. This depends on the charge carrying capacity of the polymer solution. There will be a change of shape of polymer jet at the nozzle tip by the increase of the applied electric current. This is considered as a major factor that determines the final surface morphology of the fiber [25]. There are various reports on the deviation of the average diameter of the electrospun fibers by the variation of the applied electric current. The minimum electron volt required for the deposition of ultrafine fibers during electrospinning is directly related to the needle tip-collection plate distance [26–29].

Another important factor that influences the fiber morphology is the distance between the tip of the needle and the collecting plate. Depending upon the volatility of the solvent, solvent proportion, fiber deposition time, instability interval, evaporation rate and the nature of the polymer, fibers with different morphology particularly porous, beaded, non-uniform or fibers with varying diameters were observed [27, 29]. Adjusting a proper polymer solution flow rate is important as it remarkably affects the transfer of the material and also the velocity of the jet during electrospinning. This will subsequently influence the pore diameter and fiber diameter of the nanofibers deposited [29]. The surface tension and viscosity of the polymer solution jet varies with concentration of the polymer solution [25]. An optimum concentration is essential for the fabrication of uniform and defect free ultrafine fibers. There were various reports on the occurrence of electrospraying process at very low concentrated solutions. Electrospinning was reported to be not convenient at very high concentration which results fibers with large average diameter [30–32]. Solvents play an important role during the entire process of fiber formation from solution preparation to fiber collection. The capacity to dissolve the polymer, its volatility, boiling point and charge carrying capacity have combined effect over electrospinning. The vapor pressure and the dipole moment of the solvent determine the rate of evaporation and conductivity of the polymer jet. The high dipole moment of the solvent influences the surface morphology and average diameter of the fibers [33–36].

Among a large number of promising engineering materials polycarbonate (PC) garnishes a key position with its unique mechanical and physical properties. It is a material with excellent heat resistance, resistance to acid and alkali, impact strength, rigidity, toughness and stable performance in high temperature atmospheres [34, 37]. The above mentioned properties of PC enable it to be a suitable material for filtration, bio-medical, electronics, protective clothing and many other modern applications [38]. Only limited number of studies were done to prepare micro and nano sized fibers of PC by electrospinning technology. Various electrospinning parameters and their influence on the final morphology of the polymer fibers were also reported [39–45]. As it is an amorphous material, it has the ability to possess high residual charge by electrospinning. Preparation of antimicrobial filtration membranes of PC were reported by electrospinning with the addition of quaternary ammonium salt into the polymer matrix [46]. Ultrafine PC fibers were prepared by the addition of hexadecyl trimethyl ammonium bromide (CTAB) with average pore size 504 nm and average diameter of 319 nm with high efficiency [47].

The present study systematically established the preparation of ultrafine beadless PC fibers with average diameter of 90 nm. Fixed concentration of PC solutions were electrospun by varying the solvent proportion, flow rate, applied voltage and distance between the needle tip and the collecting plate (working distance). The surface morphology and average diameter of the generated fibers were thoroughly investigated. The uniform bead free fiber mat with least average diameter was further examined for its filtration ability.

Experimental

Materials and methods

Polycarbonate (PC) pellets were purchased from Sigma Aldrich, USA with molecular weight 45,000 g/mol. Analytical grade solvents dichloromethane (DCM) and *N, N* dimethyl formamide (DMF) were procured from Merck India Ltd.

Electrospinning

In our previous published papers different concentrations of PC in the solvents DCM and DMF were electrospun under constant spinning parameters [32, 34]. A 14 w/v% PC solution in 1:1 DCM–DMF mixture was found to generate beadless fibers with least average diameter of 90 nm. So in the present work the PC concentration was kept constant as 14 w/v% and varied the solvent ratio and other spinning parameters. Electrospinning of PC solutions were done with the help of Espin Nano electrospinning machine supplied by PECO Chennai. The process of formation of fiber mat during electrospinning of PC solution is shown in Fig. 2a. The solution was taken in a 5 mL syringe with needle 0.6×25 mm^2 dimension and connected to one of the electrode. The other terminal was connected to the fiber collecting metal plate. Then voltages of 10, 20 and 30 kV were separately applied to 14 w/v% PC solutions keeping all other parameters constant. Similarly electrospinning continued by varying the flow rate as 0.5, 1 and 1.5 mL/h. Then the process was repeated by setting the needle tip-collection plate distance as 10, 15 and 20 cm. Five different proportions of solvents were experimented with values 1:1, 3:2, 7:3, 4:1 and 9:1. The conductivities and viscosities of these solutions were measured with the help of Eutech instruments Cyberscan PC 300 model conductivity meter and Brookfield digital viscometer CAP 2000 with spindle number 1 respectively. The collected fibers were characterized for surface morphology with the help of TESCAU VEGA 3 SBH scanning electron
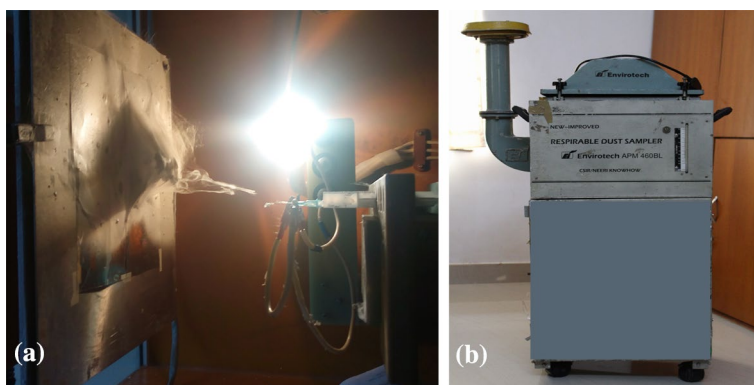

Fig. 2 **a** Formation of PC fiber mat during electrospinning. **b** Respirable dust sampler for particulate matter analysis

microscope (SEM). The water contact angles of the prepared fibers were measured using DMS 401 contact angle instrument.

Respirable dust sampler

The filtration property of PC nanofiber mat produced by electrospinning process was measured with the help of Envirotech APM 460BL Respirale dust sampler (Fig. 2b).

The indoor air pollutants were collected from the kitchen premises of a household on a busy time schedule between 8 am and 12 noon for two consecutive days. A 20.3×25.4 cm (1×8 in.) glass fiber filter paper was used to collect particles. The adsorbed respirable suspended particulate matter (RSPM) will spread over about 18×23 cm area of the glass fiber filter paper after exposure. Loosen the face plate wing nuts and remove the face plate of instrument. Remove the weighed filter paper from its jacket and center it on the support screen with the rough side of the paper facing upward. Replace the face plate and tighten the wing nuts. Set the timer for 2 h for continuous sampling. After sampling was completed, note the final flow rate by removing the wing nuts. Folded the filter in half-length by handling it along its edge with the exposed side inward. Weighed the filter paper after proper drying. Weighed another glass fiber filter paper and placed inside the chamber as discussed above. Then the prepared PC fiber mat was kept over the gap on one side of the instrument which is in between the glass fiber paper and the external sucking hood. Tighten all the screws ensuring the suction of the particulate matter properly through the fiber mat. The experiment was conducted by maintaining the time and atmosphere same as the first one. The process was repeated with fresh glass papers and fiber mat for the next 2 h. The experiment was also done by using PC fiber mats with different thickness.

The histograms of the nanofibers were prepared by using a custom code Image J software. A suitable SEM image was selected, set the scale and selected a scanned area of the image. Along with the histograms average fiber diameter and standard deviation values will be available. The standard deviation values will provide an insight into the variation of fiber uniformity. The bead density of the fibers was also calculated using this software.

Results and discussion

Polycarbonate (PC) was perfectly soluble in the solvent DCM but slightly soluble in DMF. Fibers with least average diameter was obtained for 14 w/v% PC in 1:1 DCM–DMF mixture out of a series of different concentrations experimented [34]. The average fiber diameter increases with increase in the concentration of the polymer solution. This is attributed to the increase in viscosity that can strongly opposes the bending instability of the polymer jet [48]. To confirm whether this PC concentration could produce beadless uniform fibers with least average diameter by the variation of solvent proportion, flow rate, applied potential and needle tip-collector distance, systematic investigations were performed.

Variation in solvent proportion

Different proportions of the solvents DCM and DMF were examined at constant PC concentration and spinning parameters. Both solvents in PC solutions have their own active role to modify and balance various forces acting on the polymer jet during its flight to the target [42]. Various spinning parameters applied for different solvent proportions during electrospining are provided in Table 2. The SEM images of the fibers obtained by the electrospinning of 14 w/v% of PC in different solvent proportions are given in Fig. 3.

Beadless fibers with slight variation in uniformity and average diameter were obtained from all the solvent proportions. 14 w/v% of PC in 1:1 DCM–DMF mixture has generated uniform fibers with an average diameter of 90 nm (Fig. 3a). For 3:2 solvent mixture beadless PC fibers with an average diameter of 388 nm were obtained. The average fiber diameter is 583 nm for PC in 7:3 DCM–DMF solvent system. Non-uniform but beadless fibers with average diameter 752 nm can be observed for PC in a 4:1 solvent mixture. For a 9:1 solvent system non-uniform fibers with average diameter of 816 nm and beadless morphology were obtained. The histograms drawn with the help of Image J software can easily predict the variation of uniformity of the electrospun fibers (Fig. 4). The corresponding standard deviation (SD) values of average diameters are also provided along with the histograms.

The variation in uniformity of the nanofibers obtained from different solvent proportions can be identified from the standard deviation values. This was an interesting observation that the average diameter and non-uniformity increased with decrease of DMF concentration. The large dipole moment possessed by the solvent DMF helps to maintain a high charge density to overcome the surface tension exerted in the polymer jet [34]. Volatile solvent like DCM supports faster dehydration of the nanofibrous mat deposited on the target [49]. So PC solution with higher proportion of DCM caused the formation of non-uniform fibers with
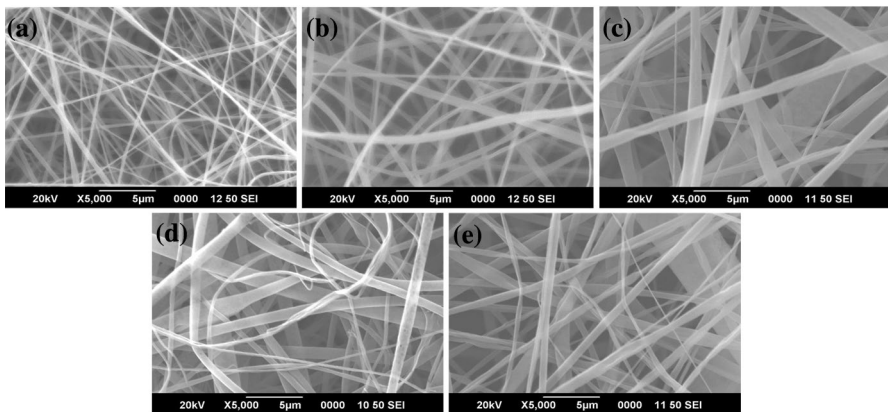

Fig. 3 SEM images of fibers of 14 w/v% of PC in various proportions of DCM–DMF mixture **a** 1:1, **b** 3:2, **c** 7:3, **d** 4:1 and **e** 9:1
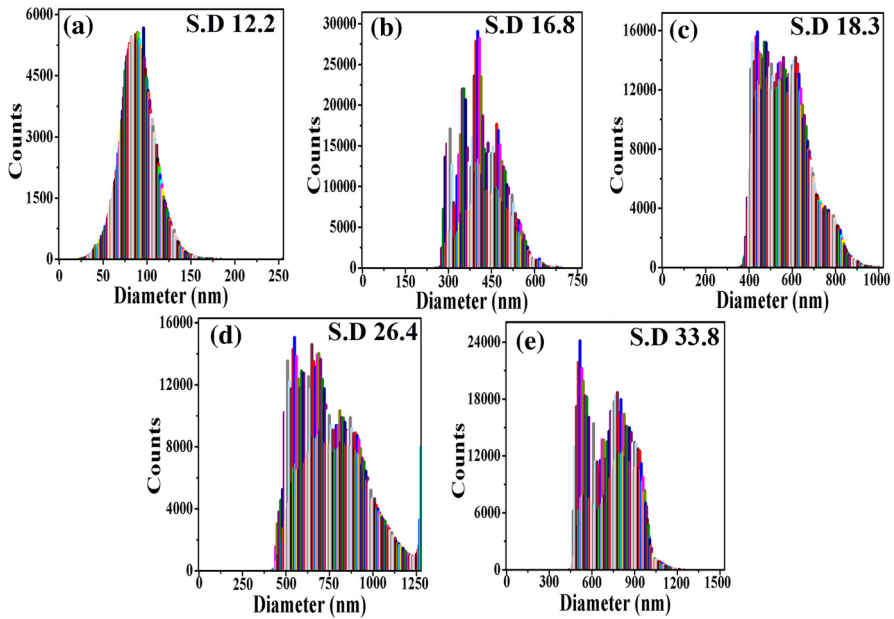
Fig. 4 Histograms of the fibers of 14 w/v% of PC in various proportions of DCM–DMF mixture **a** 1:1, **b** 3:2, **c** 7:3, **d** 4:1 and **e** 9:1. Corresponding standard deviation (SD) values in nanometer are provided in each image

large average diameter. The solution viscosities and conductivities of 14 w/v% PC in different solvent proportions are provided in Table 1.

With the increase of DCM content in the solvent mixture, solution viscosity increased gradually. Meantime the solution conductivity decreased with increase of DCM content in the mixture. The relation between viscosity of the PC solutions and the corresponding values of average diameters is in good agreement with various previous reports. With the increase of DMF content viscosity of the solution decreases and conductivity increases. All these factors together affected the final morphology of PC fibers including uniformity. The variation of average diameter of PC fibers with different solvent proportions is given in Fig. 8a.

Table 1 Solution viscosities and conductivities of PC with different DCM–DMF proportions

DCM–DMF ratio	Viscosity (cP)	Conductivity (µS)
1:1	52.3	3.53
3:2	59.1	3.12
7:3	66.7	2.69
4:1	78.9	1.88
9:1	82.1	0.92

Variation in applied voltage

The SEM images and the corresponding histograms of PC fibers obtained by the electrospinning of 14 w/v% solution in 1:1 DCM–DMF mixture under different applied voltages are shown in Fig. 5. Other spinning parameters like flow rate and working distance were kept as 0.5 mL/h and 15 cm respectively. The standard deviation (SD) values of the average fiber diameter are shown in the histograms provided.

Beaded but almost uniform fibers with average diameter of 137 nm were obtained under an applied voltage of 10 kV. Around 4% bead density was observed by the analysis of the SEM image using Image J software. Surface morphology of PC fibers under 20 kV applied voltage was already studied and the SEM image and histogram are provided in Figs. 3a and 4a, respectively. Under an applied voltage of 30 kV, beadless fibers were formed with slightly non uniform appearance with an average diameter of 382 nm.

An optimum potential was found to be suitable for obtaining uniform beadless fibers with least average diameter. An applied voltage of 10 kV was not sufficient to overcome the surface tension of the polymer solution which results beads on fibers. Applied voltage is an important parameter that has direct influence on the fluid mechanics. Stretching and acceleration of the polymer jet depend on the applied voltage that subsequently influence final fiber morphology. Low electrical conductivity of a solution results beaded fibers due to insufficient polymer jet elongation. There were reports on the decrease in average fiber diameter with increase in electrical conductivity of the solution. Very large applied voltage often results multiple jet formation and subsequently non uniform fibers [50]. The stretching of the polymer jet under the application of a high voltage has also reduced bead formation [51]. The variation of average diameter of the PC fibers with applied voltage is shown in Fig. 8b.

Variation in flow rate

Feed rate of the polymer solution during electrospinning is a prominent element for the shaping up of final morphology of the fibers. There were reports on the reduction of fiber diameter with decrease in flow rate [42]. The SEM images and the
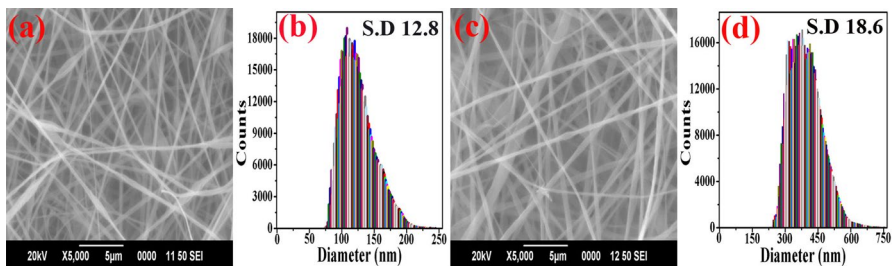

Fig. 5 **a** SEM image of PC fibers of 10 kV voltage. **b** Histogram of PC fibers of 10 kV voltage. **c** SEM image of PC fibers of 30 kV voltage and **d** histogram of PC fibers of 30 kV voltage. Corresponding standard deviation (SD) values in nanometer are provided in each image

corresponding histograms of PC fibers obtained by the electrospinning of 14 w/v% solution in 1:1 DCM–DMF mixture under different flow rates are shown in Fig. 6. Other spinning parameters like applied voltage and working distance were kept as 20 kV and 15 cm, respectively.

Almost uniform but beaded fibers with average diameters of 178 and 236 nm were obtained for 1 and 1.5 mL/h flow rates respectively. Surface morphology of PC fibers under a flow rate of 0.5 mL/h was already studied and the SEM image and histogram are provided in Figs. 3a and 4a, respectively. Large spindle shaped beads were observed for the fibers obtained under a flow rate of 1.5 mL/h. Approximate bead densities of 8 and 11% were observed for the PC fibers formed under the flow rates of 1 and 1.5 mL/h, respectively. Bead formation was due to the net result of various factors during electrospinning. High flow rates were found to be not suitable for a 14 w/v% PC solution in 1:1 DCM–DMF mixture under an applied potential of 20 kV and a working distance of 15 cm to get defect free nanofibers. The polymer jet could not get enough time for complete evaporation of solvents before depositing on the target under such a high flow rate [52]. The variation of average diameter of PC fibers with the variation of flow rate is shown in Fig. 8c.

Variation in needle tip-collector distance

The distance between the needle tip and the metallic collection plate (working distance) is another important parameter that influences electrospinning of polymer solutions. The selection of an appropriate working distance depends on the type of the polymer, solution and spinning parameters. Variation of the surface morphology of the fibers obtained by changing the needle tip-collector distance was investigated by SEM analysis. SEM images and the corresponding histograms with the standard deviation values of average diameter are provided in Fig. 7.

There was considerable difference in the fiber morphology with respect to the needle tip-collection plate distance. Working distances of 10 and 20 cm have generated beaded fibers from a 14 w/v% PC solution in 1:1 DCM–DMF mixture under an applied voltage of 20 kV and flow rate of 0.5 mL/h. Non-uniform fibers with average diameters of 136 and 238 nm were obtained at working distances 10 and 20 cm respectively. An intermediate working distance of 15 cm was found to be
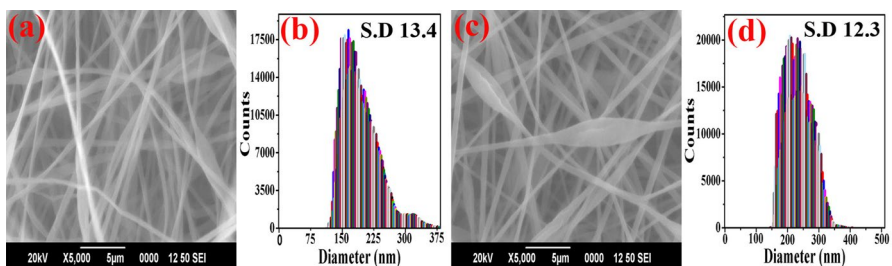

Fig. 6 **a** SEM image of PC fibers of 1 mL/h flow rate. **b** Histogram of PC fibers of 1 mL/h flow rate. **c** SEM image of PC fibers of 1.5 mL/h flow rate and **d** histogram of PC fibers of 1.5 mL/h flow rate [standard deviation (SD) values are provided]
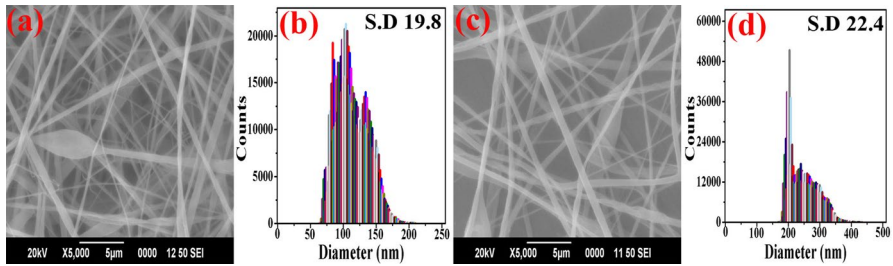
Fig. 7 **a** SEM image of PC fibers of 10 cm working distance. **b** Histogram of PC fibers of 10 cm working distance. **c** SEM image of PC fibers of 20 cm working distance and **d** histogram of PC fibers of 20 cm working distance [standard deviation (SD) values are provided]
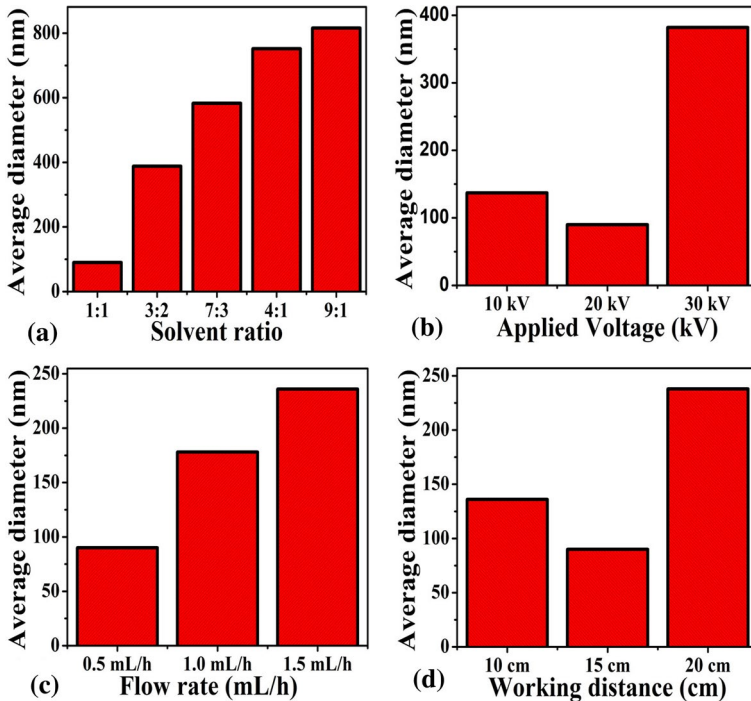

Fig. 8 The variation of average fiber diameter with **a** solvent ratio, **b** applied voltage, **c** flow rate and **d** working distance

most suitable for the production of uniform beadless fibers of least average diameter and the SEM image and histogram are shown in Figs. 3a and 4a respectively. Insufficient evaporation at a smaller distance was the reason for the formation of beads on fibers at a distance of 10 cm. Early drying of the polymer jet may be the reason for the increase in average diameter and bead formation at a distance of 20 cm. At the same time the distance tends to change the areal density due to the variation of the spread of fibers [26]. Figure 8 is given for the comparison of variation of

average diameter of fibers produced under different solution and spinning parameters. Figure 8d represents the variation of average diameter of PC fibers under different working distances.

Water contact angles are useful for the determination of wettability of polymer materials. The sessile drop method was adopted using 0.03 μL water for a sample. The water contact angles of the PC fibers prepared with different solvent proportions, flow rate and needle tip-collector distance are shown in Fig. 9.

The electrospun PC fibers exhibit hydrophobic characteristics with slight variation in the water contact angle values. It was observed that the hydrophobic character was maximum for the PC fibers with least average diameter. The surface roughness of a material with lyophilic groups on the surface is inversely related to the water contact angle [53]. Superhydrophobic porous polymer membranes were reported to have high oil/water filtration efficiency [54]. PC nanofibers prepared in the solvents DCM and DMF under different solution and spinning parameters with corresponding average fiber diameter and contact angle values are given in Table 2.

Under a thorough investigation of various spinning and solution parameters on the surface morphology and average diameter of the fibers an important information was drawn. 14 w/v% PC in 1:1 DCM–DMF mixture under an applied voltage of 20 kV, flow rate 0.5 mL/h and needle tip-collector distance of 15 cm were the most favorable parameters for obtaining beadless and uniform fibers with least average diameter.

Indoor air pollution analysis

Polymer fiber mat with ultrafine morphology was reported to have large surface area that enables efficient adsorption of particulate matter. PC fiber mat prepared by
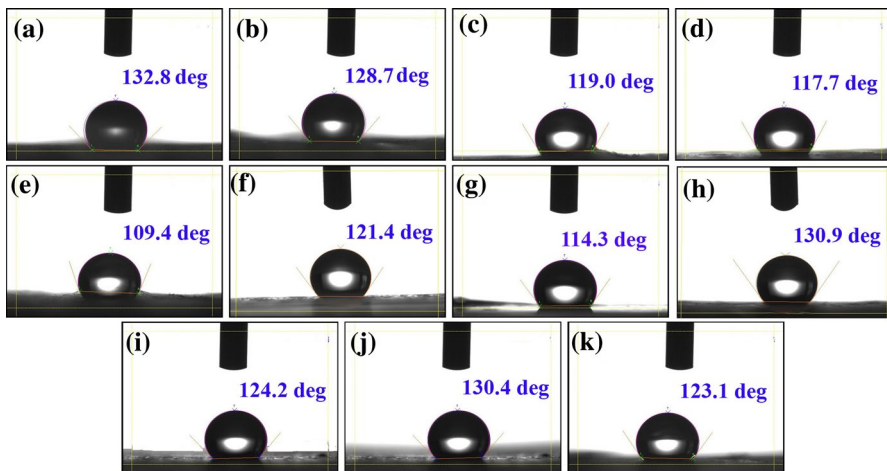

Fig. 9 Water contact angles of PC fibers prepared under different parameters **a** 1:1, **b** 3:2, **c** 7:3, **d** 4:1 and **e** 9:1 solvent ratios, **f** 1 mL/h and **g** 1.5 mL/h flow rates, **h** 10 kV and **i** 30 kV voltages, **j** 10 cm and **k** 20 cm working distances

Table 2 Solution and spinning parameters used for the preparation of PC nanofibers with the corresponding fiber average diameter and contact angle values

Sl.no.	Concentration of PC solution (w/v%)	Solvent ratio	Flow rate (mL/h)	Working Distance (cm)	Voltage (kV)	Average diameter (nm)	Contact angle (°)
1	14	1:1	0.5	15	20	90	132.8
2	14	3:2	0.5	15	20	388	128.7
3	14	7:3	0.5	15	20	583	119.0
4	14	4:1	0.5	15	20	752	117.7
5	14	9:1	0.5	15	20	816	109.4
6	14	1:1	1.0	15	20	178	121.4
7	14	1:1	1.5	15	20	236	114.3
8	14	1:1	0.5	15	10	137	130.9
9	14	1:1	0.5	15	30	382	124.2
10	14	1:1	0.5	10	20	136	130.4
11	14	1:1	0.5	20	20	238	123.1

electrospinning method has superior air and water filtration ability. By the decrease of fiber diameter adsorption capability increases due to the increase of surface area. Electrospinning of 14 w/v% PC in 1:1 DCM–DMF mixture deposited as a fiber mat which exactly functions like a filtration membrane.

The fiber mat was introduced over the slit in between the analysis chamber and the external hood of the particle dust analyzer. Particulate matter formed by the burning of firewood, coconut husk and coconut shell on a 4 h busy time period was used for the investigation of indoor air pollution. The glass fiber filter paper was exposed to fume with and without placing the PC fiber mat. Weights of the glass fiber filter paper before and after the experiment were taken. The photographs of the glass filter papers without and with using the fiber mat are shown in Fig. 10.
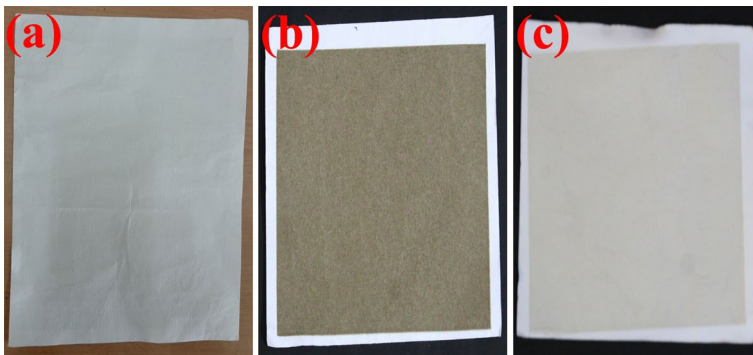

Fig. 10 Glass filter papers used for particulate matter adsorption **a** plane filter paper, **b** filter paper without using PC fiber mat and **c** filter paper with fiber mat separation

The color difference of the glass fiber filter papers with and without placing the PC fiber mat in the dust analyzer shows the extent of adsorption of the air pollutants by the fiber mat. The dark color at the exposed surface of glass fiber filter paper without the use of fiber mat shows a 2 h continuous direct exposure (Fig. 10b). But color over the glass filter paper used with the fiber mat was reduced very much due to the adsorption of particulate matter by the fiber mat barrier (Fig. 10c). Filtration efficiency of the fiber mat is directly related to reduction in adsorption of particulate matter by the glass fiber filter paper. This was calculated using the formula:

$$V = QT,$$

where V is the volume of air sampled in m^3, Q is the average flow rate in m^3/minute and T the total sampling time in minute. The flow rate of air was measured as 1.5 m^3 per minute for 2 h.

Mass concentration of the particulate matter less than 10 micron (PM_{10}) diameter was calculated by the equation:

$$\text{Mass concentration of } PM_{10} = (W_f - W_i)/V,$$

where PM_{10} is particulate matter less than 10 micron diameter (aerodynamic diameter) and unit of mass concentration of PM_{10} is $\mu g/m^3$. W_i is the initial weight and W_f the final weight of glass filter paper in g. Mass concentration of PM_{10}, average mass of PM_{10} and filtration efficiency of PC nanofiber mats with different thickness are provided in Table 3.

From the weights of glass fiber filter papers, the mass concentrations of the particulate matter deposited for 2 h time period with and without using fiber mat and their mean values were calculated. Finally the reduction in the deposited particulate matter was calculated from the average PM_{10} values. A single layer of PC fiber mat with thickness 1.64 mm has a filtration efficiency of 89.22%. Filtration efficiency was found to increase with increase in the number of layers of PC fiber mat. But there was not much difference in the filtration efficiency of three layer and four layer fiber mats. A maximum of 93% filtration efficiency was observed for PC fiber mats with 4.33 and 5.72 mm thickness. It was clearly established that the PC fiber mat acts as an efficient filter for the particulate matter passing through it. This is also

Table 3 Mass concentration of PM_{10}, average mass of PM_{10} and filtration efficiency of PC nanofiber mats with different thickness

Filtration experiment	Mass of PM_{10} ($\mu g/m^3$)		Average mass of PM_{10} ($\mu g/m^3$)	Filtration efficiency (%)
	1	2		
Without using PC fiber mat	1120	1188	1154	
PC fiber mat with 1.64 mm thickness (one layer)	124.43	124.21	124.32	89.22
PC fiber mat with 3.16 mm thickness (two layer)	95.70	93.54	94.62	91.80
PC fiber mat with 4.33 mm thickness (three layer)	80	81.66	80.83	93
PC fiber mat with 5.72 mm thickness (four layer)	80.09	79.56	79.82	93.08

worth to mention that the adsorbed particulate matter coming under a hazardous class with size less than 10 microns. The images of the PC fiber mat before and after adsorption of particulate matter are provided in Fig. 11.

The entire surface of the fiber mat was covered by particulate matter including carbon. The fiber mat did not exhibit any sign of degradation. The degree of adsorption of particulate matter on the PC nanofiber mat was further investigated with the help of SEM analysis. The SEM images of the fibers with various magnifications are provided in Fig. 12.

The micrographs show that particulate matter below 10 micron was almost adsorbed and covered over the entire surface of the nanofiber mat. It was observed that PC fiber mat with least average diameter has superior particulate matter adsorption property. Such a material could successfully deliver large surface area for minute particulate adsorption.

Conclusion

The attractive properties of polycarbonate has been utilized constructively by molding it into a versatile material with large surface to volume ratio. This was done by a systematic and a novel method by the optimization of solution and electrospinning parameters. A 14 w/v% PC was selected as the most suitable concentration from our previous research work. Suitable solvent proportion was picked from a list of different proportions of solvents with the help of electrospinning process. The selection of a solvent which has high volatility and another solvent which has large dielectric constant and dipole moment, helped to create a highly manageable electrospinning atmosphere. The interesting observation was that a solvent mixture with equal amount of these two solvents, resulted fibers which has least average diameter. Multiple experiments were conducted by varying different parameters such as
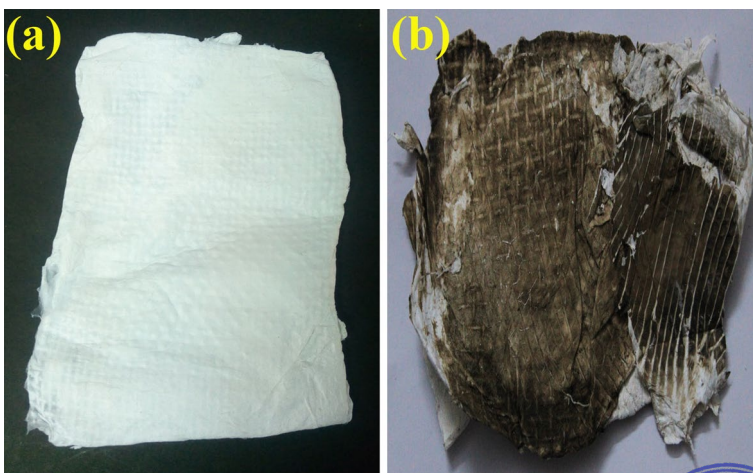

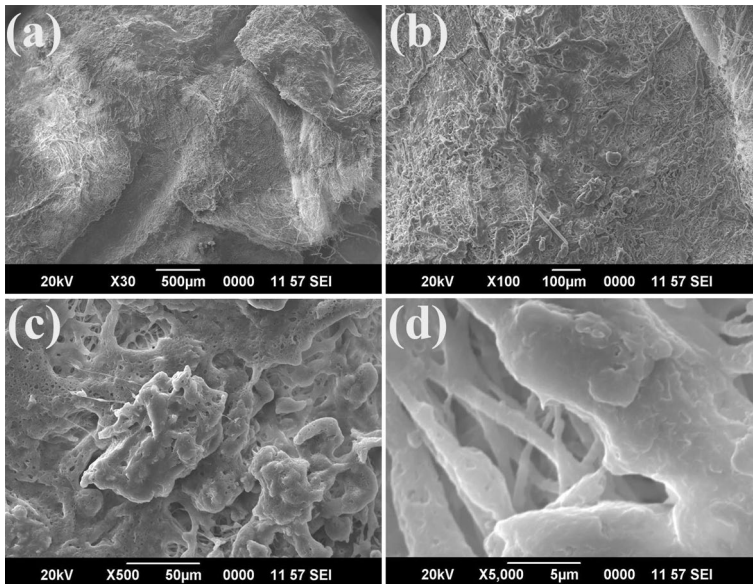Fig. 11 PC fiber mat **a** before and **b** after adsorption of particulate matter

Fig. 12 SEM images of PC nanofiber mat after particulate matter adsorption with different magnifications **a** ×30, **b** ×100, **c** ×500 and **d** ×5000

the applied voltage, flow rate and needle tip-collector distance for the electrospinning of 14 w/v% PC in 1:1 DCM–DMF mixture, and collected associated valuable information with each experiment. It is observed that a proper evaporation of the solvent and drying of the polymer jet are essential for the formation of beadless and uniform ultrafine fibers. A very low flow rate of 0.5 mL/h, medium applied potential of 20 kV and a needle tip-collector distance of 15 cm were found to be the highly favorable spinning conditions. A '14 w/v% PC in 1:1 DCM–DMF mixture' under the above spinning parameters has successfully generated a uniform layer of nanofibers with average diameter 90 nm. The PC nanofiber mat exhibited excellent particulate matter adsorption capability in indoor air pollution monitoring experiment. The efficiency of the PC fiber mat was monitored by a continuous 2 h indoor air sample exposure. There was 93% reduction in the adsorption of particulate matter by the glass filter paper which indicates a superior filtration efficiency of the PC fiber mat with least average diameter. In the current environmental challenges this would be definitely a supportive finding in the field of air quality assessment and purification.

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ORIGINAL PAPER

Green Light Emitting Cadmium Sulfide Nanoparticles with Coral Surface Morphology

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Abstract

Cadmium sulfide (CdS) is an important semiconductor material that has been utilized constructively for various modern applications. There were lot of works regarding the preparation of CdS nanoparticles. The present work has utilized a chemical precipitation method with and without using a capping agent. Even though the solvent system used for the preparation is a new one and provides a non-toxic reaction medium, this work mainly focused on the advantages of surface capping on nanoparticles. CdS nanoparticles prepared by surface capping with oleic acid (OA) exhibit many unique properties compared to the uncapped nanoparticles. The coral shaped surface morphology and the bright green fluorescence observed in OA capped CdS nanoparticles were not reported elsewhere. Strong absorption of radiation in the visible as well as in the ultraviolet region with a large band gap was also observed in capped CdS nanoparticles. Blue shift in emission with an intense peak was another unique character observed in the surface capped CdS nanoparticles. Morphological, structural, optical and thermal properties of the capped and uncapped CdS nanoparticles were systematically investigated.

Keywords Nanoparticles · Photoluminescence · Agglomeration · Band gap

Introduction

Inorganic semiconductors with attractive properties contribute a keen position among various materials of interest in nanotechnology. Large number of modern functional nanodevices of attractive utilities were prepared out of such materials [1–5]. The unique properties possessed by such materials are not usually observed in their bulk materials [6]. The large surface area possessed by a material in its nano dimension is the reason for the foresaid unique properties. The vast applications of II–VI semiconductors like ZnO, ZnS, CdO and CdS are widely accepted in the arena of nanotechnology wonders. One of the most attractive features of such a material is its size dependent optical properties. The emission bands can be observed in any part of the spectrum, ranging from ultraviolet to infrared. These luminescent characteristics are mainly due to various properties such as recombination of electron–hole pairs (excitons), conduction band-valence band radiative transitions and transitions among impurity energy levels [7]. An impressive band gap of 2.42 eV was reported to be possessed by CdS nanoparticles [8].

Applications taking advantage of CdS nanoparticles are optoelectronic devices, detectors, solar cells, nonlinear optical materials, sensors, various luminescence devices and photochemical catalysis [9–13]. It has been observed that CdS nanoparticles emit different luminescence bands such as green, yellow and red in the visible region [14]. A number of suggestions were put forward to explain the origin of these visible emissions such as involvement of cadmium vacancies, sulfur vacancies, cadmium interstitials, and sulfur interstitials [15, 16]. Nanoparticles with attractive fluorescence have immense uses as per literature [17]. Various reports established a minuscule average particle size of around 5 nm for CdS quantum dots and it could be above or below this value [18–20]. It was also reported that several tens of nanometers were possible for

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ROLE OF INDIAN STARTUP ECOSYSTEM TOWARDS SUSTAINABLE DEVELOPMENT OF INDIA

☐ **Gopu Vijayan***
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ABSTRACT

ABSTRACT

Every sector of the economy has to make their contribution towards the development of our nation in terms of social, economical and environmental needs. Out of the various sectors, industrial sector or entrepreneurship has a significant role to play. But, it is important to note that 'more of the same' will not contribute anything sustainable to our nation. Industrial sector should bring out something innovative or creative to face these social, economic and environmental challenges. Startup firms are the sources from which innovative or creative thinking comes out. India is in third position in terms of total number of startups. This paper attempts to give an insight on Indian startup ecosystem and its role in making India a sustainable nation.

Keyword: *Entrepreneurship, startups, innovation, sustainable development, startup ecosystem*

INTRODUCTION

According to the UN, sustainability is "development that meets the needs of the present without compromising the ability of future generations to meet their own needs." 'Economic growth', 'social development' and 'environmental sustainability' and are the three pillars of a nation's wealth. Making a balance between these three pillars is the main challenge faced by every nation. For this, the contribution of every sector is inevitable. Out of the various sectors, industrial sector or entrepreneurship can contribute much towards developing a sustainable India. The contribution should be in such a way that identifies the fact that 'more of the same' will not contribute anything sustainable to the nation. Innovation is the key aspect in sustainability, so our country needs something creative. That is the only way through which economic growth and environmental sustainability can be balanced.

What is a startup?

In the Indian context, a startup is a young company which is

> ➢ Formed for a period of less than 3 years.
> ➢ At funding stage.
> ➢ An entrepreneurial venture/partnership/temporary business organisation.
> ➢ Engage in the development/distribution of innovative products.
> ➢ Revenue not more than Rs 25 crores.
> ➢ Not formed through splitting/restructuring.

According to National Association of Software

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and Services Companies (NASSCOM), India ranks third globally with more than 50000 startups. India has a lot of promising startup unicorns to show before the world like Paytm, Flipkart, Justdial, freecharge etc

REVIEW OF LITERATURE

(Abhyankar, 2014)In his article'The Government of India's Role in Promoting Innovation through Policy Initiatives for Entrepreneurship Development', he is in the opinion that In spite of having a large publicly funded science and technology infrastructure and a sizeable education base, India has not been able to realize its innovative potential due to a fragmented innovation ecosystem.

(Hockerts & Wustenhagen, 2009)discussed in detail the contribution of small emerging and established firms towards sustainability transformations and found that small emerging firms are showing more interest on sustainability opportunities as they do not have anything to lose as they are on the primary stage.

(Zahra, Newey & Li, 2014) are in the opinion that when sustainability factor is considered, we need a different startup ecosystem. In order to increase its impact, sustainability oriented startups need an ecosystem which understands the goal and purpose of sustainability-oriented entrepreneurship.

(Venkatanarayana, 2016)deals withstartups in India and their role in making India sustainable. As per the author, startups are playing a significant role in India's sustainability. It creates an innovative environment which directs every developmental activity towards sustainability.

(Kalyani, 2016)pointed the relevance of innovation and creativity in entrepreneurship and how these can lead to sustainability. Author concluded that, to become creative and innovative, startup firms significantly need the support of various allied agencies related to funding, mentoring, research and development etc.

SIGNIFICANCE OF THE STUDY

Sustainability indicates the ability to satisfy the needs of the coming generation without interrupting the needs of the present generation.

Sustainable development is an essential need for any country. Each and every sector of the economy has the responsibility to secure the future of our nation. Out of the various sector, industrial sector has a special role as it can contribute economically, socially and in terms of environment needs.

Startup ecosystem is a crucial member of industrial sector which can bring innovation in a way that contributes much towards sustainability. This paper attempts to give a conceptual background of the role of Indian startup ecosystem towards sustainable development. Thus, it has got relevance in the present scenario.

OBJECTIVES OF THE STUDY

➢ To make an overview of Indian Startup ecosystem.
➢ To understand how the Indian Startup ecosystem can contribute towards making India sustainable.

METHODOLODY

The study is purely based on secondary data. The objectives of this study is fulfilled through historical data collected from various journals, articles, bulletins, official websites of Indian government and allied agencies.

WHAT IS A STARTUP ECOSYSTEM…....??

A startup ecosystem is formed by various stakeholders such as people, startup in their various stages and various types of organisations interacting as a system to create and flourish new startup companies. These organisations can be further classified into universities, research organisations, supporting organisations (such as incubators, accelerators etc), funding organisations, service providers and big companies. This can be illustrated with the help of the following diagram
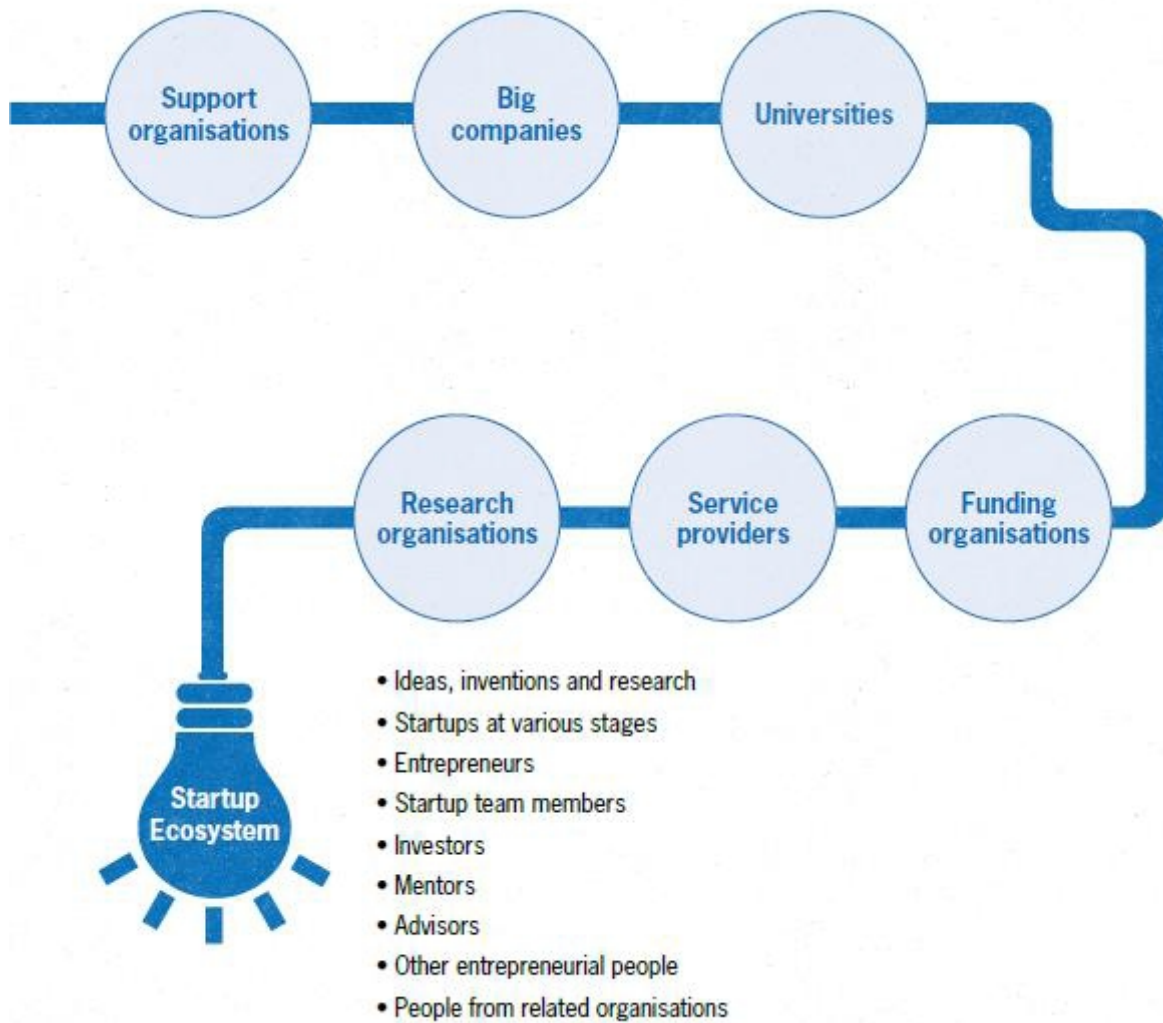
INDIAN STARTUP ECOSYSTEM

India is one of the top five countries in the world with more than 50000 startups and also with an annual increase of 800 startups.

Technology based startups					
E- commerce	B2B	Consumer Internet	Mobile apps	Saas	Others
33 %	24 %	12 %	10 %	8 %	13 %

Non technology-based startups							
Engineering	Construction	Agri products	Textile	Printing & packaging	Transport & Logistics	Outsourcing & Support	Others
17 %	13 %	11 %	8%	8 %	6 %	5 %	32 %

Some of the key features of Indian startup ecosystem are
❖India is the third largest startup hub in the world.
❖India is the youngest startup nation in the world average age of startup founders in India is 28 years.
❖Majority of start-ups/investors are from metro cities.
❖Only 9 % of the startup founders are women.
❖Startups have created approximately 80000-100000 jobs

INDIAN STARTUP ECOSYSTEM – A COMPARISON WITH OTHER COUNTRIES

PARAMETERS	INDIA	USA	UK	ISRAEL	CHINA
Global InnovationIndex[1]	35.59	60.56	59.78	53.55	53.28
Total Number of Startups	40000-50000	100000-150000	10000-15000	6000-8000	50000-60000
Time taken to set up a new business (Days)	15-30	4-8	4-6	10-15	30-40
Corporate tax rate	30 %[2]	39 %	20 %	26 %	25 %
Number of VC firms	300+	800+	NA	200+	NA
Number of angel investors	1800	300000	18000	600+	NA
Number of incubators/accelerators	140+	1500+	50+	130+	2400+

Source: NASSCOM Report on Indian Startup ecosystem

[1]The Global Innovation Index (GII) is an annual ranking of countries by their capacity for, and success in, innovation
[2]Tax exemption for the first three years

Goal 1	End poverty	⬆
Goal 2	Zero hunger	↗
Goal 3	Good health and well being	↗
Goal 4	Quality education	00
Goal 5	Gender equality	➡
Goal 6	Clean water and sanitation	↗
Goal 7	Affordable and Clean Energy	➡
Goal 8	Decent Work and Economic Growth	⬆
Goal 9	Industry, Innovation and Infrastructure	↗

Goal 10	Reduced Inequalities	00
Goal 11	Sustainable Cities and Communities	➡
Goal 12	Responsible consumption & Production	00
Goal 13	Climate Action	⬆
Goal 14	Life Below Water	↗
Goal 15	Life on Land	➡
Goal 16	Peace, Justice and Strong Institutions	➡
Goal 17	Partnerships for the goals	➡

Source: SDG Index and Dashboards Report 2020

- *Green indicates SDG achievement*
- *Yellow, Orange and Red indicates increasing distance from SDG achievement*

From the above table, it is clear that India is not having a good position in sustainable development. It is time to find suitable remedies to address this problem

STARTUP ECOSYSTEM AND INDIA'S SUSTAINABLE DEVELOPMENT

Sustainable development is the sum of 'economic growth', 'social development' and 'environmental sustainability'. A nation is said to be sustainable when it balances these three aspects. As far as India is concerned, sustainability is a big challenge because of its diverse nature in terms of economically, socially and geographically. So, our nation needs an environment where every sector joints their hands towards a common goal that is India's sustainability.

However, India's startup ecosystem has a crucial hand in making the nation sustainable. Following are some of them;

> **Innovation:**
Innovation is the key driving force behind economic, social as well as environmental sustainability of any country. Innovation brings new and effective way of doing a particular thing which can secure the future of the nation. As far Indian startup community is concerned, innovation is one of the pre-requisites to become a startup. It is the power source from which innovative ideas comes out. Government agencies and various accelerators are encouraging young minds to make their participation in the field of innovation. 'Startup India' initiative by the government of India is an example.

> **Can bring new competitive dynamics in the economy:**
Startup firms can be considered as the most dynamic economic organization in the world. This is because, they offer additional dynamics and competitiveness in the economy. This will indirectly contribute towards sustainability as dynamics and competitiveness from a small startup firm will force others to find new and innovative ways to stay in the market. Our nation will be the ultimate beneficiary of all these.

> **Brings the values of propensity into the society:**
Startup ecosystem has the power to bring values of proclivity into the society. Through its activities, it changes the mind set of the society, imparts knowledge and creativity. These all will force the society to do something which is innovative in nature. This propensity from the society will benefit the nation in terms of economically, socially and geographically.

> **New job creation:**
With its continuous efforts in flourishing startup firms in India, startup ecosystem brings abundant number of job opportunities which uplifts an individual economically as well as socially. In order to see it in the long run, government should encourage investors to invest in the bunch of companies having the potential to create employment in the long run.

> **Creates research innovation system:**

Knowledge based service startups and high tech startups are always in connection with research institutions. Thus, research institutions have a great prominence in startup ecosystem. Promoting these research organizations will help young minds to gain access to it and bring out their ideas in the form of a startup company.

CONCLUSION

According to Prof. Schumacher, 'small is the ever best to the economy'. This statement is exactly true in the case of sustainable development of a nation because, startup that is a budding business venture can be treated as an agent of economic, social and ecological development of a nation. But, Indian startup ecosystem is not as stronger as other nation even if the country is ranked in the third position. This is because; the third position is not justified by its numbers. However, with all the positive initiatives from government, corporates, investors, mentors and other stakeholders, Indian startup ecosystem has the capacity to hold the future growth of our nation in economic, social and ecological terms.

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FINANCIAL CAPABILITY AS A PATH TO SUSTAINABLE GROWTH - A CONCEPTUAL STUDY

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ABSTRACT

The paper aims to highlight the importance of financial capability for achieving sustainable growth in an economy. The paper deals with financial capability, components of financial capability and benefits of attaining financial capability.Briefly explains the Sustainable

Development Goals (SDG's) of 2030 by United Nations. The paper shows the linkage between financial capability and financial inclusion. Specifically examining the behavior and wellbeing of an individual and its effect on financial capability. Also examining the impacts of financial capability especially eradication of poverty, improving the wellbeing of families and communities and increasing the level of investments for ensuring the growth of economy in a sustainable manner**.**

Keywords: Financial capability, Components of financial capability, Sustainable Development Goals (SDG's), Financial Inclusion ,Well-being,Poverty and Capability

INTRODUCTION

Finance is an important input for economic growth.The ability to access appropriate financial services shows the development of a society.The rural folks in India still do not have access to the formal financial services mainly due to insufficient knowledge and the inability to provide collateral for loans.The situation shows the financial exclusion in India.Now the question about financial capability arises.

Financial capability is the combination of attitudes ,behaviors,knowledge and skills.Financial capability is best judged by the actual behavior of an individual.We need to innovate and use technology to deepen financial capability among individuals. Improving financial capability has thus emerged as a strategic policy objective that complements governments' financial inclusion and consumer protection agendas .Building financial capability often involves the development of the literacy and numeracy skills which underpin everyday financial activities, such as reading and understanding written information and filling in forms. Physical distance from the financial literacy contact centers and trainers and the social-cultural contexts are major impediments in extending financial literacy. Therefore, there is a need to use interfaces that allow people to access financial literacy easily, conveniently and without disturbing their contexts. India has witnessed revolutionary penetration of mobile phones even in the hinterlands. We need to ensure that every individual who owns a mobile phone or has access to one is able to use it for educating themselves and managing their own finances. Financial capability has an important role in the development of communities . It also seeks to empower individuals and groups and to promote participation, inclusion and equal opportunities for those individuals and groups.

SCOPE AND SIGNIFICANCE OF THE STUDY

Our economy is growing fast .There arises dynamic financial environment where new financial products ,services,technology and other innovations are going on.Individuals need to change according to the current conditions.Hence they are required to acquire wide range of capabilities.Financial capability is must for taking financial decisions at the right time or in the case of choosing financial products .In India Financial Inclusion is of national priority but to attain financial inclusion financial capability is essential.So sustainability of an economy is affected by the financial structure as finance is the nerve of the economy.

REVIEW OF LITERATURE

Taylor(2011) Impact of financial capability on psychological health is independent of income and other resources.Individual financial capability highly depends upon psychological health.it shows the direct impact between capability and psychological wellbeing.

Kumar M(2015) Only a financially capable economy can make a well developed economy.It acts as a basis for macro economic growth.It is an important predictor for the success of financial inclusion .

FMA(2016) Feelings and fears influence the financial decision of an individual.Financial capability recognizes the impact of behavior

CFEB(2010) Introduces the MINDSPACE elements to build financially capable behavior.The report states that absence of financial capability leads to economic resources unproductive

METHODOLOGY OF THE STUDY

The study is highly conceptual in nature.Hence secondary sources of information are used.Journals ,books and various other sources are used.

WHAT IS FINANCIAL CAPABILITY?

We can understand the meaning of financial capability through simple equation

> **FINANCIAL CAPABILITY =ATTITUDES+BEHAVIOURS+SKILLS+KNOWLEDGE+MINDSET+SEL FEFFICACY**

Financial capability is the internal capacity to act in one's best financial interest, given socio- economic environmental conditions. It encompasses the knowledge (literacy), attitudes, skills

and behaviors of individuals in managing their resources, and understanding, selecting, and making use of financial services that fit their needs. In short it is the ability to make right financial decision at the The term 'financial capability' is of recent origin.

Financial Capability Concepts

Knowledge	Skills	Attitudes	Behaviors
■ Knowledge of financial concepts (inflation, compound interest etc.) ■ Awareness of financial products and services ■ Practical Know-how (how to make payments, how to open a bank account etc.	■ Numeracy Skills ■ Literacy Skills	■ Reasons for or for not saving, borrowing, investing, etc. ■ Attitudes Towards the future ■ Confidence in own plans for old age ■ Proclivity towards budgeting, saving, lending etc.	■ Money management (managing day-to-day finances). ■ Long-term planning (preparing for emergencies and retirement) ■ Financial decision-making (ability to choose appropriate financial products) ■ Seeking financial advice.

http://responsiblefinance.worldbank.org/~/media/GIAWB/FL/Documents/Misc/Financial-Capability-Review.pdf

The Center for Financial Inclusion's states, "Financial capability is the combination of attitude, knowledge, skills, and self-efficacy needed to make and exercise money management decisions that best fit the circumstances of one's life, within an enabling environment that includes, but is not limited to, access to appropriate financial services."

IMPORTANCE OF FINANCIAL CAPABILITY

Financial capability is important as people are faced by increasingly complex financial decisions. Financial choices and decisions will have significant consequences for future financial well-being. Financial capability is an important life skill for everyone: the ability to make financial decisions is the key to identifying and making best use of the opportunities in today's dynamic world.

KEY COMPONENTS OF FINANCIAL CAPABILITY

1. Making Ends Meet :

   A key building block of financial capability is the ability to make ends meet, which can be measured by examining the extent to which people balance monthly income and expenses to avoid over-spending and how they deal with everyday financial matters.

2. The future is inherently uncertain:

   Individuals and families need to make provisions to buffer themselves against financial shocks. Being able to weather shocks not only contributes to financial stability at the individual and family level but also increases the stability of the economy as a whole.

3. Managing Financial Products:

   It deals with how people manage cash, how they borrow, which assets they own and their exposure to financial market risks.

4. Financial Knowledge and Decision-Making:

To make sound financial decisions, individuals need to be equipped not only with at least a rudimentary level of financial knowledge, but also with the skills to apply what they know to actual financial decision-making situations. As the survey data demonstrate, all too often, a gap exists between self-reported knowledge and real-world behavior.

FINANCIAL INCLUSION AND FINANCIAL CAPABILITY

Financial inclusion broadly means the provision of affordable financial services, viz., access to payments and remittance facilities, savings, loans and insurance services by the formal financial system to those who tend to be excluded. Financial capability is a broader concept.It is an important ingredient for financial inclusion.The overall objective of these measures is to increase the people's ability to manage their money. However, financial inclusion is not only limited to opening of bank accounts but also the banking education to make use of banking facilities and products to better manage their money and capabilities. So the significance of financial capability arises.Financial inclusion is the process of ensuring access to appropriate financial products and services needed by vulnerable groups such as weaker sections and low income groups at an affordable cost in a fair and transparent manner by mainstream institutional players.Financial capability is necessary for each and every individual to take complex financial decisions in the current scenario. The significance of Financial Inclusion in the context of a developing country like India wherein a large population is deprived of the financial services which are very much essential for overall economic growth of a country.

> **FINANCIAL INCLUSION=FINANCIAL LITERACY+FINANCIAL CAPABILITY+FINANCIAL SELF EFFICACY**

POVERTY AND FINANCIAL CAPABILITY

Amartya Sen (2000) convincingly argued that poverty is not merely insufficient income, but rather the absence of wide range of capabilities, including security and ability to participate in economic and political systems. Today the term 'bottom of the pyramid' refers to the global poor most of them live in the developing countries. These large numbers of poor are required to be provided with much needed financial assistance in order to sail them out of the poverty trap.

Accordingly, there is felt a need for policy support in channeling the financial resources towards the economic upliftment of resource poor in any developing economy.

Below Poverty Line is an economic benchmark and poverty threshold used by the Government of India to indicate economic disadvantage and to identify individuals and households in need of government assistance and aid. It is determined using various parameters which vary from state to state and within states.Credit is an important pillar for the rapid development of poor people living in a country like India. It is the alternative way of livelihood opportunity for the self- employed and casual laborers those who have uncertainty in agricultural income. Access of finance make them living with minimum requirement of life and can help poor people climb out of poverty, giving them the freedom to earn in a sustainable approach.Since poor people often have insufficient traditional forms of collateral to offer, they are often excluded from traditional financial markets, transaction costs are often high relative to the small loans typically demanded by poor people and in areas where population density is low, physical access to banking services can be very difficult. These are numerous reasons that jointly lead to exclude the poor households from financial services and compels them remaining vicious circle poverty. Efforts to strengthen financial capability among low-income households can build on these time- honored financial survival strategies. Financial information, education, and training can improve people's knowledge and skills. However, families also need access to quality financial products. Low-income households cannot address the deficiencies of mainstream and alternative financial services industries alone. Policy and regulatory changes are required to build financial capability in low- income households. People needs to acquire knowledge and opportunity to participate fully in the life of their community if they want to

flourish and realise their potential. But certain sections in the society suffer from prolonged financial as well as social exclusion.

Linking Financial Literacy and Financial Inclusion: Toward Financial Capability:

Following figure shows the relationship between financial education and financial stability and well-being through improved financial literacy and improved use of financial products.
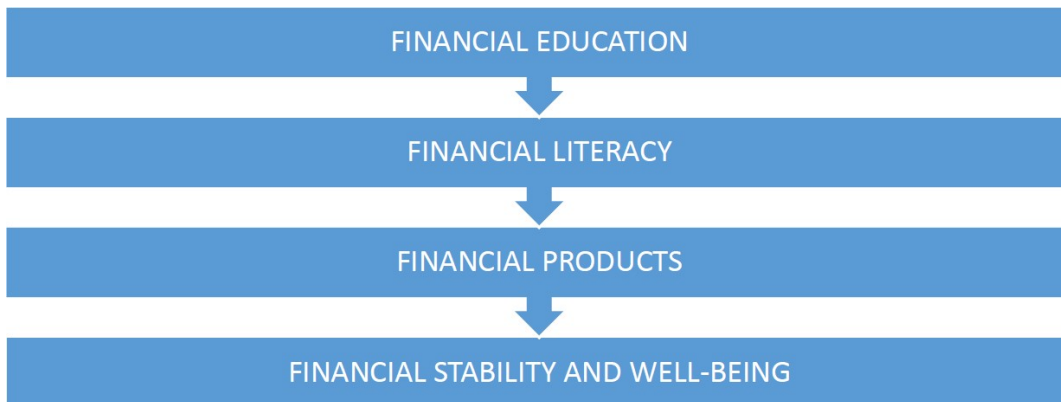
In the following figure, financial knowledge and skills (from economic socialization and financial education), generates improved financial literacy. At the same time, accessible, affordable, financially attractive, easy to use, secure, and reliable financial products lead to financial inclusion. Together financial literacy and financial inclusion build financial capability in low-income households.
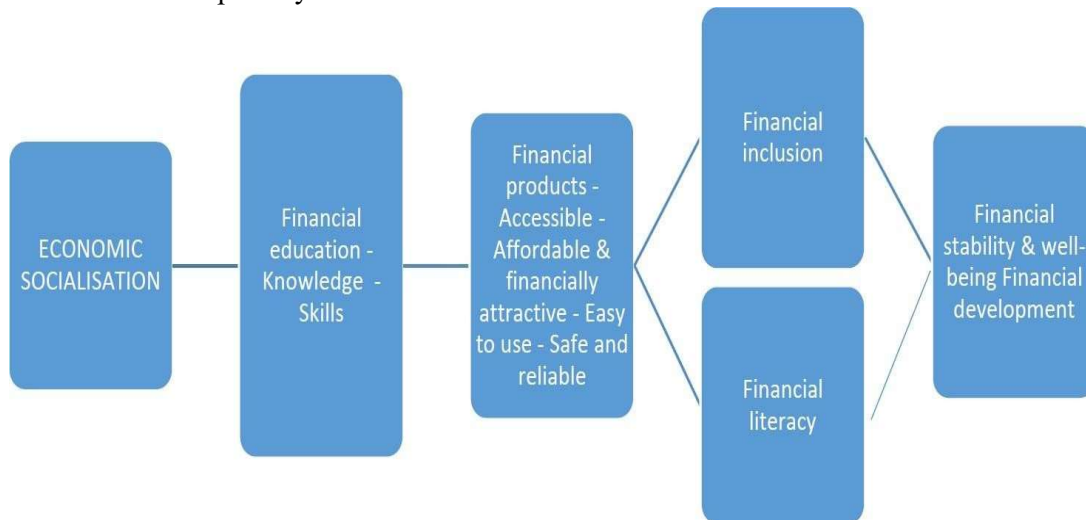
BENEFITS OF BEING FINANCIALLY CAPABLE

The major benefits of being financially capable are the following:

1. Ability to control economic resources efficiently

2. Control future finance

3. Improves material & economic wellbeing

4. Ability to exploit knowledge of financial information

5. Understand bank statements, bills, pay slips and other basic financial records.

6. Understand the implications of borrowing money and that it must be paid back, usually with interest.
7. Use cash and non- cash methods of payment.
8. Manage a day to day budget and prioritize essential and non- essential spending.
9. Understand why we pay tax and national insurance and how it affects wages.
10. Understand percentages and how interest rates have an impact on the amount of money borrowed or saved.
11. Seek advice when needed, knows where to go to get it and has the confidence to ask.
12. More control over the external environment

SUSTAINABLE DEVELOPMENT GOALS

The Sustainable Development Goals are a collection of 17 global goals set by the United Nations Development Programme.The formal name for the SDGs is: "Transforming our World: the 2030 Agenda for Sustainable Development."The Sustainable Development Goals are the blueprint to achieve a better and more sustainable future for all. They address the global challenges we face, including those related to poverty, inequality, climate, environmental degradation, prosperity, and peace and justice.

CONCLUSION

Financial capability is a broader concept.There are internal and external factors which affects financial capability.

EXTERNAL ENVIRONMENT AND FINANCIAL CAPABILITY

http://responsiblefinance.worldbank.org/~/media/GIAWB/FL/Documents/Misc/Financial-Capability-Review.pdf Financial
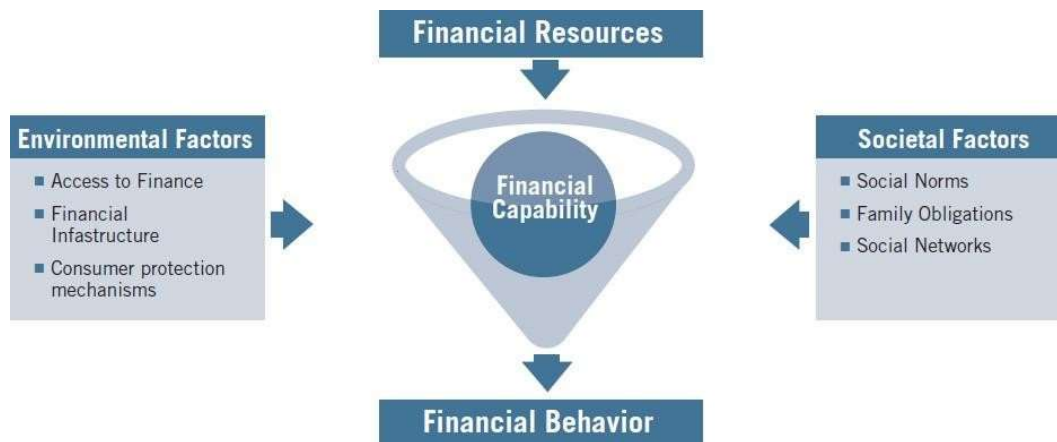
It acts as tool for policymakers for future economic growth. Financial decision making wholly depends upon the capability of an individual to take right financial decision. The whole economy is affected by the individual financial decisions. It is difficult to measure the financial capability of an individual since it is highly influenced by behavior of an individual which is qualitative in nature. Impact of financial capability of an individual's psychological health is independent of other factors like income,financial resources, financial shocks etc.Various studies revealed that capability and well being establishes a relation. At the same time capability acts as an important determinant of mental disorder. By promoting and improving financial capability it helps people to overcome financial shocks, improves psychological health, improves savings and investments.

Ensures better standards of living, reduces poverty, and thereby enhances economic growth in a sustainable manner.

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CHALLENGES OF INTERNATIONALISATION AND INNOVATION MANAGEMENT IN INDIAN SMEs AND STARTUPS

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ABSTRACT

SMEs and startups constitute majority of Indian industrial sector. There is a maturity stage if they stay in the domestic market. So, SMEs and startups in India realised the importance of internationalisation. Internationalisation is the process by which a company takes steps to increase its customer base outside of its home country. This is a significant stage in the life of a company. After attaining maturity from its home country, it is vital for the firm to expand its market to stay alive. This is why the relevance of internationalisation arises. But, the process of internationalisation is not smooth. They will have to overcome various challenges throughout the process on internationalisation. Here, the significance of innovation arises. SMEs and startups won't be successful in the international market if they offer the same product or services there as they are offering in its home country. So, innovation contributes significantly towards internationalisation procedure. For that, a thorough understanding of the target market should be made their product or services should be restructured as per the market needs. It needs an efficient system of innovation. A culture of innovation should be developed in the organisation. This paper aims to make a theoretical view of the challenges faced by SMEs and startups in their internationalisation process and how innovation management can contribute towards internationalisation.

Keywords: Startups, SMEs, Internationalisation, Innovation management

INTRODUCTION

Internationalisation refers to a process by which a company takes steps to increase its footprint or client base outside of its country of domicile and into international markets. Internationalisation is regarded as one of the significant and popular step in the life of a firm. It helps SMEs and startups to remove the barriers of borders and gain benefits from the international market. Globalisation results a large number of opportunities for SMEs startups to grow and expand. But, the pathway for them to become global is not as simple as it looks. They have to overcome various challenges. Innovation is considered as one of the best and widely accepted way for any firm to smoothen their path to become global. But, going international through innovation certainly will involve huge investment risk.

For an SME or startup, internationalisation is a huge task since they don't have enough resources to follow all the strategic steps for it. They have to develop a strategy to utilise their available resources at its optimum level. Through optimum utilisation of resources, SME or startup can find ways for innovation. This innovation can become a competitive advantage or core competency for them to make their presence at the global level. Thus, innovation is the base a firm to become global. If they have an idea, they definitely will get market
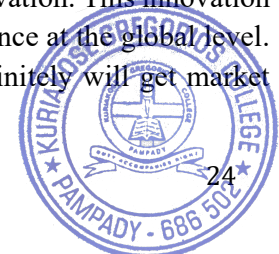
across the globe. Since an SME or startup is in a seed stage, managing innovation along with internationalisation is a complex task. So, it is important to have specific strategy to balance innovation and internationalisation.

REVIEW OF LITERATURE

Many studies have been conducted on internationalisation of business. This study is intended to analyse previous studies on the following basis;

  - ➢ **Internationalisation and business performance**
  - ➢ **Challenges affecting internationalisation of business operations**
  - ➢ **Innovation and internationalisation**

  - ➢ **Internationalisation and business performance**

(Bloodgood, Sapienza, & Almeida, 1996) states that firms are required to have international operations to remain competitive in the market as it allows access to international expertise, innovations and advanced technology. Further, it provides firms avenues for "knowledge growth, capability development and revenue enhancement" which boost their global competitiveness.

(Burpitt & Rondinelli, 2000) made their point clear that financial success in initial years through exporting activities motivates firms to further internationalize in subsequent periods. The partial correlation analysis in the study showed that both financial success and learning oriented variables are positively associated with the likelihood of continued exporting by small firms.

(Parnel, 2002) explained the conceptual and empirical challenges facing strategy researchers and suggested the inclusion of qualitative measures instead of traditional metrics such as returns on investment, return on asset, sales revenue growth, market share etc. to provide deep insights into organizational processes and resources. Overall, there is a positive association between internationalising operations and firm performance.

  - ➢ **Challenges affecting internationalisation of business operations**

(Biswas, Khan, & Sultana, 2017) investigated the challenges faced by SMEs from Bangladesh to expand their business operations across national boundaries. Instead of identifying few challenges, authors listed a total of 39 challenges faced by SMEs in Bangladesh. They suggested that, all these challenges can be eradicated with the help of government, NGOs, industry associations and external donor organisations.

(Wilkinsona & Brouthersb, 2006) pointed that The success for SMEs export operation depends on firm level strengths as well as business level opportunities and challenges. A favourable business environment both in home and foreign markets is very important for getting success in international business operation for the SMEs. An unfavourable business environment in home or international market hurts more to the SMEs than to a large company in international operation.

(Yener, Dogruoglu, & Ergun, 2014) analysed the main challenges faced by SMEs in Turkey for cross border business transactions. Authors found that uncertainty, conflict in a network, profitable domestic market and lack of experienced management involvement hold a major part in decreasing international activities.

  - ➢ **Innovation and internationalisation**

(Carneiro, 2005) emphasises the importance of technological innovations and innovation through new products and technologies. As In his opinion sustainable growth and profitability require technological innovation, because growth plans rely on more than new products; they include innovation management and adequate management mentalities to adopt new technologies within several processes.

(Lopez Rodriguez, Rodriguez, & Rafael.M, 2005) divided innovation phenomenon into process innovation

and product innovation. Authors pointed that both these innovation can generate competitive advantage for the firm. Process innovation results in process efficiencies while product innovation lead to a competitive advantage in customer value via the development of greater differentiation in product characteristics.

Ruzzier, Hojnik, & Lipnik, 2013) explores the relationship between strategic directions, innovation and internationalisation. For that, authors divided innovation into product innovation and process innovation. Study concluded that product innovations are determinants of internationalization for Slovenian internationalized companies, while process innovations, were not statistically significant based on research conducted on Slovenian internationalized companies.

All the reviews state that internationalisation is an essential part in the life of a business. But, the process is not simple. Business organisations have to overcome various challenges to fulfil the dream of internationalisation. To make the procedure smoother, firm will have to make their concentration on innovation management. Both these innovation and internationalisation are directly related.

SIGNIFICANCE OF THE STUFY

No firm can stay in the domestic market for long. Once, they achieve maximum maturity from the domestic market, they have to find new markets where their products or services can be offered. Here, the need for internationalisation arises. It is an essential procedure in the lifecycle of an organisation. Internationalization is seen as an advantage for transfer of capital, labour, and technology in new geography as market creates lots of opportunities to learn about the latest technology, economy, and market. Collaborating with other companies can help to acquire new expertise which can assist in strengthening the organisations position. Innovation management is an important element in internationalisation. Efficient system of innovation management is essential for SMEs and startups to make cross border business effectively.

But, it is not as easy for an SME or startup to fulfil internationalisation dream since they lack enough resources. They are facing so many challenges. If the firm has constitutes an efficient system of innovation, it can overcome the challenges to an extent. Thus, the study aims to understand internationalisation challenges and innovation system has got relevance in the present context.

RESEARCH METHODOLOGY

The study is purely theoretical in nature. For conducting the study, various dimensions of internationalisation and innovation management are taken into consideration and these dimensions were evaluated theoretically. Secondary data were collected from books, journals and various websites.

CHALLENGES OF INTERNATIONALISATION

Internationalization is a practice to expand services and products into other international markets where there is a need and scope for acceptance and large user base. During the process internationalisation, SMEs or startups are facing various problems which are illustrated as follow

How to select a new market?

SMEs and startups take the process of internationalization to find new customers for their products and services. Selecting an international market is the most important challenge faced by every startups and SME. They should adopt a systematic approach in selecting international market. But, majority of SMEs and startups adopt a 'non systematic' approach in selecting target market. "Opportunistic" approach is adopted by the

organizations considering the weaker administrative capacities for market analysis and research. Selecting the right market is also influenced by various external factors like economic policies, business environment and political stability of the target country. It is found that lack of international managerial experience also affects the decision of selecting the new international markets.

➢ *How to design an internationalisation strategy?*

A strong internationalisation strategy is a pre requisite for any firm to make their presence at the global level. In India, there are two forms of SMEs or startups namely 'traditional firms' and 'Born global' organisations. Traditional firms are those firms which have a stronghold in the domestic market and they gradually moved to international market. 'Born global' firms are those which design their strategies only for international market.

Traditional firms design their strategies exclusively for the domestic market. They have a good hold on the domestic markets and technical ability to meet the demands. Gradually, with capacity building and attaining saturation at the domestic market, the organisation will make their move towards the global market based on the available resources and information. This form lacks enough exposure at the international level especially during implementation stage. Organisations may not be able to redesign their business model to meet the demand of the global customers. They will have to introduce new methods and practices in the organisation which is also a tedious task for them.

'Born global' firms, as its name suggests born for international market. These firms go directly to the global market from its beginning itself. The growth and expansion of these firms will be much faster than the traditional form. But, the main challenge before them will be the initial capital needed from the initial stage onwards. It also requires competitive and sustainable technical capabilities for international markets. The observation is SMEs and startups have a big challenge to manage the funds to run different operations inside and outside the organizations at the initial stage. 'Born global' firms have to invest more into their different operations to meet the criteria of international markets to compete and earn the revenue.

Designing an internationalisation strategy should be made systematically and should be implemented in such a way that does not affect the performance of the firm negatively. Strategy for internationalisation should integrate various factors such as time, resource utilisation, target market and business objectives.

➢ *How to manage technology competency?*

Advanced technology, new product capability and responsiveness to market changes are the key elements of every business organisation to survive in domestic as well as international market. An SME or startup should gain more responsiveness towards their product or services to make successful internationalisation. To gain market response, the product or services should not be repetitive. It should be the result of an innovative idea. Innovation is one of the best way through which an SME or startup can access a place in the global market.

When the product or service offered by the firm is the result of an advanced innovative technology, and which is capable of satisfying market needs, it will automatically acquire more market response. Thus, the firm can ensure a stable place in global market but, requires an approach beyond the local markets and understanding of the global market needs.

To adapt to the changes and the highly responsive strategies, startups and SMEs do not have extra resources and excess of capital funds to invest into specialized technological advancements. It requires a thorough understanding of the consumer needs and current business practices. Partnering with the existing companies in the international market can be an inviting step but there should be proper business terms between both the parties which should help the organization to learn and perform with flexibility and efficiency.

> ➤ *How to manage people?*

Regardless of the size, every organisation is made up of people. Employees are the key element in the success of every organisation. As far as internationalisation is concerned, employees are the most critical element for the firm to cross their business activities beyond national frontiers. Managing human resources in an international market is a big challenge for SMEs and startups because, existing philosophy of people management in domestic markets may not work for operations in international markets. So, there should be a serious effort from SMEs and startups to understand the cultural and behavioural difference of people.

International market is highly complex where the challenge for doing is high. So, SMEs and startups should focus on decisions on target market, internationalisation strategy, technology competency and human resources effectively to achieve successful internationalisation. In addition to this, they should also consider Adoption of globalized culture, management of knowledge and effective methods of communication during internationalisation procedure.

INNOVATION MANAGEMENT FOR SMEs AND STARTUPS

In a developing country like India, SMEs are very important for the growth of the economy. Increasingly SMEs and established startups are creating a competitive environment. Product life cycles is shortening due to cut-throat competition in the market This changing market, forces SMEs and startups to adopt the new strategies and develop new technologies frequently to be in the competitive market. It is essential for them to reinvent their business models according to the dynamic market needs. Varying business model is considered as inconvenient for the SMEs. Due to limited resources and experiences, SMEs cannot survive in the market without innovating.

Innovation in business process and product or services helps SMEs or startups to acquire an edge over the market. Innovation can be made in collaboration with other departments or firms. Expanding to different regions and partnering with international firms for resources and technology are important for SMEs or startup growth. Innovation in different processes provides SMEs a competitive advantage. Innovation is an approach essential for consistent growth to meet the dynamic market need and competition. SMSs and startups should constitute an innovation system to improvise the traditional form of process development or product development.

Innovation process not completely stick on research and development process. It also has an influence on the organisational culture. To develop a culture of innovation in the organisation, there should be innovativeness in each process of the organisation. Strategic and disciplined implementation of the innovative processes helps the organization to provide sustainable innovations to the market with consistency.

INTERNATIONALISATION, INNOVATION MANAGEMENT AND FIRM'S PERFORMANCE

Internationalisation and innovation management are two key process in the life of a business organisation. They are interrelated as well. Innovation helps an organisation to gain a consistent position in the global market. Thus, business performance can be improved. Following diagram illustrates the relationship between internationalisation, innovation management and business performance;

Resource and capabilities   Strategy of the firm   Competitive advantage
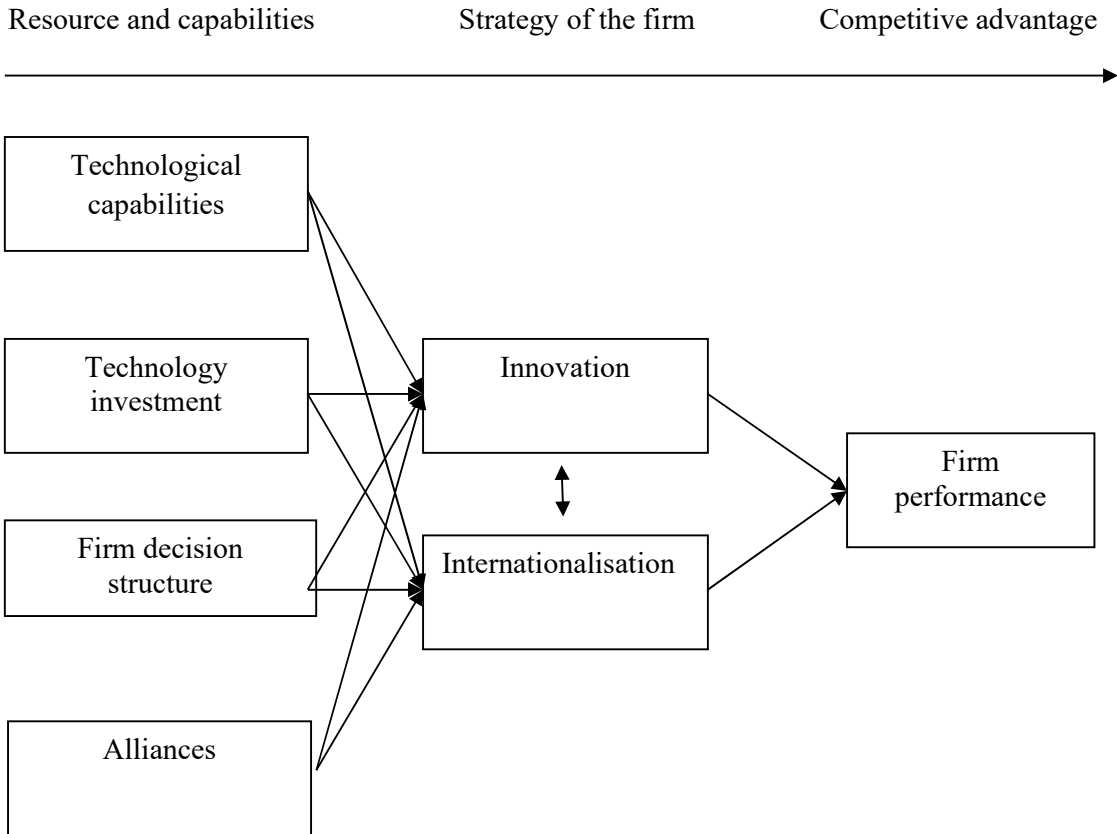
Above diagram illustrates the relationship between internationalisation and innovation. Technological capabilities of the firm, technological investments, alliances with other departments and firms and the decision structure constitutes by the organisation lead to achievement of innovation and internationalisation. Both innovation and internationalisation combine together to improve business performance.

CONCLUSION AND RECOMMENDATION

Indian economy is highly dependent on SMEs and startups as they contribute majority of the industrial firms in the nation. SMEs and startups have witnessed the importance of internationalization and leveraged the benefits of globalization to expand into new countries. Internationalisation involves huge challenges as it involves in depth understanding of market behaviour. So, it is important for SMEs and startups to understand the relevance of innovation management in the business. It helps the firm to attain technological core competencies which helps them to face competition. To develop an effective innovation management system, it is important for them to understand the relevance of developing a good system of knowledge management. For that, SMEs and startups can arrange partnership with technology firms for resource sharing. Organisational leadership should be focused and it should be capable of developing a culture of innovation in the organisation. All these innovative processes will guide firms towards global market without any barriers.
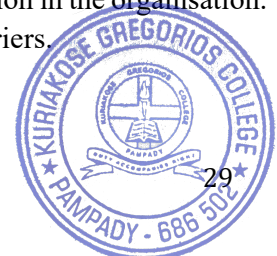
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HYDROLOGY OF ARUVIKKUZHI WATERFALLS, KOTTAYAM, KERALA

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ABSTRACT

To provide information on the physico-chemical characteristics of Aruvikkuzhi waterfalls, monthly samples were taken from three stations along the length of waterfalls for 6 months from September 2019 to February 2020 covering wet and dry seasons. Air and water temperature was low during wet season which can be connected with the rain and cooling of atmosphere itself. Mean pH was comparatively low at the waterfall area (7.28) while the value calculated for TDS was higher at this station (10.8 mg/l) and lower at the upstream station (9.35 mg/l). Chloride content in the water was comparatively higher at station III (upstream) followed by station II (waterfall). Total alkalinity was low at all stations, varied from 1.6 to 4.2 mg/l $CaCO_3$. Total hardness (mean) was comparatively higher at station III (21 mg/l $CaCO_3$) followed by station II (18.5 mg/l $CaCO_3$). There is considerable increase in dissolved oxygen in the waterfall area together with total absence of carbon dioxide. Concentration of the nutrients nitrite and phosphate were comparatively higher at the upstream station and lower in the waterfall area. Low organic enrichment and greater turbulence leads to comparatively better physico-chemical characteristics in the immediate vicinity of waterfall. Low level of sewage mixing from the surrounding human settlements along the banks and the digestion of sewage wastes lead to comparatively higher values of nutrients, chloride, carbon dioxide and total hardness at the upstream station.

KEY WORDS: Physico- chemical parameters, waterfall ecosystem, tourism.

INTRODUCTION

A waterfall is an area where water flows over a vertical drop or a series of steep drops in the course of streams and rivers. Waterfalls are generally considered as natural monuments for revenue generation, because of their ecotourism potentials and as source of quality water for drinking, irrigation and other domestic purposes. Tourism is said to be one of the fastest growing economic activities world over. Tourism planning requires sustainability because its growth usually brings increasing pressure on the natural environment. Sustainable tourism development projects in any aquatic ecosystems can be carried out only if the ecology of these systems in the region is well understood.

Aruvikkuzhi waterfalls, one of the well known waterfalls in Kerala is located at Pallickathodu panchayath in Kottayam district between 9.6035° N latitude and 76.6670° E longitude. The waterfall is about 30ft in height, falling in five steps is a real feast for eyes, especially during monsoon season. Aruvikkuzhi waterfalls are loved for the natural beauty they possess along with the quaint charm of the surrounding rubber plantations. The trails surrounding the area along with the cool water falling from over 100 ft. make it a picnicker's paradise. One gets the distinct feeling of being hugged directly by nature when stand there in this monsoon wonder and it attracts plenty of visitors during season.

The intensity of waterfalls and pressure generated from it due to gravity has given the impression of a lifeless zone and water quality researchers had given little attention to waterfalls. Only few investigations have been carried out so far on parameters of the waterfall ecosystems in Kerala (Priyanka Prabhakaran and Kakkassery, 2018) and absolutely no information of Aruvikkuzhi waterfalls. The present study aimed at the investigation of physical and chemical properties in the ecological system of Aruvikkuzhi waterfalls, Kerala.

MATERIALS AND METHODS

The study was carried out at three selected stations located along the length of Aruvikkuzhi waterfalls for 6 months from September 2019 to February 2020 covering wet and dry seasons. Station I was selected at the downstream part of the waterfalls, about 50 meters away from the falling area, Station II in the immediate vicinity of the waterfall just below the falling steps and Station III in the upstream part of the waterfall about 50 meters upward to the falling steps. The physical and chemical parameters included in the study are air and water
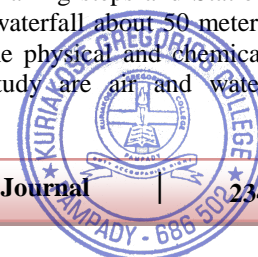
temperature, pH, total dissolved solids, chloride, total alkalinity, total hardness, dissolved oxygen, free carbon dioxide, nitrite-nitrogen and phosphate- phosphorus. The water quality parameters were estimated following the standard methods (Strickland and Parson, 1972; Grasshoff *et al.*, 1983; Trivedy and Goel, 1984; APHA, 1998).

Air and water temperature recorded immediately on the site by mercury thermometer. The pH value of water samples are measured by using digital pH meter. TDS of water samples were measured using gravimetric method. Total alkalinity of the water samples were determined by titrating with H_2SO_4 using methyl orange as indicator. The total hardness was determined by the complex titration with EDTA using Erichrome black T as indicator. The chloride was determined by titration against standard solution of silver nitrate using potassium chromate as an indicator. Dissolved oxygen was determined by the modified Winkler method. The carbon dioxide was determined by titrating with NaOH using phenolphthalein as an indicator. Nitrite and phosphate

was estimated using spectrophotometer at 543nm and 882 nm respectively.

RESULTS AND DISCUSSION
The water quality characteristics of Aruvikkuzhi waterfalls are shown in Table I.

Water resource is one of the major components of environmental resources threatened by exploitation and pollution due to human activity. Physico-chemical characteristics are very vital water quality monitoring parameters due to their instability once water is extracted from its source. Knowledge of physico-chemical parameters provides information on the productivity of water resource, type of water treatment process to be adopted and permit better understanding of the ability of populations of organisms to survive in them (Boyd and Lichtkpoppler, 1985; Ayodele and Ajani, 1999). As an aquatic ecosystem, the waterfall has several functions such as provide clean water, control pollution and supporting with some critical chemical substances in the ecosystem (Offem, 2011; Shaikh Parveen *et al.*, 2013).

Table I. Range and mean of water quality characteristics of Aruvikkuzhi waterfalls (Sept. 2019- Feb. 2020).

Parameter	Downstream		Waterfall		Upstream	
	Range	Mean	Range	Mean	Range	Mean
Air temperature (^{0}C)	29-31.5	29.8	28-32	29.8	28-32	28.8
Water temperature (^{0}C)	27-31.5	28.6	26.5-31	28	27-31.5	28.7
pH	6.74-7.9	7.33	6.7-7.8	7.28	6.66-7.9	7.31
TDS (mg/l)	7.2-14.2	10.02	9.1-15	10.8	6.9-11.1	9.35
Chloride (mg/l)	15.62-24.28	19.83	15.62-24.22	20.08	18.46-34.2	26.23
Total alkalinity (mg/l. $CaCO_3$)	3-4.2	3.4	1.6-4.2	2.85	2.2-4.2	3.15
Total hardness (mg/l. $CaCO_3$)	14-24	18.25	14-24	18.5	13-32	21
Dissolved oxygen (mg/l)	7.2-9.2	8.25	10.2-14.4	11.95	7.6-9.2	8.52
Carbon dioxide (mg/l)	0-1.2	0.6	0	0	0.6-1.4	1.32
Nitrite-nitrogen (µg/l)	15.75-68.46	43.91	17.5-66.4	41.59	26.5-116.3	72.47
Phosphate- phosphorus (µg/l)	1.22-6.06	3.1	1.22-6.06	3.09	1.86-6.34	4.71

Physico-chemical parameters recorded in the present study are an indication of the level of water quality of the different sections of the Aruvikkuzhi waterfall during the period September to February. In general there exists a positive correlation between water level and rainfall which indicate that the water level increases with increasing rainfall. Variation in amount and duration of rainfall had been found to affect physico-chemical parameters of water (Adebisi, 1981; Egborge, 1994). In the present study September - December received considerable amount of rainfall in the area while other months January and February can be considered as low wet period. Air and water temperature was low during wet season (Sept - Dec) which can be connected with the rain and cooling of atmosphere itself. There observed an increase in air as well as water temperature during February since smaller water bodies react quickly with changes in atmosphere. Water temperature (mean) was low at waterfall (28 ^{o}C) compared to that at downstream (28.6 ^{o}C) and upstream (28.7 ^{o}C) stations.

Every water body shows diurnal, monthly as well as seasonal variation in pH. The relationship between CO_2 and pH is also well known in limnology (Boyd, 1990). pH values in the present study indicated slightly acidic conditions during November and December which might be due to higher input of allochthonous organic matter and increased acidification from rain water and land runoff. The dry season pH levels in this study indicate moderate quality of water. pH values obtained in this study agree with those documented by Fakayode (2005) as values most suitable for maximum productivity of aquatic organisms. Total dissolved solids of water sample represents dissolved organic and inorganic matters excepting gases and suspended inorganic substances. None of the samples used for determining TDS in the present study was up to maximum admissible concentration (600 mg/l) of total solids as stipulated by WHO(2004). The chloride concentration was however high in the study area, with increasing trends towards the dry season and also from the downstream towards upstream, is an indication that the area has influence due
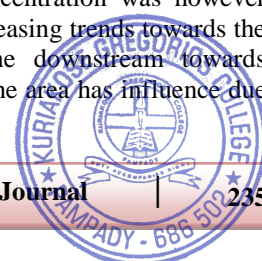
to organic pollution by domestic sewage(Goel *et al.*,1980).

Dissolved oxygen level recorded in the waterfall region (station II) of the study area was higher compared to other downstream (station I) and upstream (station III) stations. Low organic enrichment and turbulence nature of waterfall had been suggested as the possible reason responsible for such high oxygen values (Mason, 1992; Offem and Ikpi, 2012). On the other hand, low dissolved oxygen observed downstream of the waterfalls could be attributed to low water velocity, thus reducing the movement of the waters and dissolution of oxygen. The values of dissolved oxygen fell within the ranges 7.2 – 14.4 mg/l can be considered as good water quality suitable for aquatic organisms (Alabaster, 1982). Dissolved oxygen content will be higher during the rains due to lower water temperature and increased aeration due to increased agitation of the water (Offem, 2011). During the present study free CO_2 was totally absent at the water fall region (station II) and the values among the other stations were comparatively higher at the upstream station (station III). Greater turbulence and the associated greater oxygen saturation may be the reason for the absence of CO_2 in the water fall area while sewage mixing and the digestion of sewage wastes may be the reason for the higher values at the upstream station surrounded by human settlements along the banks (Varma and Shukla, 1969).

Total alkalinity is a measure of the capacity of water to neutralize a strong acid (Boyd, 1990). In natural fresh water alkalinity is generally caused by carbonates of calcium and magnesium, calcium forming the major constituent. Total alkalinity values have utmost importance in aquatic habitats as water with low alkalinity is biologically less productive (Sakhare, 2006). Alkalinity in the Aruvikkuzhi waterfalls during this study was very low favouring to low productivity but found to be within tolerance limit of biota. Total hardness indicates the concentration of divalent cations present in water. Total hardness of 13-32 mg/l in Aruvikkuzhi waterfalls was far less than values from Sahastrakund Waterfall, Maharashtra (170 mg/l). The value relates to soft water according to the classification of water in terms of hardness and softness: 0-50 (soft), 50-100 (moderately soft), 100-150 (moderately hard), and 250 and above (hard).

Phosphorus, although present in very small quantity in natural water plays a key role in photosynthesis and intermediary metabolism and forms constituent of nucleic acids and proteins. Phosphorus occurs in natural water in the form of phosphates. The probable source of phosphate-phosphorus of running waters is fertilizer run off, decayed organic matter and phosphate mineral. In the present study phosphate was higher at the upstream section of waterfall where the possibility sewage mixing is found maximum. Nitrite occurs fairly widely in natural waters, which may probably be derived from the reduction of nitrate. High values of nitrite usually occur in regions of low oxygen which is in agreement with the higher concentration at the upstream section of the waterfall. However, the low level of nitrite at all the stations indicates that the biological oxidation of nitrogenous organic matter of both autochthonous and allochthonous origin such as domestic sewage, agricultural runoffs and effluents from industries etc., the major source of aquatic nitrogen, are at their minimum in the study area(Saxena, 1998).

CONCLUSION

A general outlook of the entire results shows that the water of Aruvikkuzhi waterfall is of good quality and relatively clean which may be explained as resulting from high flushing rate in the waterfalls, particularly during wet season. The influx of the stream water has sufficient energy to cause turbulent water movements which could result in flushing of the water body. The cool breeze and affable climate make Aruvikkuzhi waterfalls among the best picnic spots in the district and families are regularly seen camping in this wonderful spot in the landlocked district of Kottayam**.** Recently tourism department of the state is trying to develop this place as a spot of monsoon tourism and giving funds for its development. It is needed to make many facilities in future for the development of this place. However, proper attention should be given for sustainable development of this waterfall for tourism.

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Fabrication of photoluminescent electrospun poly(styrene-co-methyl methacrylate) nanofibers integrated with LaPO$_4$:Eu^{3+} for optical applications

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ABSTRACT

Organic luminescent nanofibers owing to their flexibility and anisotropic emission along the axis when compared to direction perpendicular to axis are gaining much importance as luminescent probes and in a variety of other optic applications. Of the different organic luminescent nanofibers the one which is of recent interest is the rare earth integrated electrospun polymeric nanofibers. Among different host matrices the most suitable one is polymer in view of electrospinning technique as it facilitates the spinnability of the solution which is a matter of concern when coming to electrospinning technique and also enhances the flexibility of the product. Rare earths are the most apt material of choice when the research focus into luminescent applications. Among a number of rare earths of choice the one with greater potential is undoubtedly europium ion because of its intense emission in the orange red region on UV excitation. In the present study the polymer chosen is poly (styrene-co-methyl methacrylate) which is a copolymer of polystyrene and polymethyl methacrylate and the rare earth integrated is LaPO$_4$:Eu^{3+}. The surface morphologyanalysis and optical characterizations are done by SEM, EDX, XRD, PL and IR techniques. The sem analysis shows that the average fiber diameter distribution increased from the range of 70 nm to 120 nm on integration of LaPO$_4$:Eu^{3+}. The shift of maximum excitation wavelength in the UV spectra and presence of characteristic bands of Eu^{3+} ions in the region 579 to 610 nm in the integrated nanofibers shows that the rare earth is very well distributed into the polymer matrix. Also there is significant enhancement in the intensity of integrated nanofiber.

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1. Introduction

Researches focusing on the development of novel materials for optic applications such as transmission, sensing and construction of new photonic devices identified polymer nanofibers [1] as one of the top materials of preference. For many years glass and semiconductor fibers were being used but poor mechanical property, incompatibility with other materials, high fabrication cost, drastic processing conditions like high temperature and pressure restricted its extensive applications. With the advent of use of polymers either directly by making use of luminescent conjugated polymers [2] or as host matrices for luminescent particles [3,4] technology defined a new pathway for the device fabrications for

photonic applications [5,6]. Both two dimensional and one dimensional materials can be used for the aforementioned applications, but 1D structures like nanofibers offer more tight confinement especially for optical sensing. Of the different nanofabrication techniques like drawing, template synthesis, self-assembly, phase separation etc. [7] electrospinning technique is more preferred as the fibers produced can be easily tailored to different architectures of our demand [8,9] simply by adjusting the spinneret or collector assemblies in addition to cost effectiveness. Also it can be used to produce a wide range of organic and organic–inorganic nanofiber composites [10,11]. The basic principle behind electrospinning is that when sufficient voltage is applied to the polymer solution or melt, charges will be induced in the droplet and at a particular point the droplet will be stretched towards the collector in the form of fibers whose morphology is determined by a number of

parameters like solution properties, applied voltage, tip to collector distance etc. [12,13].

Luminescent electrospun nanofibers can be organic, inorganic or hybrid depending on the host matrix nature. Electrospun organic luminescent nanofibers can be made of either luminescent conjugated polymers [14–16] or with spinnable non-luminescent polymers functionalized with dyes [17–19] metals [20–23] or rare earth complexes [24–26]. More research is going on with non-luminescent polymers as they offer the required molecular weight and good solvent interaction which are the prime requisites for electrospinning. Also among the dopants such as dyes, metal complexes etc. rare earths are more preferred for its strong emission characteristics. The sizeable energy gap displayed by europium and terbium ions among other rare earths made them more interesting candidates towards optic applications. Works with europium salts and complexes doped in different polymer matrices such as PVP, PAN, PVDF, PMMA, PS were already been reported [27–29]. In this study a novel polymer, poly (styrene-co-methyl methacrylate), which is a copolymer, is being used. Both PS and PMMA are well known for its optic properties. PSMMA is an amorphous polymer which offers excellent optical property and good flexibility with respect to the phenyl ring in the PS fragment. PSMMA would be a suitable candidate where flexible optic devices are required. Dopant used here is 3% Eu^{3+} doped lanthanum phosphate [30,31]. In this study the main aim is to establish the possibility of exploiting the electrospun PSMMA as a host matrix for the luminescent particles especially rare earths for optic applications like display lamps, panels etc.

2. Experimental

2.1. Materials and methods

Poly(styrene-co-methyl methacrylate) with average Mw 100,000–150,000 and Lanthanum Nitrate hexa hydrate purchased from Sigma Aldrich, Europium(III) Nitrate hexahydrate from CDH, Sodium hexametaphosphate and the solvents Tetrahydrofuran (THF) and N,N-Dimethylformamide (DMF) were used for the study. The study proceeds in two steps. First is the synthesis of $LaPO_4$: Eu^{3+} and second step is the electrospinning of $LaPO_4$:Eu^{3+} doped PSMMA fibers.

2.1.1. Synthesis of LaPO4:Eu3+

$La(NO_3)_3$ and $Eu(NO_3)_3$ solutions were mixed with $(NaPO_3)_6$ solution at mole ratios of P/(La + Eu) = 3. After stirring for 2 h the mixture was heated at 120C for 8 h in a teflon coated stainless steel container. The mixture was then centrifuged decanted and dried at 60C

2.1.2. Fabrication of electrospun LaPO4:Eu3+ integrated PSMMA nanofiber

The homogeneous polymer solution for electrospinning was prepared by dissolving 3 wt% PSMMA in 1:1N,N-Dimethylformamide and Tetrahydrofuran binary solvent mixture. After complete dissolution of polymer, $LaPO_4$:Eu^{3+} was added into the polymer solution, by keeping a ratio of 1:10. The solution is subjected to vigorous magnetic stirring for 24 h at room temperature and sonicated for 1 h before electrospinning. The electrospinning was done using ESPIN NANO and the processing conditions employed are given in Table1. The detailed report of optimization

Table 1
Condition for Electrospinning.

Applied Voltage	Tip to Collector distance	Flow rate
25 kV	20 cm	0.5 ml/h

of electrospinning conditions are reported in published work [32]. The nonwoven fiber mats were collected in aluminium foil and glass substrates.

2.2. Characterization

The morphology of the electrospun nanofibers was investigated by using Zeiss Field Emission Scanning Electron Microscope (SEM) after sputter coating with gold. The UV–Visible studies were performed using UV-2600 UV–Visible spectrophotometer. Fourier Transform Infrared analysis was performed using Thermo Nicolet, Avatar 370 FTIR spectrometer. The photoluminescence analysis was done with Fluoromax4 spectrofluorometer. The XRD analysis was performed using Rigaku MiniFlex 600 X-ray Diffractometer.

3. Results and discussions

3.1. Structural studies

The FESEM images of PSMMA and PSMMA nanofibers incorporated with $LaPO_4$:Eu^{3+} mentioned as integrated PSMMA nanofibers electrospun under the same processing conditions are shown in the Fig. 1(a) and (b) respectively. It is evident from the images that both the electrospun nanofibers are in the form of nonwoven fiber mats with smooth defect free surface morphology.

Fig. 2 gives the histogram of the fiber diameter measurement studies done by using image j software. For PSMMA nanofibers, the diameter distribution ranges from about 40 nm to 110 nm with an average fiber diameter distribution in the range of of 70–80 nm. In the case of integrated PSMMA nanofibers the range is from 60 nm to 130 nm with an average fiber diameter distribution ranging from 110 to 120 nm. The diameter of the fiber is significantly influenced by both solution parameters and processing conditions [33]. But here since the processing conditions are same the fiber diameter increase is attributed to the changes in the solution parameter. Among the different solution properties the factors that influence fiber diameters are conductivity and viscosity of the solution. By integrating rare earth there would be change in the conductivity and viscosity of solution. It is reported in the literature that with the loading of inorganic molecules there will be changes in the fiber diameter due to the variation in its solution properties [34]. The increase in the average fiber diameter is a clear evidence for the successful incorporation of $LaPO_4$:Eu^{3+} into the polymer.

Fig. 3 gives the EDX spectral analysis of the integrated PSMMA nanofibers done along with the SEM analysis to confirm the presence of $LaPO_4$:Eu^{3+}in the fibers. The elemental detection of Europium and Lanthanum ion is clear from the image.

Also the elemental mapping image given in the Fig. 4 shows the uniform distribution of $LaPO_4$:Eu^{3+} in the integrated PSMMA nanofibers. The peak due to aluminium is from the foil that is used to collect the nanofibers.

3.2. XRD analysis

XRD spectra of $LaPO_4$:Eu^{3+}, PSMMA and integrated PSMMA nanofibers are shown in Fig. 5. The peaks at 28°, 48.1° and 59.4° of $LaPO_4$:Eu^{3+} are also present in the integrated PSMMA nanofiber.

Also xrd pattern of the integrated psmma nanofibers shows more sharp peaks when compared to PSMMA fibers. This is an evidence of the successful integration of $LaPO_4$:Eu^{3+} onto PSMMA nanofibers

V. Varkey, A.R. Chandran, E. Tomlal Jose et al.
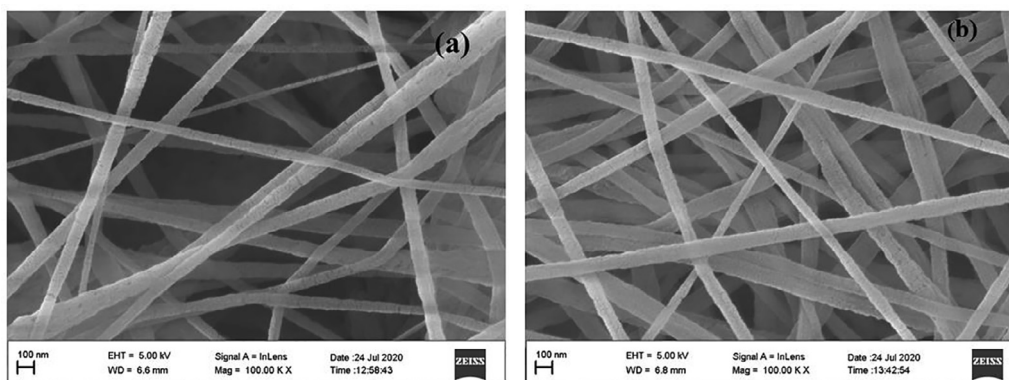
Fig. 1. FESEM Images (a) PSMMA fibers (b) Integrated PSMMA fibers.
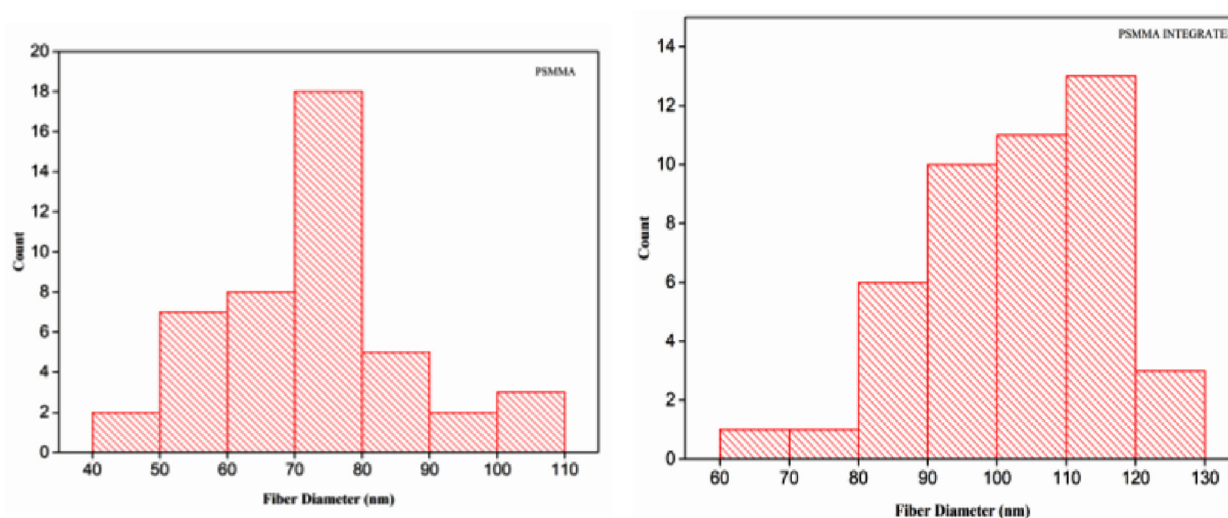
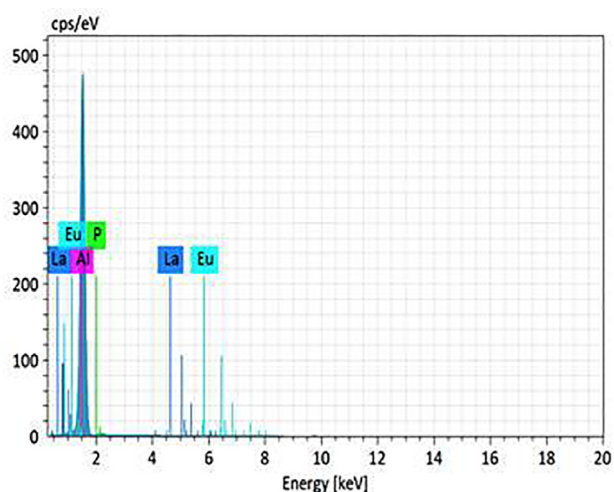**Fig. 2.** Histogram of PSMMA and LaPO$_4$: Eu^{3+} integrated PSMMA fibers.

Fig. 3. EDX spectra and of integrated PSMMA nanofibers.

Fig. 4. EDX mapping image of integrated PSMMA nanofibers.

3.3. FTIR studies

The FTIR spectra of PSMMA and integrated PSMMA nanofibers are shown in Fig. 6. In the PSMMA nanofibers peak at 2947 cm^{-1} corresponds to C–H stretching vibration and at 1726 cm^{-1} is the characteristic peak of C=O stretching of the PMMA fragment. Peaks at 1453 cm^{-1}, 1602 cm^{-1} corresponds to the vibration of benzenoid rings of PS fragment. In the case of PSMMA doped nanofibers the peaks corresponding to the C–H stretching and C=O stretching vibrations shifted to the high frequency side to 2955 cm^{-1} and 1734 cm^{-1} respectively and it may be due to the interaction of the integrated material with the polymer matrix

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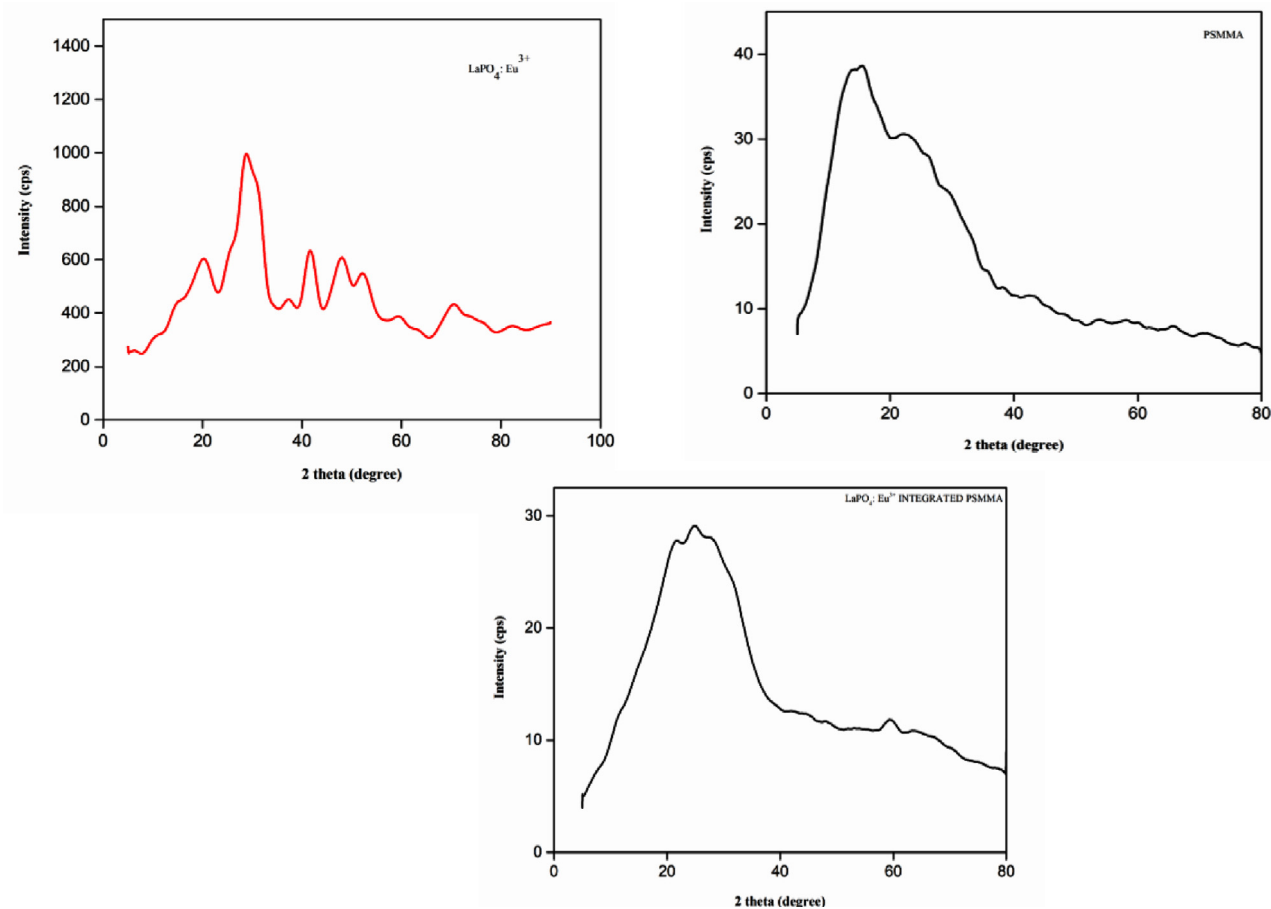
Fig. 5. XRD spectra of LaPO$_4$: Eu^{3+}, PSMMA and integrated PSMMA nanofibers.
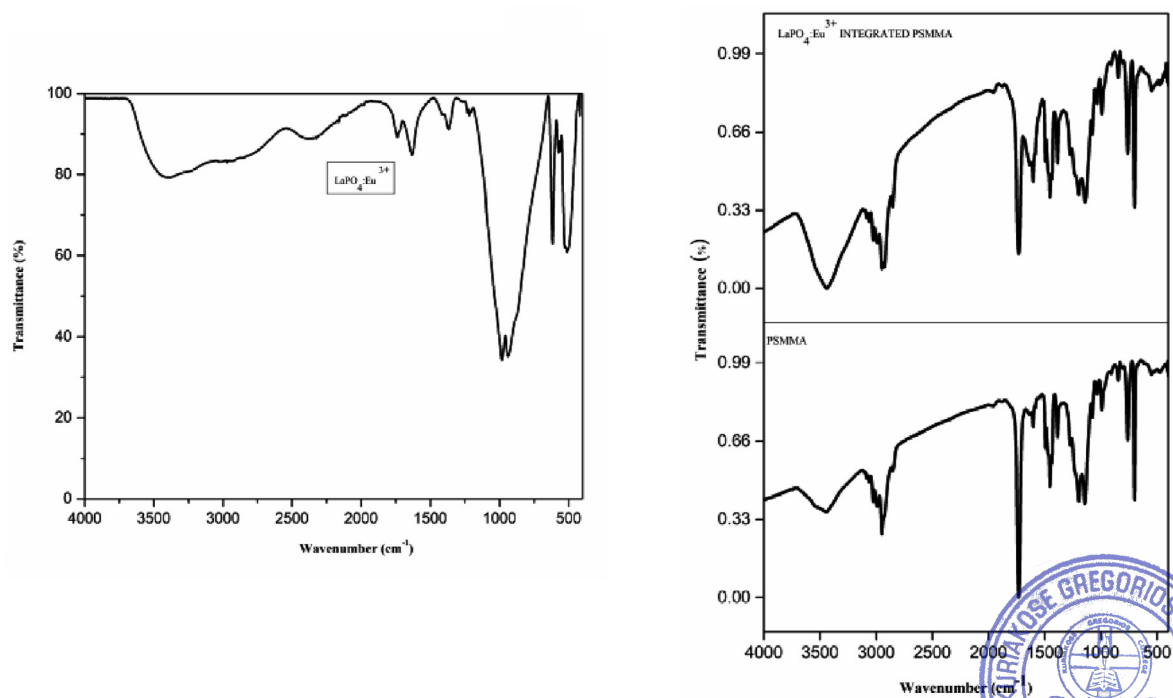
Fig. 6. FTIR image of LaPO$_4$: Eu^{3+}, PSMMA and integrated PSMMA nanofibers.

V. Varkey, A.R. Chandran, E. Tomlal Jose et al.
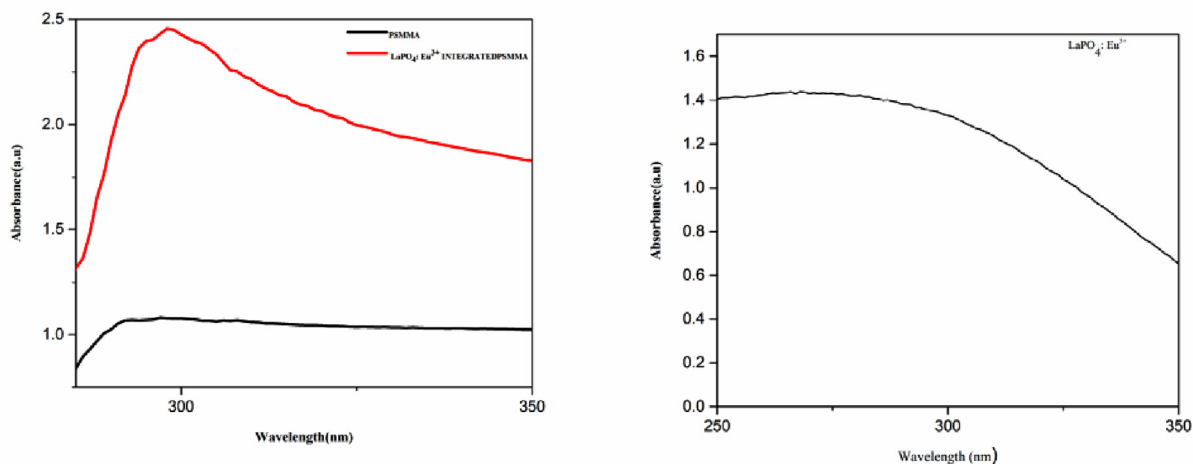
Fig. 7. UV–Visible Absorption spectra of LaPO$_4$: Eu^{3+}, PSMMA and integrated PSMMA fibers.

which is in agreement with the reported work [35]. Also additional peaks are observed at around 2916 cm^{-1} and 2850 cm^{-1} which also may be due to the interaction of the integrated material with polymer matrix.

3.4. UV –Visible absorption studies

The UV – Visible spectra of PSMMA and integrated PSMMA nanofibers given in Fig. 7 shows a shift in the wavelength of maximum absorption from 290 nm to 298 nm in the case of integrated PSMMA nanofibers. This may also be due to the interaction of LaPO$_4$:Eu^{3+} with the polymer matrix. The UV– Visible Spectra of LaPO$_4$:Eu^{3+} shows a broad peak in the range of 250 to 300 nm which is consistent with the peak of integrated nanofibers.

3.5. Photoluminescence analysis

PL emission spectrum recorded at λ_{exc} 393 nm of PSMMA, integrated PSMMA nanofibers and LaPO$_4$:Eu^{3+} are shown in Fig. 8 and Fig. 9 respectively. In the case of PSMMA nanofibers no characteristic emission band is observed in the region 575 to 595 nm whereas for integrated PSMMA nanofibers peaks corresponding

Fig. 9. Emission spectra of LaPO$_4$:Eu^{3+}.

to the transitions obtained for LaPO$_4$:Eu^{3+} is seen and also there is significant enhancement in the intensity of PSMMA nanofibers on integrating LaPO$_4$:Eu^{3+}. This can be explained on the basis of the fact that there is an increase in the luminescent centres of integrated PSMMA nanofibers when compared to psmma nanofibers.

The peaks observed in the region 579 to 610 nm corresponds to $^5D_0$ -$^7F_0$, $^5D_0$ -$^7F_1$, $^5D_0$ - $^7F_2$ transitions.

4. Conclusion

Electrospun nanofibers find applications in diverse fields. In the present work the possibility of using electrospun PSMMA nanofibers as a host matrix for luminescent rare earth phosphates is been investigated. The surface morphology analysis revealed that there is an increase in the fibre diameter of PSMMA when integrated with LaPO$_4$:Eu^{3+}. Also from EDX analysis the presence of rare earth ion is confirmed. The FTIR and UV–Visible analyses also supported the above observations thereby confirming our aim to establish the use of PSMMA nanofibers as host matrix for luminescent particles. Furthermore investigations are required to understand clearly the nature of interaction between the host and dopant. PL analyses showed a significant enhancement in the intensity of integrated

Fig. 8. Emission spectra of PSMMA and integrated PSMMA fibers.

nanofibers ascertaining that PSMMA integrated nanofibers can be used in various optic and photonic devices.

Declaration of Competing Interest

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

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Review

Recent studies in Suzuki-Miyaura cross-coupling reactions with the aid of phase transfer catalysts

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A R T I C L E   I N F O

A B S T R A C T

Under increasing environmental awareness and with the increasing interest in green chemistry processing, Suzuki-Miyaura coupling reaction can be proceeded using phase transfer catalyst (PTC), instead of using toxic ligands and organic solvents is a great stride in synthetic organic chemistry. The phase transfer catalyst allows transferring substance from one system to another in a chemical reaction between the two non-miscible, heterogeneous systems, which itself has both functional sites to get solubilized in both system. This review highlights the use of various PTC's, and the importance for the reaction outcome and applicability in Suzuki-Miyaura coupling reaction from 2009 to 2020.

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1. Introduction

Phase-transfer catalyst (PTC) has been well-known for more than four decades in synthetic organic chemistry [1]. It allows the reaction in a heterogeneous system between general organic compounds soluble in organic solvents and inorganic salts soluble in water [2]. A phase-transfer catalyst is to assist transfer of the reagent from one phase (eg. Hydrophilic) to another phase (eg. Lyophilic) which are immiscible and it is regenerated to its original state so the amount of PTC needed is catalytic [3]. This versatile method is used industrially because, reactions usually progress under mild reaction conditions, inexpensive and environmentally benign reagents and solvents are employed, simple experimental operations with higher yield of product, eliminate hazardous waste and the possibility to conduct large-scale preparations and hence the methodology is regarded as good for Green Chemistry [4]. Typical phase-transfer catalysts are quaternary ammonium salts [5], crown ethers [6], phosphonium compounds [7], non-ionic PTC etc [8]. This review aims to highlight the recent advances in use of phase transfer catalysis in Suzuki coupling reaction [9] and covers literature from 2009 to 2020. For simplicity and clarity, the topic is classified based on the different types of PTC's used in Suzuki reaction.

2. Suzuki-Miyaura cross-coupling reactions with the aid of phase transfer catalyst

Cross-coupling reactions indicate an important synthetic organic conversion that consist of the combination of an organometallic reagent with an organic electrophile with the support of group 8–10 metal catalysts to accomplish a C–C [10], C–N [11,12], C–S [13,14], C–Se [15], or in general C–M bond formation. Suzuki reaction is an important organic coupling reaction between organoboron reagents with organohalides, using palladium (0) complex as catalyst and is one of the most versatile and successful synthetic tools for carbon–carbon bond formation [16-25]. This reaction is named after the Japanese Nobel Laureate Akira Suzuki, who first published the work on this reaction in 1979. The general scheme for the Suzuki coupling reaction follows a catalytic cycle involving three primary steps, viz. oxidative addition, transmetalation, and reductive elimination (Scheme 1).

To realize cleaner and environmentally benign products, studies have been progressed on Suzuki cross-coupling reactions under solvent-free or on-water conditions. In many cases, reactions proceed slowly due to the poor solubility of substrate/reagents in water. Aryl boronic acid showed very slow or incomplete conversion of products. Also, it showed difficulty to isolate the products from the reaction mixture. These difficulties can be solved by adding phase transfer catalysts [26] and use of water soluble salt of reagents or catalysts [27,28]. This review discusses various types of phase transfer catalysts used in Suzuki-Miyaura cross-coupling reactions. By adding phase transfer catalysts which can bridge the

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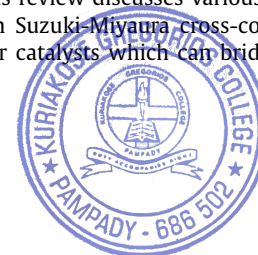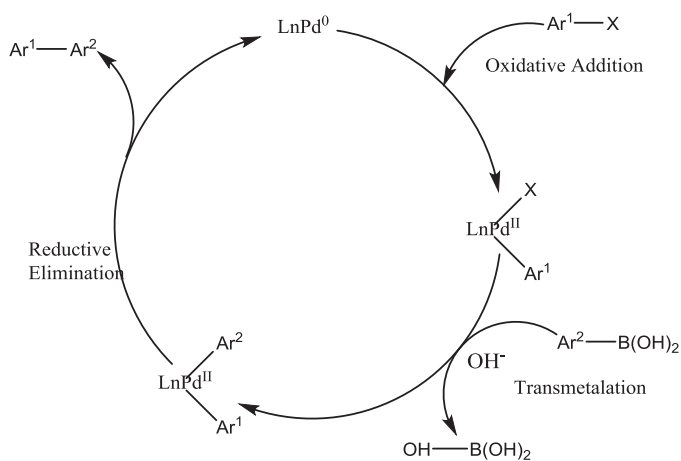
Scheme 1. General Mechanism for Suzuki Reaction.

gap between these two immiscible phases and can make molecular interactions possible between two phases [29]. The PTC molecules can transport reactant molecules from the organic phase (e.g., heteroaryl bromides) to the aqueous phase (Pd-catalyst and phenylboronic acid) and vice versa. Hence, direct interactions among molecules in the mixture could be possible and it leads to the transmetalation between heteroaryl bromides and phenylboronic acid via the transporting functions of PTC.

2.1. Quaternary ammonium salt in Suzuki reaction

2.1.1. Tetra butyl ammonium halide support in Suzuki reaction

Heterogeneous (hydrophobic) palladium catalysts are good promise towards green approach where water acts as a cheap, non-toxic and safe reaction medium. The presence of PTC such as tetra butyl ammonium halide plays a vital role for the smooth reaction by activating the catalytic species in the reaction. In 2009, Jin and co-workers designed a very original approach based on a recoverable palladium supported magnetite Fe_3O_4–ionic liquid catalyst. Pd-NHC complex is used as the catalyst source which has been immobilized onto magnetite Fe_3O_4–ionic liquid hybrid matrix based on supported ionic liquid system. HR-TEM images showed that the particle size was around 30-40 nm (Scheme 2) [30]. The immobilized Pd- NHC catalyst such as Pd- NHC@Fe_3O_4–IL has shown excellent catalytic activity and high stability for the Suzuki coupling reaction of bromoarenes with a variety of arylboronic acids in water. The catalyst system required K_3PO_4 as the base and TBAB (tetrabutylammonium bromide) as the phase transfer agent in water at temperatures ranging from 40–85 °C. Numerous examples were reported with 0.5 mol% Pd indicating that the protocol was particularly efficient even in the presence of challenging substrates. This catalyst can be recycled five times without any significant loss in the catalytic activity. Due to the magnetic properties of nano-Fe_3O_4, the hybrid complex catalyst could be separated from the reaction mixture by an external magnet avoiding the usual filtration or centrifugation process.

In the same year, Cai *et al.* reported an eco-friendly protocol of Suzuki–Miyaura cross-coupling reactions using perfluorotagged palladium nanoparticles supported on a fluorous silica gel (Pd-1/FSG) as the catalyst, K_2CO_3 as the base and TBAB in water, affording the corresponding biphenyls in moderate to high yields (Scheme 3) [31]. Arylbromides with either electron- withdrawing or donating substituents in the *ortho* or *para* positions give good yields of product. Chlorobenzene has not effectively resulted the product. The catalyst could be recovered by simple filtration and reused again several times. The catalyst activity was

decreased slightly in each recycling, and Pd leaching was less than 10 ppm. The phase-transfer catalyst, tetra-n-butyl ammonium bromide (TBAB) remarkably stabilizes Pd-1/FSG by preventing the aggregation of nanoparticles, which effectively accelerates the reaction and gives good yields of the products.

Another environmental friendly report on the coupling of bromoarenes with sodium tetraphenylborate has been described by Bai using Pd/C catalyst in water under microwave irradiation (Scheme 4) [32]. Excellent yields were obtained in less than twenty minutes at 120 °C in the presence of K_2CO_3 as the base and TBAB as phase transfer catalyst with a comparatively higher palladium loading (5 mol% Pd). Aryl bromides with various substitutions, dibromobenzene, tribromobenzene and some heterocycles could effectively couple with Ph_4BNa forming cross-coupled products in excellent yields. The Pd/C catalyst was found uncontaminated with ligands or transition metals and it showed excellent recycling ability over more than five cycles and could be easily separated from the reaction mixture.

A study describing the highly enantioselective asymmetric Suzuki–Miyaura biaryl coupling was carried out in water for the first time with a recyclable palladium complex of a chiral imidazoindole phosphine ligand supported on an amphiphilic polystyrene–polyethylene glycol copolymer (PS–PEG) resin by Uozumi and co-workers (Scheme 5) [33]. Excellent yields of a variety of biaryl compounds with very good enantioselectivities (88–99% *ee*) with broad substrate tolerance were obtained in water with the aid of palladium complex of PS–PEG-supported imidazoindole dicyclohexylphosphine (PS–PEG–L*) in the presence of tetrabutylammonium fluoride (TBAF) as PTC at 80 °C. A large amount (10 mol%) of the palladium catalyst (PS–PEG–L*–Pd) was required, but it could be reused four times without further purification and further charging of it with palladium.

In a subsequent study, Zhang *et al.* reported more environmental friendly Suzuki-Miyaura cross-coupling reaction using air and moisture stable palladium-phosphinous acid catalyst POPd, that is $[(t\text{-}Bu)_2P(OH)]_2PdCl_2$ with K_2CO_3 as base and $(n\text{-}Bu)_4NBr$ (TBAB) as PTC using water as solvent under reflux. (Scheme 6) [34]. This efficient Suzuki cross-coupling reaction resulted biphenyls in good to excellent yields from variety of aryl halides with phenyl boronic acid have various functional groups without requirement of organic co-solvents. Water-PTC palladium-catalyst system can be reused and the yield was 70% even after the fourth cycle. Also, the catalyst possessed high stability in air, good solubility in water and it could resolve the basic difficulties of catalyst separation and recovery.

In another report following their earlier studies, the same team used this catalytic system for the coupling of heteroaryl halides with phenylboronic acid in high yields and demonstrated excellent tolerance to a wide range of sensitive functional groups on substrate (Scheme 7) [35]. TBAB was effectively used as phase transfer catalyst, among the three sets of PTCs studied such as tetramethylammonium bromide (TMAB) cetyltrimethylammonium bromide (CTAB) and Tetrabutylammonium bromide (TBAB). POPd has excellent tolerance to a broad range of heterocyclic halides and it can be conveniently handled due to its air stability.

In the next year, Yuan *et al.* explored water-mediated coupling reactions of aryl chlorides over heterogeneous palladium nanoparticles deposited on a zeolite-type Metal-Organic Framework (Scheme 8) [36]. This work represents the first example of an active catalyst, composed of a MOF as the support for metal NPs, for the coupling reactions of aryl chlorides. Pd/MIL-101 was prepared by the impregnation of activated MIL-101 with a $Pd(NO_3)_2$ precursor that was diluted in N,N-dimethylformamide. X-ray diffraction showed that palladium loading did not change the MIL-101 framework and the TEM image revealed that the palladiums NPs were greatly dispersed, with a mean diameter of 1.9–0.7
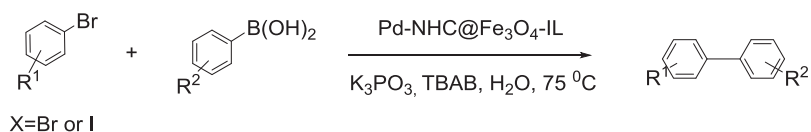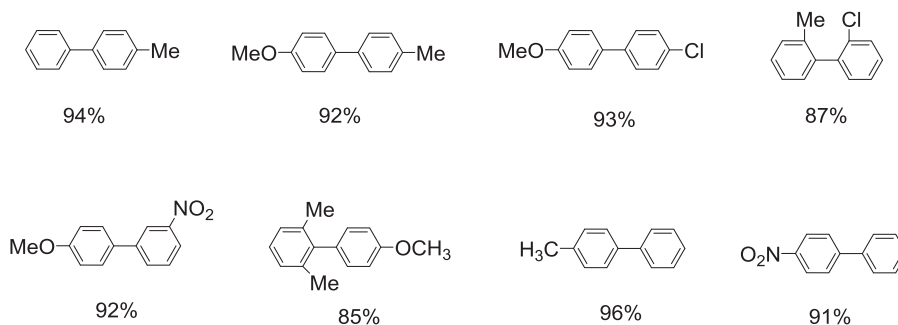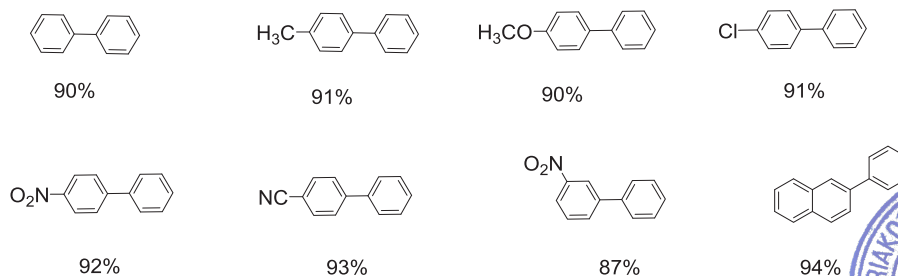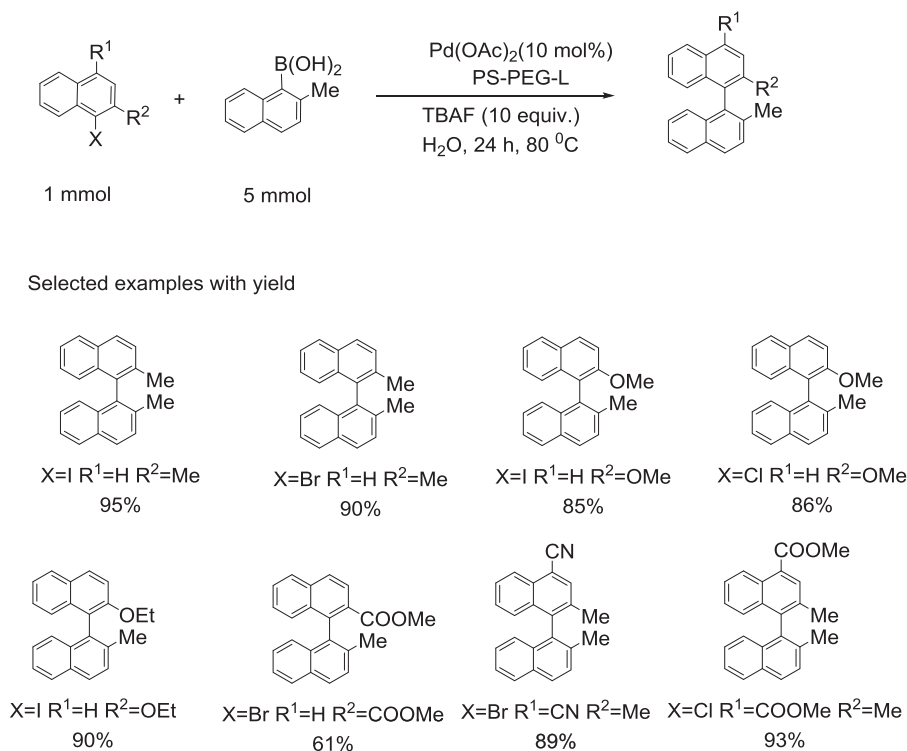
Scheme 2. Suzuki coupling of phenyl bromide with Phenylboronic acid in water.
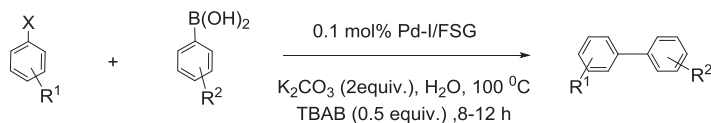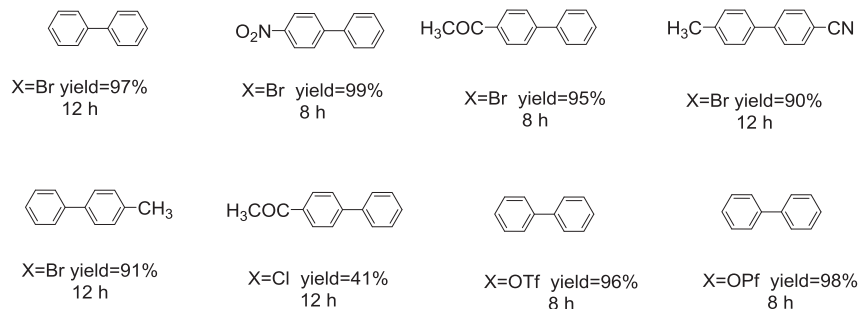

Scheme 3. Pd–C/FSG-catalysed Suzuki–Miyaura reactions.
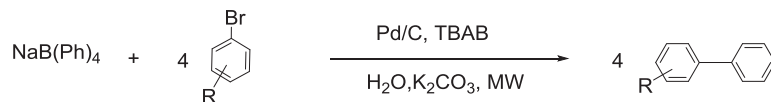
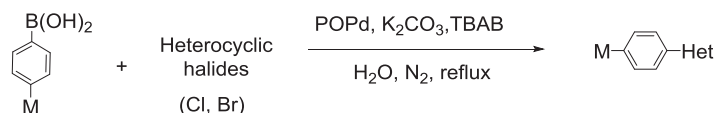**Scheme 4.** Cross-coupling of aryl bromides with sodium tetraphenylborate.

Selected examples with yield

X=I R^1=H R^2=Me
95%

X=Br R^1=H R^2=Me
90%

X=I R^1=H R^2=OMe
85%

X=Cl R^1=H R^2=OMe
86%

X=I R^1=H R^2=OEt
90%

X=Br R^1=H R^2=COOMe
61%

X=Br R^1=CN R^2=Me
89%

X=Cl R^1=COOMe R^2=Me
93%

Scheme 5. Selected examples of the asymmetric Suzuki–Miyaura reaction by Uozumi et al.

Selected examples with yield

X=Br 99%

X=Br 98%

X=Br 99%

X=Br 92%

X=Cl 57%

X=Cl 55%

X=Cl 58%

X=Cl 19%
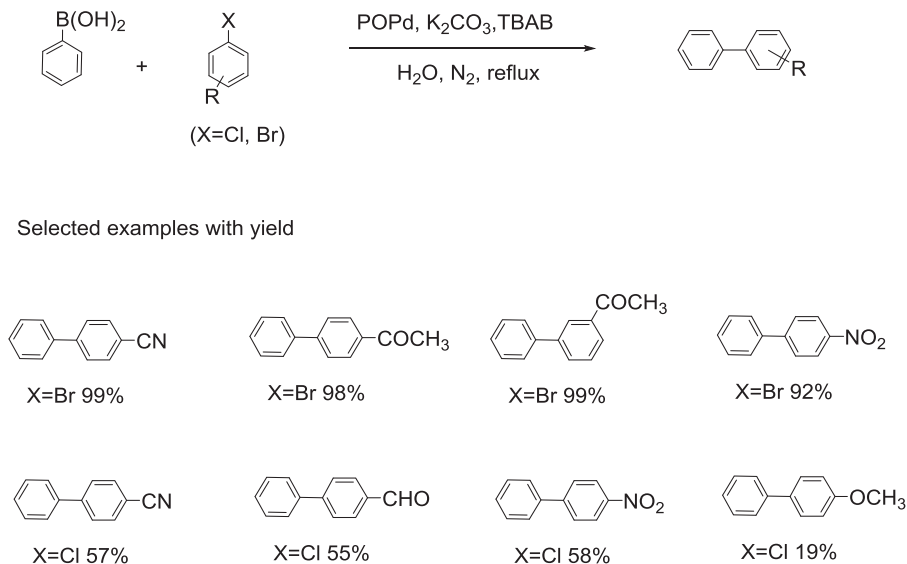
Scheme 6. POPd-catalyzed Suzuki coupling reaction of phenyl boronic acid with substituted phenyl halides.

nm. XPS studies proved that most of the palladium was in the reduced form, and palladium in the reduced form is the active site for the Suzuki–Miyaura coupling reaction. Phenyl boronic acid react with aryl chlorides having both electron-rich and electron-poor substituents, affording the corresponding biphenyl compounds in excellent yields under the optimized reaction conditions such NaOMe as base, TBAB in neat water at 80 °C for 20 hours. The addition of TBAB as PTC enriched the yield considerably. The crystalline structure of the catalyst was mostly retained after five catalytic cycles. A very low amount of dissolved palladium (less than 0.2% of the total palladium) was detected in the solution at the end of the reaction.

A facile one-step synthetic strategy for a catalyst system by immerging a porous ionic copolymer (PIC) into a Pd(OAc)$_2$ in acetone solution was demonstrated by Jun Huang and co-workers in 2011 (Scheme 9) [37]. Acetone was then removed by evaporation to give the Pd catalyst Pd(OAc)$_2$/ PIC. The Pd nanocatalyst (Pd/PIC) was a heterogeneous catalyst formed in situ with Pd(OAc)$_2$/PIC with a diameter of mainly around 2–5 nm in the Suzuki– Miyaura reaction in which aryl bromides and chloride reacted with phenylboronic acid in water in the presence of TBAB and base (NaOH and Na$_2$CO$_3$). TBAB used as the phase transfer agent has enhanced the yield significantly. Also, it played a role for the stabilization of the Pd nanocatalyst. Pd/PIC can be separated easily by filtration and

B(OH)₂ on M + Heterocyclic halides (Cl, Br) → M——Het

$$\text{B(OH)}_2 \text{ (M)} + \text{Heterocyclic halides (Cl, Br)} \xrightarrow[\text{H}_2\text{O, N}_2,\text{ reflux}]{\text{POPd, K}_2\text{CO}_3,\text{TBAB}} \text{M}-\text{Het}$$

Selected examples with yield

heterocyclic halide = 2-bromothiophene
M=H yield=82%

heterocyclic halide = 3-bromopyridine
M=H yield=88%

heterocyclic halide = 2-bromothiophene
yield=79%

heterocyclic halide = 2-bromopyridine
yield=55%

heterocyclic halide = 4-chloropyridine
yield=77%

heterocyclic halide = 5-chloro-2-fluropyridine
yield=79%

Scheme 7. POPd-catalysed Suzuki-Miyaura cross-coupling of heterocyclic halides with pheylboronic acid.

$$\underset{\underset{0.05 \text{ mmol}}{}}{\text{Cl}-\text{R}} + \underset{0.75 \text{ mmol}}{\text{B(OH)}_2} \xrightarrow[\text{TBAB (0.3 mmol),80 }^0\text{C, 20 h, under N}_2]{\substack{\text{Pd/MIL-101 (0.9 mol\%)} \\ \text{NaOMe (1.5 mmol), H}_2\text{O (4 ml),}}} \text{R}-\text{biphenyl}$$
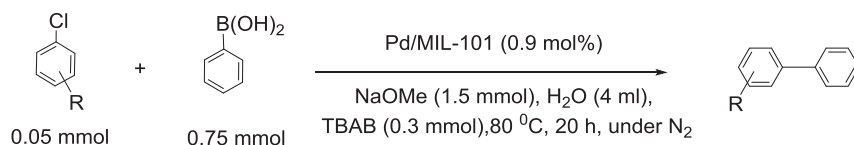
Some selected examples

97%

MeO— 96%

MeOC— 96%

OMe 81%
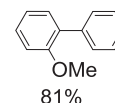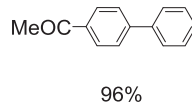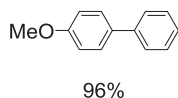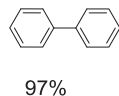
Scheme 8. Suzuki–Miyaura coupling reactions of aryl chlorides over supported palladium catalysts.

without loss of efficiency and have excellent recyclability. The TEM image of the catalyst after 5 times reaction indicates that the mean diameter of the nanoparticles is around 2–5 nm, which is similar to the catalyst separated from the reaction mixture firstly. Moreover, Pd/PIC were well tolerated for the coupling reaction of aryl bromides and chlorides, and functional groups, such as methoxyl, nitriles, nitro, aldehydes, ketones and ester groups.

In 2012, Wu and Gu developed tetrabutyl ammonium fluoride (TBAF)-assisted palladium-catalysed Suzuki reaction in neat water under the ligand and base-free conditions (Scheme 10) [38]. The cross-coupling of aryl or heteroaryl bromides with arylboronic acids generated the corresponding products in good to excellent yields using Pd(OAc)₂ (0.5 mol%) with TBAF at 95 °C for 3 hours in air. The presence of TBAF was very significant in this reaction, and two equivalents of TBAF were satisfactory to perform the reaction well. Therefore, under the Suzuki reaction conditions, TBAF

may play simultaneously two roles as the phase transfer catalyst and the base. Various electron-donating and electron-withdrawing were well tolerated to give the desired unsymmetrical biaryls in good to excellent yields tetrabutylammonium halide.

The synthesis of hydroxyapatite supported novel palladium catalyst and its application to the Suzuki–Miyaura cross-coupling reaction in water under atmospheric conditions was demonstrated by Indra and co-workers in 2013 (Scheme 11) [39]. Two types of supported palladium catalyst, one by immobilization of [Pd(COD)Cl₂] (COD = 1,5-cyclooctadiene) on hydroxyapatite (HAP) (catalyst 1) and another catalyst by subsequent reduction of the catalyst 1 with sodium borohydride (catalyst 2). The powder XRD studies revealed that Pd-loading does not change the bulk structure of HAP. TEM images showed that the size of the catalyst particles were in the range of 1-5 nm. The catalyst with Pd²⁺ was found to be almost five times more active than the reduced catalyst un-
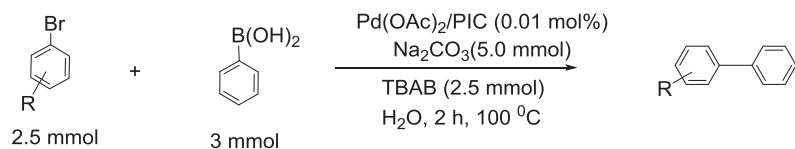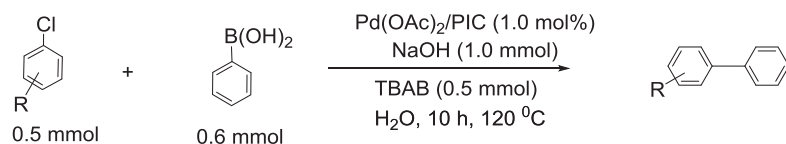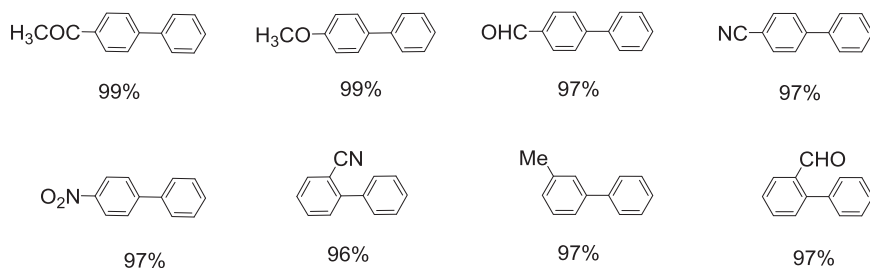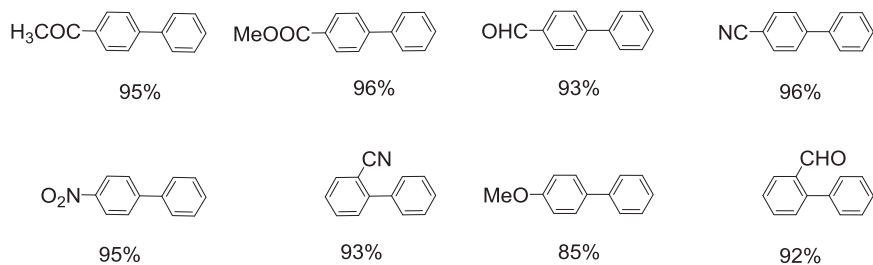
Scheme 9. Suzuki coupling of aryl bromide/chlorides and phenylboronic acid.
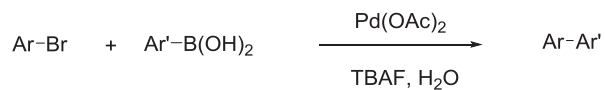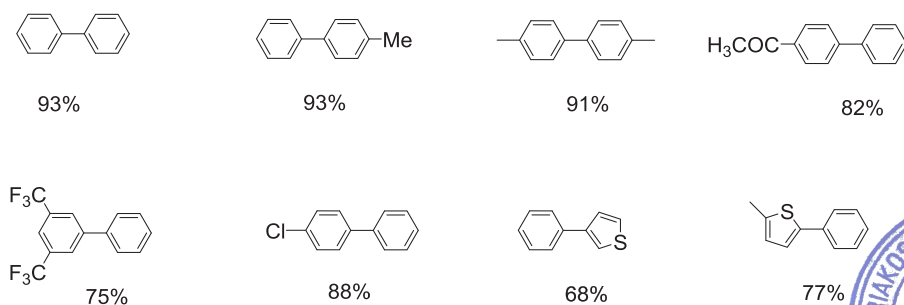
Scheme 10. Cross-coupling of aryl and heteroaryl bromides with arylboronic acids
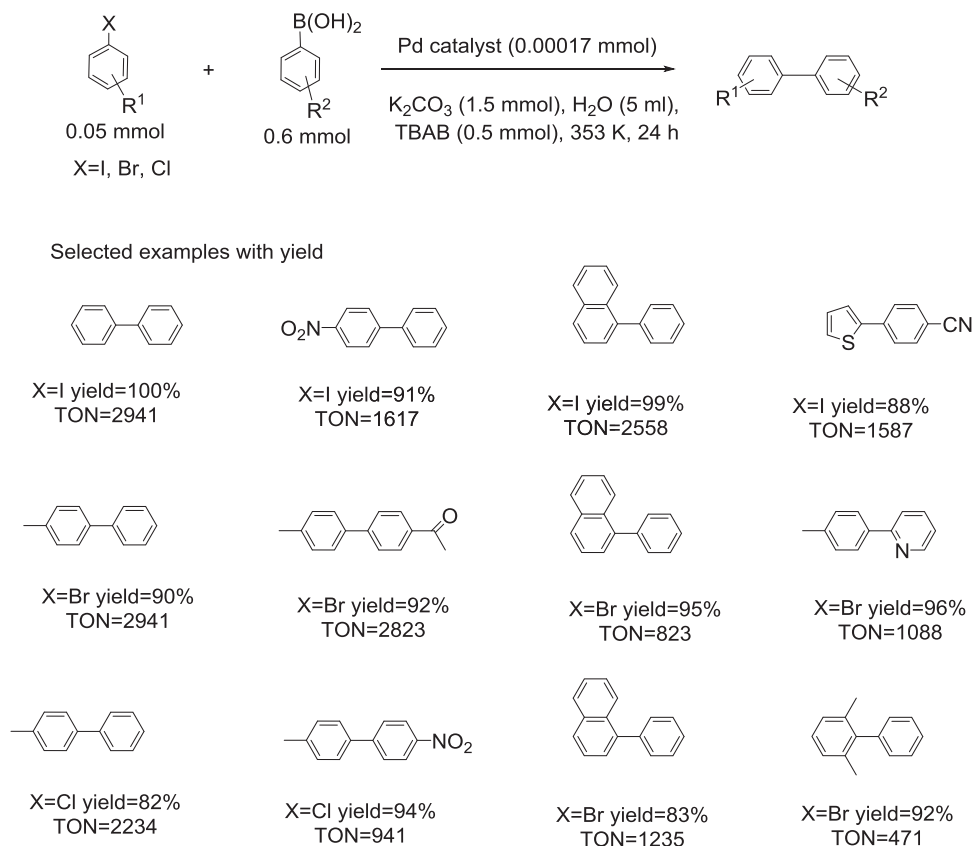
Scheme 11. Suzuki–Miyaura reactions using the Pd–HAP catalyst.

der similar reaction conditions. This catalyst system has been effectively tested for different electronically neutral, electron-rich, electron-poor and sterically hindered aryl boronic acids, and several different aryl halides including aryl chlorides. TBAB acts as PTC and stabilises the active catalytic intermediate in coupling reactions, and its presence showed a significant increase in turnovers. More than one thousand turn overs and high selectivities toward the hetero-coupled products have been observed in most cases. Catalyst 1 can be recycled ten times without any metal leaching and activity. A negligible drop in activity was observed over ten cycles. It was recovered by simple filtration and the product yields for the 2nd and 3rd cycle were nearly the same (93%) but reduced during the 4th cycle (88%).

In the same year, Amadio and co-workers prepared a new eco-friendly water-soluble nitrogen ligand, which has been prepared by coupling of 2-(azidomethyl)pyridine with but-3-ynyl sodium sulphate in t-BuOH using $Cu(OAc)_2$ (Scheme 12) [40]. The mixture of the new ligand with $[Pd(\eta^3-C_3H_5)Cl]_2$ (Pd:ligand=1:1) provides a greatly dynamic catalytic system for the Suzuki–Miyaura reaction. The experiments were carried out in the presence of tetra-butylammonium bromide (TBAB) as phase transfer catalyst in order to make sure a good movement of the organic substrate into the aqueous phase using K_2CO_3 as the base. TBAB, owing to its inexpensiveness, makes the process more cost-effective. The use of water as the solvent in catalysis promises the easy recycle of catalyst and the product can be recovered promptly by filtration or extraction with organic solvent. The air stable catalytic system works under conventional heating and catalyst can be recycled effectively for three successive runs. After the second run, the catalytic activity was found reduced due to the loss of PTC, and was found accumulated along with saline by-products. A variety of aryl bromides and heteroaryl bromides reacted effectively with phenyl-

boronic acid in this coupling reaction with low catalyst loading and reasonable reaction times.

Koleychev and co-workers developed series of novel 6- and 7-membered NHC (N-heterocyclic carbene)palladium(II) complexes and studied its catalytic activity in Suzuki cross coupling of heteroaryl chlorides in aqueous media under air(Scheme 13) [41]. (NHC)Pd(cinn)-Cl (cinn = cinnamyl = 3-phenylallyl) were synthesized and characterized structurally in the solid state. These complexes can be obtained by direct interaction of free carbenes with a palladium source or via transmetalation in (NHC)AgCl. The (6-Dipp)Pd(cinn)Cl complex (cinn = cinnamyl = 3-phenylallyl) based on six-membered ring carbene bearing bulky Dipp (Dipp = 2, 6-diisopropylphenyl) substituents was found to be the most active precatalyst in the Suzuki– Miyaura cross-coupling reaction of heteroaryl chlorides and bromides with boronic acid in aqueous media. High quantitative yields of biaryls were resulted with boronic acids bearing donor, acceptor as well as sterically bulky substituents using water as solvent, under air, using low catalyst and low loadings of phase transfer agent TBAB and with mild and environmentally benign base $NaHCO_3$. As an additional benefit, the precatalyst (6-Dipp)-Pd(cinn)Cl is air- and moisture-stable and can be prepared in multigram quantities in high yields.

In 2013, Li *et al.* proposed palladium-phosphinous acid complexes used in Suzuki cross-coupling reaction of heteroaryl bromides under mild reaction conditions (Scheme 14) [42]. The catalyst was highly active and air stable. Suzuki cross-coupling reaction of heteroaryl bromides with phenylboronic acid happened well using palladium phosphinous acid complexes (POPd) and tetrabutylammonium bromide or PEG as phase transfer catalyst in water/ethanol mixture with the presence of base K_2CO_3 resulted the corresponding yields of cross-coupling heteroaryl-aryls were satisfied. Notably, in the presence of TBAB, addition of alcoholic sol-
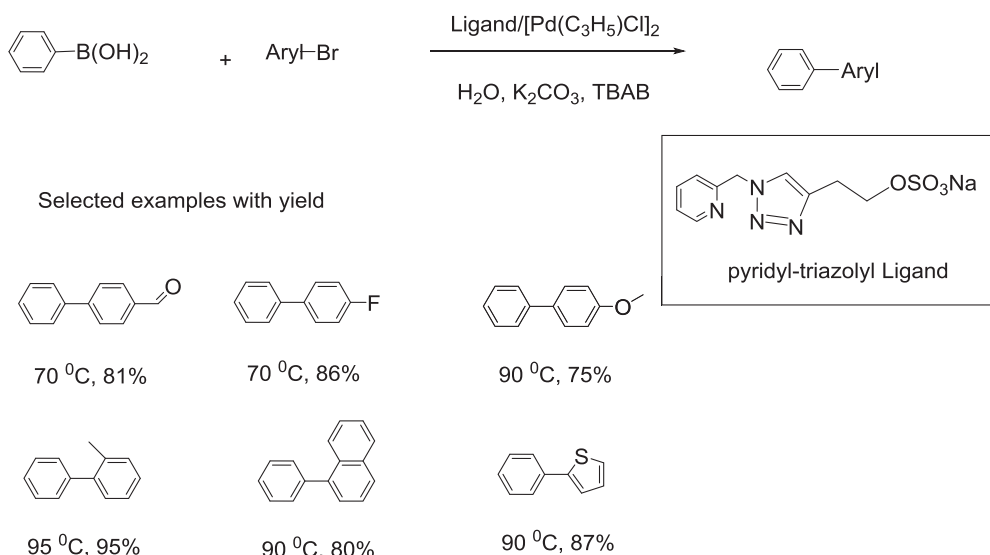
Scheme 12. Palladium catalysed coupling of phenylboronic acid with various aryl bromide.
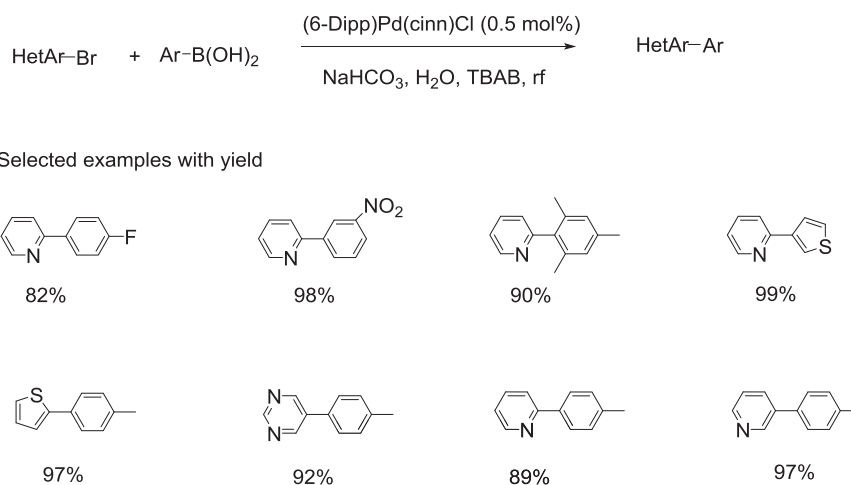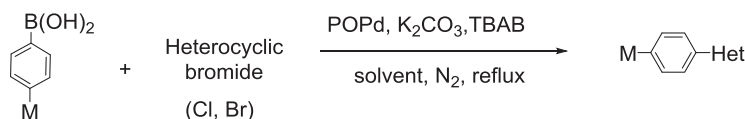

Scheme 13. Suzuki–Miyaura coupling of heteroaryl bromides with arylboronic acids.

vents into water enhanced the yields of the target products. The yield of the product could be enhanced with the increase of PTC concentration, and decreased with the increase of POPd amount due to the high reactivity of POPd triggering potential homo-coupling reaction of phenyl boronic acid molecules. However in terms of the liquid phase transfer catalyst of PEGs, mixing water into PEGs could slightly decrease the yields with respect to the water free PEGs bulk phase, which was probably due to the ho-mogenous liquid conditions in pure PEGs and weak interactions between PEGs and heteroaryl bromide molecules in water depend-ing on their molecular chain lengths.

The Pd-PEPPSI complexes (PEPPSI implies pyridine-enhanced precatalyst preparation, stabilization, and initiation) with N-heterocyclic carbenes (NHC) ligands of the 1,2,4-triazole series and it was studied for the first time as catalysts of the Suzuki Miyaura reaction by Chernenko et al. in 2018 (Scheme 15) [43]. A' proce-dure for the synthesis of bromide and iodide Pd-PEPPSI complexes by the reactions of PdCl$_2$ with 1,4-dialkyl-1,2,4-triazolium salts in pyridine in the presence of KBr or KI as sources of halide ions was studied. With the aid of PTC such as tetrabutylammonium bromide (TBAB), the excess KBr or KI makes to increase the yield of the bro-mide and iodide Pd-PEPPSI complexes (up to 99%) with short dura-tion such as 3 hours. 1,2,4-Triazole Pd-PEPPSI complexes have high

catalytic activity and followed a simple synthesis method. Also, it showed comparable activity with generally applied PEPPSI-IPr cat-alyst. The Suzuki cross-couplings of phenylboronic acid reacted ef-fectively with various aryl bromides and iodides in propan-2-ol in the presence of catalyst resulted good yield of products (70-98%)

A novel heterodonar bidentate perfluorinated phosphine-imine ligands complexed with divalent palladium(II) soluble in supercrit-ical carbon dioxide (ScCO$_2$) solvent showed good catalytic activ-ity in the Suzuki C-C coupling reactions under mild conditions was introduced by Yilmaz in 2018 (Scheme 16) [44]. ScCO$_2$ is a preferred solvent in green chemistry research, because it is non-toxic, inert, inexpensive, nonflammable, environmentally friendly and readily available. Also, perfluorinated phosphine-imine ligands have been synthesized from the 3-(heptadecafluorooctyl)aniline and 2-(diaryl)phosphinobenzaldehyde and it is complexed with dichloro(1,5- cyclooctadiene) palladium(II). These palladium(II) complexes having perfluoroctyl ponytails (-C$_8$F$_{17}$) are completely soluble in supercritical carbon dioxide (ScCO$_2$) at 80 °C under 122 atm of CO$_2$ pressure. ^{31}P, ^{1}H, ^{19}F, ^{13}C NMR and FTIR spectroscopies and high resolution mass spectroscopy revealed that phosphine-imine ligands acted as PN bidentate ligand and have bonded to the palladium(II) centre via nitrogen and phosphorus donors. Ho-mogenous palladium catalysed Suzuki C-C coupling reactions us-
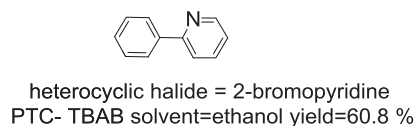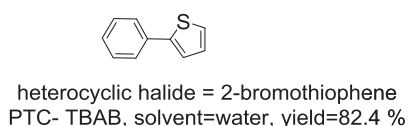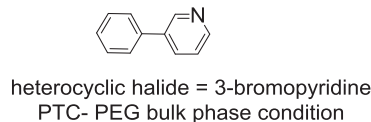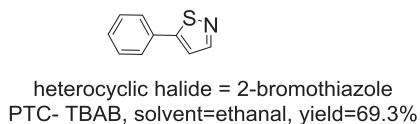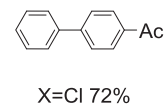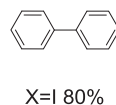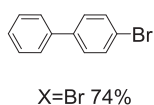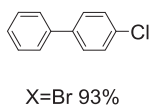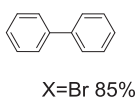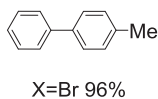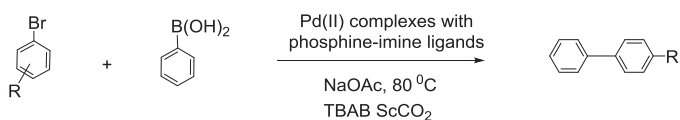
Scheme 14. POPd-catalysed Suzuki-Miyaura cross-coupling of heterocyclic halides with pheylboronic acid.
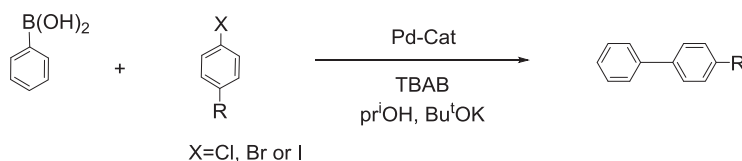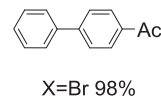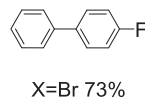
Scheme 15. Cross-coupling of aryl halides with PhB(OH)$_2$.
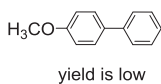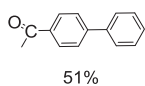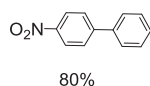

Scheme 16. Suzuki C-C coupling reactions of aryl bromides with phenyl boronic acid in ScCO$_2$.

ing palladium(II) complexes were carried out at 353 K under the pressure 135 atm. Tetrabutyl ammonium bromide (Bu$_4$NBr) used as phase transfer catalyst to facilitate the movement of the sodium salt into a ScCO$_2$ solution with NaOAc which gave the best effect for the coupling reaction. The catalytic activities of Pd (II) complexes in ScCO$_2$ were found to be greater in the Suzuki C-C coupling reactions of phenyl boronic acid with aryl bromides having electron-withdrawing groups than those deactivated species under mild conditions.

2.1.2. Tetrapropyl ammonium halide support in Suzuki reaction

In 2017, Mpungosea *et al.* reported greener and highly efficient bimetallic catalyst such as single-phase palladium and copper combination using the Pd$_{0.04}$Cu$_{0.04}$Ce$_{0.92}$O$_{2-\delta}$ (PdCuCeO) solid-solution oxide and its application in quasi-heterogeneous Suzuki-Miyaura cross-coupling reactions (Scheme 17) [45]. This catalyst could be prepared by simple, inexpensive and quick solution combustion synthesis method. It was characterised fully using X-ray diffraction (XRD), XPS, XANES, Raman spectroscopy, EXAFS and
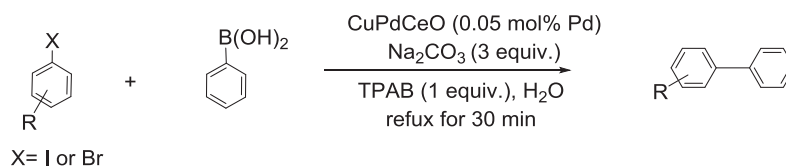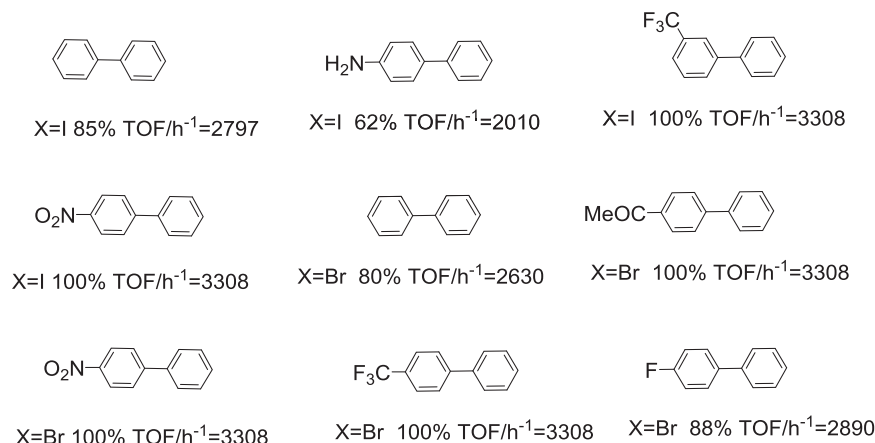
Scheme 17. Suzuki cross-coupling of iodo- and bromoarenes with phenylboric acid.

high-resolution transmission electron microscopy (HR-TEM) and all the characterisation techniques strongly suggest that the Pd^{2+} and Cu^{2+} ions were successfully incorporated into the ceria lattice. The crystal size of the prepared solid-solution oxide ranges from 11-14 nm and their surface areas ranges between 31-34 m^2/g. The Pd-CuCeO solid-solution oxide was effectively used in Suzuki-Miyaura cross-coupling reactions under ligand-free conditions using water as a sole solvent and tetrapropylammonium bromide (TPAB) as a phase transfer catalyst with Na$_2$CO$_3$ as base at 100 °C. The catalyst leaching and recyclability studies showed that Pd doped metal oxides act as precatalysts, and it act as a palladium reservoir, that slowly releases extremely reactive Pd species. This released Pd is taken by TPAB and creates a highly active quasi-heterogeneous Pd/TPAB catalyst. Suzuki-Miyaura coupling of aryl iodides, bromides as well as activated aryl chlorides was efficiently performed by this active PdCuCeO-TPAB catalytic system. The PdCuCeO-TPAB catalytic system also displayed good functional group tolerance, and good to excellent isolated yields were obtained. ICP-OES detected Only a negligible amount of palladium (<0.1 ppm) in the product solution because TPAB removed most of the palladium from the solution. Hence, catalytic system can be recycled three times and it resolved the difficulties of catalytic separation and recovery, which minimizes the metal contamination of products. The catalytic cycle followed the usual steps such as oxidative addition, transmetalation and reductive elimination.

2.1.3. Tetrabutylammonium hydroxide (TBAOH) support in Suzuki reaction

In 2010, Monopoli *et al.* introduced a composite resulting from the electrochemical impregnation of palladium nanoparticles on a tetragonal zirconium oxide nanopowder, can be used as an appropriate eco-friendly heterogeneous catalyst in three significant Pd catalysed C-C coupling processes such as Heck, Ullmann and Suzuki reactions (Scheme 18) [46]. TEM studies revealed that, Pd-NPs/ZrO$_2$ composite catalyst was of nanosize whereas the ZrO$_2$ support particle size was 150 ± 70 nm, also the whole catalyst surface was fully covered by the small sized palladium nanophases.
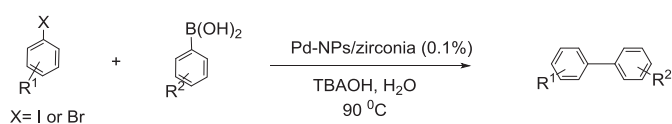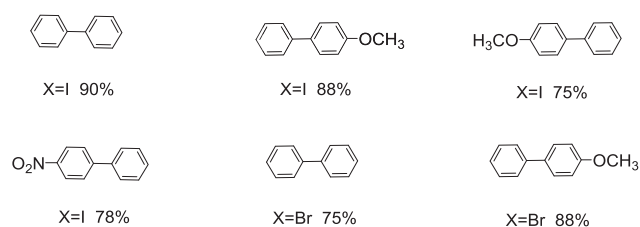

Scheme 18. Suzuki reaction catalysed by Pd-NPs/ZrO$_2$ in water.

The Suzuki cross-coupling reactions between aryl bromide or iodide with phenyl boronic acid couild be carried out in the presence of Pd/NPs/Zirconia (0.1%) catalyst in water, using TBAOH as PTC at 90 °C. TBAOH could act as base as well as PTC in reaction forming an emulsified reaction mixture, which helped to solve the solubility problems of the low polar starting materials in neat water. Also, the aqueous medium helped to increase the reaction rate because of its capability to dissolve boron side products coating the catalyst surface. In addition, the catalyst could be effectively recycled up to ten times without any considerable loss of activity and it was found efficient at low loadings also.
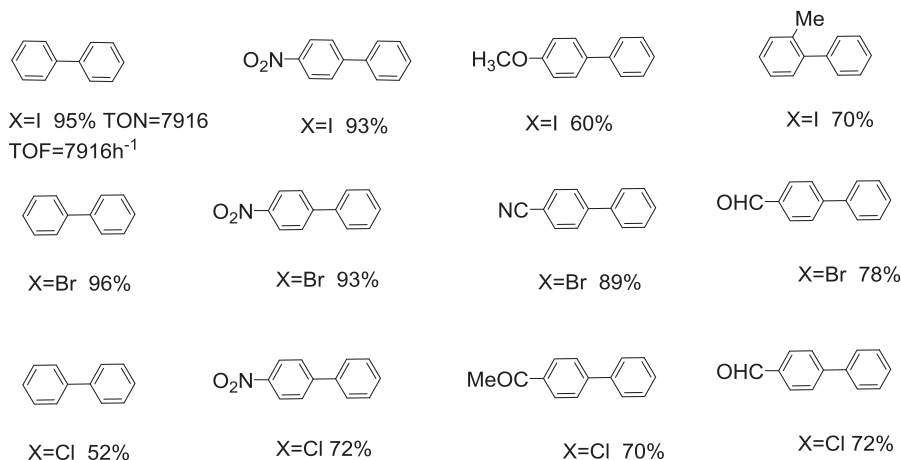
2.2. Quaternary phosphonium phase transfer catalyst support in Suzuki reaction

Hajipour and Azizi demonstrated a new supported matrix containing palladium and PTC and its application in the cross-coupling reactions of aryl halides and water-soluble
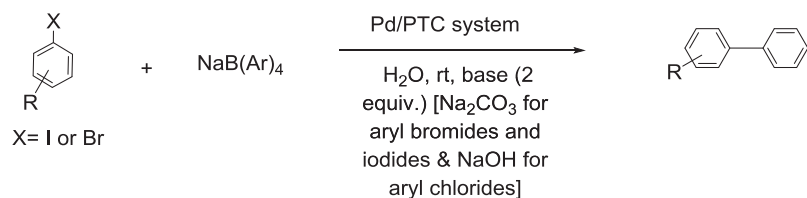
Scheme 19. Suzuki coupling reaction of various aryl halides with sodium tetraphenylborate catalysed by Pd/PTC system.

sodium tetraphenylborate have been developed based on simple simultaneous covalent anchoring of palladate anion–phosphonium cation matrix and PTC matrix immobilized on silica nanoparticles (Scheme 19) [47]. The silane coupling agent, triphenyl(3-trimethoxysilylpropyl)phosphonium iodide, was first synthesized by the reaction of triphenylphosphine and 3-(iodopropyl)trimethoxysilane in refluxing toluene. Complexation of excess quaternary phosphonium silane coupling agent with palladium chloride under an inert atmosphere at reflux temperature for 2 h in dry $CHCl_3$ afforded a dark purple solution. Silica-supported Pd/PTC matrix system can be prepared by simultaneous immobilization of PTC and palladium catalyst on a support of silica nanoparticles for 5 h at reflux temperature.

A transmission electron microscopy (TEM) image of the catalyst indicated the average diameter of the catalyst nanoparticles is about 12 nm with a very narrow size distribution. The successful covalent attachment of the catalyst matrix onto the silica surface was revealed from (FT-IR) spectrum, ^1H NMR spectrum, UV–visible spectrum, Scanning electron microscopy. Pd/PTC matrix immobilized on silica nanoparticles have an application in the Suzuki coupling reaction of a variety of different haloarenes and sodium tetraphenylborate in neat aqueous media using Na_2CO_3 or NaOH as base as based on haloarenes choosed, under aerobic condition at room temperature, without the addition of any organic co-solvent, thus rendering this process economically and ecologically acceptable. The catalyst can be reused and even for the seventh reuse without any activating procedure, the yield is 80%.
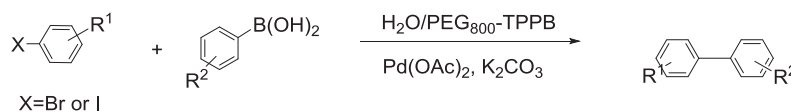
2.3. PEG support in Suzuki reaction

Polyethylene glycol (PEG) is a non-toxic, recoverable, thermally stable and inexpensive polymer that can be used as a medium or solid-liquid phase transfer catalyst in organic reaction. PEG is available in a broad range of average molecular weights (the mostly used are from 200 to 4000) Sin, Yi and Lee developed a chitosan-g-mTEG (methoxy triethylene glycol)- or mPEG (methoxy polyethylene glycol)-supported palladium (0) catalyst in 2010 (Scheme 20)

[48]. CS-g-mPEG350 Pd (0) catalyst showed excellent catalytic activity in Suzuki cross-coupling reaction without any additional phase transfer reagents. The grafted PEG chain in this catalyst acted as an effective solubilizing agent for the organic substrates in aqueous media. CS-g-mPEG350 Pd (0) catalyst was prepared by following method. mPEG (methoxy polyethylene glycol) was added to the triazine-grafted chitosan-supported palladium (0) catalysts in polypropylene tubes with a frit with 15 mL of pyridine. The mixture was shaken at a temperature 60 °C for 19 hours. After filtration and washing with ether, acetone, ethanol and water, the catalyst was freeze-dried for 24 h. The Suzuki cross coupling reactions of various aryl halides with phenylboronic acids were carried out using the CS-g-mPEG350 Pd (0) catalyst using NaOH as base at 150 °C in water. Aryl iodides and aryl bromides produced the coupling products with good yield. For aryl chlorides, 4-chloroacetophenone gave a 55% product yield even though the truth that aryl chlorides are particularly tough to be coupled with phenylboronic acids in water. CS-g-mPEG350 Pd (0) catalyst was recycled upto third cycle, after that the activity was found decreased due to the aggregation of palladium nanoparticles inside the chitosan beads. So after the fifth cycle, a longer reaction time ensured the product yield comparatively high.

In 2013, Xiang *et al.* reported the water-surfactant-ligandless palladium catalyst system can achieve Suzuki Miyaura coupling (Scheme 21) [49]. Using $Pd(OAc)_2$ as catalyst, with polyethylene glycol triphenylphosphonium bromide salt (PEG$_{800}$–TPPB) as phase transfer catalyst resulted in very rapid reactions of aryl halides with phenylboronic acids in pure water. PEG$_{800}$–TPPB showed the best performance than the other PTCs studied such as PEG$_{200}$–TPPB, PEG$_{600}$–TPPB, PEG$_{2000}$–TPPB and PEG$_{6000}$–TPPB. PEG$_{800}$–TPPB attaches effortlessly to insoluble solid substrates and could stimulate reactions effectively through reduction of Pd(II) to Pd(0). Here the surfactant acts as a stabilizer for Pd nanocluster formation and it also provides a strong micellar effect. The best yield was obtained when Suzuki reaction was carried out at 80 °C in H_2O in the presence of PEG$_{800}$–TPPB (0.6 equiv.) using K_2CO_3 (2.0
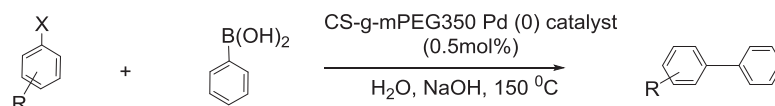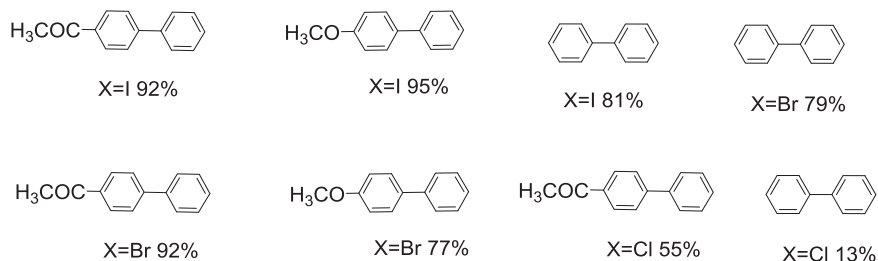
Scheme 20. Suzuki cross-coupling reaction of various aryl halides and phenylboronic acid.
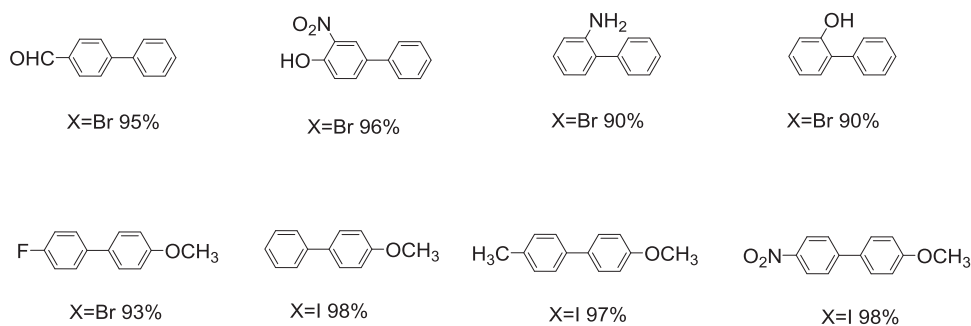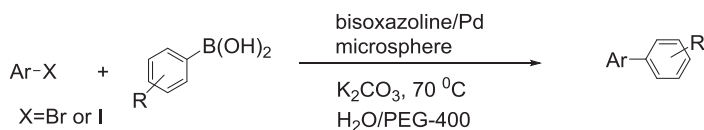
Scheme 21. Suzuki coupling reaction of various aryl halides with arylboronic acids.

equiv.) as base and 1.5 mmol% Pd(OAc)$_2$. It was found that both the electron-rich and electron-deficient aryl bromides delivered the desired products with high yields about 1.5 hours whereas, aryl iodides resulted the high yield products even in a short time of about 0.5 hour. For the use of aryl chlorides as substrate, instead of K$_2$CO$_3$, DABCO (1, 4- diazabicyclo[2.2.2]octane) was used as base to get the better yield of product.

Pd-phosphine complexes are frequently used as catalysts in Suzuki coupling reaction, however, phosphine ligands are toxic, have low thermal stability, difficulty in synthesis, and are non-recoverable. In the past few years, many studies have been done to develop phosphine-free palladium catalysed Suzuki–Miyaura coupling reactions. Wang and co-workers reported the synthesis of a novel non-phosphine solid, self-assembled bisoxazoline/Pd composite microsphere catalyst in 2016 (Scheme 22) [50]. A pale yellow powdered bisoxazoline/Pd composite microsphere catalyst was obtained by self-assembled coordination of Pd(OAc)$_2$ to the solution of the ligand 4,4′-oxybis(N-(4,5-dihydrooxazol-2-yl)benzamide) in acetonitrile. The catalyst showed high thermal stability and it was detected to be insoluble in polar solvents. So it can be effectively used as a good solid catalyst for organic reactions. The structure and composition of the solid catalyst were as-signed by SEM, ^{1}H NMR, TGA and FT-IR. SEM images showed that the particle diameter ranges from 0.53 to 0.55 μm. This catalyst exhibits high catalytic activity for Suzuki–Miyaura cross-coupling reactions of various aryl halides and arylboronic acids in aqueous media. The best condition of this reaction is the combination of as a base and a mixture of water and PEG-400 (H$_2$O: PEG-400 = 10: 1) as the solvent at 70 °C in air for 4 hours. PEG-400 can play an important role as the phase transfer catalyst (PTC) and the addi-tion of it into H$_2$O improved the yield of product (85 - 99%) re-markably. Various arylboronic acids showed good yield of products with aryl bromides and iodides having electron-donating and elec-tron withdrawing groups. However, aryl chlorides are less active towards bisoxazoline/Pd microsphere catalytic activity. Catalyst can be recycled eight times without any loss of its activity. The yield of catalyst was remained as 95% even after the eighth cycle.

Another report on series of N, O-bidentate ligands were synthe-sized using the Vilsmeier–Haack reaction and oximation by Song *et al.* in 2017 (Scheme 23) [51]. 2,5-Dihydroxyterephthaldehyde dioxime was used as an efficient N,O-symmetrical bidentate lig-and and was prepared from hydroquinone via a Vilsmeier–Haack reaction and oximation. This ligand has the highest activity due to its electron-rich character and the existence of multiple bonding
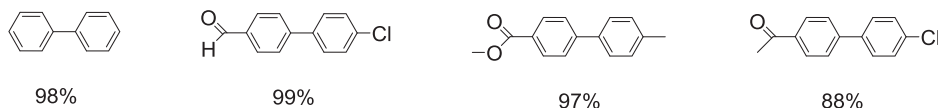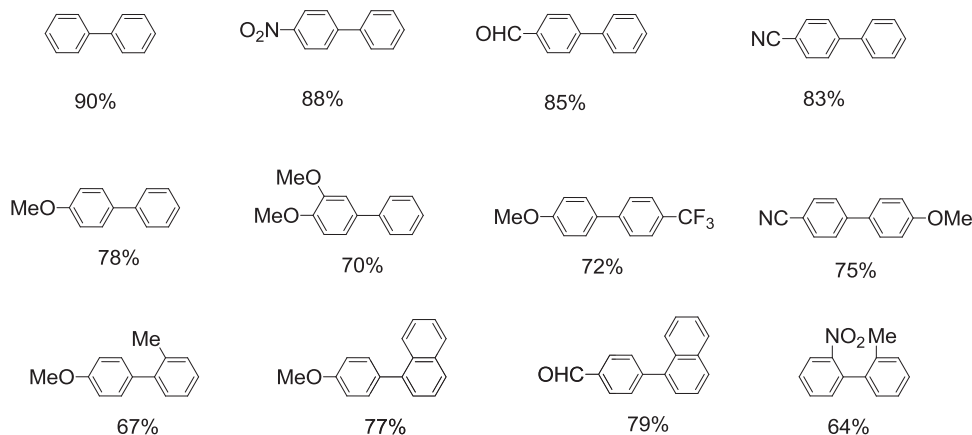
Scheme 22. Suzuki–Miyaura cross-coupling catalyzed by a bisoxazoline/Pd microsphere.
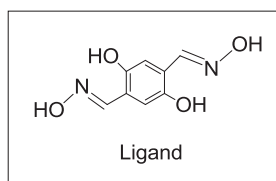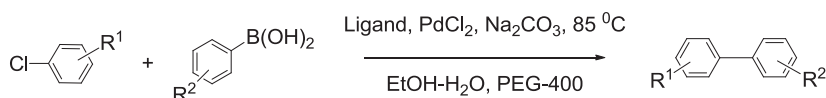
Scheme 23. Suzuki reactions of various aryl chlorides with arylboronic acids using L8.
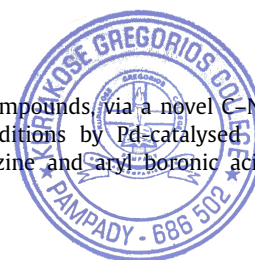
sites which are considered to increase the steric congestion around the metal centre. The coupling reactions were performed in the presence of PdCl$_2$ as the catalyst, 2,5-dihydroxyterephthaldehyde dioxime as the ligand, Na$_2$CO$_3$ as the base, PEG-400 as the PTC and in ethanol/water (1:1) as an environmentally benign solvent at 85 °C. PdCl$_2$ catalyst is relatively inexpensive as compared with Pd(OAc)$_2$. PEG-400 likely acts as a stabilizer for some low ligated palladium species, and its presence increased the yield from 55% to 80%. Abundant biaryls were obtained from Suzuki–Miyaura cross-coupling reactions of a number of aryl chlorides with arylboronic acids having either electron-withdrawing or electron-donating groups with excellent yields at a small palladium loading of 0.20 mol%.
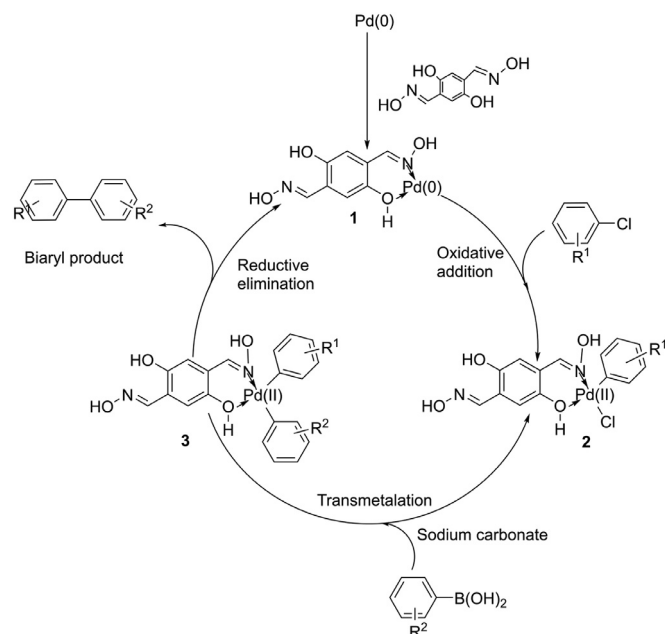
They proposed that the mechanism of the Suzuki–Miyaura reaction could be shown as in (Scheme 24). Firstly, Pd(0) is formed by

the reduction of Pd(II) in the Suzuki reaction system. Pd(0) is then stabilized by the ligand L8 and the complex **1** is formed, which act as an effective catalyst for further reaction. Then an oxidative addition take place between the aryl chloride and complex **1** to produce the intermediate **2**. transmetalation occurs between intermediate **2** with the arylboronic acid to give the intermediate **3** in the presence of Na$_2$CO$_3$. Lastly, a reductive elimination results the biaryl products. complex **1** is regenerated by this means continuing the catalytic cycle.

2.4. SDS support in Suzuki reaction

For the preparation of biaryl compounds, via a novel C–NHNH$_2$ bond activation under green conditions by Pd-catalysed Suzuki cross-coupling between arylhydrazine and aryl boronic acid was

Scheme 24. Proposed mechanism.

withdrawing groups were effectively participated in coupling reaction in good yields. Heteroaryl substituted boronic acids were also employed in the coupling reaction which showed moderate yields.

A possible mechanism for this hydrazine Suzuki reaction via C–NHNH$_2$ bond activation has been proposed (Scheme 26). Firstly, arylhydrazine **4** could quickly react with TsCl to form *N'*-tosyl arylhydrazine **5**, which was dehydrogenated in the presence of base K$_2$CO$_3$ and O$_2$ in the air to deliver the aryl diazonium ion **6** and tolylsulfinate. As a relay process, the tolylsulfinate could be used as another efficient oxidant for the formation of aryl diazonium ion **6** and thiosulfonate (Ts-S-Tol), and the thiosulfonate could be identified by GC-MS. Then an oxidative addition of diazonium ion to Pd catalyst provided the organopalladium intermediate **7**, which stimulated the transmetalation of the aryl boronic acid to result the diaryl palladium species **8**. To end with a reductive elimination of **E** resulted biaryl product **9** and Pd-catalyst was regenerated.

2.5. Pd@COF-QA: A phase transfer composite catalyst for aqueous Suzuki-Miyaura coupling reaction

In 2020, Wang and team reported a palladium nanoparticle loaded and paraffin-chain quaternary ammonium salt(*N, N*-dimethyldodecyl ammonium bromide) decorated covalent organic framework based composite catalytic system, that is Pd@COF-QA. It can act as very good phase transfer catalyst for aqueous Suzuki-Miyaura coupling, leads to the carbon-carbon coupling in water under mild reaction conditions even at gram scale level (Scheme 27) [53]. N,N-Dimethyldodecyl ammonium bromide decorated COF(COF-QA) can be prepared by Schiff-base condensation between quaternary ammonium salt decorated dihydrazide (L-QA)) and 1,3,5-triformylbenzene under solvo-thermal conditions. COF-QA was loaded with palladium nanoparticles resulted in Pd@COF-QA. High-resolution transmission electron microscopy (HR-TEM) showed that the loaded Pd NPs were well dispersed in the COF-QA matrix with an average particle centred at ca. 2.4 nm. From
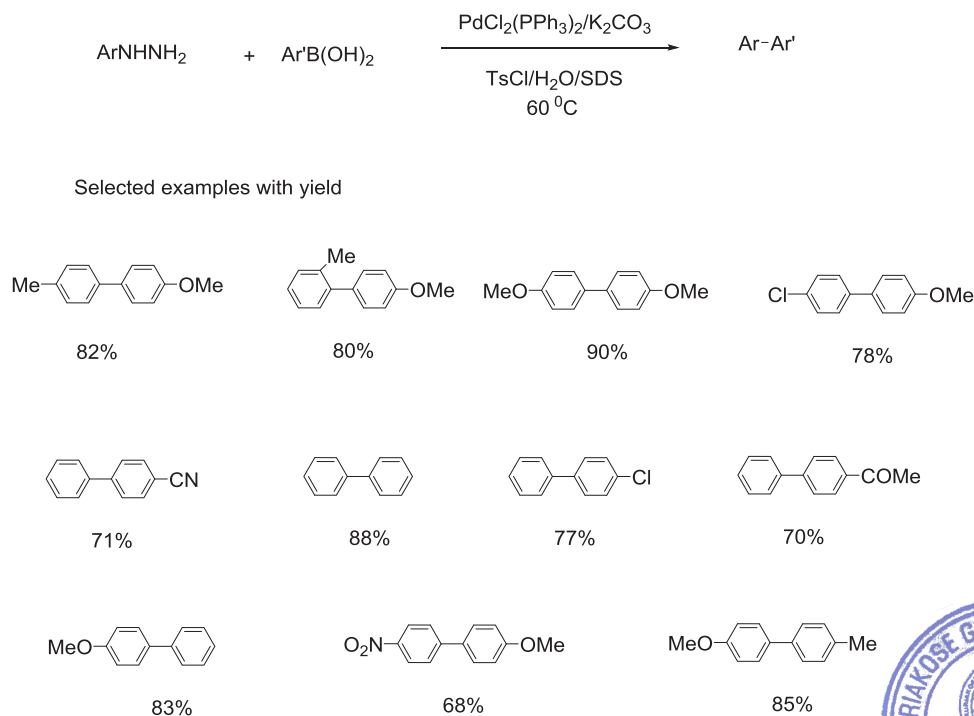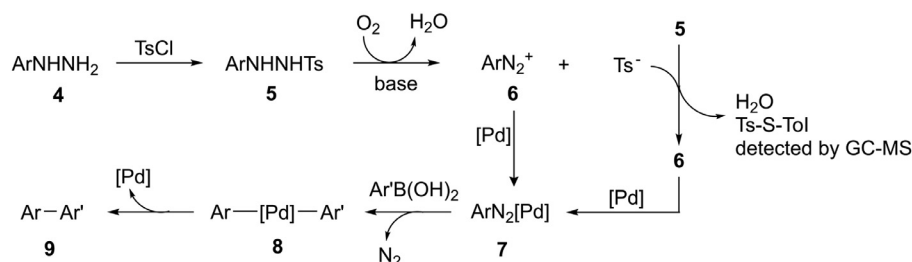
proposed by Liu, Zhou and Peng in 2014 (Scheme 25) [52]. This method involved mild and green reaction conditions, high substrate generality and good yields. 10 mol% of sodium dodecyl sulphate (SDS) acts efficiently as phase transfer catalyst than various other phase transfer catalysts (TBAB, DTAC, PEG, *β*-CD). The scope of Pd-catalysed Suzuki cross-coupling of arylhydrazines with aryl boronic acids was studied under the optimized conditions using PdCl$_2$(PPh$_3$)$_2$ (5 mol %) as catalyst, K$_2$CO$_3$ (3.0 equiv.) as base, with SDS (10 mol %) as PTC, activated by Tosyl Chloride (1.2 equiv.) in H$_2$O, at 60 °C. Both arylhydrazines and aryl boronic acid with electron-donating and electron-
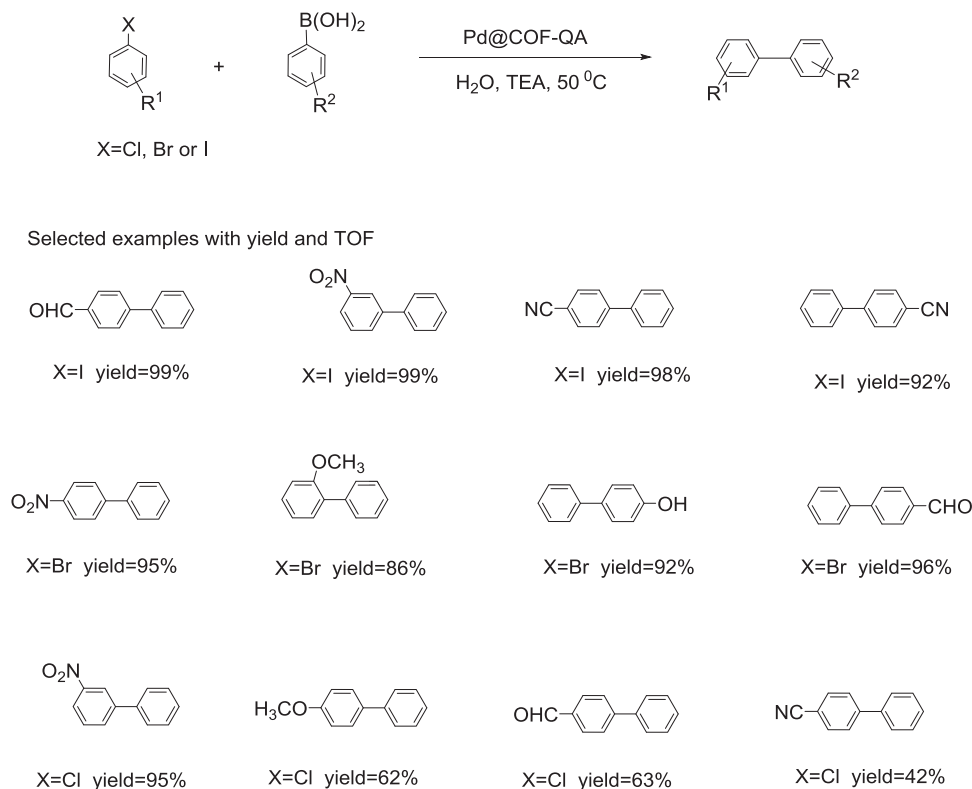

Selected examples with yield

Scheme 25. Pd-catalyzed Suzuki cross-coupling of arylhydrazines with aryl boronic acids.

Scheme 26. Proposed mechanism.

Selected examples with yield and TOF

Scheme 27. Pd@-COF-QA-catalysed Suzuki-Miyaura coupling reaction.

XRD studies, oxidation state of the loaded Pd NPs in Pd@COF-QA was found to be zero. SEM-EDX mapping indicated a homogeneous distribution of Pd, N, and C elements in the COF matrix. Thermogravimetric analysis (TGA) showed the thermal stability of the catalyst. It could be stable till temperature over 200°C and could be effectively used as catalyst in organic reactions at relatively high temperature. Pd@COF-QA (1.7 mol % Pd equiv.) could effectively use at lower reaction temperature such as 50 °C, using triethylamine (TEA) (0.4 mmol) as base in water at relatively lower reaction time (6 h). Due to large extraction constant, phase transfer catalysts with longer paraffin chains such as, N,N-dimethyldodecyl ammonium bromide are more efficient to prepare the catalyst. For gram scale coupling reaction, a continuous flow-through reactor equipped with Pd@COFQA@chitosan aerogel catalysing column was implemented.

Under the optimized PTC conditions, the excellent catalytic activity of Pd@COF-QA was observed for the various substituted iodobenzene and bromobenzene with substituted phenylbonic acids regardless of electron-withdrawing or electron-donating groups at different substituted positions. Also, Pd@COF-QA could be a important substitute to the heterogeneous catalysts for the aqueous chlorobenzene based Suzuki-Miyaura coupling reaction. This catalytic system promoted Suzuki-Miyaura coupling reaction to be more cost-effective and environmental friendly and it can be recycled more than ten runs.

The summary of discussed catalysts with the aid of PTC's and the necessary reaction conditions with the yield percentages are listed below.

3. Conclusion

During the last decade, attractiveness of PTC in organic synthesis is significant and much effort has been devoted towards its improvement of the sustainability of these reactions, such as catalyst recovery and atom efficiency. The recent advances discussed herein the role of PTC in Suzuki-Miyaura coupling illustrate the potential of this chemistry. We conclude this review by hoping that it will encourage researchers to further explore and develop this interesting field of research Table 1.

Table 1
Summary of reported catalysts with the aid of PTC's and the necessary reaction conditions with the yield percentages.

Catalyst	PTC used	Base	T (°C)	Time (h)	Yield (%)	Catalytic recovery	Ref
Pd- NHC@Fe$_3$O$_4$–IL	TBAB	K$_3$PO$_4$	40–85	0.4-6	85-95	5	30
Pd-1/FSG	TBAB	K$_2$CO$_3$	100	8-12	83-99	several	31
Pd/C	TBAB	K$_2$CO$_3$	120	0.25-0.40	87-95	5	32
Pd(OAc)$_2$/ PS–PEG–L	TBAF	-	80	24	53-96	4	33
POPd	TBAB	K$_2$CO$_3$	100	1-8	55-99	4	34
POPd	TBAB	K$_2$CO$_3$	reflux	2-8	32-98	4	35
Pd/MIL-101	TBAB	NaOMe	80	20	80-97	5	36
Pd(OAc)$_2$/ PIC	TBAB	Na$_2$CO$_3$	100-120	2-10	93-99	-	37
Pd(OAc)$_2$	TBAF	-	95	3	68-95	-	38
Hydroxyapatite supported palladium catalyst	TBAB	K$_2$CO$_3$	80	24	80-98	10	39
[Pd(η^3-C$_3$H$_5$)Cl]$_2$	TBAB	K$_2$CO$_3$	70-100	22	55-95	3	40
(6-Dipp)Pd(cinn)Cl complex	TBAB	NaHCO$_3$	reflux	1	80-99	-	41
POPd(palladium phosphinous acid complexes)	TBAB or PEG	K$_2$CO$_3$	-	3.5	60-82	-	42
Pd-PEPPSI complexes	TBAB	Bu^{t}OK	80	2-5	70-98	-	43
ScCO$_2$ soluble bidentate perfluorinated phosphine -imine ligands complexed with divalent palladium(II)	Bu$_4$NBr	NaOAc	80	3.5	30-80	-	44
(PdCuCeO) solid-solution oxide	TPAB	Na$_2$CO$_3$	100	0.5	70-100	3	45
Pd/NPs/Zirconia	TBAOH	TBAOH	90	14	75-90	10	46
Silica-supported Pd/PTC matrix system	quaternary phosphonium silane	Na$_2$CO$_3$ or NaOH	Room temp.	Ambient	50-96	7	47
CS-g-mPEG$_{350}$ Pd (0) catalyst	PEG	NaOH	150	1	55-95	3-5	48
Pd(OAc)$_2$	PEG800-TPPB	K$_2$CO$_3$	80	0.5-1.5	90-98	-	49
Bisoxazoline/Pd composite microsphere	H$_2$O: PEG$_{400}$ = 10: 1	K$_2$CO$_3$	70	4	85 -99	8	50
L/PdCl$_2$ (L= 2, 5-Dihydroxytereph thalaldehyde dioxime)	PEG$_{400}$	Na$_2$CO$_3$	85	5	60-90	-	51
PdCl$_2$(PPh$_3$)$_2$	SDS	K$_2$CO$_3$	60	4-8	68-90		52
N, N-dimethyldodecyl ammonium bromidebrk decorated Pd@COF-QA	N, N-dimethyldodecyl ammonium bromide	TEA	50	6	83-99	More than 10	53

Declaration of Competing Interest

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REVIEW

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Palladium-catalyzed cross-coupling reactions of coumarin derivatives: An overview

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Coumarins are omnipresent in several plants and exhibit a plethora of pharmacological properties, making them an important scaffold in organic synthesis. Naturally, the chemistry of this motif has attracted ever-increasing attention, among which palladium-catalyzed coupling reactions are the most prevalent one. Numerous useful, easy, and concise syntheses and reactions have been achieved using palladium-catalyzed coupling reactions. This review focuses on recent advances in palladium-catalyzed cross-coupling reactions such as Suzuki, Heck, Stille, Sonogoshira etc. reactions of coumarin derivatives and covers the literature from 2001 to 2020.
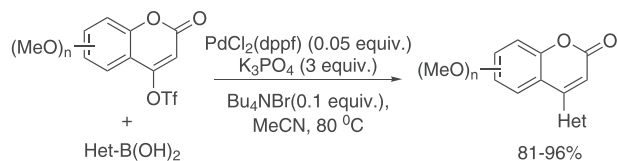
KEYWORDS
catalysis, C–C, coumarin, cross-coupling, palladium

1 | INTRODUCTION

Coumarins belong to a class of benzopyrones commonly present in plant species in either a free or combined state.[1–6] The prominence of coumarins in natural products and biologically active molecules has prompted researchers to put more effort into their synthesis. Coumarins find diverse applications due to their pharmacological properties such as antiprotozoal,[7] antimalarial,[8,9] antibacterial,[10] anticancer,[11–13] and anti-HIV properties,[14] and cytotoxicity.[15] They also possess some outstanding optical properties.[16–21] They are well known for their various photophysical applications and therefore they are widely used in organic light emitting diodes and as optical brighteners, nonlinear optical chromophores, fluorescent whiteners, and fluorescent labels and probes for physiological measurements.[22–30] The coumarin scaffold may be substituted on any of the six carbons by the introduction of various substituents in the coumarin ring. The derivatives can have a wide range of modifications, providing flexibility to fit various applications in natural products and synthetic organic chemistry. For the synthesis of various substituted coumarins, several procedures have

SCHEME 1 Pd(0)-catalyzed Stille reaction using 4-triflate substituted coumarins

been adopted, such as Pechmann, Knoevenagel, Perkin, Wittig, and Reformatsky reactions, Claisen rearrangement and many more.[31–33] Most of these reactions are multistep and time-consuming, but this has been solved by the introduction of metal-catalyzed intermolecular or intramolecular coupling reactions. Owing to the great importance of this small, but useful, moiety, much attention has been given to the development of synthetic methods for substituted coumarins using transition-metal catalysts such as palladium,[34] iron,[35] gold,[36] silver,[37] copper,[38] platinum,[39] nickel,[40] cobalt,[41] rhodium,[42] gallium,[43] and zinc.[44] Recently, a review based on the efficient synthetic methods for 4-arylcoumarins has been reported.[45]

To the best of our knowledge, there is no review focused on palladium (Pd)-catalyzed cross-coupling reactions involving coumarin derivatives. Therefore, we describe here the recent advances in Pd-catalyzed cross-coupling reactions of coumarin derivatives, covering the literature up to 2020. For simplicity and brevity, the topic is categorized based on the different types of Pd-catalyzed cross-coupling reactions using coumarins.

2 | CROSS-COUPLING REACTIONS

Cross-coupling reactions furnishing carbon–carbon (C–C) bonds are of great importance in organic synthesis.[46–48] The most commonly used coupling reactions are Kumada coupling (1972), the Heck reaction (1972), Sonogashira coupling (1975), Negishi coupling (1977), Stille coupling (1978), the Suzuki reaction (1979), Hiyama coupling (1988), and most recently Liebeskind–Srogl coupling (2000). The proper choice of ligand and catalytic system in these coupling reactions has resulted

in a large variety of new synthesized organic molecules. Pd-catalyzed cross-coupling reactions are the most widely used and popular. In 2010, Heck, Negishi, and Suzuki shared the Nobel Prize in Chemistry for their contributions to coupling reactions utilizing Pd catalysts. The first transition metal mediated cross-coupling using coumarin was reported by Wattanas in 1988.[49] He demonstrated the feasibility of Pd(0)-catalyzed Stille coupling for the synthesis of 4-arylcoumarins from 4-triflate-substituted coumarin and aryl stannane species (Scheme 1). Thereafter, several methodologies appeared for coupling reactions involving coumarin derivatives using transition metals such as Pd, Ni, and Fe.[50–52]

2.1 | Suzuki cross-coupling reaction

Yang et al. introduced an efficient Pd-catalyzed reaction between 4-tosyl coumarin and arylboronic acids to synthesize diversified 4-arylcoumarins in which boronic acids with an electron-donating group gave better yields (Scheme 2).[53] The best catalyzed reaction was obtained by employing $PdCl_2(PPh_3)_2$ in tetrahydrofuran (THF) at 60°C in the presence of Na_2CO_3. This protocol illustrates 4-tosylcoumarin as an alternative substrate for the palladium-catalyzed Suzuki reaction. The superiority of 4-tosylcoumarin versus its corresponding triflate in terms of its stability, synthetic reagent cost, and easy preparation should make it an ideal synthon for combinatorial synthesis of coumarin using Pd catalyst.

Beletskaya et al. developed an efficient protocol for Pd-catalyzed coupling of 4-trifluoromethylsulfonyloxycoumarins with heteroarylboronic acids under Suzuki reaction conditions which gave 4-heteroaryl-substituted coumarins in good to excellent yields (Scheme 3).[54] The optimized catalytic system comprising $Pd(dppf)Cl_2$ (0.05 equiv.)–K_3PO_4 (3.0 equiv.)–Bu_4NBr (0.1 equiv.) was selected for the subsequent cross-coupling reactions of triflates with heteroarylboronic acids. The cross-coupling products were isolated in good to excellent yields (81–96%) irrespective of the number of methoxy groups present in the coumarin substrate and the nature of the heteroaryl fragment of the boronic acid.

Selected examples with yield
R^1 = H; R^2 = H (63%),1-OMe (80%),1-F (62%), 2-CHO (51%)
R^1 = 7-OMe; R^2 = H (91%), 1-OMe (81%)
R^1 = 6-OMe; R^2 = H (68%), 1-OMe (76%)

SCHEME 2 Pd-catalyzed synthesis of diversified 4-arylcoumarins by Suzuki coupling

**SCHEME 3** Pd-catalyzed coupling between triflates and heteroarylboronic acids

Zhang et al. introduced Pd-catalyzed site-selective cross-coupling reactions of 3-bromo-4-trifloxycoumarin or 3-bromo-4-tosyloxycoumarin, providing an efficient and facile route for the synthesis of diversified 3,4-disubstituted coumarins, which include 3,4-diarylcoumarins, 3-amino-4-arylcoumarins, and 3-aryl-4-aminocoumarins.[55] The order of reactivity of the (pseudo) halide substituents in the coumarins was

found to be 4-OTf > 3-Br > 4-OTs. The Pd-catalyzed reaction of 3-bromo-4-trifloxycoumarinandarylboronic acid with Pd(PhCN)$_2$Cl$_2$ as a catalyst and NaHCO$_3$ as a base was used. The result established that the coupling reaction proceeds essentially at C4 rather than at C3 of the coumarin. Remarkably, both electron-rich and electron-poor arylboronic acids were found to be suitable partners in this process, affording the corresponding mono-substituted products in good to excellent yields (Schemes 4 and 5).

An efficient protocol for the synthesis of a variety of 4-methyl-7-aryl/heteroarylcoumarins has been developed by utilizing a Pd-catalyzed Suzuki cross-coupling reaction of 4-methyl-7-nonafluorobutylsulfonyloxycoumarin with a wide range of electronically diverse boronic acids under microwave irradiation (Scheme 6).[56] Here the dual role of Tetra-n-butylammonium fluoride (TBAF)·3H$_2$O as a
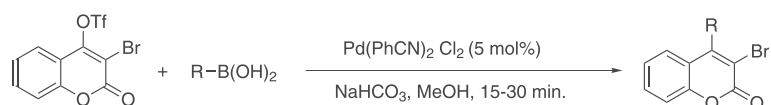
Selected examples with yield
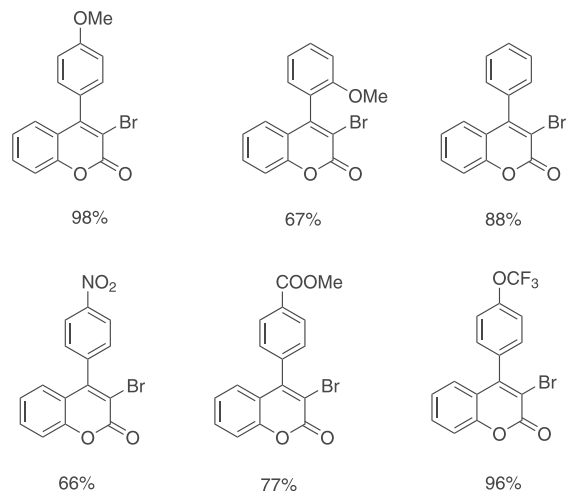
SCHEME 4 Pd-catalyzed synthesis of 3-bromo-4-arylcoumarins
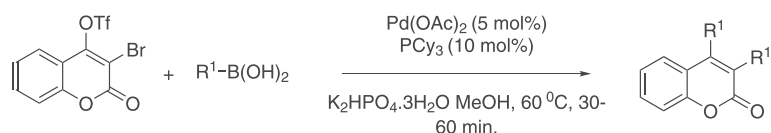
Selected examples with yield
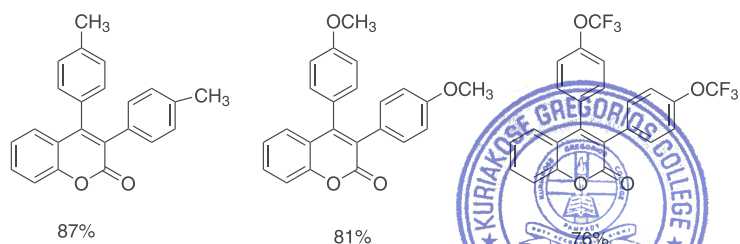
SCHEME 5 Pd-catalyzed synthesis of 3,4-diarylcoumarins

Pd(OAc)$_2$ (0.05 mmol)
dppp (0.1 mmol)
TBAF.3H$_2$O (2 mmol)
DME/MeOH (3;1)
M.W, 80 ^{0}C

R = Aryl/Heteroaryl

ONf = (nonaflate group structure)

Selected examples with yield

92%   82%   93%

77%   86%   82%

SCHEME 6 Pd-catalyzed synthesis of various 4-methyl-7-aryl/heteroarylcoumarins
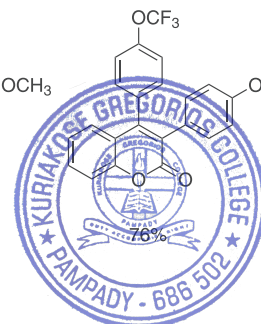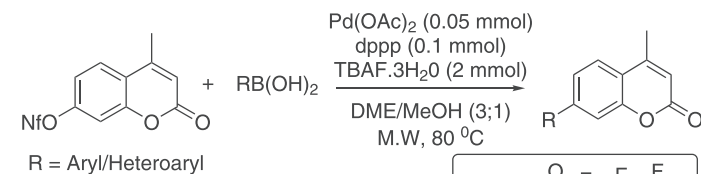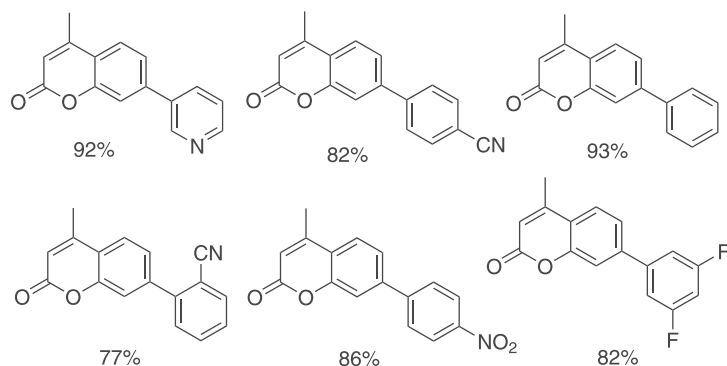
base and a solvating agent was found to be the key factor in the success of the reaction.

Birney et al. described an efficient synthesis of 4-substituted coumarin derivatives by Pd-catalyzed Suzuki cross-coupling reaction.[57] A series of novel alkyl-, aryl-, and vinyl-substituted coumarin derivatives in good to excellent yields was obtained using this method from sterically crowded 4-chlorocoumarin derivatives with air- and moisture-stable potassium organotrifluoroborates. In the optimized reaction conditions, Pd(dppf)Cl$_2$-CH$_2$Cl$_2$ (5–10 mol%) and Et$_3$N

(1.5 equiv.) as base in toluene–H$_2$O (10:1) were chosen for the cross-coupling reactions of 4-chlorocoumarin with a range of organotrifluoroborates and the cross-coupling with phenyl trifluoroborate under the optimized conditions gave a high yield (90%) for the cross-coupled product. The nature of the aryl group introduced at the C4 position did not significantly influence the yield of the cross-coupling reaction. Both electron-rich and electron-deficient aryltrifluoroborates gave good yields (Scheme 7).

Pd-catalyzed Suzuki–Miyaura couplings of potassium aryl trifluoroborates with 4-tosyloxycoumarins or 4-tosyloxyquinolin-2(1H)-one afforded the corresponding 4-substituted coumarins or 4-substituted quinolin-2(1H)-ones in good to excellent yields (Scheme 8).[58] Here, Pd(PPh$_3$)$_4$ was used as the catalyst and toluene as the best solvent with Cs$_2$CO$_3$ (1.0 M in water) as the best base. The advantages of this protocol are good substrate generality, use of air-stable and inexpensive tosylate under mild conditions, and ease of operation.

The Suzuki–Miyaura reactions of 4-trifluoromethylsulfonyloxy-6-bromocoumarin with arylboronic acid offer convenient access to arylated coumarins, and the reaction proceeds with excellent chemoselectivity in favor of the C4 position.[59] The yield of the reaction was about 60–88% and both electron-rich and electron-poor arylboronic acids were successfully employed in this reaction (Scheme 9).

The Suzuki–Miyaura cross-coupling of 4-halo and 4-bromomethyl coumaryl substrates with different aryl boronic acids has been explored using [Pd(PPh$_3$)$_2$(saccharinate)$_2$] as catalyst.[60] The desired products were obtained in excellent yields under

R^{1}BF$_3$K (1 equiv.)
PdCl$_2$(dppf).CH$_2$Cl$_2$ (5 mol%)
NEt$_3$ (1.5 equiv.),
toluene:H$_2$O, 100 ^{0}C

Selected examples

92%   92%   82%

68%   76%   74%
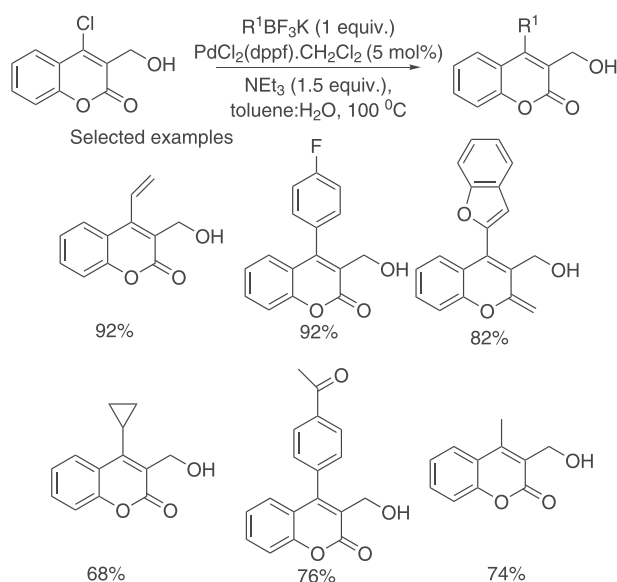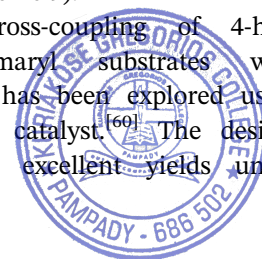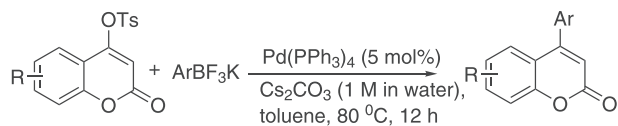
SCHEME 7 Pd-catalyzed synthesis of 4-substituted coumarin derivatives
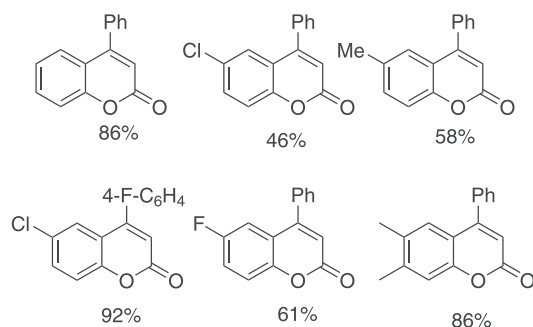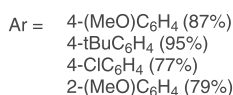
SCHEME 8 Pd-catalyzed Suzuki–Miyaura cross-coupling reactions of tosylates with potassium aryl trifluoroborates
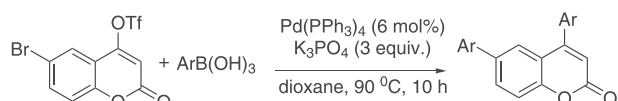
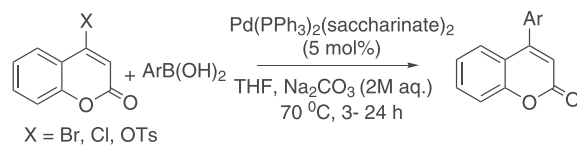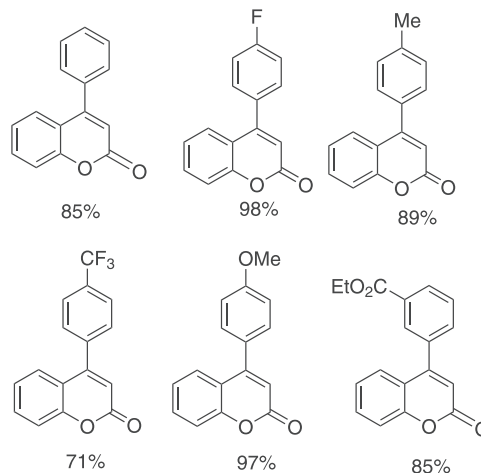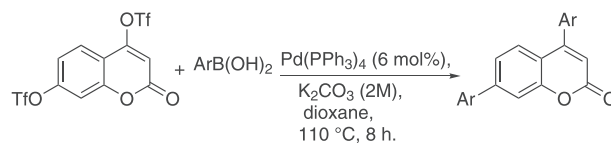**SCHEME 9** Suzuki–Miyaura coupling of 4-trifluoromethyl-sulfonyloxy-6-bromocoumarin with arylboronic acids


SCHEME 10 Suzuki–Miyaura cross-coupling of 4-halo coumarins

SCHEME 11 Pd-catalyzed Suzuki–Miyaura cross-coupling reaction of bis(triflate) of 4,7-dihydroxycoumarin

competitive reaction times and relatively mild conditions (Scheme 10).

The first report of a Suzuki–Miyaura coupling reaction of bis(triflate) of 4,7-dihydroxycoumarin was developed by Langer et al.[61] The reaction proceeds with excellent regioselectivity in favor of position 4, which provides a convenient approach for various arylated coumarin derivatives which cannot be synthesized by other methods. Both electron-rich and electron-poor arylboronic acids were successfully employed in this reaction (Scheme 11).

Pd-catalyzed Suzuki coupling reactions are also used in the synthesis of some novel coumarin derivatives which find applications as potent antibacterial agents.[62]

2.2 | Heck cross-coupling

Martins et al. introduced a new and easy protocol for the synthesis of diversified 3-aryl coumarin by using Heck coupling reactions between coumarin and aryliodides.[63] The introduction of the aryl moiety occurred

regioselectively at the C3 position of the heteroaromatic ring rather than at the C4 position on the coumarin ring. The system containing coumarin (3.0 equiv.), PhI (1.0 equiv.), Pd(PPh$_3$)$_4$ (0.1 equiv.), MeCO$_2$Ag (1.1 equiv.), and N, N-dimethyl formamide (DMF) at 80°C for 72 hr provided most efficient conditions to obtain the desired aryl substituted coumarin in 52% yield while 1-bromo-4-iodobenzene afforded the cross-coupled product in 66% yield. Electron-withdrawing as well as electron-donating substituents on the aryl iodide were suitable partners in this process, affording the corresponding mono-substituted products in fair to good yields, although electron-withdrawing groups gave the best results, as expected. Indeed, with electron-donating groups the yield of the reaction decreased substantially (Scheme 12).
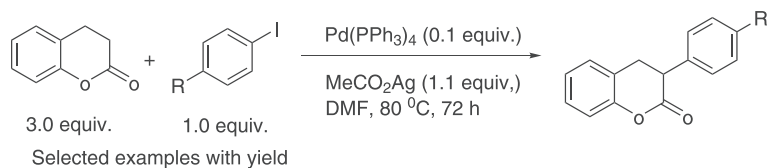
SCHEME 12 Pd-catalyzed synthesis of 3–aryl coumarins
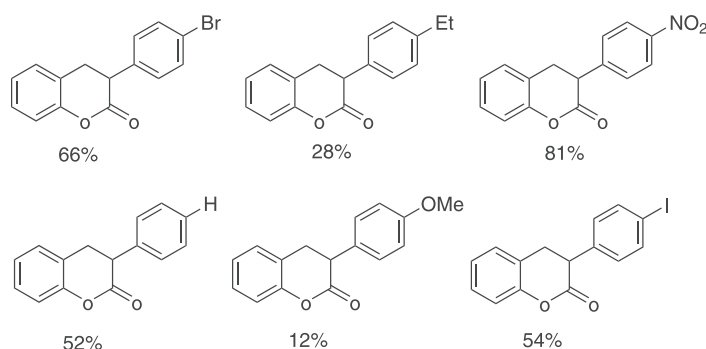
With the success of this method, a tandem Heck reaction of iodine derivative with methyl acrylate under the same conditions was performed, which provided the corresponding (E)-methyl-3-[4-(coumarin-3-yl)phenyl]acrylate in 96% yield. This promising result illustrates the potential of this strategy to diversified coumarins for numerous synthetic applications.

An efficient protocol was developed for the direct synthesis of 4-arylcoumarins via a Pd-catalyzed oxidative Heck coupling reaction using coumarins and arylboronic acids in DMF as solvent.[64] The products were obtained in moderate to excellent yields, and the reaction also showed tolerance towards functional groups such as hydroxy, methoxy, diethylamino, nitro, and chloro groups (Scheme 13).
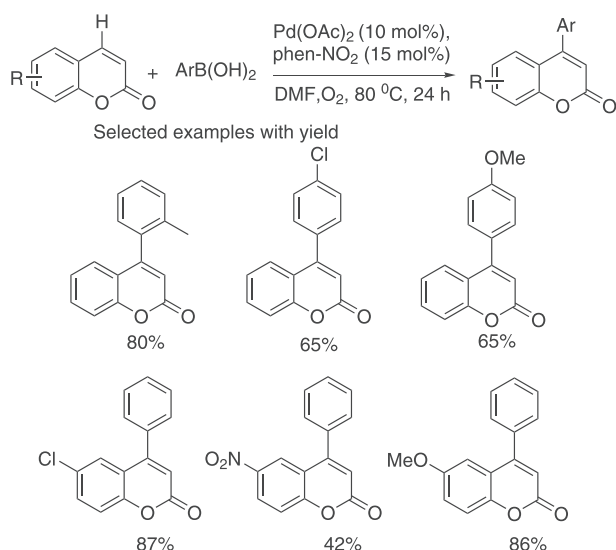
SCHEME 13 Pd-catalyzed coupling of coumarins and arylboronic acids

2.3 | Cross-dehydrogenative coupling

A direct C–H cross-coupling of 3-bromocoumarins with heteroarenes using Pd catalyst provides an efficient route to 3-heteroarylcoumarins.[65] The reaction scope for the transformation is fairly broad, affording modest to good yields of various 3-heteroaryl coumarin scaffolds, which are privileged structures and prevalent motifs in many biologically active compounds and fluorophores. The optimized reaction conditions are Pd(PPh$_3$)$_4$ (2.5 mol%) with CuI (3 equiv.), Cs$_2$CO$_3$ (2 equiv.), and 1,4-dioxane at 110°C. The Pd-catalyzed direct cross-coupling of various coumarins with benzoxazole or benzothiazoles is shown in (Scheme 14).

A wide range of 4,5-benzocoumarins with potential fluorescence properties were synthesized in good yields by Wang et al. (Scheme 15).[66] In this method simultaneous C–I and vicinal C–H bond activation of diaryliodonium salts took place. The advantages of this method are the non-necessity of ligands, assisting groups, and additional oxidants as well as the direct formation of two C–C bonds in one step. This method finds wide application in the preparation of the relevant pigments used in various applications.

A catalytic mechanism was proposed as shown (Scheme 16). The reaction is initiated by cleavage of the hypervalent iodine–aryl bond to generate a palladium species **1** which acts as a Lewis acid in association with the activation of the carbonyl group of coumarin **2**. Then an oxidative attack at C4 with synergetic activation of the vicinal C–H bond of coumarin **2** forms aryl palladacycle **3** in DMF. Reductive elimination forges only one aryl–aryl bond. A second oxidative addition of **4** with the assistance of [Ph$_2$I]OTf gives a Pd(IV) complex **5**, and another reductive elimination regenerates the catalyst with the formation of two C–C bonds of **6**.
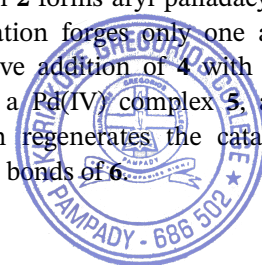
SCHEME 14 Pd-catalyzed direct cross-coupling of various coumarins with benzoxazole or benzothiazole

Selected examples with yield

84%

61%

56%

76%

64%

50%

48%

81%

72%

X = OTf, BF$_4$, OTs

Selected examples with yield

58%

95%

87%

65%

772%

88%
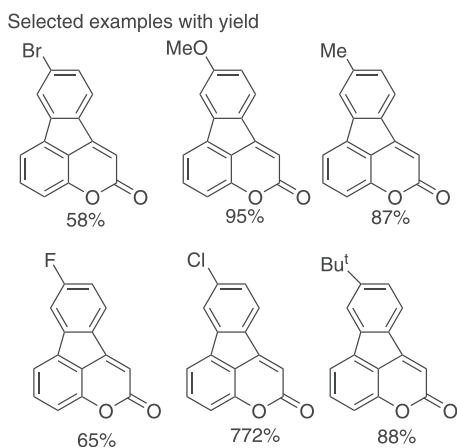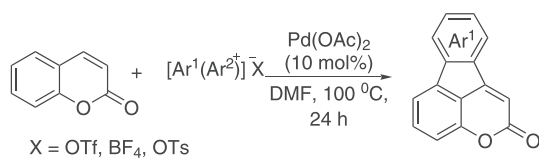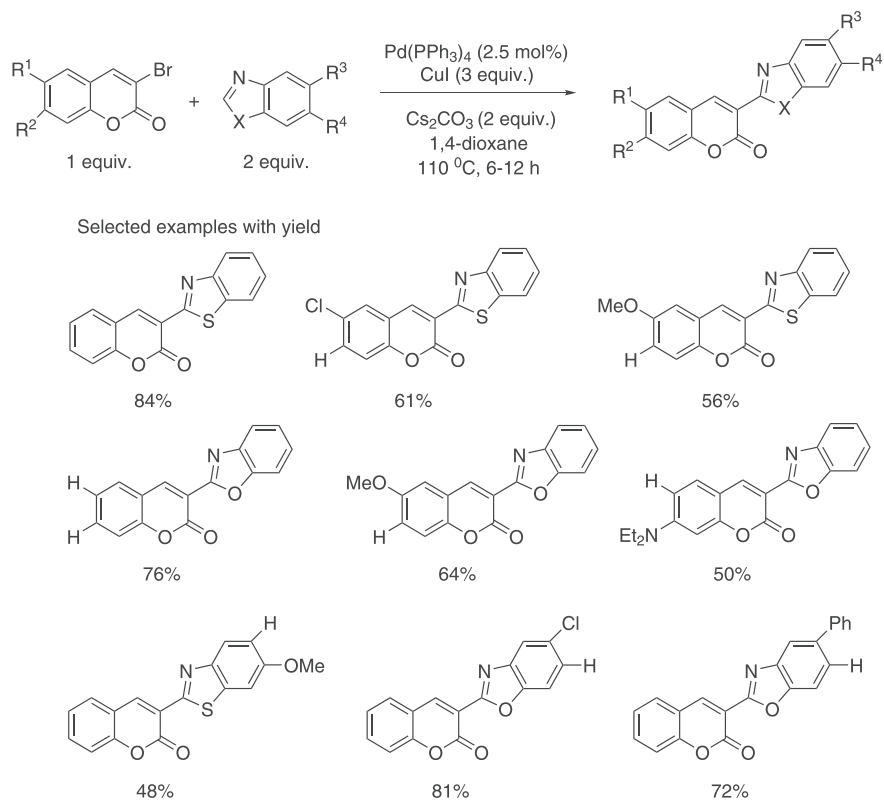
SCHEME 15 Pd-catalyzed synthesis of various 4,5-benzocoumarins

Hajra and co-workers synthesized indole-fused coumarin derivatives via Pd-catalyzed cross-dehydrogenative coupling reaction of coumarin and aniline.[67] They used a one-pot procedure that is operationally simple and the use of molecular oxygen as an oxidant makes this protocol more sustainable and environmentally benign. This method serves as a practical, versatile, and atom economical alternative to existing synthetic methods. Good yields were obtained for the target compounds from commercially available precursors. The reaction was optimized using 4-hydroxycoumarin and para-toluedine. DMF has come out to be the better solvent, providing 68% yield of the desired product in the presence of 10 mol% of Pd(OAc)$_2$ and 3 equiv. of Cu(OAc)$_2$.H$_2$O as an oxidant at 150°C. Simple aniline and para-substituted anilines such as 4-fluoro, 4-chloro, 4-methoxy, and 4-phenyl anilines worked well to give the desired indole fused coumarins with 53–78% yields. It was observed that electron-rich anilines produced better yields than electron-deficient anilines due to the better nucleophilicity of electron-rich anilines whereas anilines containing strong electron withdrawing groups like NO$_2$ and CN did not give any desired product under the standard reaction conditions (Scheme 17).

Xu et al. reported a Pd-catalyzed highly efficient and atom economical intramolecular cross-dehydrogenative coupling reaction to access fused polyheterocycles containing a coumarin nucleus.[68] A wide variety of coumestans and indole coumarins with good functional group tolerance and good to excellent yields (up to 99%) were synthesized. Using this methodology, some biologically active molecules, such as coumestrol and
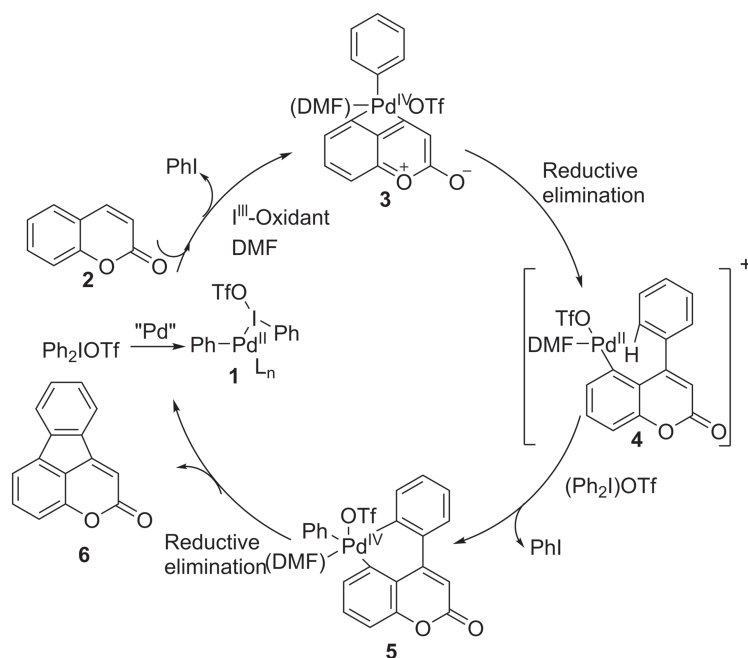
SCHEME 16 Proposed mechanism for Pd(OAc)$_2$ catalyzed diarylation of coumarin
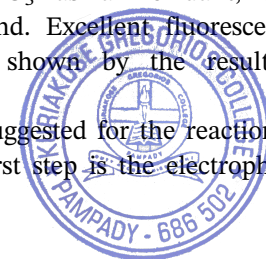

Selected examples

78%   53%   77%

81%   65%   58%
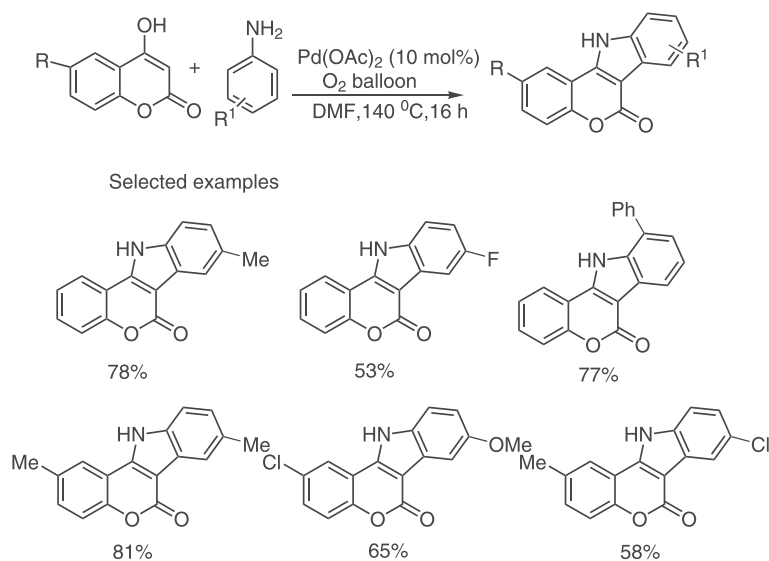
**SCHEME 17** Pd-catalyzed synthesis of indole-fused coumarin derivatives

flemichapparin C, were easily synthesized in good yields. The best results were obtained on 4-aryloxy coumarin using a catalytic amount of Pd(OAc)$_2$ (10 mol%), 2 equiv. of AgOAc as the oxidant, and 2 equiv. of CsOAc as the base in PivOH. A wide range of 4-aryloxy coumarins with diverse electronic properties with substituents on either the phenyl ring of the coumarin nucleus or the C4 substituted aryloxy participated in this reaction, providing a diverse set of coumestans generally in good to excellent yields (73–99%).The reaction is tolerant of various electron-donating or electron-withdrawing substituents on the coumarin ring (Scheme 18).

2.4 | Decarboxylative cross-coupling

A highly efficient and novel protocol for the regioselective synthesis of 3-styrylcoumarins from cinnamic acids and coumarins was reported (Scheme 19).[69] In this work the reaction proceeds *via* a decarboxylative cross-coupling mediated by a catalytic amount of Pd(OAc)$_2$, Ag$_2$CO$_3$ as an oxidant, and 1,10-phenanthrolineas a ligand. Excellent fluorescence quantum yields were also shown by the resulting 3-styrylcoumarins.

A plausible mechanism suggested for the reaction is shown in Scheme 20. The first step is the electrophilic
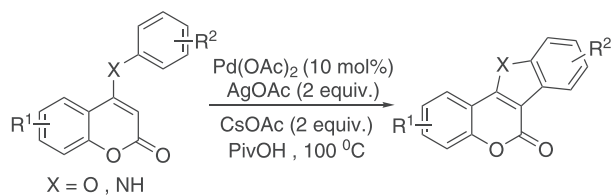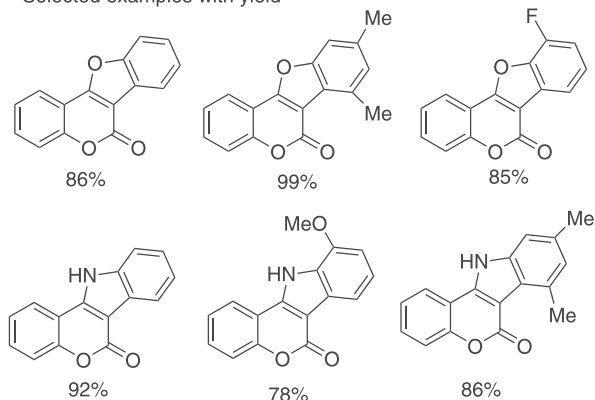
SCHEME 18 Intramolecular cross-dehydrogenative coupling reaction of 4-aryloxy coumarins and 4-arylamino coumarins

palladation of coumarin at the C3 position with the Pd-ligand species, which was more favorable due to the more nucleophilic 3-position, thereby giving intermediate **7**. In parallel, the silver-mediated decarboxylation of cinnamic acid affords alkenyl–silver species, which then transfer the alkenyl group to intermediate **7** to form intermediate **8** by transmetallation. Finally, the desired product **9** is released, regenerating the initial palladation species and resuming the catalytic cycle.

Messaoudi et al. developed an efficient and practical PdBr$_2$/diphenoxyethane (DPE) phos-catalyzed decarboxylative cross-coupling reaction of quinolin-4 (1H)-one 3-carboxylic acids with (hetero)aryl halides (Scheme 21).[70] This method proved to be general, and a variety of 3-(hetero)aryl-4-quinolinones and related heterocycles, such as 3-aryl-1,8-naphthyridin-4(1H)-ones, 3-arylcoumarins, 3-arylquinolin-2(1H)-ones, and 2-arylchromones, were prepared in good to excellent yields. The reaction proceeded under conditions of PdBr$_2$ (5 mol %), DPEPhos (10 mol%), and Ag$_2$CO$_3$ (1 mmol) in toluene/Dimethylacetamide (DMA) (9:1) in a sealed Schlenk tube at 150°C for 1 hr under microwave irradiation. Both aryl iodide and bromide reacted well, providing the desired compound in excellent yields, whereas no reaction occurred when aryl chloride was used as a coupling partner. Electron-rich and electron-deficient, *meta* and *para*-substituted aryl iodides and bromides efficiently underwent decarboxylative coupling with good yields.

To expand the scope of this method, a range of quinolin-4(1H)-one 3-carboxylic acids as well as related heterocyclic carboxylic acids were subjected to a coupling protocol with aryl iodides. It was observed that N-alkyl- and N-arylquinolin-4(1H)-one 3-carboxylic acids with electron-donating or -withdrawing groups on the aromatic nucleus led to the formation of the corresponding product with good yields. The reaction proceeded in satisfactory yields with 1,8-naphthyridin-4(1H)-one, coumarin, quinolin-2(1H)-one 3-carboxylic acids, and chromone 2-carboxylic acids to afford the corresponding arylated heterocycles in moderate to good yields.

2.5 | Sonogashira coupling

Kabalka et al. developed an efficient method for the synthesis of 4-alkynylcoumarins utilizing a Pd-catalyzed coupling reaction of 4-bromocoumarin with potassium alkynyltrifluoroborates in the presence of Cs$_2$CO$_3$ as base under mild conditions.[71] The reaction procedures are straightforward and the yields are excellent. The
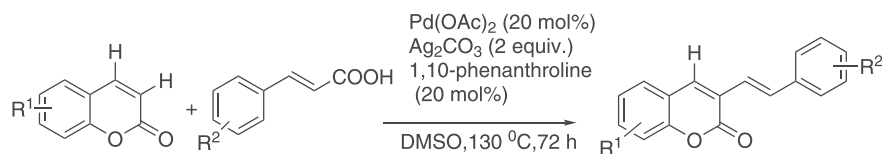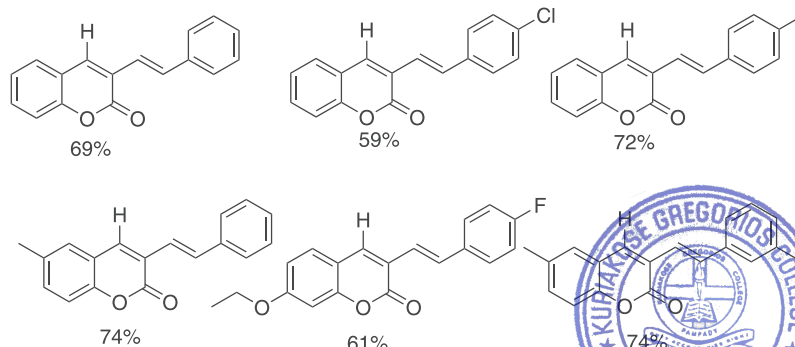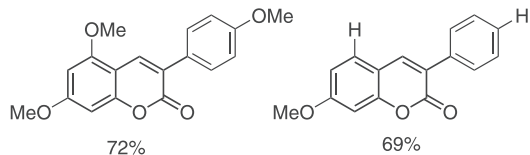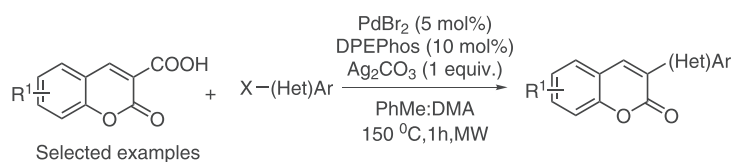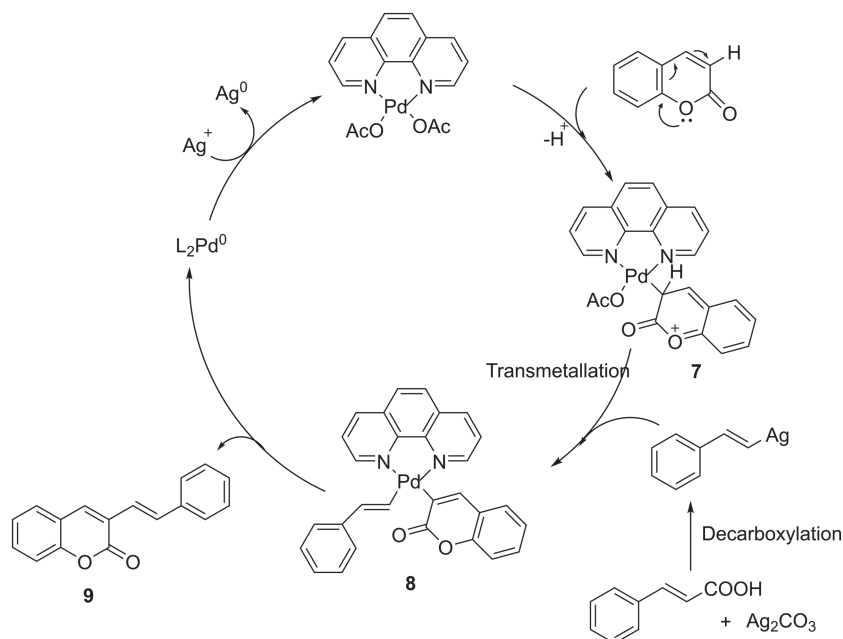

**SCHEME 19** Pd-catalyzed synthesis of 3-styrylcoumarins

SCHEME 20 Proposed mechanism for the synthesis of 3-styrylcoumarins

SCHEME 21 Pd-catalyzed decarboxylative coupling of heterocyclic carboxylic acid derivatives with various aryl iodides

cross-coupling reactions of 4-bromocoumarin with various potassium alkynyltrifluoroborates are shown (Scheme 22).

Wu and co-workers put forward a Pd-catalyzed direct cross-coupling reaction of 4-hydroxycoumarins with various alkynes under copper-free conditions with an efficient catalytic system such as [PdCl$_2$(PPh$_3$)$_2$] (5 mol%),

iPr$_2$NEt, TsCl, MeCN].[72] This transformation is highly effective under mild conditions and the desired products are obtained in good yields. The scope of the Pd-catalyzed direct cross-coupling reactions of various 4-hydroxycoumarins and alkynes was studied (Scheme 23). In all cases, 4-alkynylcoumarins were obtained in moderate to good yields. Both electron-rich
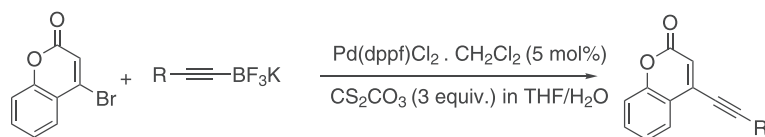
Selected examples

R	Yield (%)
t-Butyl	97
n-Butyl	91
1-cyclohexenyl	82
Phenyl	92
p-Tosyl	85

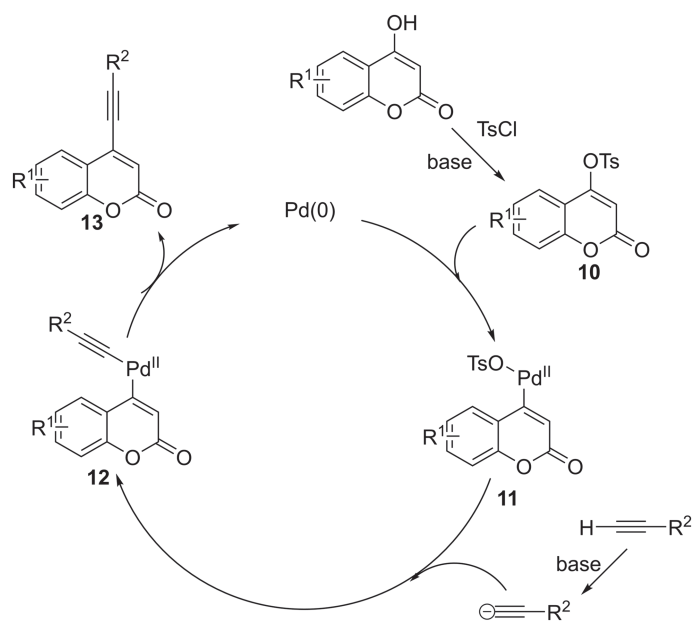**SCHEME 22** Cross-coupling reactions of 4-bromocoumarin with various potassium alkynyltrifluoroborates
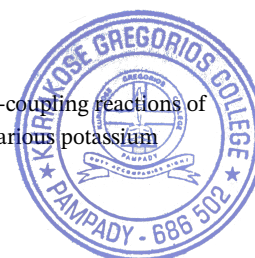
SCHEME 23   Pd-catalyzed direct cross-coupling reactions of 4-hydroxycoumarins with various alkynes

Selected examples with yield

81%   86%   78%

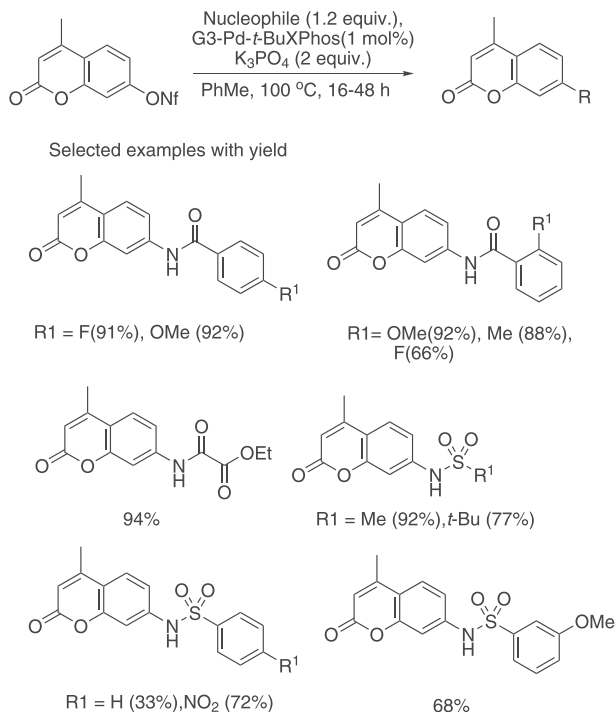
91%   48%   81%
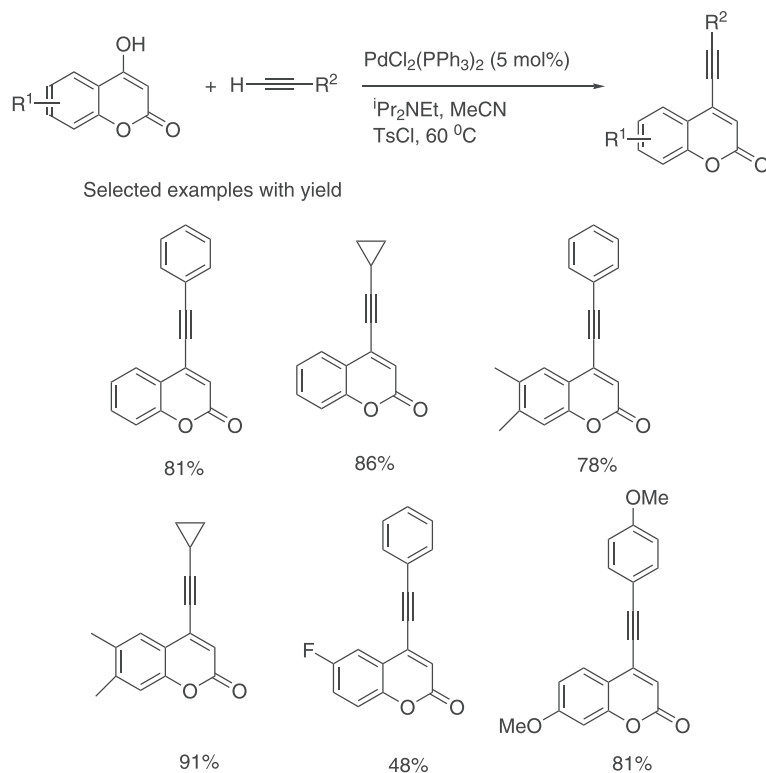
and electron-poor 4-hydroxycoumarins were suitable partners in this process. However, better results were displayed when electron-donating groups were attached on the aromatic ring of 4-hydroxycoumarins.

The mechanism proposed for the reaction is shown in Scheme 24. Due to the presence of *p*-toluenesulfonyl chloride an *in situ* activation of 4-hydroxycoumarin takes place. Therefore, an oxidative addition of Pd(0) to
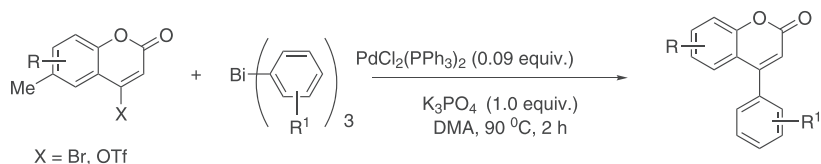
4-tosyloxycoumarin **10** generates intermediate **11**, which then reacts with alkyne, leading to intermediate **12**. The latter then undergoes subsequent reductive elimination to afford the corresponding product **13**.

Raffa et al. put forward a novel idea of Pd-catalyzed cyclofunctionalization of 3-alkynyl-4-methoxycoumarins with aryl halides resulting in the selective formation of 3-arylfuro[3,2-*c*]coumarins in lieu of the
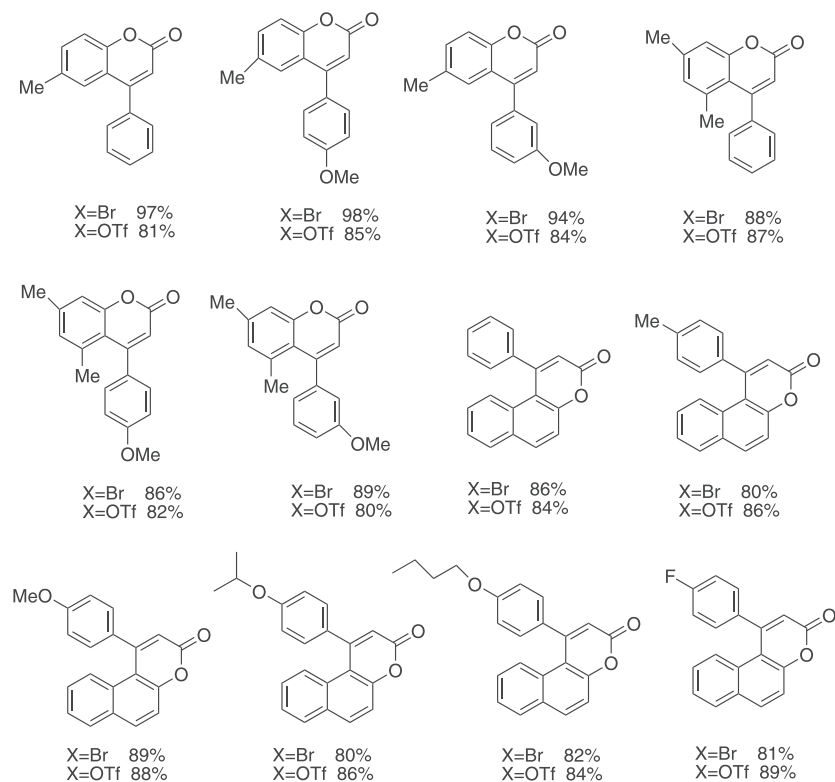

SCHEME 24   Possible mechanism for the Pd-catalyzed direct coupling reaction of 4-hydroxycoumarin with alkyne

SCHEME 25 Pd-catalyzed synthesis of 3-arylfuro[3,2-c]coumarins

Selected examples with yield

R^1 = Ph; R^2 = p-COOMe (64%), p-NO$_2$ (82%), p-F (52%), H(49%), p-OMe (6%), m-CF$_3$ (82%)

R^1 = p-COOMeC$_6$H$_4$; R^2 = p-COOMe (92%), p-NO$_2$ (87%)

R^1 = p-MeOC$_6$H$_4$; R^2 = p-NO$_2$ (65%)

expected regioisomeric 3-arylfuro[2,3-b]chromones (Scheme 25).[73] The model substrates used in the reaction are 4-methoxycoumarin and (p-MeO$_2$C)-phenyl iodide. Pd(PPh$_3$)$_4$ was found to be a particularly effective catalyst for this transformation when used in DMF at 100°C.

Aryl halides bearing electron-withdrawing groups resulted in moderate to good yields of product. Conversely, as illustrated with the reaction of p-methoxyphenyl iodide, the presence of an electron-donating group on the aryl coupling partner resulted in poor yields of the desired furocoumarins, probably reflecting a decreased electrophilicity of the organo Pd(II) complex. A range of substituted aryl as well as alkyl groups on the alkyne were also successfully employed in the cyclization coupling. A mechanism involving the linear to angular rearrangement of a Pd-containing furan intermediate was also proposed.

2.6 | Negishi coupling

In 2001, Wu et al. discussed the Pd-catalyzed cross-coupling reactions of substituted 4-tosylcoumarins with acetylenes or zinc reagents under very mild conditions with satisfactory yields (Scheme 26).[74] In this work, 4-tosylcoumarins with a variety of terminal acetylenes in the presence of diisopropylethylamine and a catalytic amount of PdCl$_2$(PPh$_3$)$_2$ and CuI in acetonitrile resulted in the formation of a series of enynes in good to excellent yields. All the selected terminal acetylenes (except trimethylsilylacetylene) with functional groups (such as bromo, chloro, hydroxy, and cyano) reacted smoothly with tosylate under Sonogashira conditions between

Selected examples

Alkyne	Yield (%)
H≡ phenyl	81
H≡ C$_6$H$_4$-Br	78
H≡(CH$_2$)$_4$CH$_3$	98
H≡(CH$_2$)$_3$Cl	83
H≡(CH$_2$)$_3$CN	82
H≡(CH$_2$)$_3$OH	92

SCHEME 26 Pd-catalyzed cross-coupling of substituted 4-tosylcoumarins with acetylenes

R^1	R^2ZnBr	Yield (%)
H	phenyl-ZnBr	71
H	phenyl-CH$_2$ZnBr	85
H	NC(CH$_2$)$_3$ZnBr	85
H	cyclohexyl-ZnBr	42
H	thiophene-ZnBr	91
6-Me	phenyl-ZnBr	66
6-Me	phenyl-CH$_2$ZnBr	61
6-Me	NC(CH$_2$)$_3$ZnBr	82

SCHEME 27 Pd-catalyzed cross-coupling of tosylates with organozincs

50 and 60°C in less than 12 hr, resulting good to excellent yields of enynes (72–92%).

Further studies have been done to evaluate the coupling of 4-tosylcoumarin with a variety of organozinc reagents. The reactions proceeded very well when aryl, benzyl, and even 3-cyanopropylzinc bromides were used to react with the tosylates (Scheme 27). However, cyclohexylzinc bromide gave low yield.

Rieke et al. reported the synthesis of 4-arylcoumarins by a Negishi-type reaction of 4-coumarinylzinc bromide with aryl halides (Scheme 28).[75]

Negishi cross-coupling of 4-coumaryl tosylate with aryl and alkylzinc reagents has also been performed with good yields of the cross-coupled products using [Pd(PPh₃)₂(saccharinate)₂] as the catalytic system.[76] Good to excellent yields of the cross-coupled products were obtained under relatively mild conditions, suggesting the efficiency of the catalytic system for such transformations (Scheme 29). Also alkylzinc reagents under the given set of conditions gave good yields of the coupled products in contrast to the examples already reported.

2.7 | Stille coupling

Stille coupling of 4-chloro-7-methoxy-2H-1-benzopyran-2-one using β-diketiminatophosphane-Pd catalyst to get the expected product has also been reported.[77] Here, CsF was found to be a suitable base in THF solvent (Scheme 30).

2.8 | Buchwald–Hartwig coupling

Recently, Ashton and coworkers described the Pd-catalyzed Buchwald–Hartwig cross-coupling reaction between 4-methylumbelliferone derived nonaflates with amides, carbamates, and sulfonamides.[78] The reactions were carried out using 4-methylumbelliferone derived nonaflate with various nucleophiles in the presence of G3-Pd-xantphos (1 mol%) and Cs₂CO₃ (1.4 equiv.) as base in 1,4-dioxane as solvent at 100°C. Good to excellent yields were obtained for a wide variety of N-substituted 7-amino coumarin derivatives (Scheme 31).

2.9 | Miscellaneous

Rao et al. investigated a Pd-catalyzed cross-coupling reaction of 4-bromo- and 4-(trifluoromethylsulfonyloxy)coumarins with triarylbismuth compounds furnishing 4-arylcoumarins in excellent yields.[79] The reactions demonstrate excellent reactivity under the established general catalytic conditions using [PdCl₂(PPh₃)₂] as catalyst with K₃PO₄ as base in DMA at 90°C for 2 hr (Scheme 32). Triarylbismuth compounds serve as atom-efficient multicoupling organometallic nucleophiles, reacting efficiently with either 4-bromo- or 4-(trifluoromethylsulfonyloxy)coumarins to furnish 4-arylcoumarins. The reactions with triarylbismuth

SCHEME 28 Negishi coupling of 4-coumarinylzinc bromide with aryl halides

SCHEME 29 Negishi cross-coupling of 4-coumaryl tosylates

SCHEME 30 Stille coupling reaction of 4-chloro-7-methoxy-2H-1-benzopyran-2-one

SCHEME 31 Synthesis of *N*-substituted 7-amino coumarin analogues

compounds as multicoupling organometallic nucleophiles proceeded smoothly in short reaction times to afford excellent yields of an array of functionalized 4-arylcoumarins.

The plausible catalytic cycle of this coupling reaction was also discussed (Scheme 33). The various steps involved in the catalytic cycle are oxidative addition, transmetallation, and reductive elimination.

Pd-catalyzed cross-coupling reactions of functionalized 3-bromo-4-trifloxycoumarins with three-fold arylating triarylbismuth reagents to synthesize 3-bromo-4-arylcoumarins in good to high yields were also reported (Scheme 34).[80] The Pd-catalyzed arylations of functionalized 3-bromo-4-arylcoumarins occur in the second arylation to give functionalized 3,4-diarylcoumarins in high yields. The method works well with triarylbismuth in structural elaborations, leading to mono-, di-, and triarylated coumarins, and has high practical and synthetic scope that find further applications in organic synthesis.

A convenient and efficient approach for the synthesis of 4-indolyl coumarins was developed via a Pd-catalyzed coupling reaction between 4-coumarinyl triflates and

SCHEME 32 Pd-catalyzed synthesis of 4-arylcoumarins using triarylbismuth
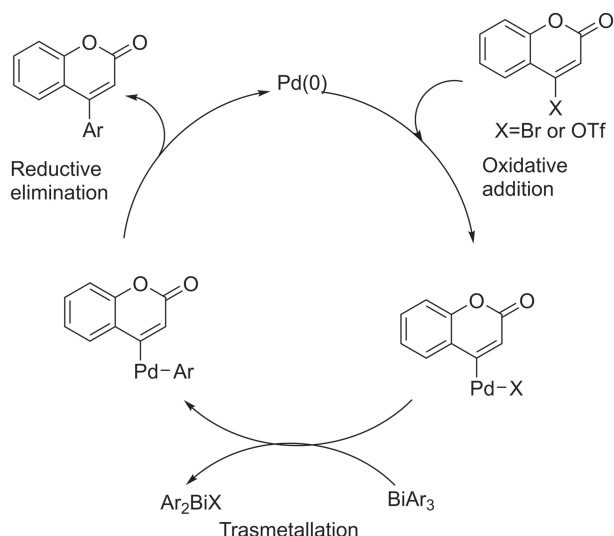
SCHEME 33   Proposed Pd catalytic cycle for the coupling of halo coumarins with triarylbismuth

SCHEME 35   Pd-catalyzed synthesis of 4-indolyl coumarins

SCHEME 34   Pd-catalyzed synthesis of 3-bromo-4-arylcoumarins
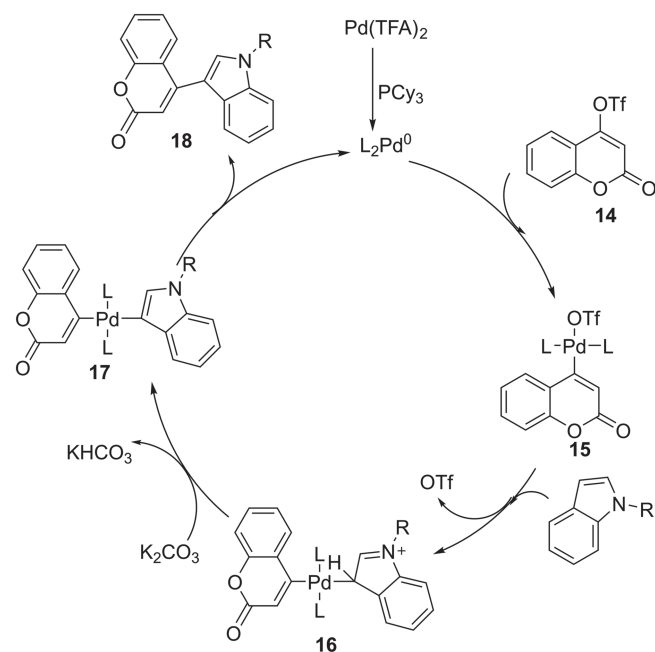
SCHEME 36   Plausible mechanism for the synthesis of 4-indolyl coumarins

indoles.[81] The model substrates used for the optimization of the reaction were 4-coumarinyl triflate and 1-methylindole. Here, Pd(TFA)$_2$ was found to be the best catalyst and gave the best result, better than Pd (OAc)$_2$, PdCl$_2$, PdBr$_2$, Pd (PPh$_3$)$_2$(OAc)$_2$, and PdSO$_4$. Xylene as solvent in the presence of tricyclohexylphosphine as ligand and K$_2$CO$_3$ as base with 4 equiv. of 1-methylindole gave the corresponding product in 75% yield (Scheme 35).

The coupling of 1-methylindole or N–H indole and coumarins with electron-donating and electron-withdrawing groups (CH$_3$, OCH$_3$, Cl, Br, F) at positions 6 or 7 were found to be favored in the reaction to afford the corresponding products in moderate to good yields.

The chloro and bromo groups on the phenyl ring of coumarins were tolerated under these coupling conditions. Polycyclic triflate also reacted smoothly with N–H indole, leading to the formation of the corresponding product in 85% yield. When indoles with an electron-withdrawing group (CO$_2$Me) and electron-donating groups (Et, OCH$_3$) were used, electronic effects in the indole turned out to be stronger and sharper, and as a result reduced yields were obtained. When indole bearing CH$_3$ at position 2 was reacted under typical conditions, the desired

product was obtained in 29% yield, but the indole bearing a $-CH_3$ group at position 3 did not yield the product. A plausible mechanism for the reaction was also proposed (Scheme 36**)**. The reaction begins with the reduction of the Pd(II) catalyst to Pd(0) by PCy_3. Then oxidative addition of 4-coumarinyl triflate **14** to the Pd(0) catalyst generates the electrophilic palladiumcomplex **15**, which can then undergo attack at the C3 position of indole to give the intermediate **16**. Later, rearomatization via C−H bond cleavage to **17** followed by reductive elimination gives the product **18**, regenerating the Pd(0) catalyst.

3 | CONCLUSION

In this review, Pd-catalyzed reactions of coumarin derivatives using various cross-coupling reactions are discussed. All these reactions demonstrate the excellent reactivity of coumarines under optimized general catalytic conditions to obtain the substituted coumarin products in good to excellent yields. Coumarins generally have a broad range of biological activities, which vary with thier structure. Even though coumarins with different substituents at C3, C4, and C7 are explored using various reaction types, the positions C5, C6, and C8 remain relatively unexplored. Hence, there is a significant scope in this type of cross-coupling reaction in coumarin chemistry for the development of functionalized and structurally diverse novel coumarin derivatives through placement of appropriate functional groups around the coumarin nucleus at different positions, and this may be of potential biological interest.

AUTHOR CONTRIBUTIONS
Thomas Mathew: Project administration.

DATA AVAILABILITY STATEMENT
Data sharing not applicable as no new data generated.

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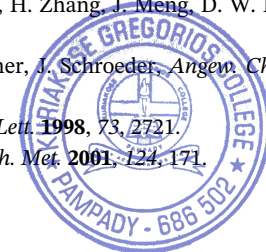
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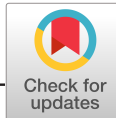
REVIEW

Recent developments in the metal catalysed cross-coupling reactions for the synthesis of the enone system of chalcones

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For the last two decades, chalcones and their derivatives have attracted special interest among researchers due to their pharmaceutical properties. Numerous research works have been still going on to improve the methodologies of chalcone synthesis. Chalcone has displayed a remarkable curative efficiency to cure numerous diseases and it continues to show promise for new drug investigations. This review highlights the metal catalysed cross-coupling reactions for the synthesis of chalcone and its derivatives from 2009 to 2020.

KEYWORDS
Chalcone, cross-coupling, flavonoids, α,β-unsaturated ketones

1 | INTRODUCTION

1,3-Diaryl prop-2-en-1-ones, *viz.* chalcones, belong to flavonoid family.[1] Chalcones give yellow pigmentation in many yellow flowered ornamental species such as Dahlia, Cosmos, Coreopsis etc.[2] In addition to flowers, chalcone is also present in spices, vegetables and fruits.[3] There are several natural and synthetic chalcones are considered as mediators for various synthesis of therapeutic compounds.[4] They cover a wide class of pharmacological activity,[5] including anti-malarial,[6] anti-fungal,[7] anti-diabetes,[8] anti-oxidant,[9] anti-inflammatory,[10] anti-cancer,[11] anti-nociceptive[12] etc. In chalcones, the α,β-unsaturated carbonyl system allows them to be biologically active, and omission of the carbonyl system makes them biologically inactive.[13]

Several synthetic strategies for chalcones have been reported in the past decades such as Claisen-Schmidt condensation,[14] Photo-Fries rearrangement,[15] Julia-Kocienski olefination,[16] Mukaiyama-aldol reaction,[17] Friedel-Craft acylation,[18] Coupling reaction[19] etc. A cross coupling reaction is a reaction where two fragments are fused together with the support of metal catalyst. Suzuki–Miyaura coupling,[20–22] Heck reaction,[23,24] Stille coupling,[25] and Sonogashira coupling[26,27] are some of the most versatile and successful synthetic tools for carbon–carbon bond formation. Synthetic methodologies for chalcones have some drawbacks like requirement of strong basic or acidic reaction conditions, low yield of products, harsh reaction conditions, long reaction time, usage of toxic reagents, and low selectivity. Chalcone based compounds have attracted much attention in

medicinal chemistry, where various bioactive moieties are possible to be introduced in the two aromatic rings and the α,β unsaturated ketone fragments. Some chalcone family drugs such as metochalcone,[28] sofalcone,[29] ilepcimide[30] have been approved for clinical use. Metochalcone (vesidryl®) is isolated from heartwood of *Pterocarpus marsupium* and effectively used as a choleretic and diuretic drug. Sofalcone is used as an anti-peptic ulcer and mucosal protecatnt drug. Triazole-benzimidazole-chalcone heterocyclic hybrid bearing varied aromatic substitutions[31] effectively used in cancer therapy. Also, various natural and synthetic chalcones are used as antibacterial scaffold[32] and anti-osteoprotic activity[33] in medicinal chemistry. This review focuses on the novel progress in chalcone synthesis through metal catalysed cross-coupling reactions and covers literature from 2009 to 2020. The chemistry of Pd catalysed cross-coupling reaction for the synthesis of chalcones was not included in detail in this review as the topic has been reviewed recently in 2019 by Rullah *et al.*[34] For simplicity and clarity, the topic is classified based on the metal used as catalyst for the coupling reaction.

2 | SYNTHESIS OF CHALCONES VIA METAL CATALYSED CROSS-COUPLING REACTIONS

2.1 | Synthesis of chalcones via silver catalysed cross-coupling reaction

A silver-catalysed double-decarboxylative protocol has been proposed in 2015 by Zhang *et al.* for the synthesis of chalcone derivatives under mild aqueous conditions by cascade coupling of substituted α-keto acids with cinnamic acids (Scheme 1).[35] The reaction was carried out under nitrogen atmosphere with water as solvent, using 10 mol% silver nitrate as the catalyst, 1 equiv. of sodium persulphate as the oxidant, 2 equiv. of potassium carbonate as the base at 100 °C. Cinnamic acids with an electron donating substituent (CH_3, $COCH_3$) underwent rapid conversion than the substrate having an electron withdrawing group. Moreover, steric hindrance in α-keto acids has not much affected the catalytic efficiency. This simple and effective way could expanse the synthetic methods for the preparation of diverse chalcones.

The proposed tentative mechanism is illustrated in Scheme 2. Initially, using sodium persulphate, Ag(I) cation get oxidised to Ag (II) cation. In the next step, Ag (II) cation reacts with α-keto acid anion **1** to form acyl radical **2** with the release of Ag(I) cation and CO_2. Then, the addition of acyl radical **2** to the α-position of the double bond of cinnamate anion **3** results the intermediate **4**. Lastly, this intermediate **4** reacts with Ag (II) giving chalcones **5** with carbon dioxide as by-product.

In 2017, Wu *et al.* developed a silver-catalysed decarboxylative cross-coupling reaction using easily available starting materials such as α-keto acids with alkenes under the reaction condition of 10 mol% of silver carbonate as catalyst, 3 equivalent $K_2S_2O_8$ as oxidant using acetonitrile as solvent at 100 °C (Scheme 3).[36] This base free methodology delivers an appropriate way to produce chalcone derivatives with mild operation conditions and wide substrate tolerance giving the corresponding products. Different α-keto acids and alkenes were tested which resulted moderate to good yield of products.

In the proposed mechanism, silver plays a significant role in decarboxylative cross-coupling of α-keto acids and it follows free radical pathway (Scheme 4). Initially, Ag(I) cation get oxidised to Ag (II) cation by $K_2S_2O_8$. Then

Selected examples with yield

62 % 75 % 68 %

80 % 80 % 92 %

72 % 54 % 66 %
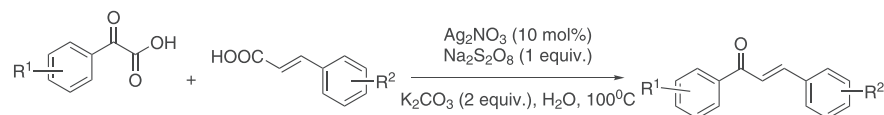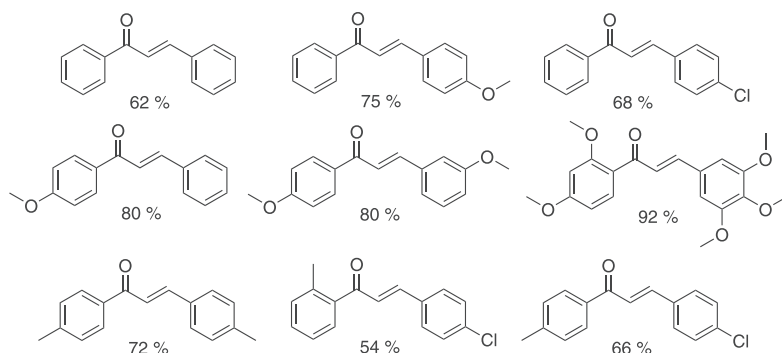
SCHEME 1 Silver catalysed synthesis of chalcone derivatives via decarboxylative coupling
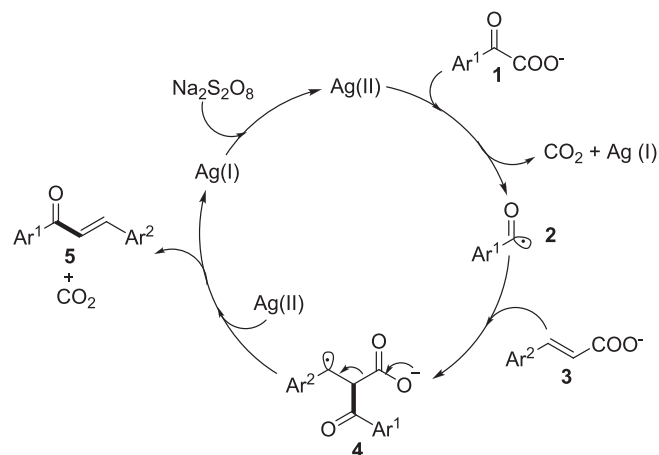
SCHEME 2 Plausible mechanism for the Silver catalysed synthesis of chalcones.Reprinted with permission from Ref. No 35

α-keto acid **6** reacts with Ag (II) cation producing an acyl radical **7** with the liberation of CO_2. Subsequently, a radical intermediate **9** is formed by radical addition process of **7** to **8**. Ultimately, the final product chalcone **10** is produced from **9**, with immediate oxidation by the high valent silver species and coordinated with a deprotonation process. Ag(I) cation again get oxidised to Ag (II) cation by $K_2S_2O_8$.

2.2 | Synthesis of chalcones via iron-catalysed cross-coupling reaction

In 2015, Guo *et al.* reported a new approach for the synthesis of α,β-unsaturated carbonyls in aqueous solution by iron-facilitated oxidative radical decarboxylative cross-

SCHEME 3 Decarboxylative cross-coupling of *α*-keto acids
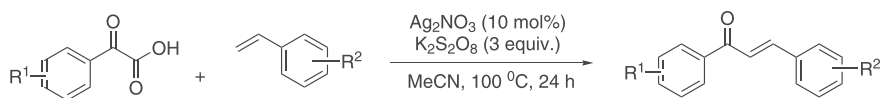
Selected examples
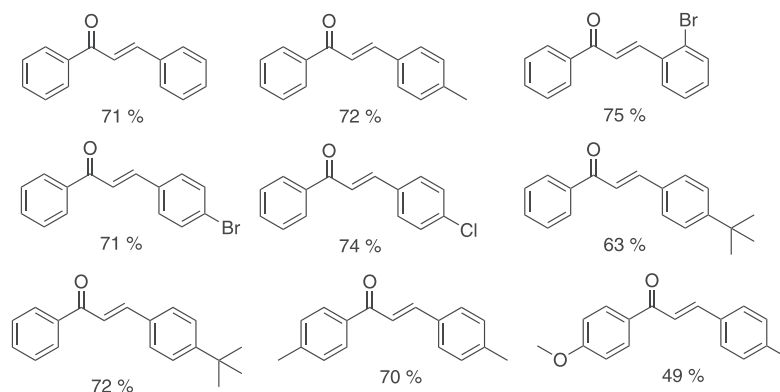
SCHEME 4 Proposed mechanism for the decarboxylative cross-coupling of *α*-keto acidsReprinted with permission from Ref. No. 36
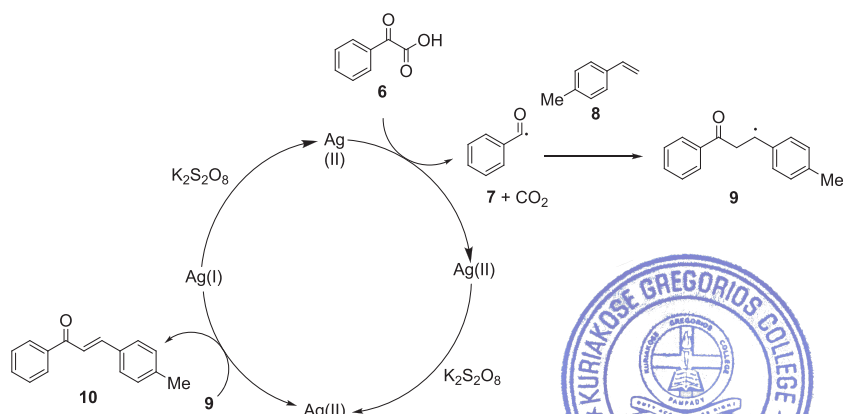
coupling between α-oxocarboxylic acids and acrylic acids (Scheme 5 & 6)[37] The optimised reaction condition involves $FeCl_2$ (10 mol%) as the catalyst precursor, $HCOONa \cdot 2H_2O$ (2.0 equiv.) as base, $K_2S_2O_8$ (2.5 equiv.) as oxidant and solvent as $H_2O/DMSO$ in the ratio 17:3 at 120 °C in N_2 atmosphere for 15 hr. The presence of both electron withdrawing and electron donating groups in the benzoylformic acids afforded good yields (64–92%) of

SCHEME 5 Reaction of various α-oxocarboxylic acids with cinnamic acid

Selected examples

83 %   81 %   87 %   92 %

82 %   78 %   64 %   67 %

64 %   64 %   62 %

52 %   42 %   41 %   51 %

Selected examples

83%   90%   82%

60%   70%   65%

63%   74%   60%
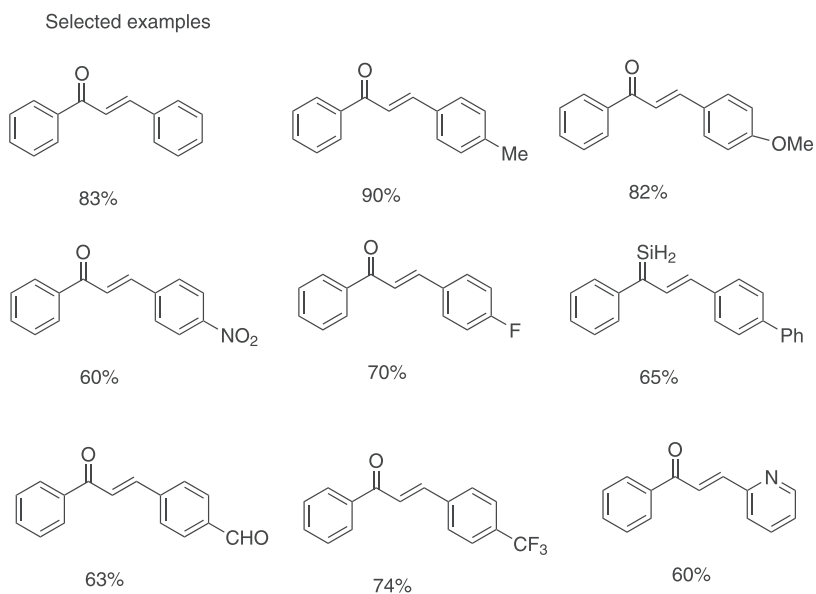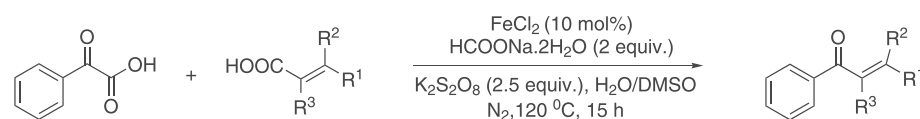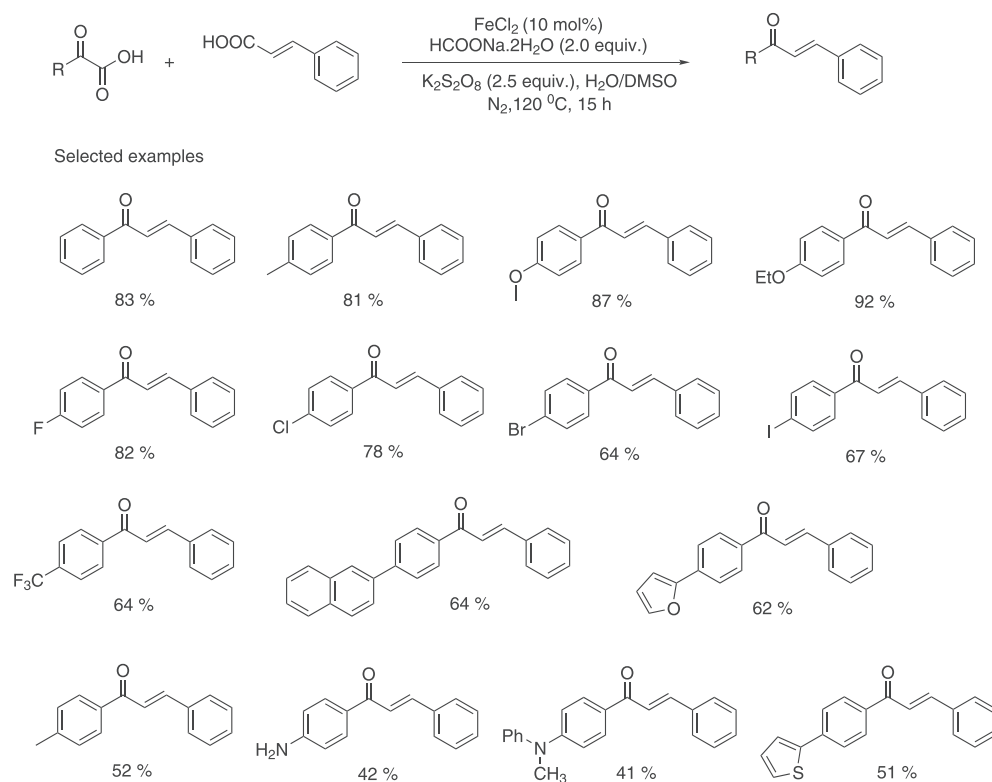
SCHEME 6 Reaction of various α-oxocarboxylic acids with cinnamic acid

α,β-unsaturated carbonyls on reaction with cinnamic acid. In addition to this, naphthyl oxocarboxylic acid and heterocyclic α-keto acids also effectively gave the corresponding products in moderate yields.

Subsequently, a variety of acrylic acids and benzoylformic acid underwent reaction. Cinnamic acids with electron-donating or electron-withdrawing functional groups provided moderate to good yields of the products. Acrylic acids with pyridyl, thiophen-2-yl, and furan-2-yl substitution gave the corresponding products with 42–72% yields.

A possible free-radical mechanism suggested by the authors is discussed in Scheme 7. In the presence of $FeCl_2$ and $K_2S_2O_8$, acyl radical **12** is generated from α-oxocarboxylates **11** via an oxidative radical decarboxylative process. Then, addition of the benzoyl radical **12** to the double bond of acrylic acid **13** results the alkyl radical **14**. Lastly, the intermediate **14** undergoes β-elimination to form the preferred product **15** with the liberation of CO_2.

2.3 | Synthesis of chalcones via gold-catalysed cross-coupling reaction

In 2009, Park and co-workers reported a simple sol–gel method for the synthesis of α,β-unsaturated ketones by the coupling of various primary alcohols with ketones immobilizing gold nanoparticles in aluminium oxyhydroxide support (Scheme 8).[38] The catalyst system Au/AlO (OH) was made from a solution of aluminium tri-sec-butoxide, hydrogen tetrachloroaurate hydrate, and

SCHEME 7 Proposed mechanism for the synthesis of chalcones via Iron-catalysed cross-coupling reactionReprinted with permission from Ref. No 37

SCHEME 8 Synthesis of chalcones catalysed by gold nanoparticle catalyst

Pluronic P123 in ethanol. TEM images showed gold nanoparticles of 5–13 nm size and aluminium oxyhydroxide fibres. XRD and XPS results confirmed that these nanoparticles were metallic gold and ICP data showed that almost all gold source is entrapped in the support. The reaction was carried out on 1.0 mmol of ketone and 3.0 mmol of alcohol dissolved in 3.0 mL of toluene with 1.0 mol% Au and Cs_2CO_3 (3 equiv.) at 25 °C under O_2 balloon for 24–30 hours. This gold nanoparticle catalyst was reusable although additional caesium carbonate was required in reuse.

Later, in 2011, a convenient and general protocol for gold-catalysed Meyer-Schuster rearrangement of secondary and tertiary propargylic alcohols with boronic acids at room temperature developed by Pennell and co-workers (Scheme 9 & 10).[39] This reaction was carried out in toluene in the presence of 0.2 equiv. of 4-methoxyphenylboronic acid and 1 equiv. of methanol with secondary and tertiary alcohols in the presence of 1–2 mol% gold catalyst such as PPh_3AuNTf_2, at room temperature resulting enones with good to excellent yields. In most cases, this reaction offered high selectivity for E-alkene.

Liu *et al.* established a direct and effective C-C cross-coupling of primary and secondary alcohols via solid multifunctional Au–Pd/HT through a facile BH pathway.[40] This bimetallic Au–Pd/HT catalyst can effectively catalyse the aerobic cross-coupling of benzyl alcohol and 1-phenylethanol to produce the corresponding chalcone, with a high yield under 1 bar O_2 (Scheme 11).

In 2016, highly selective tandem nucleophilic cross-coupling reactions of alkynes have been developed by Glorius and co-workers using visible-light-promoted dual gold/photoredox catalysis.[41] α-Arylenones were resulted by the reaction between propargyl alcohols and aryldiazonium salts in the dual gold/photoredox catalysed arylative Meyer–Schuster rearrangement (Scheme 12). [Ph_3PAuCl](10 mol%), [Ru (bpy)$_3$] (PF$_6$)$_2$(2.5 mol%) acts as gold/photoredox catalyst in KH_2PO_4 (0.90 mmol) under argon. The reactions proceed at room temperature under irradiation with visible light from readily available sources or even sunlight.
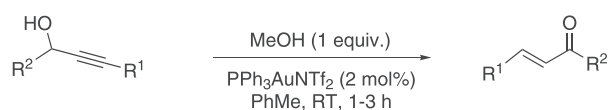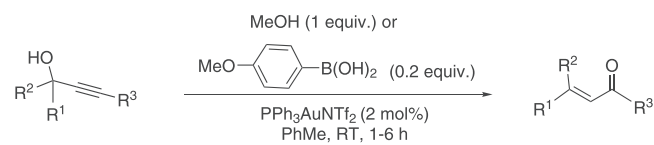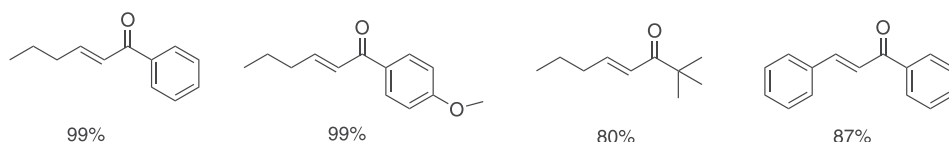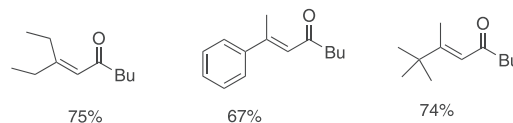
SCHEME 10 Gold-catalysed Meyer-Schuster rearrangement of secondary propargylic alcohols
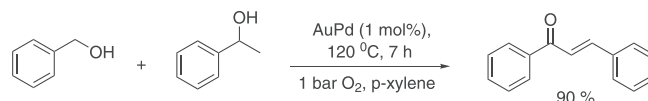
SCHEME 11 Aerobic cross-coupling reaction under O_2

In 2017, Varma and Maya reported a green synthetic method for the preparation of α,β-unsaturated ketones by oxidative C-C coupling reaction of ketones with primary alcohols with water as the only by-product. This reaction was carried out at room temperature using bentonite–gold nanohybrid (Au–MPBen) as a heterogeneous catalyst in the presence of weak base such as Cs_2CO_3 (Scheme 13).[42] This catalyst was reused for five runs without significant loss of activity and it was found to be environment friendly and cost-effective. Ketones and primary alcohols with electron donating and electron withdrawing groups gave chalcones with good to excellent yields. The catalyst also showed high TOFs and TONs.

The suggested reaction mechanism is given in (Scheme 14). At the initial stage, metal alkoxides are generated by the adsorption of alcohol molecules on the surface of gold nanoparticles. Thereafter, metal alkoxide is subjected to β-hydride elimination resulting metal hydride intermediate and aldehyde. By oxidation, metal hydride intermediate regains the gold surface and produces water as the by-product. Finally, α,β-unsaturated ketone is

SCHEME 9 Gold-catalysed Meyer-Schuster rearrangement of primary propargylic alcohols
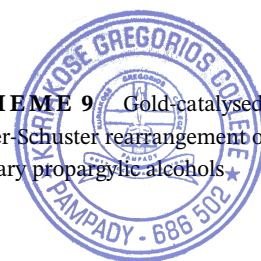
SCHEME 12 Dual gold/photoredox-catalysed arylative Meyer-Schuster rearrangement

Selected examples with yield

61%   68%   15%

74%   79%   66%
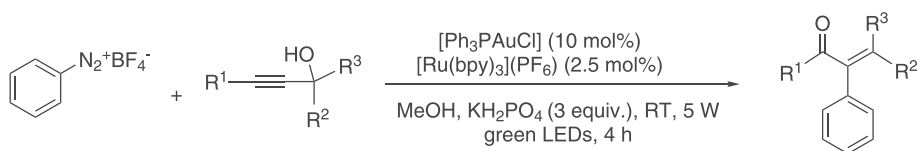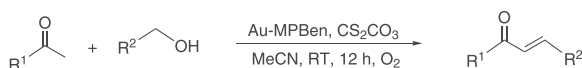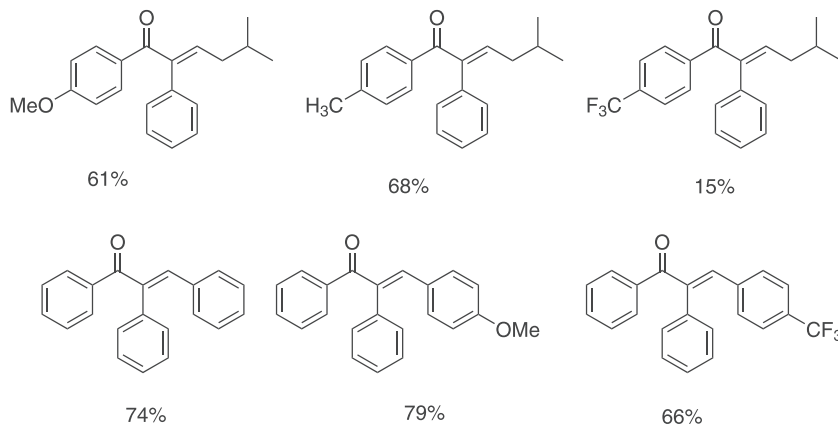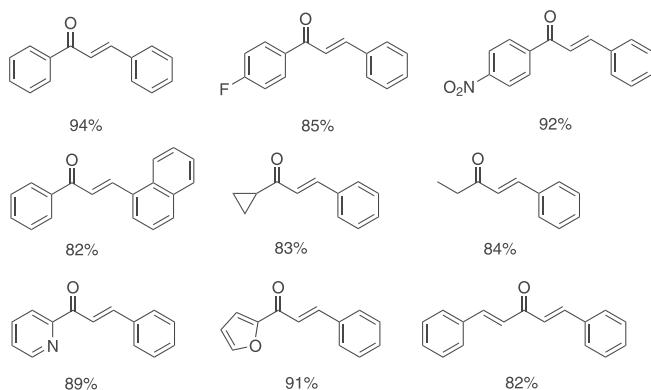
SCHEME 13 Synthesis of chalcones catalysed by Au–MPBen catalysed C-C coupling of ketones with primary alcohols

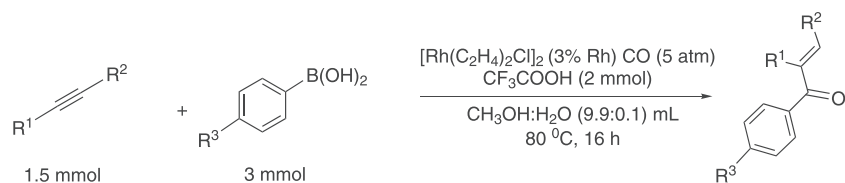Selected examples with yield

94%   85%   92%

82%   83%   84%

89%   91%   82%

formed by aldol condensation reaction between aldehyde and ketone in the presence of base (Cs_2CO_3).

2.4 | Synthesis of chalcones via rhodium-catalysed cross-coupling reaction

In 2009, Artok and co-workers introduced a method in which, under CO atmosphere, in the presence of a rhodium(I) catalyst, organoborons and alkynes resulted mainly 5-aryl-2(5H)-furanones, α,β-unsaturated ketones, and indanones (Scheme 15).[43] To favour the formation of selectivity of product, the reaction condition was tuned by modifying the reaction conditions. In the presence of $[Rh(C_2H_4)_2Cl]_2$ complex (3% Rh), diphenylacetylene reacted with several arylboronic acids in the presence of trifluoroacetic acid and water as additives in methanol solvent, generating mixtures of both *Z*- and *E*-isomers of enones.

SCHEME 14 Oxidative cross-coupling reaction of primary alcohols with ketones catalysed by Au-MPBenReprinted with permission from Ref. No 42
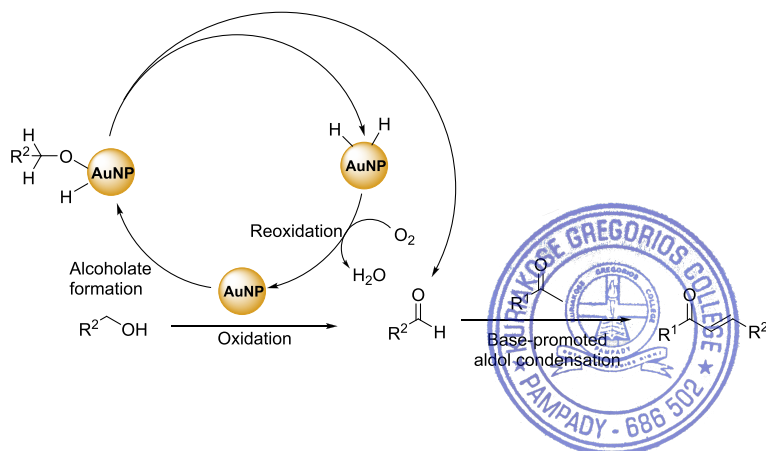
SCHEME 15 Synthesis of enones by carbonylative addition of various arylboronic acids to alkynes

Selected examples with yield
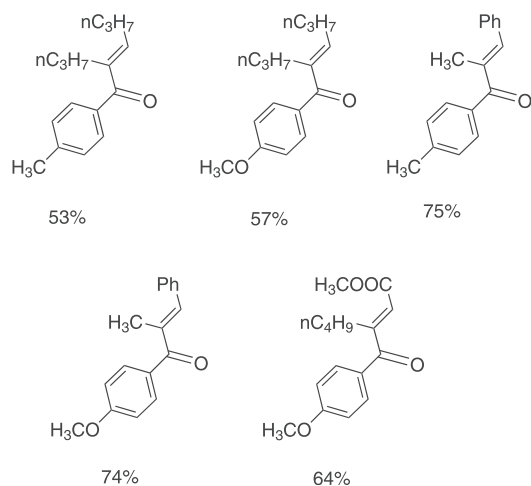
Later, in 2014, Yu and Li reported another unique way for the synthesis of chalcones by C − C coupling of cyclopropenones with arenes using the redox-neutral Rh (III)- catalyst. The reaction proceeds using 2.5 mol% of [Cp*RhCl₂]₂ and 15 mol% of AgSbF₆ as catalyst, in DCM solvent at 45 °C for 20 hours, sealed under argon (Scheme 16).[44] Coupling of symmetrical diphenyl-cyclopropenones and 2-phenylpyridines with either electron-donating or -withdrawing groups at the *para*, *meta* or *ortho* position of the phenyl ring, afforded the corresponding products in good yields. The substituent on the pyridinyl ring also showed broad functional group compatibility. Also, coupling of symmetrical diphenyl-cyclopropenones bearing electron-donating or electron-withdrawing groups with 2-phenylpyridine gives good yields of product.

This C − H functionalization reaction was applied to other arene substrates with the same reaction condition, but the temperature was increased up to 60 °C. Under mild reaction condition, diphenylcyclopropenones reacted with arenes having directing groups such as 2-pyridyl, 2-pyrimidyl, N-pyrazyl and oxime resulted chalcones in admirable yields (Scheme 17).

In 2018, Gao *et al*. developed a novel scheme for the synthesis of benzofuran and chalcone derivatives by synergistic dual directing groups enabled C–H functionalization reaction between various *N*-phenoxyaceta-mides with propargyl alcohols in a solvent-controlled chemoselective manner using mild Rh (III)-catalyst

(Scheme 18).[45] At room temperature, *N*-phenoxyaceta-mides and propargyl alcohols reacted in the presence of rhodium catalyst such as [Cp*RhCl₂]₂ and caesium acetate in acetonitrile as solvent under air for 24 hr. *N*-Phenoxyacetamides substituted with functional groups like alkyl, halogens, cyano and ester were well tolerated.

2.5 | Synthesis of chalcones via copper catalysed cross-coupling reaction

Lei and co-workers developed the first Cu-catalysed oxidative coupling of alkenes with aldehydes using CuCl₂ (20 mol%), TBHP (2.5 equiv.) at 80 zero C for 12 hr (Scheme 19).[46] The presence of electron donating and electron withdrawing groups both in aldehyde and alkenes gave α,β-unsaturated ketones in excellent yields.

A plausible mechanism was also suggested for the reaction via a single-electron transfer process (Scheme 20). Initially, copper species **17** and the alkyloxy radical form the low valent copper species **16** by donating an electron to TBHP. Acyl radical **19** is formed by the abstraction of hydrogen atom from aldehyde **18** by alkyloxy radical. The radical addition of acyl radical **19** to alkene **20** generates the benzylic radical **21**. This benzylic radical **21** undergoes the direct oxidation by copper species **17** and deprotonation to give α,β-unsaturated ketones **22**. The low valent copper species **16** get regenerated and it allows continuing the catalytic cycle.
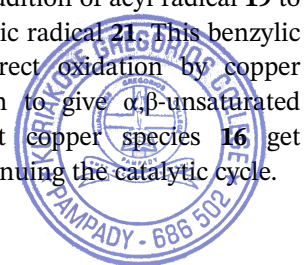
SCHEME 16 Reaction between 2-arylpyridines and cyclopropenones

Selected examples with yield

91%   88%   74%

72%   85%   79%

79%   93%
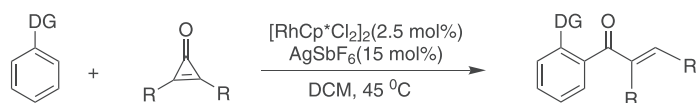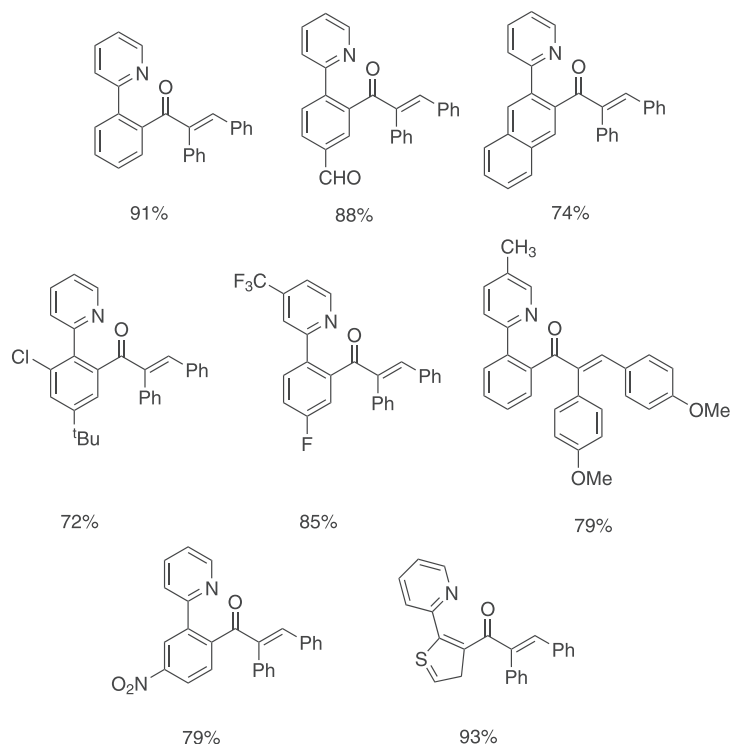
SCHEME 17 Scope of other arene substrates on C − H functionalization reaction

Selected examples with yield

R= H (82%), CH₃ (85%), COCH₃(78%)   R= H (71%), OCH₃ (77%), Cl (47%)   72%   89%
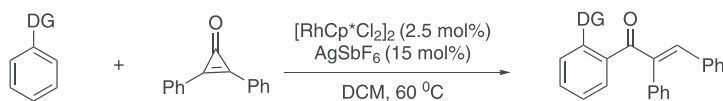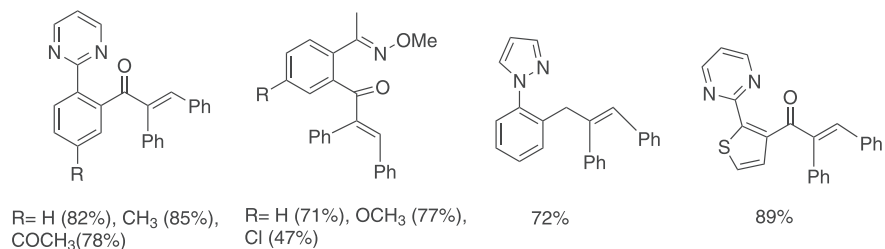
In the same year, Yus *et al.* described a new methodology for the copper-catalysed multicomponent synthesis of indolizines from 2-pyridinecarbaldehyde derivatives, secondary amines, and terminal alkynes using CuNPs/C as catalyst in dichloromethane solvent at 70 °C (Scheme 21).[47] Interestingly, the same starting materials and catalyst used for this purpose produced the heterocyclic chalcones in moderate yields with exclusive *E* stereochemistry in the absence of solvent.

In 2015, Gonzalez-Soria and co-workers synthesized indolizines using copper nanoparticles on activated carbon (CuNPs/C) in dichloromethane from pyridine-2-carbaldehyde derivatives, secondary amines, and terminal alkynes at 70 °C (Scheme 22).[48] In the absence of solvent such as dichloromethane, the same procedure was used to synthesise heterocyclic chalcones, where piperidine was used as the secondary amine. Nonheterocyclic chalcones were also produced by this method, where electron withdrawing substituent underwent rapid conversion than the substrates having an electron donating group. Moderate to good yields of product were obtained and the catalyst was
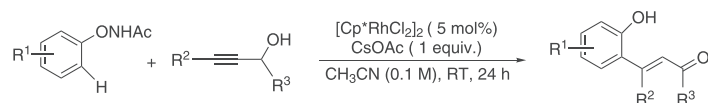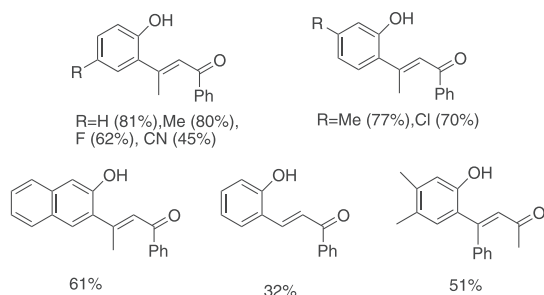
SCHEME 18 C–H Alkenylation reaction for the synthesis of chalcone derivatives using Rh (III)-catalysed system
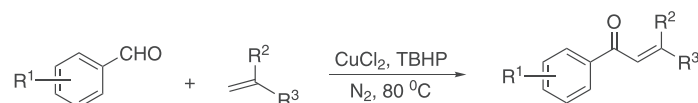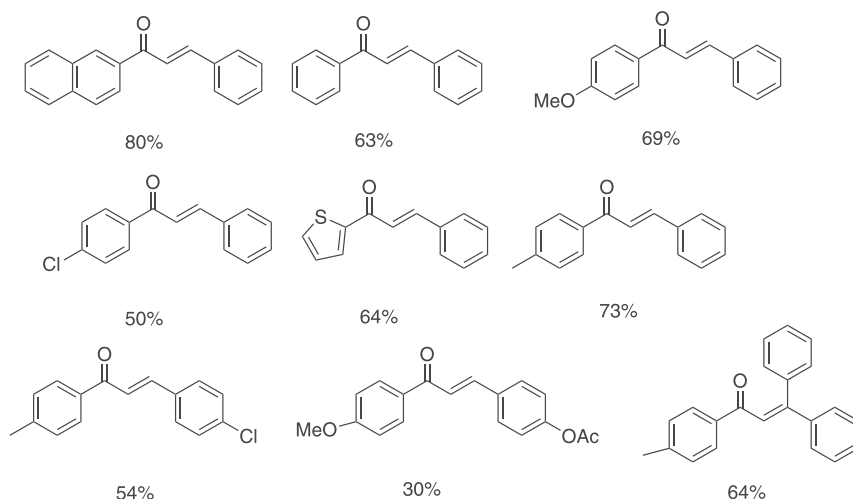
SCHEME 19 Synthesis of chalcones from various aldehydes and alkenes

recycled and reused over four cycles (yield decreased from 85% to 64%).

Further studies have been done for developing truly recyclable heterogeneous catalysts under green reaction conditions. In 2015, Rawat *et al.* reported an easy one-pot synthesis of aminoindolizines and chalcones with CuI/CSP nanocomposites (Scheme 23).[49] CuI/CSP nanocomposites were synthesised by refluxing the mixture of carbon spheres (CSP) and CuI in ethanol, then the CuI was stabilized on polysaccharide surface of CSP at conventional reflux condition. The CuI/CSP nanocomposites were characterized by using various techniques such as PXRD, FT-IR, SEM, TEM, TGA, XPS, ICP-AES etc. SEM image shows the presence of spheres, distorted spheres, and cubes of various size from 2 to 8 μm and shows the presence of CuI nanoparticles on the surface and in between the carbon spheres. The internal morphology studies give the

idea that the assembling of porous rods in the spherical shape and its length varies from 100 to 320 nm. The porous and crystalline nature of carbon and CuI NPs were confirmed from TEM and SAED respectively.

One-pot synthesis of aminoindolizines and chalcones from pyridine-2-carboxaldehydes, secondary amines, and terminal alkynes at 60 °C using CuI/CSP nanocomposites was also achieved. Depending on the secondary amines and solvents, the product selectivity could be controlled. For the synthesis of aminoindolizines, ethylene glycol was used as the best recyclable solvent. In contrast, chalcones were resulted under solvent free condition, by using the secondary amines such as piperidine, pyrrolidine and piperazine, 3-Methylpiperidine with good to excellent yield (75–93%). This method follows green and sustainability principles with smaller E-factor such as 0.06 and high atom economy (94%). The CuI/CSP nanocomposites catalyst
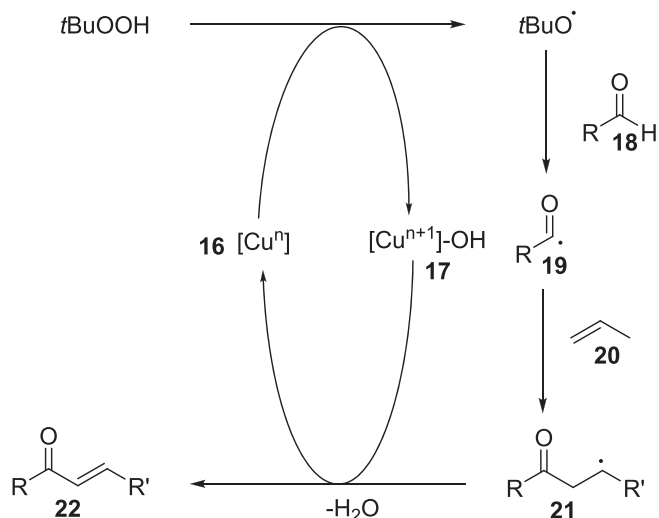
SCHEME 20 Proposed mechanismReprinted with permission from Ref. No 46

showed good performance parameters, such as high efficiency, mild and green reaction condition, selectivity, and good recyclability (four times), which makes this catalyst suitable for future industrial applications.

In 2017, Rani and co-workers reported copper nanoparticle supported Cu-BTC-MOF as catalyst for the synthesis of indolizines and chalcones (Scheme 24).[50] Different amount of copper nanoparticles were loaded on Cu-BTC-MOF, and Cu(10%)/Cu-BTC-MOF showed the highest activity for the synthesis of chalcones. The XRD pattern showed that Copper nanoparticles were decorated on the surface of Cu(10%)/Cu-BTC-MOF. N_2-Adsorption–desorption measurements revealed the texture property of catalyst showing that loading of copper nanoparticles penetrates into the inter-particle mesopores and it reduces surface area. Surface morphology of catalyst was studied by SEM and TEM. To study various oxidation state of copper species present in Cu(10%)/Cu-BTC-

SCHEME 21 Synthesis of heterocyclic chalcones catalysed by CuNPs/C
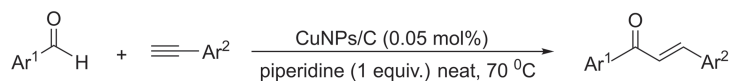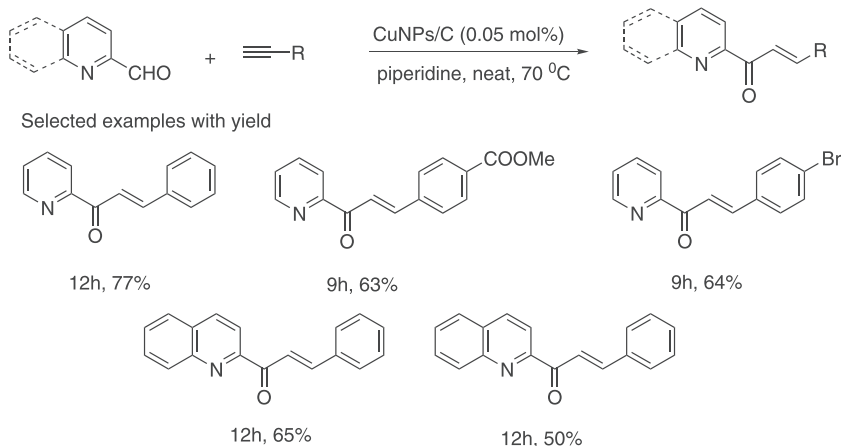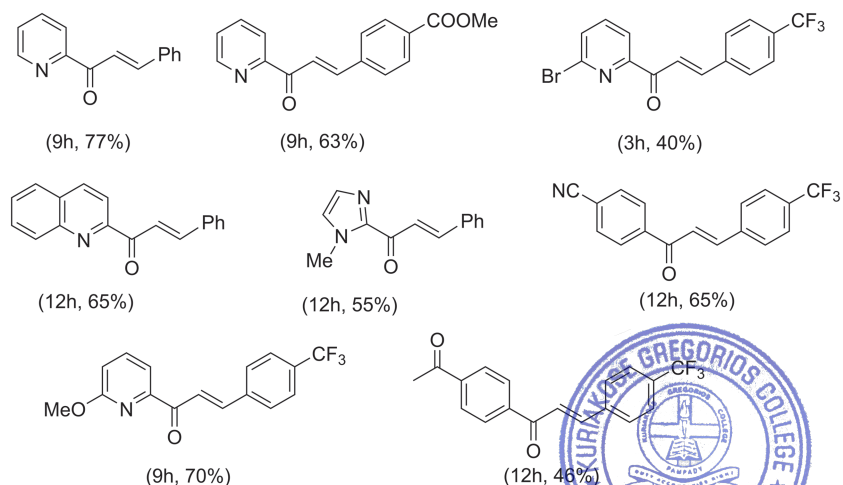
SCHEME 22 Synthesis of chalcones from aldehydes and alkynes catalysed by CuNPs/C
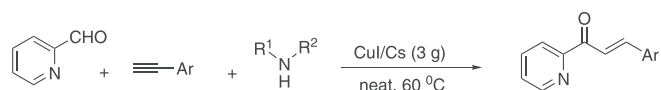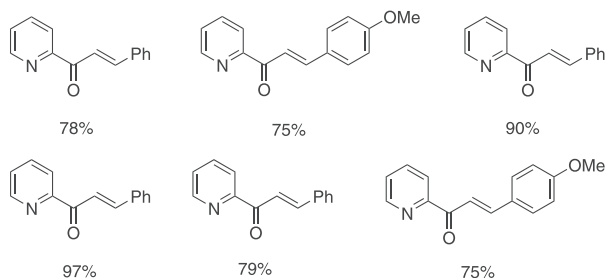
SCHEME 23 CuI/CSP catalysed synthesis of chalcones under solvent free condition

MOF, CV and XPS techniques were carried out. 2-Pyridinecarboxaldehyde reacts with 2^0 amine and phenyl acetylene using the catalyst Cu(10%)/Cu-BTC-MOF (40 mg) for 9 hours at 70 °C resulted a wide range of chalcones with good yield, in the absence of solvent. Piperidine, pyrrolindine, diethylamine, dipropylamine can be used effectively as secondary amine. Catalyst can be recycled even after fifth cycle, without significant change in activity and selectivity.

2.6 | Synthesis of chalcones via cerium catalysed cross-coupling reaction

In 2016, Wang *et al.* demonstrated an efficient method for the synthesis of α,β-unsaturated ketones in the
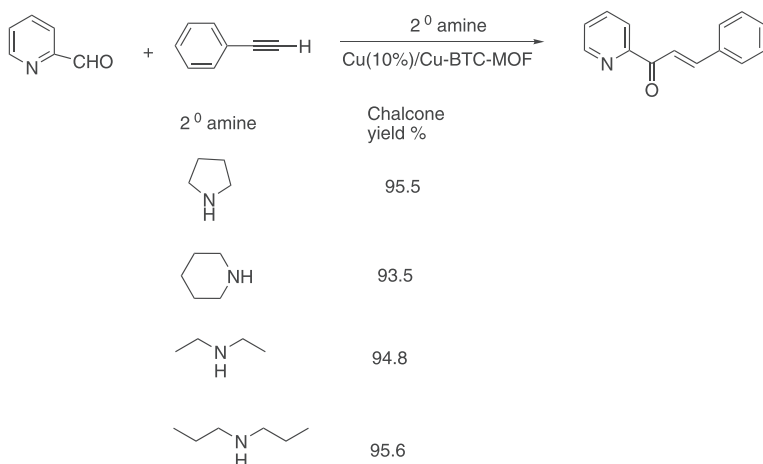
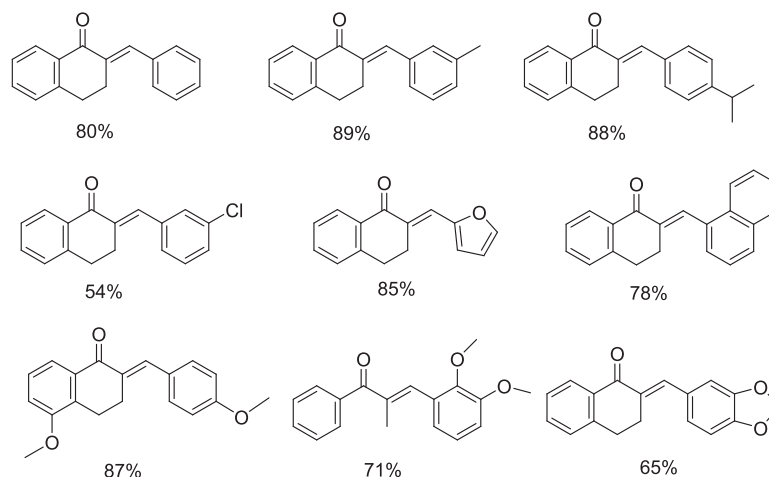**SCHEME 24** Selective synthesis of chalcone in neat condition using Cu catalysts
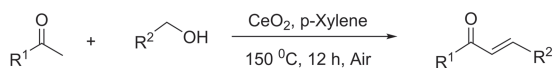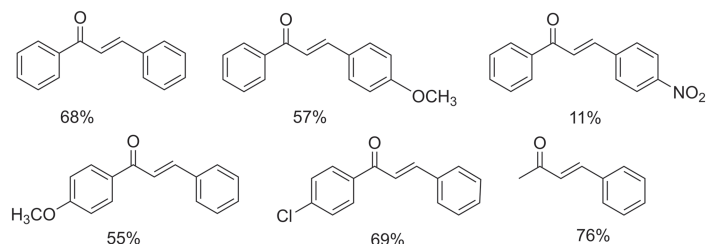
SCHEME 25 Synthesis of chalcones catalysed by CeO_2 by C-C coupling of ketones with primary alcohols
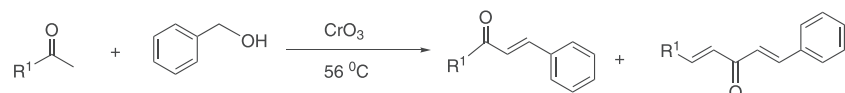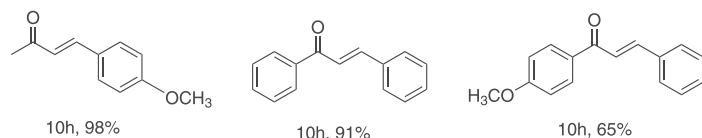
SCHEME 26 Synthesis of chalcones catalysed by CrO_3 by C-C coupling of ketones with aromatic alcohols

SCHEME 27 Manganese catalysed reaction between ketones and primary alcohols

$$R^1 \overset{O}{\underset{R^2}{\bigcirc}} + R^3 \diagup OH \xrightarrow[\text{tert-amyl alcohol, 135 }^0C, 20\text{ h}]{\substack{\text{Mn catalyst (0.3 mol\%)} \\ Cs_2CO_3 \text{ (5 mol\%)}}} R^1 \overset{O}{\underset{R^2}{\bigcirc}} R^3 + H_2O + H_2$$

Selected examples with yield

80%   89%   88%

54%   85%   78%

87%   71%   65%
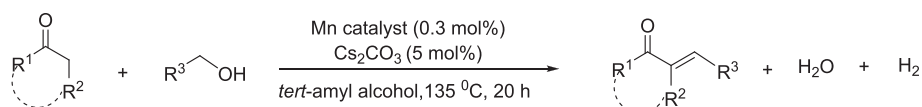
absence of alkaline additives, by carbon–carbon coupling of primary alcohols and ketones using CeO₂ catalyst (Scheme 25).[51] These reactions were carried out for 12 hours in the presence of *p*-xylene as solvent in air at 150 °C. Various substituted primary alcohols and ketones resulted moderate to good yields of the product. The calcinated catalyst CeO₂ was reused and this calcination was done to remove the surface-adsorbed substances. The catalytic performance is related to CeO₂ crystal plane in the order of (110) > (111) > (100).

2.7 | Synthesis of chalcones via chromium-catalysed cross-coupling reaction

Li and Chen put forward an effective and simple method with CrO₃ as catalyst for preparing α,β-unsaturated carbonyl compounds such as benzalacetones and chalcones using aromatic alcohols and ketones at 56 °C for 10 hours (Scheme 26).[52] Aromatic alcohols and ketones with various substitutions gave good yield of the product. Electron-donating or electron-withdrawing substituents have no significant effect on the product yields. But aliphatic primary alcohols did not give the product with ketones. The possible mechanism was also suggested.

2.8 | Synthesis of chalcones via manganese-catalysed cross-coupling reaction

In 2019 Gunanathan and co-workers developed sustainable and economical catalytic method using Kempe's manganese

PNP pincer complexes for selectively producing α-alkenyl ketones by dehydrogenative coupling of ketones with primary alcohol (Scheme 27).[53] Lower yield of catalyst

[P] = P^{i}Pr₂
R³ = aryl, alkyl
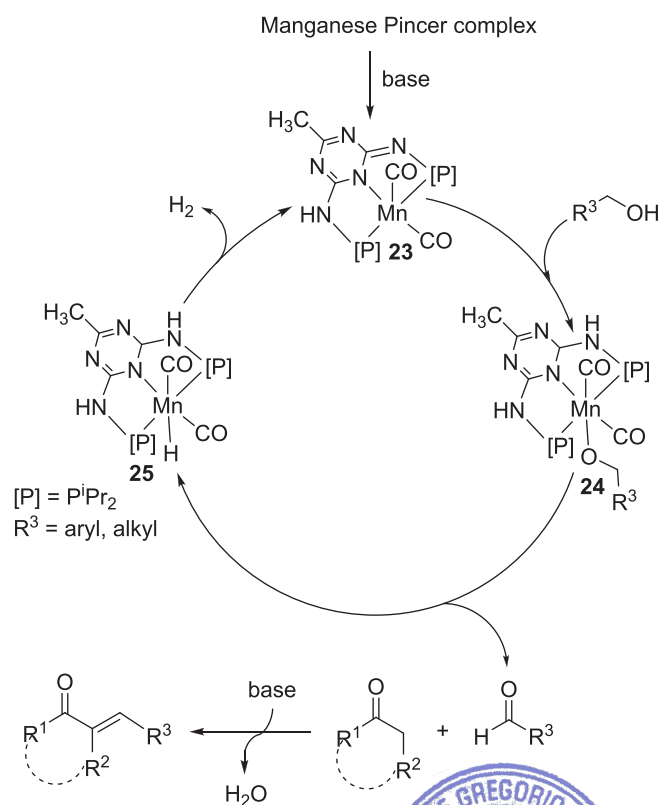
SCHEME 28 Proposed reaction mechanism for dehydrogenative α-alkenylation of ketones catalysed by manganese pincer complexReprinted with permission from Ref. No 53

(0.3 mol%) and a mild base caesium carbonate (5 mol%) provided moderate to good yields of α-alkenyl ketones from various cyclic and acyclic benzylic ketones with primary alcohols. Water and molecular hydrogen were formed as by-products is another advantage of this method. Primary alcohols bearing electron donating substituents quickly offered good yield of product than that of electron-withdrawing substituents.

A plausible mechanism was suggested (Scheme 28). Initially, manganese pincer complex reacts with base Cs_2CO_3 providing an intermediate **23**. Subsequently, this intermediate reacts with alcohol resulting alkoxy-ligated manganese complex **24**. This complex **24** further undergoes β-hydride elimination giving aldehyde and Mn-hydride complex **25**. Afterward, aldehyde undergoes aldol condensation with ketone to give α-alkenyl ketones as product and water as by-product. Finally, the intermediate **25** liberates hydrogen and completes the catalytic cycle.

2.9 | Synthesis of chalcones via titanium catalysed cross-coupling reaction

Goettmann *et al.* studied different class of early-transition-metal carbide and nitride nanoparticles and its application in alkylation of ketones with alcohols.[54] In this work, they mentioned the reaction between acetophenone with benzyl and 4-methylbenzyl alcohol to the action of TiN nanoparticles at 150 °C for 24 hr in xylene resulted 1, 3-diphenyl-1-propanone (Scheme 29). The urea-synthesised TiN used here appeared to be much more active than the C_3N_4 TiN.
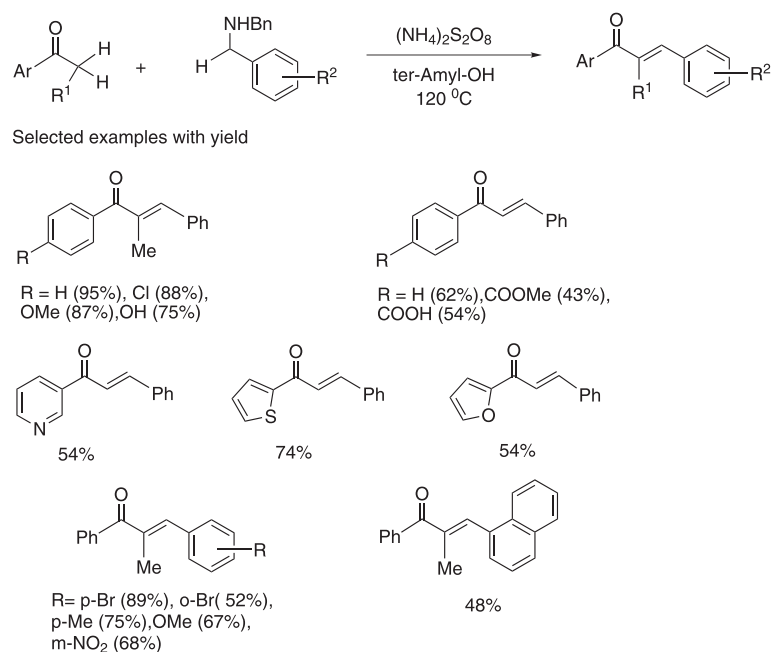
2.10 | Synthesis of chalcones via magnesium catalysed cross-coupling reaction

In 2018, Yatabe *et al.* successfully developed a $Mg_3Al–CO_3$ layered double hydroxide (LDH) catalysed formal hydroacylation of terminal alkynes for the synthesis of α,β-unsaturated ketones (Scheme 30).[55] Aromatic terminal alkynes and aromatic aldehyde undergo formal hydroacylation reaction in the presence of heterogeneous catalyst $Mg_3Al–CO_3$ LDH using Argon balloon (1 atm.) at 120 °C for 15 hr in toluene. Akynes and aldehydes with various substitutions effectively gave moderate to good yield of products. This environmentally friendly reaction was repeated with the same catalyst three times without loss in its catalytic property).

SCHEME 29 Synthesis of chalcones catalysed by TiN
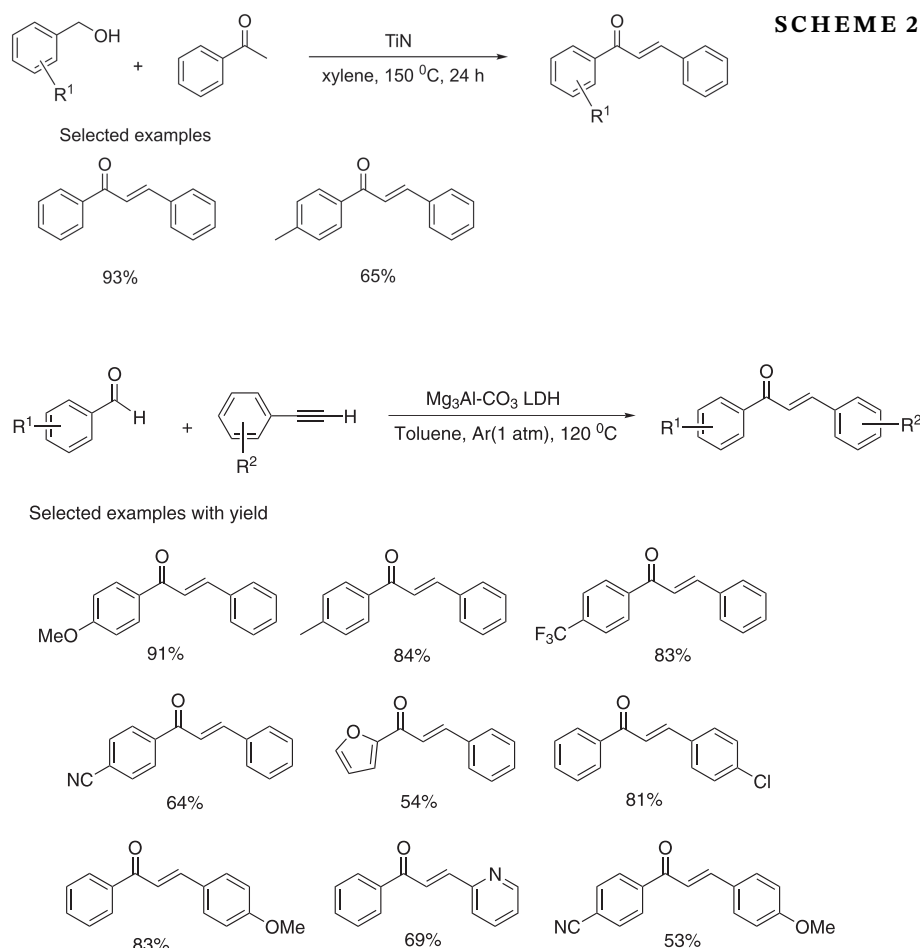
SCHEME 30 Transition metal-free formal hydroacylation of terminal alkynes
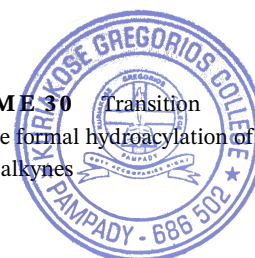
SCHEME 31 Synthesis of chalcone derivatives by metal-free tandem CDC-elimination reaction

Selected examples with yield

R = H (95%), Cl (88%), OMe (87%),OH (75%)

R = H (62%),COOMe (43%), COOH (54%)

54%

74%

54%

R= p-Br (89%), o-Br(52%), p-Me (75%),OMe (67%), m-NO₂ (68%)

48%

2.11 | Synthesis of chalcones via metal-free cross-coupling reaction

Zeng *et al.* developed a simple protocol to prepare chalcone derivatives using inexpensive ammonium persulfate salt via cross-dehydrogenative-coupling (CDC)/elimination reaction (Scheme 31).[56] The CDC transformation takes place between ketones and benzylamine in the presence of ammonium persulfate in *tert*-Amyl-OH at 120 °C for 24 hr resulting chalcones with high stereo selectivity. The presence of electron rich and poor substituents in the ketones gave good yield of chalcones. Heterocyclic motif on ketones also resulted moderate yield of chemoselective product.

3 | CONCLUSION

Chalcone derivatives are widely found in natural products and are extensively applied as therapeutic agents. In this review, we presented a comprehensive coverage of the main synthetic methods of formation of chalcone via cross-coupling reaction for the last 11 years. The other existing methods for the synthesis of chalcone have been caught up by some limitations such as harsh reaction condition, lengthy reaction time and poor selectivity. It is evident from the forgoing discussion that cross coupling reaction involving palladium, silver, iron, gold, rhodium, copper, cerium, chromium, manganese, and magnesium catalysts are the most common methods involved; however, metal-free reactions also attracted attention. The recent advances discussed in the synthesis of chalcones illustrate the potential of this chemistry and, the most complex chalcones can be synthesized with good efficiency in minimum reaction time. Another significant feature is that in most of the methods discussed, the catalyst was effectively reused. This information regarding the existing methods, provide data for the development of more practical and environmentally-benign approaches in future for the synthesis of chalcone and its derivatives with better yield, less reaction time and minimum cogeneration of by-products. We conclude this review by presuming that it will stimulate researchers to further explore and expand this interesting field of research. We anticipate that the years ahead will be a noteworthy period for the development of chalcone-based pharmacologically significant medicinal agents for the treatment of various diseases.

AUTHOR CONTRIBUTIONS
Thomas Mathew: Conceptualization; project administration. **Gopinathan Anilkumar:** Conceptualization.
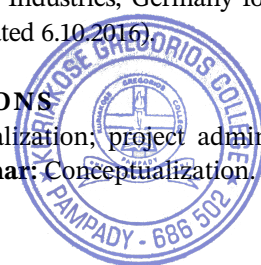
CONFLICT OF INTEREST

There are no conflicts to declare.

DATA AVAILABILITY STATEMENT

Data sharing not applicable – no new data generated.

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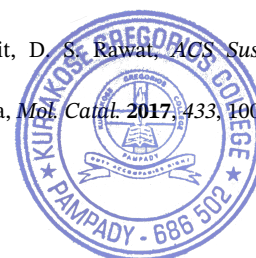
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ECONOMIC CHALLENGER

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Contents

THE ECONOMY IN LIMELIGHT

SPECIAL ARTICLES

MERGERS AND ACQUISITIONS IN BANKING SECTOR WITH SPECIAL REFERENCE TO STATE BANK OF INDIA

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ABSTRACT

The roots of the State Bank of India lay in the first decade of the 19th century when the Bank of Bengal was established on June 2, 1806. The Bank of Bengal was one of the three Presidency banks, the other two being the Bank of Bombay (1840) and the Bank of Madras (1843). These three Presidency banks amalgamated on January 27, 1921, and the reorganized banks' entity took as its name Imperial Bank of India. In 1955, the Imperial Bank of India was nationalized. It was given the name "State Bank of India" to act as the principal agent of RBI and handle banking transactions worldwide. State Bank of India (SBI) is a government-owned corporation with its headquarters in Mumbai, Maharashtra. First Nationalization was on July 19 1969. The Reserve Bank of India describes this bank nationalization as the single most important economic policy decision taken by any Government after 1947.

State Bank of Travancore was established in 1945 as the Travancore Bank Ltd. It was the people's bank, and it was sown, watered, and nourished by the rulers from time to time. It was the last major institution that the last ruling Maharaja of Travancore, his Highness Chithira Thirunal Balarama had founded. In 1960, it became a subsidiary of State Bank of India under the SBI Subsidiary Banks Act 1959 enacted by the Parliament of India. It thus achieved the name "State Bank of Travancore." State Bank of Travancore (SBT) was a major Indian Bank headquartered in Thiruvananthapuram, Kerala, and was a principal associate of State Bank of India. It was the premier bank of Kerala. Overall, as of March 31, 2015, it had 1157 branches and 1602 ATMs covering 18 states and three union territories.

OBJECTIVES OF THE STUDY

The major goals of the study are;

1. To study the changing pattern of operation in the Commercial Banking Sector

2. To find out the socio-economic effects due to banking polarization.

3. To find out the extent of reduction in Non-Performing Assets resulting in more income and consumption.

4. To find out the extent of erosion or enrichment of banker customer
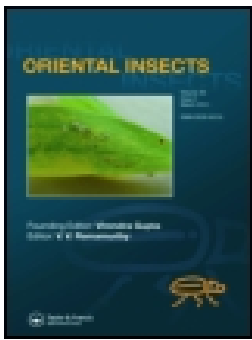
A new species and a new record of *Dicuspiditermes* Krishna (Blattodea: Isoptera: Termitidae) from the Kerala part of Western Ghats, India

Poovoli Amina , Keloth Rajmohana & Shilimol C. Aliyas

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A new species and a new record of *Dicuspiditermes* Krishna (Blattodea: Isoptera: Termitidae) from the Kerala part of Western Ghats, India

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ABSTRACT

A new species, *Dicuspiditermes leghugathrae* Amina and Rajmohana **sp.nov**. (Termitidae) is described and illustrated based on the morphological characters of soldiers and workers. *Dicuspiditermes hutsoni* (Kemner), a termite species hitherto endemic to Sri Lanka, is reported for the first time from India. Both the species are recorded from the Kerala part of Western Ghats. An identification key to the species of *Dicuspiditermes* found in India (based on soldier caste), along with a species distribution map is also provided.

http://www.zoobank.org/urn:lsid:zoobank.org:act:44AB093B-6A02-4A35-BC1B-3277259A3104

Introduction

The genus *Dicuspiditermes* Krishna belongs to the *Pericapritermes*-group and was first erected by Krishna (1965). *Dicuspiditermes* is limited to the Oriental Region, and has 20 species of which 9 are from India. Out of these, seven species, *Dicuspiditermes achankovili* Verma, 1985, *Dicuspiditermes boseae* Chhotani, 1997, *Dicuspiditermes cornutella* (Silvestri, 1922), *Dicuspiditermes fontanellus* Thakur and Chatterjee, 1971, *Dicuspiditermes gravelyi* (Silvestri 1922), *Dicuspiditermes obtusus* (Silvestri, 1923) and *Dicuspiditermes sisiri* Chhotani, 1997 are endemic to India (Krishna et al. 2013).

As a part of our taxonomic investigations on termites of Kerala part of the Western Ghats, we hereby describe and illustrate a new species, Dicuspiditermes leghugathrae Amina and Rajmohana **sp. nov.**, and also report for the first time from India, *Dicuspiditermes hutsoni* (Kemner, 1926), hitherto known only from Sri Lanka. Both the species have their distribution limited to the Western Ghats. An identification key to the species of *Dicuspiditermes*

found in India (based on soldier caste), along with a species distribution map is also provided (Fig. 4).

Materials and methods

All the specimens were collected from the part of colony in the soil underneath boulders, during the field surveys undertaken in the Kerala part of Western Ghats during 2013–2016. The specimens were preserved in 80% Himedia alcohol. Dissections and measurements were also made in 80% alcohol under a stereo zoom microscope, Leica EZ4HD, at magnifications between 8 and 35 ×. Mandibles of worker castes of the proposed new species were slide mounted in Canada balsam and then examined for diagnostic characters. Images were taken using a Leica 205-A stereomicroscope fitted with DFC 500 camera, and processed with the help of extended focus software, LAS version 3.6.

Morphological characters follow Chhotani (1997), while studies on the worker mandibles are after Fontes (1987), Gathorne-Hardy (2001) and Eggleton (2011). Species occurrence maps were generated by using Q GIS software version 3.10.8.

All specimens including the holotype and the paratypes are deposited in the National Zoological Collections of the Zoological Survey of India (ZSI), at Calicut (Kozhikode), Kerala, India.

Taxonomy

Genus *Dicuspiditermes* Krishna, 1968

1968. *Dicuspiditermes* Krishna in: Krishna, *Bull. Am. Mus. nat. Hist.*, 138 (Art.5): 265, 267, 268, 269, 270, 271, 286–290, 291, 292, 320.Type: *Capritermes obtusus* Silvestri.

Diagnosis

Imago: Head subcircular, fontanelle long, narrow, antennae 14–15 segmented; mandible each with an apical and two marginal teeth; first+ second marginal with long and sinuate posterior margin, shorter than apical; third marginal prominent, separated from first by a deep cut; molar prominence not extending up to level of first marginal. Right mandible: First marginal triangular with slightly longer posterior margin; second marginal prominent with incurved posterior margin.

Soldier: Head subrectangular, anterolateral corners extending into tubercle-like projections; fontanelle generally transverse; antennae 14 segmented. Labrum asymmetrical with anterior margin deeply incurved; anterolateral corners produced into needle-like, long processes; lateral margins with or without serrations anteriorly. Mandibles asymmetrical; left mandible
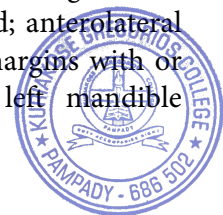
strongly twisted at middle and with or without a beak at tip; right mandible blade-like. Pronotum saddle-shaped.

Worker: Head subcircular. Fontanelle plate translucent, round or oval. Antennae with 14 segments. Pronotum strongly saddle-shaped.

Bioecology. Soil dwellers. Commonly seen in soil, under stone, barks, logs and mounds of other termites, etc. (Krishna et al. 2013). Nesting pattern of *Dicuspiditermes* is remarkably species-specific and it ranges from subterranean line galleries in soil to elaborate structures in trees or on tree trunks that show ventilation pores or slits through the outer surface (Krishna 2001).

Key to the species of *Dicuspiditermes* Krishna found in India (based on soldier caste, modified from Chhotani 1997)

1. Head without frontal protuberance; frons weakly and gradually inclining in front at an angle of about 45°-60°. Fontanelle gland small **2**
-. Head with frontal protuberance; frons sharply inclining in front at an angle of about 75°. Fontanelle gland large .... ***D. laetus*** (Silvestri)

2. Head small (head length with mandibles 3.30–3.68 mm; length to the base of mandibles 1.68–1.84 mm; maximum head width 1.10–1.14 mm) **3**
-. Head generally large (head length with mandibles 3.60–5.60 mm; length to the base of mandibles 1.70–2.33 mm; maximum head width 1.15–1.15 mm) **4**

3. Labrum with a few serrations on anterolateral margins (Fig. 2D) ....
.... ***D. cornutella*** (Silvetri)
-. Labrum without any serration (Fig. 1D) on anterolateral margins ....
.... ***D. leghugathrae*** Amina and Rajmohana **sp. nov.**

4. Anterolateral tubercle of head short and blunt (Fig. 3A) ....
.... ***D. obtusus*** (Silvestri)
-. Anterolateral tubercle of head long and pointed (Fig. 3B) **5**

5. Head small (head length with mandible 3.6–4.0 mm; length to the base of mandibles 1.85–2.47 mm; maximum head width 1.15–2.33 mm). Head sharply inclined in front at about 50°-60° angle; anterolateral processes of head somewhat small. Postmentum short (0.75–0.99 mm) ....
.... ***D. gravelyi*** (Silvestri)
-. Head large (head length with mandible 3.9–5.6 mm; length to the base of mandibles 2.08–2.55 mm; maximum head width 1.33–1.55 mm). Head weakly inclined in front at 45° angle; anterolateral processes of head somewhat short to long. Postmentum comparatively long (1.0–1.24 mm) **6**

6. Left mandible tip with a beak (Fig. 3C); right mandible apex long and thin and apical blade strongly incurved **7**
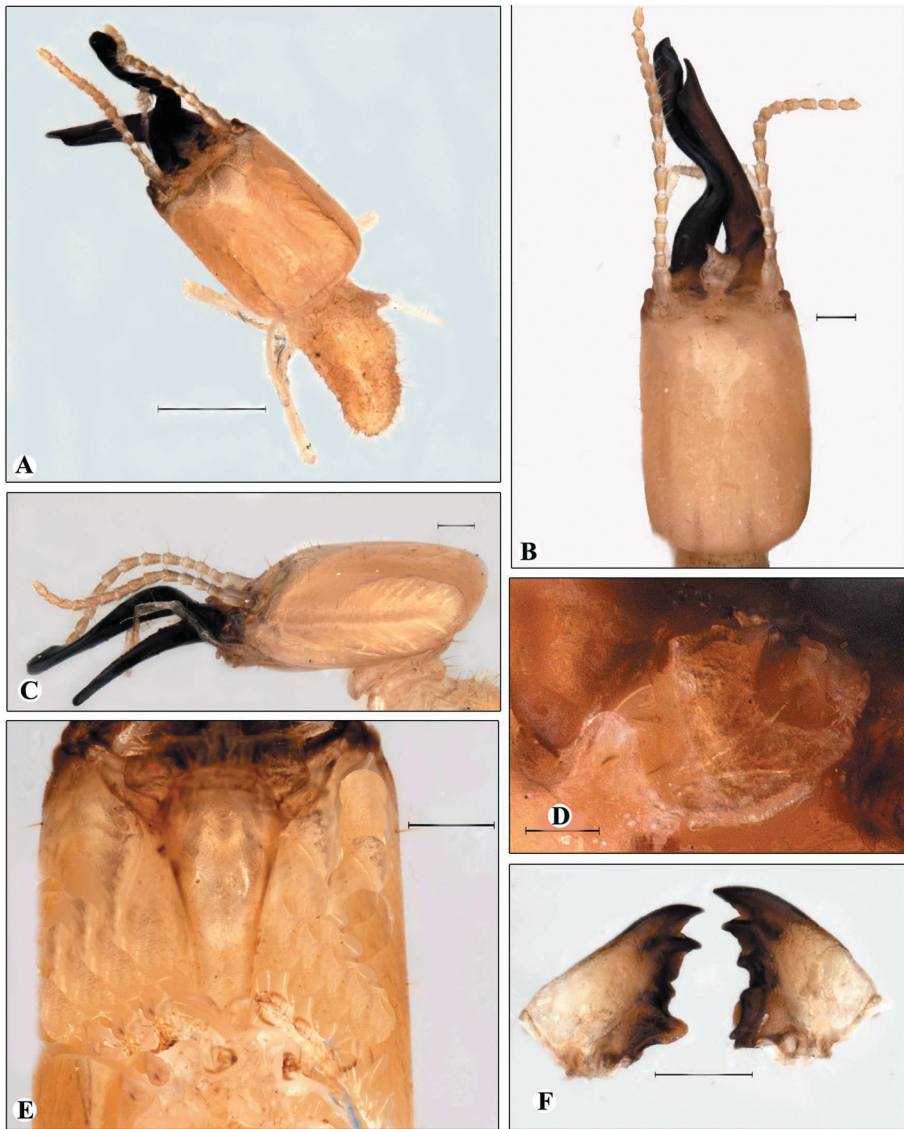
Figure 1A–F. *Dicuspiditermes leghugathrae* **sp. nov**. A, body dorsal view; B, head dorsal view; C, head profile view; D, labrum; E, Postmentum; F, worker left and right mandible (Scale bar A = 1 mm; B, C, E, F = 0.3 mm; D = 0.1 mm).

-. Left mandible tip without beak (Fig. 2B), with or without a point at tip; right mandible apex short and somewhat thick and apical blade weakly incurved **8**

7. Head small and narrow (head length to base of mandible 2.08–2.13 mm; maximum head width1.15–1.20 mm, index width/length 0.57–0.58). Left mandible more twisted and shorter in comparison to head length (left
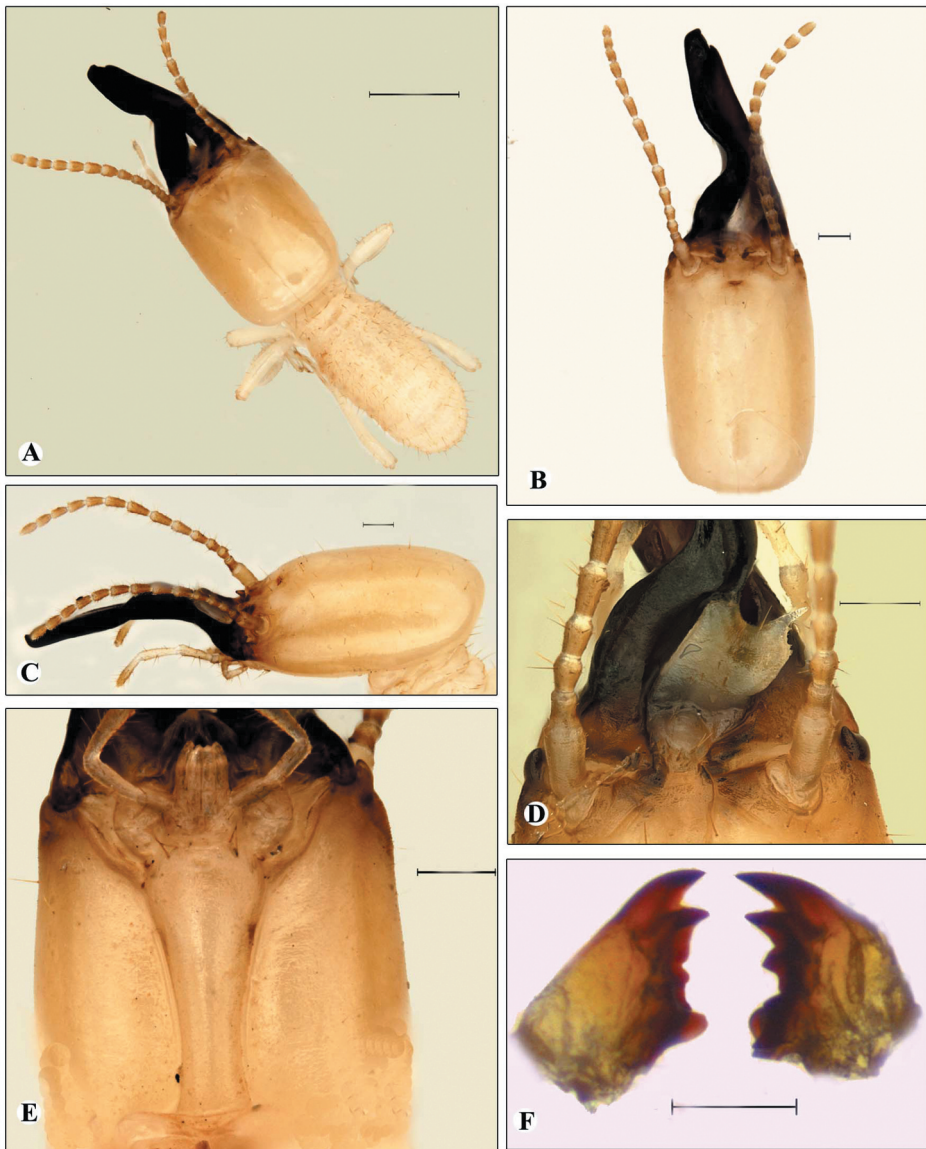
Figure 2A–F. *Dicuspiditermes hutsoni* A, body dorsal view; B, head dorsal view; C, head profile view; D, labrum; E, postmentum; F, worker left and right mandible (Scale bar A = 1 mm; B, C, D, E, F = 0.3 mm).

mandible length 1.67–1.50 mm, index left mandible length/head length 0.81) .... ***D. boseae*** Chhotani

-. Head large and wide (head length to base of mandible 2.08–2.45 mm; maximum head width 1.33–1.45 mm, index width/length 0.57–0.65). Left mandible less twisted and longer in comparison to head length (left mandible length 1.80–2.20 mm, index left mandible length/head length 0.80–0.95) .... ***D. incola*** (Wasmann)
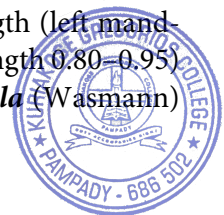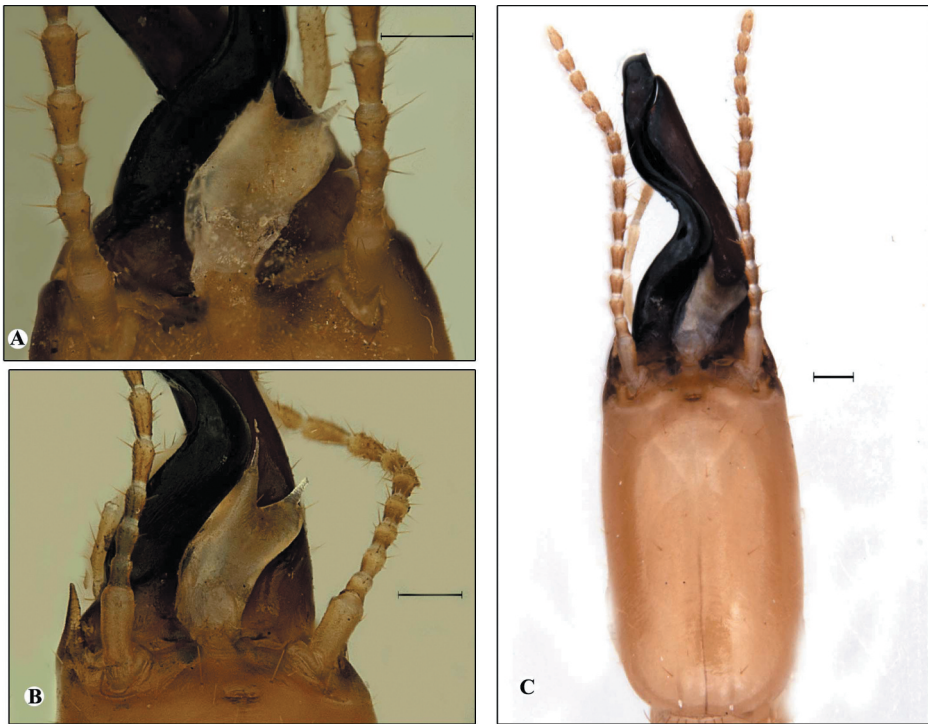
Figure 3A–C. A, anterolateral tubercle of *Dicuspiditermes obtusus*; B, anterolateral tubercle of *Dicuspiditermes sisiri*; C, dorsal view of head capsule of *Dicuspiditermes incola* (Scale bar A, B, C = 0.3 mm).

8. Generally small: head length with mandible (3.70–4.05 mm); head length to lateral base of mandible (1.94–2.05 mm); maximum head width 1.16–1.26 mm .... **D. hutsoni** (Kemner)
-. Generally large: head length with mandible (4.00–5.60 mm); head length to lateral base of mandible (2.22–2.55 mm); maximum head width 1.38–1.55 mm **9**

9. Small: head small (length with mandibles 4.00–4.44 mm, length to lateral base of mandibles 2.22–2.43 mm); left mandibles comparatively short (length 1.84–2.00 mm) and strongly twisted .... **D. achankovili** Verma
-. Large: head large (length with mandibles 4.40–5.60 mm; length to lateral base of mandibles 2.40–2.55 mm); left mandibles comparatively long (length 2.00–2.13) and less so twisted .... **D. sisiri** Chhotani

Dicuspiditermes leghugathrae Amina and Rajmohana **sp. nov**. (Fig. 1A–F)

Type material
INDIA: Kerala: Palakkad (Chulliyar Dam site, 10.5906 N, 76.7690E), 19. ix. 2013, Amina Poovoli. Colony code: Vial No. PA 62 (ZSI/WGRC/IR/INV/
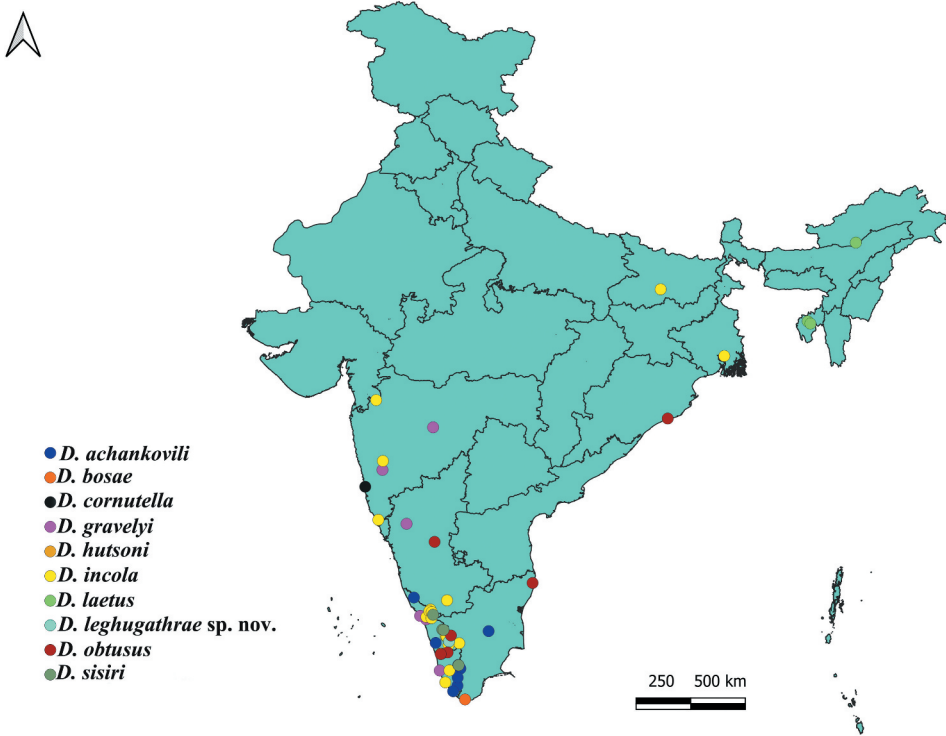
Figure 4. Distribution map of *Dicuspiditermes* spp. in India.

6333). Holotype (soldier in alcohol, in a separate vial); Paratype-6 soldiers and 8 workers. This species is known only from the type locality.

Diagnosis

Of the 20 known species of *Dicuspiditermes* from the Oriental Region, *D. leghugathrae* **sp. nov**. shows affinity to *D. obtusus* and keys to couplet number 3 of the key to Indian species by Chhotani (1997). It resembles *D. obtusus* in having a short and blunt anterolateral tubercle on head, but differs in the following characters. *Dicuspiditermes leghugathrae* is comparatively a smaller species (4.14–4.40 mm), head capsule small (head length with mandibles 3.30–3.66 mm; head length without mandibles 1.68–1.83 mm) and narrow (head width 1.10–1.14 mm), but *D. obtusus* is generally a large species (4.5–7.00 mm), head capsule large (head length with mandibles 3.8–4.40 mm; head length without mandibles 1.70–2.33 mm) and broad (1.15–1.40 mm). Anterior margin of labrum in the proposed new species is deeply incurved (Fig. 1D) and without any anterolateral serrations, but in *D. obtusus* these serrations are present.

Description

Imago: Unknown

Soldier (Fig. 1A–E, Table 1): Head capsule pale yellow to pale brownish yellow; antennae pale brown; labrum translucent; left mandible black; right mandible reddish brown; legs and body creamish to pale yellow. Head sparsely and body densely hairy. In dorsal view head capsule subrectangular; slightly converging at anterior end; anterolateral processes short and blunt. Frons gradually sloping in front; median suture of head long, extending up to middle; fontanelle transverse, situated anteriorly at distal one-fifth of head; fontanelle gland small. Antennae with 14 segments; segment 2, 3 and 4 subequal; 5–9 gradually increasing in length and remaining segments subequal. Labrum asymmetrical, anterior margin deeply incurved with long needle-like anterior points, lateral margin without any serrations, length a little longer than width. Mandibles asymmetrical, a little shorter than head capsule; left mandible twisted at middle and with a weak beak at tip. Right mandible blade-like, with long, sharply pointed tip, apical part incurved. Postmentum club-shaped; length less than half of head length; with a narrow waist lying posteriorly. Pronotum saddle-shaped, anterior margin without notch; posterior margin indistinctly emarginate. Legs with 3:2:2 apical tibial spurs. Abdomen short; cerci short; 2 segmented.

Worker: Head capsule and antennae creamish yellow; thorax and legs cream coloured; abdomen transparent, intestinal content showing through. Head moderately and body densely hairy. Total body length 4.20–4.40 mm. Head capsule subcircular, broader than long (head length to tip of labrum 1.14–1.18 mm, length to base of mandibles 0.73–0.80 mm, maximum head width 0.90–0.95 mm). Fontanelle plate round, translucent to white (diameter 0.1–0.12 mm). Antennae with 14 segments; segment 2 broader and longer than 3 and 4; segment 3 and 4 subequal. Postclypeus swollen; length about less than half of width (length 0.25–0.27 mm, width 0.50–55 mm). Labrum dome-shaped. Mandibles (Fig. 1F) with apical and two marginals. Left mandible: First+ second marginal with long and sinuate posterior margin, shorter than apical; third marginal prominent, separated from first by a deep cut; molar prominence not extending up to the level of first marginal. Right mandible: First marginal triangular with slightly longer posterior margin; second marginal prominent with incurved posterior margin; molar plate without ridges, cockroach notch present. Pronotum strongly saddle-shaped; anterior margin without notch (length 0.27 mm-0.30 mm, width 0.53–0.56 mm); legs with 3:2:2 apical tibial spurs; foreleg somewhat swollen; tarsi 4-segmented.

Etymology: The species is named after its small body size. In Sanskrit 'leghugathrae' (leghu = small, gathra = body) meaning small body.
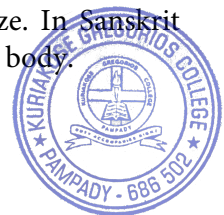
Table 1. Measurements of *Dicuspiditermes leghugathrae* Amina and Rajmohana sp. nov.-Soldier (n = 7).

Body parts	Measurements		
	Range	Mean	Holotype
Head length with mandibles	3.30–3.66	3.44	3.33
Head length to base of mandibles	1.68–1.83	1.76	1.68
Maximum head width	1.10–1.14	1.12	1.11
Maximum head height	0.74–0.79	0.77	0.77
Occipito- fontanelle distance	1.44–1.50	1.47	1.44
Head index (maximum head width/head length to base of mandible	0.62–0.67	0.64	0.67
Fontanelle head index (fontanelle distance/head length to base of mandibles	0.82–0.87	0.85	0.857
Length of labrum	0.26–0.31	0.275	0.27
Width of labrum	0.24–0.26	0.25	0.26
Left mandible length	1.6–1.72	1.65	1.63
Right mandible length	1.5–1.6	1.56	1.53
Mandible head length index (left mandible length/head length to base of mandibles)	0.91–0.97	0.93	0.97
Length of Postmentum	0.7–0.83	0.75	0.71
Maximum width of Postmentum	0.30–0.35	0.33	0.32
Width of postmentum at waist	0.16–0.19	0.17	0.18
Postmentum-head length index (postmentum length/head length to base of mandible)	0.40–0.46	0.43	0.42
Postmentum contraction index (Width at waist/maximum width)	0.51–0.57	0.55	0.56
Pronotum length	0.28–0.31	0.29	0.31
Pronotum width	0.51–0.56	0.54	0.51
Total body length	4.14–4.40	4.26	4.28

Bioecology: Soil dwellers. The samples were collected from underneath boulders from mango plantations. No mounds could be seen in the vicinity. The worker mandibles indicate they are humus/organic-rich soil feeders.

Dicuspiditermes hutsoni (Kemner, 1926) (Fig. 2A–F)

Capritermes hutsoni Kemner, 1926 in: *Bull. ent. Res.*, 16(4): 391–392
1965. *Dicuspiditermes hutsoni* (Kemner), Krishna in: *Am. Mus. Novit.*, No. 2210:18.

Specimens examined: India: Kerala: Wayanad: Thalappuzha, (762 m, 11.8403 N, 75.9492E).06. vii. 2015. Shili. Colony code, Vial No.SH-2 (Register No. ZSI/WGRC/IR/5598), 2 soldiers, 4 workers and Vial No.SH-11 (Register No. ZSI/WGRC/IR/5597), 4 soldiers, 3 workers.

Redescription

Soldier (Fig. 2A–E, Table 2): Head capsule pale yellow; antennae yellowish brown; labrum translucent yellow; left mandible black; right mandible reddish brown; legs and body whitish yellow. Head sparsely hairy with many long hairs near fontanelle region and body densely hairy.

Head capsule subrectangular; sides substraight; anterolateral tubercle of head short. Frons gradually inclining in front at 40°–45° angle; median suture of head
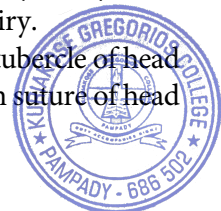
Table 2. Measurements of *Dicuspiditermes hutsoni* (Kemner) – Soldier.

Body parts	Measurements (mm)
Head length with mandibles	3.70–4.05
Head length to base of mandibles	1.94–2.05
Maximum head width	1.16–1.26
Head index (maximum head width/head length to base of mandible	0.62–0.64
Length of labrum	0.38–0.42
Width of labrum	0.27–0.29
Left mandible length	1.74–1.87
Right mandible length	1.65–1.76
Mandible head length index (left mandible length/head length to base of mandibles)	0.86–0.94
Length of postmentum	0.75–0.88
Maximum width of postmentum	0.37–0.40
Width of postmentum at waist	0.20–0.23
Pronotum length	0.34–0.36
Pronotum width	0.70–0.77
Total body length	5.40–6.10

faintly distinct extending up to middle or sometimes indistinct. Fontanelle small, transverse, situated anteriorly at distal one-fifth of head; fontanelle gland small. Antennae 14 segmented; segment 2, 3 and 4 subequal; segments 5–8 gradually increasing in length and remaining segments slightly decreasing in size except last segment. Labrum asymmetrical, anterior margin deeply incurved with long needle-like anterolateral points, lateral margin with a few serrations, a little longer than width. Mandibles asymmetrical, a little shorter than head capsule; left mandible twisted at middle and with a small point at tip and sometimes point-tip seen damaged. Right mandible blade-like, apical part incurved. Postmentum short and club-shaped; length less than half of head length; with a narrow waist lying medially. Pronotum saddle-shaped, anterior and posterior margin without any notch. Legs with 3:2:2 apical tibial spurs. Abdomen oblong; cerci short; 2 segmented.

Worker: Head capsule and antennae pale yellow; thorax and legs transparent yellow; abdomen transparent, intestinal content showing through. Head moderately with many short and long hairs and body densely hairy. Total body length 4.30–4.75 mm. Head capsule subcircular, broader than long (head length to tip of labrum 1.20–1.25 mm, length to base of mandibles 0.73–0.76 mm, maximum head width 0.92–0.99 mm). Fontanelle plate round, translucent to white. Antennae with 14 segments; segment 2 a little longer than 3 and 4; segment 3 and 4 subequal. Postclypeus swollen; length about half of width (length 0.23–0.26, width 0.48–0.50 mm). Mandibles (Fig. 2F) each with an apical and two marginal teeth. First+ second marginal of left mandibles with long and sinuate posterior margin, shorter than apical; third marginal prominent, separated from first+ second by a deep cut or notch; molar tooth present; molar prominence more prominent and not extending up to the level of first marginal. First marginal of right mandible triangular with slightly longer posterior margin; second marginal prominent and with incurved posterior margin; distance between first and second marginal

subequal to or a little shorter than the distance between apical and first marginal; cockroach notch present. Pronotum strongly saddle-shaped; anterior margin without notch (length 0.23 mm-0.27 mm, width 0.50–0.54 mm); legs with 3:2:2 apical tibial spurs; foreleg somewhat swollen; tarsi 4-segmented.

Remarks

Both the soldier and worker castes of this species are redescribed here, since the original description as well as that in Chhotani (1997) were inadequate.

This is the second documentation of *D. hutsoni* after its initial discovery in 1926 from Pelmadulla, Sri Lanka. The study by Chhotani (1997) was based on the original description only. The finding of a taxon hitherto assumed to be 'endemic' to Sri Lanka, in south Kerala is not surprising, since the island was once broadly connected to southern India during Pleistocene when sea levels were much lower than at present (Amina and Rajmohana 2013). Another Sri Lankan endemic species *Hospitalitermes monoceros* (König, 1779) and a new species of *Ceylonitermellus* Emerson, 1960, a Sri Lankan endemic genus were reported recently from the Kerala parts of the Western Ghats (Amina et al. 2013; Amina and Rajmohana 2013)

In Sri Lanka, *D. hutsoni* was previously reported as a pest of tea (Krishna et al. 2013). Interestingly, the present collections are also from a tea plantation, in the Western Ghats of Kerala.

Acknowledgments

Disclosure statement

No potential conflict of interest was reported by the author(s).

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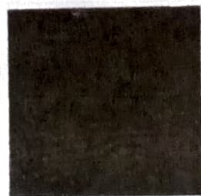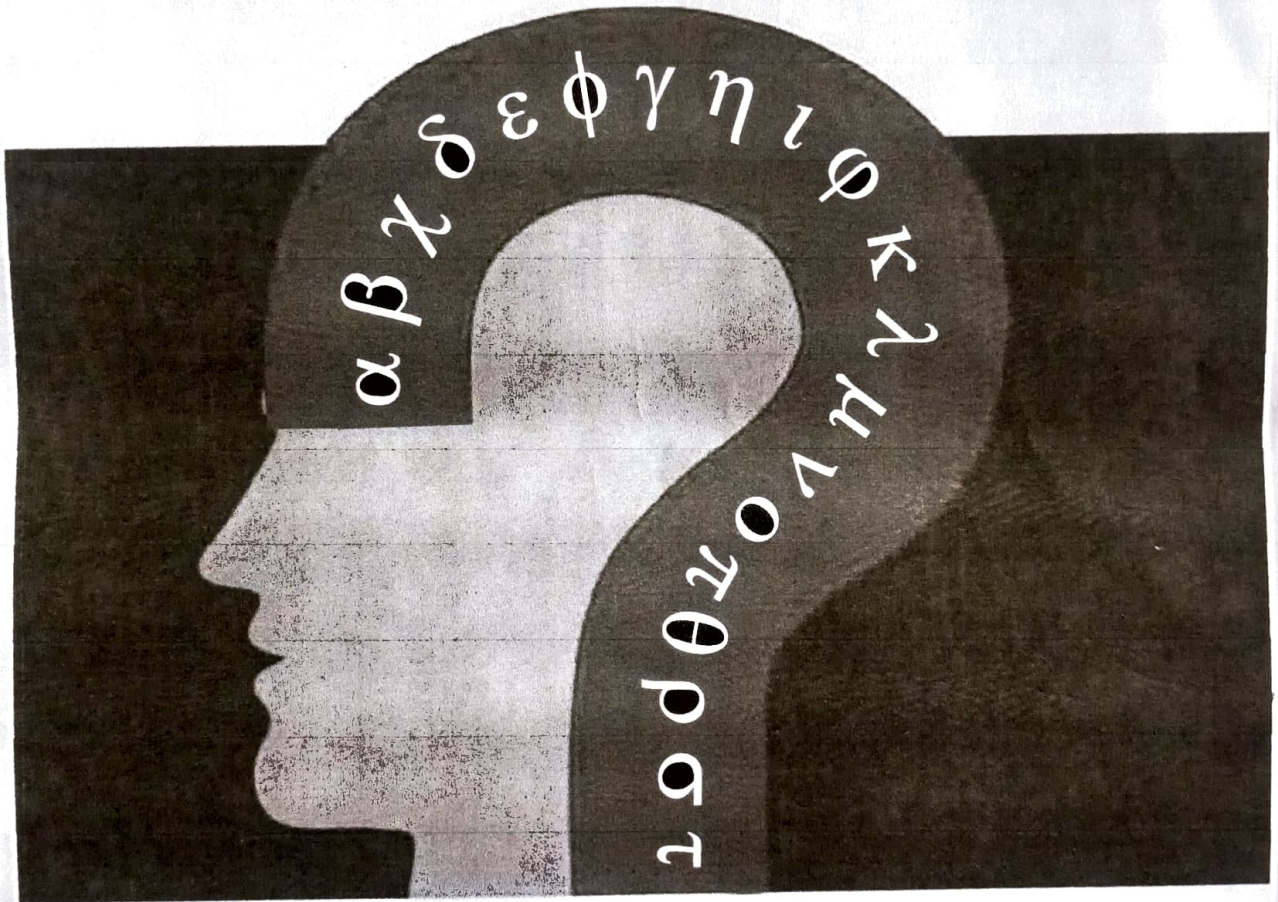
HYGIENE AND SANITATION IN SPORTS DURING THE POST COVID TIMES

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ABSTRACT

Globally there are copious amounts of people participating in some sort of sports. The coronavirus disease 2019 (COVID-19) pandemic forced the world's population to alter daily routines, including exercise and sporting habits. Like the flu, COVID-19 is spread from person to person by droplets of saliva. When an infected person coughs, sneezes or talks, they may generate droplets containing the virus. These droplets settle on surrounding surfaces. People may get infected by the virus if they touch those surfaces or objects, and then touch their mouth, nose or eyes. The high-intensity sports activities lead to an open window of susceptibility to infection. Subsequently good hygiene practices, and regular cleaning are critical to controlling the spread of COVID-19. The guidance on good hygiene, cleaning sports equipment and shared facilities, to ensure the prevention of virus spread is unavoidable. It is important to teach athletes about ensuring hygiene in sports. Good hygiene should be an integral part in every sportsman's life.

KEYWORDS: Coronavirus Disease, Susceptibility to Infection

INTRODUCTION

The word 'Hygiene' is derived from 'Hygeia', the goddess of health in Greek mythology. Hygiene is defined as the science of health and embraces all factors which contribute to healthy living. Hygiene has two aspects – personal and environmental. The aim of personal hygiene is to promote standards of personal cleanliness within the setting of condition where people live. Personal hygiene includes bathing, clothing, care of nails, feet and teeth, spitting, cough, sneezing and personal appearance. The environmental hygiene has two aspects-domestic and community. Domestic hygiene comprises of the