Proceedings of the Golden Jubilee Seminar Series in EMERGING TRENDS IN PURE AND APPLIED DISCIPLINES
January 15-23, 2014

Chief Editor
Jino Nainan
ST. GREGORIOS COLLEGE  
KOTTARAKARA  
Affiliated to University of Kerala  
Accredited by NAAC with B++

Proceedings of the  
Golden Jubilee Seminar Series  
in  
Emerging Trends in Pure and Applied Disciplines  
January 15 – 23, 2014

*Chief Editor*  
Jino Nainan

Pulamon P.O., Kottarakara,  
Kollam, Kerala, Pm. 691 531  
e-mail: gregorioscolle@yahoo.co.in  
http://www.gregorioscollege.org
Preface

The Management, Staff and students of the College realise that 2013-14, being the Golden Jubilee Year of the College, is an appropriate time for retrospection, correction and innovation. The Golden Jubilee Seminar Series is an outcome of that realisation and a part of the innovative programmes planned by the College for the Jubilee Year. There are eight departments in the College offering undergraduate programmes, of which four are offering post graduate programmes also. The Golden Jubilee Seminar Series is an eight-day programme from 15 January, 2014, allocating a day for each of the eight departments to conduct seminars on topics relating to their respective disciplines. Every day, there was two technical sessions-one in the forenoon and one in the afternoon. The objective of organising the programme is to promote interdisciplinary learning, particularly in the emerging areas of various academic disciplines.

The seminar was supported financially by the community of St. George (Bethlehem Ashram), Chengamanadu, Kottarakara - the sponsoring body of the college founded by Late lamented H. H. Moran Mar Baselios Marthoma Mathews II. His Grace Mathews Mar Theodosios, Metropolitan, Idukki Dioces of Malankara Orthodox Church is the manager and Fr. Dr. K Geevarghese was the administrator of the college. His Grace Mathews Mar Theodosios was the chief patron and Fr. Dr. K Geevarghese was the patron of the organising committee.

In the seminar series (January 15 – 23, 2014), experts in the respective disciplines were invited to give research/expository lectures in the topic of their expertise. The articles in this proceeding are mostly the expanded version of the invited talks and the selected papers. Apart from the sponsoring body of the college, the programme also received financial support from Krishna Tulsi Pharmaceuticals, Kollam, Kerala and the St. Gregorios College Co-operative Society. I am indebted to the speakers of the programme and the authors of the articles for their contributions, without which this venture would never achieve its objectives. As a member of the organising committee, I also thank all the sponsors for their financial support and the enthusiastic and cheerful support throughout the programme.

I would also like to express my sincere gratitude to the members of the organising committee for their enthusiastic and meticulous support in organising the seminar series. I would like to acknowledge Dr. Leni V for giving the technical know-how.
and unconditional efforts for the success of this programme. Overall I am truly
greatful to Mr. Jino Nainan for his whole hearted efforts. I also thank Mr. Sibin
Soman, computer lab assistant, who took full effort for capturing each session in ve-
dio format. I am greatful to all my colleagues and non teaching staff viz. Jijumon,
Baby John, Arun and Lenju in the college for undertaking various responsibilities
in organizing this programme.
Finally I am thankful to the reviewers for their services rendered in screening the
contributed papers for inclusion in the proceedings.

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Kottarakara

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Programme

INAUGURATION
Wednesday, January 15, 2014
09.45AM

Chair: Dr. P K Josekutty (Principal)
Benedictory Speech: H. G. Mathews Mar Theodosius
(Manager)
Inaugural Address: Dr. ACHUTHSANKAR S NAIR
(Head, Dept. of Computational Biology and Bioinformatics, and the State Inter University Centre of Excellence in Bioinformatics, University of Kerala)

Wednesday, January 15, 2014
Department of Zoology

11.00 AM Technical Session I
Topic: Endosulfan Toxicity on Fresh water Fish
Resource Person: Dr. Treesa Radhakrishnan
(Professor, Dept. of Aquatic Biology, University of Kerala)

2.00 PM Technical Session II
Topic: Climate Change: Impact in Kerala and Green Technology
Resource Person: Dr. M K P Royee
(Director, Centre for Community Health Research, Kollam, Kerala)

3.30 PM Paper Reading Session
Biju A et al. Ecology of mysids(Crustacea: Mysida) from the Cochin backwater.
Lincy A et al. Plankton pigments as a trophic state forecasting tool along Kerala coast, India.
Rani S D On Wild Animal - Human Interaction at Kuryanayam in Kumaramkudy Forest Range, Kerala.
Volga S S et al. Role of Germline Polymorphism XRCC3 Thr241Met in Familial and Sporadic Breast Cancer Susceptibility.
Thursday, January 16, 2014
Post Graduate Department of Commerce

10.00 AM
Technical Session III
Topic: Contemporary Marketing Intelligence in the Indian Context
Resource Person: Dr. K S Chandrasekhar
(Director, School of Management and Legal Studies, University of Kerala)

2.00 PM
Technical Session IV
Topic: The Changing Scenario of Indian Capital Market
Resource Person: Dr. G Raju
(Associate Professor, Dept. of Commerce, Govt. College for Women, Thiruvananthapuram)

Friday, January 17, 2014
Department of Botany

10.00 AM
Technical Session V
Topic: Taxonomy: Its Relevance
Resource Person: Dr. Mathew Dan
(Senior Scientist, JNTBGRI, Palode, Thiruvananthapuram)

2.00 PM
Technical Session VI
Topic: Orchids of Western Ghats and its Conservation
Resource Person: Dr. A Ganga Prasad
(Assistant Professor, Dept. of Botany, University of Kerala)

3.30 PM
Paper Reading Session
Chithira C et al. Screening of Antimicrobial property of Adathoda against respiratory infection causing organisms.

Saturday, January 18, 2014
Post Graduate Department of Chemistry

10.00 AM
Technical Session VII
Topic: Group Theory and its Applications I

2.00 PM
Technical Session VIII
Topic: Group Theory and its Applications II
Resource Person: Dr. V Sadasivan
(Associate Professor, Dept. of Chemistry, University College, Thiruvananthapuram)
3.30 PM  Paper Reading Session
Sivakala S  Facile Seed Mediated Cum Capping Strategy For The Preparation
Of Silver Nano Particles And Anti Bacterial Activity Studies

Monday, January 20, 2014
Department of Political Science

10.00 AM  Technical Session IX
Topic:  Indian constitution: A Contemporary Reading
Resource Person:  Dr. Biju B L
(Original Professor, Dept. of Political Science,
Central University of Hyderabad)

2.00 PM  Technical Session X
Topic:  Environment and Development
Resource Person:  Dr. Shaji Varkey
(Head, Dept. of Political Science,
University of Kerala)

Tuesday, January 21, 2014
Post Graduate Department of Mathematics

10.00 AM  Technical Session XI
Topic:  Analysis: From Abstract to Concrete
Resource Person:  Dr. E Krishnan
(Former Professor and Head, Dept. of Mathematics,
University College, Thiruvananthapuram)

2.00 PM  Technical Session XII
Topic:  Introduction to Finite Field
Resource Person:  Dr. A R Rajan
(Former Professor and Head, Dept. of Mathematics,
University of Kerala)

3.30 PM  Paper Reading Session
Manil T. Mohan  Some Notes on the Navier-Stokes Equations in Unbounded
Channel Domains.

Wednesday, January 22, 2014
Post Graduate Department of Physics

10.00 AM  Technical Session XIII
Topic:  Recent Trends in Materials Research
Resource Person:  Dr. Sam Solomon
(Head, Dept. of Physics, St. John’s College, Anchal)
2.00 PM  Technical Session XIV
Topic:  Concept of Quantum Mechanics: Vectors and Tensors
Resource Person:  Dr. V Biju
(Associate Professor, Dept. of Physics, University of Kerala)

3.30 PM  Paper Reading Session
A Devarajan  Synthesis and structural study of nanostructured calcium carbonate.
Fergy J et al.  Dielectric studies of Nano crystalline NdTiNbO₆ ceramic through combustion technique.
Ansu P J et al.  XRD and FTIR characterisation of ZnS nanoparticles synthesized by novel aqueous chemical method.
Sharon T et al.  Chemical synthesis and FTIR characterisation of NiO nanoparticles.

Thursday, January 23, 2014

10.00 AM  Technical Session XV
Topic:  Sharpening Soft Skills for Success
Resource Person:  Dr. Noel Jose
(Vice Principal, F M N College, Kollam)

1.30 PM  Technical Session XVI
Topic:  Reading: The Contemporary Dilemma
Resource Person:  Mr. P Harikrishna
(Associate Professor, PG Dept. of English, N S S College, Pandalam)

Valedictory Function
Thursday, January 23, 2014
3.00 PM
List of Speakers

Dr. Achuthsankar S Nair
(Head, Dept. of Computational, Biology and Bioinformatics, and the State Inter University Centre of Excellence in Bioinformatics, University of Kerala)

Dr. E Krishnan
(Former Professor & Head, Dept. of Mathematics, University College, Thiruvananthapuram)

Dr. A R Rajan
(Former Professor & Head, Dept. of Mathematics, University of Kerala)

Dr. Treesa Radhakrishnan
(Professor, Dept. of Aquatic Biology, University of Kerala)

Dr. M K P Royee
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Dr. K S Chandrasekhar
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Dr. Mathew Dan
(Senior Scientist, JNTBGRI, Palode, Thiruvananthapuram)

Dr. A Ganga Prasad
(Assistant Professor, Dept. of Botany, University of Kerala)

Dr. V Sadasivan
(Associate Professor, Dept. of Chemistry, University College, Thiruvananthapuram)

Dr. Biju B L
(Assistant Professor, Dept. of Political Science, Central University of Hyderabad, Hyderabad)
Dr. Shaji Varkey
(Head, Dept. of Political Science, University of Kerala)

Dr. Sam Solomon
(Head, Dept. of Physics, St. John’s College, Anchal)

Dr. V Biju
(Associate Professor, Dept. of Physics, University of Kerala)

Dr. Noel Jose
(Vice Principal, F M N College, Kollam, Kerala)

Mr. P Harikrishna
(Associate Professor, PG Dept. of English, N S S College, Pandalam, Kerala)
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Orchids of Western Ghats and Its Conservation

A Gangaprasad
Department of Botany
University of Kerala, Thiruvananthapuram
Kerala, India - 695 581
e-mail: agangaprasad@yahoo.com

1 Introduction

Biodiversity, which encompasses all life forms on earth, can be auto-sustainable and self regenerating if there are no natural or manmade perturbations. India is one of the 12 mega biodiversity countries of the world. Indiscriminate exploitation and various anthropogenic pressures lead to depletion of this valuable gift of nature. Western Ghats, one of the richest floristic regions in the country is having about 4000 flowering plant species which is about 30% of the flowering plants in the country[10].

According to the IUCN Action Plan, orchids are among the world’s most diverse and widely distributed plants. Orchids constitute a very large and immensely fascinating group of flowering plants. The diversity of forms found in the orchid family is quite amazing. Orchids belong to the most diverse plant family known to man. They have complex life cycle, mycorrhizal association and specific pollination syndrome. It is a family of considerable economic importance particularly in horticulture and floristry. Apart from the horticultural value, orchids are used in traditional herbal medicine. Many orchid species are threatened globally by over collection from the natural habitat for horticultural purpose. Many orchids are rich in alkaloids and other phytochemical contents and many of them are effectively used to cure a wide range of ailments. Plant tissue culture and micropropagation technique play an important role in conservation programme and management of botanical collections. Orchids are beautiful, fascinating flowers that have long held a grip on the human imagination, perhaps due to their sexual appearance. The bloom of an orchid plant is so gorgeous and distinctive that one botanist was led to describe orchids as ‘living jewels’[13]. These perennial plants have adapted to almost every environment on earth, and this has led to a great diversity in orchids. There are between 25,000 to 30,000 different kinds through the world. Additionally, there are also approximately 60,000 known types of orchid hybrids that have been created by orchid growers. They have emerged as leaders in floriculture and account
for multimillion dollar cut flower industry in several countries[6]. The majorities of orchids in cultivation are native of tropical belt and occur in their profusion in humid tropical forests of Central and South America, India, Sri Lanka, Burma, South China, Australia, Thailand, Malaysia, Philippines, New Guinea etc. In addition to horticultural importance, the species Vanilla planifolia needs special mention the source of vanilla essence.

2 Orchid wealth of India

The widely diverse climatic regions of India are reflected in the wide diversity of its orchid flora. India with 1129 species in 184 genera[14] is one of the major orchid habitats of the world. The Indian Himalayan region alone harbours about 876 species in 151 genera[29]. The Indian orchids grow at altitude up to 5,000 m, and in areas having an annual rainfall of as low as 600 mm to as high as 1,100 mm. The epiphytic orchids are abundant up to 1,800 m and their frequency progressively decreases with further increase in altitude. Majority of the terrestrial orchids, on the other hand, are confined to temperate regions. In general, the ground growing taxa are more common in north Western Himalayas, the epiphytic ones in north eastern India, and the small flowered ones in the Western Ghats.

The Western Ghats region in the peninsular India is a known mega diversity centre and is one of the richest orchid habitats in the world[1]. The Western Ghats which extends from Tapti valley in Gujarat to Kanyakumari in Tamil Nadu is a water shed of peninsular India and an area of high plant genetic diversity and high endemism[24]. The genera Smithsonia, Aenhendya, Cottonia and other species like Paphiopedilum druryi, Ipsea malabarica, Dendrobium jerdonianum, Seidenfade-niella rosea, Euophia cullenii, Aerides crispa, A. maculosa etc are endemic to this region. Altogether, the Western Ghats harbour 288 species of orchids in 76 genera. It has been reported that many of our native orchids are an untapped resource. They are showy and promising and hence have great potential in breeding programme to raise novel hybrids of immense beauty. Some of the rare and exquisite orchids of the western Ghats is presented in the table1. Among the orchids of the Western Ghats, at least thirty species are reported to be rare and endangered, of which ten are known from a single location[28]. Preservation of the threatened and endangered orchids in situ is most desirable to ensure their survival and breeding, and evolution in association with related taxa but its success largely depends on the stability of the ecosystem, which cannot be guaranteed at present.

Conservation of the shrinking plant gene pool especially of the rare and endangered taxa of known potential economic source is a well-debated issue all over the world. Plant tissue culture is an effective tool to conserve plant genes and guarantee the survival of endangered and overexploited genotype is derived from the fact that it makes sure of small units (cell and tissues) without losing the mother plant, take the pressure of waning wild populations and makes available large number of
faithful copies of plants for reintroduction and wide distribution. Particularly for orchids, seed (embryo) cultures offer opportunities of easy and rapid multiplication, maintenance of diversity within species and facilitate reintroduction and restoration of taxa into the native habitat. In orchids, seed propagation in vitro holds considerable significance as each orchid produces up to 4,000,000 dust like seeds in a single capsule[33], of which less than 1% germinate in nature and nearly all seeds germinate in a simple defined medium. Seed germination, therefore, can play a significant role in retaining the diversity within species and achieving practical conservation via reintroduction and restoration in native habitats.

Orchids are grown primarily as ornamentals and are valued as cut flowers not only because of their exotic beauty but also for their long shelf life. Though orchids are grown primarily as ornamentals some are employed as herbal medicines and food[4]. Vanilla is one of the rare examples of orchids being used as spice.

At present the orchids figure prominently in the Red Data Book prepared by IUCN. In fact, the entire family is now included in Appendix-II of the Convention on International Trade in Endangered Species of Wild Fauna and Flora(CITES). Nearly 250 species of Indian orchids are threatened of survival whereas some like Anoectochilus rotundifolius, Aphyylorchis gollani, Coelogyne treutleri, Paphipedilum charlesworthii, Pleione tagenaria etc have probably already vanished from their Indian natural habitats[32]. The Western Ghats region, which extends from Tapi valley in Gujarat to Kanyakumari in Tamil Nadu is a water shed of Peninsular India, and an area of high plant genetic plant genetic diversity and rich in orchids[24]. Out of the 85 species of endemic orchids of Western Ghats, over 15 are reported to be rare and endangered[28].

The Indian government has established Biosphere Reserves, National Parks and Sanctuaries in the orchid rich regions of the country besides banning the export of orchids collected in wild. Unfortunately, in situ conservation is not always a viable option because of reasons like fragmented habitats, absence of pollinators, indiscriminate use of pesticides or other modifications of the biome etc.

3 Embryo culture

The culture of immature seeds from green capsule is widely followed for multiplication of different types of species and hybrid orchids. Asymbiotic seed germination in epiphytic orchids is easy and in some terrestrial species is difficult. Orchid seeds are unique in several aspects. They are minute and non endospermic with undifferentiated embryos and are produced in large numbers. As many as 1,300 to 4000000 seeds per capsule are produced[33]. In nature, the orchid seeds require mycorrhizal association for germination[2]. However, less than 5% of the seed germination occurs in their natural environment. The seeds of orchids, produced in large numbers in each capsule, are highly fragile and possess virtually no stored food material or endosperm[19].
Development of asymbiotic germination methods of orchid seed took place following the formulation of Knudson B and Knudson C\[16, 17\]. The propagation of orchid through in vitro germination of seeds has been emphasized by many workers\[2, 3, 4, 8, 17, 18, 19, 20\]. Many media have been used for the axenic germination of orchid seeds\[11\]. The commonly used nutrient media for orchid seed culture are those proposed by Knudson\[17\], Vacin and Went\[38\], and Mitra et al.\[21\].

Seed culture of a number of species including tropical epiphytes, tropical lithophytes, tropical terrestrials and temperate terrestrials are developed with varied levels of successes. Among tropical, the seeds of terrestrials and lithophytic species are more difficult to germinate and many require special media\[9\].

4 Tissue culture

Plant tissue culture as a means of multiplication of orchids is not new and has been employed for the rapid clonal propagation of outstanding orchid hybrids for more than 50 years. The benefits of meristem culture attracted the attention of many researchers and work on various valuable orchid hybrids was initiated in different laboratories.

Orchids represent the first horticultural crop successfully cloned by tissue culture method on a commercial scale. The earliest report of using tissue culture technique in orchids goes back to 1949 when it was demonstrated that, Phalaenopsis plantlets could be developed from the buds of inflorescence stalk\[26\]. However, the credit for achieving mass clonal propagation of orchids goes to Morel\[22\], who produced virus free Cymbidium from diseased plants by culturing shoot apices. Wimber\[40\] published the first detailed protocol for in vitro production of Cymbidiums starting with meristem culture. Following this technique, many orchid genera have been successfully cloned. The technique of shoot meristem culture has limited utility in the monopodial orchids as it involves the sacrifice of the mother plants. Consequently, attempts have been made in recent years to test the regeneration of excised leaves, rhizomes, node and tubers\[35, 37, 39\].

The major advantage of clonal propagation is that the plant lets produced are usually identical to their parents. During the last forty five years, tissue culture techniques have been extensively exploited, not only for the rapid and large scale propagation of orchids but also for their ex situ conservation\[7\]. Different protocols have been developed for the large scale propagation of a number of orchid species through in vitro culture of various parts including shoot tips, flower stalk, nodes, buds, root tips, rhizome segments. For mass propagation, regeneration from tissue cultured explants is advantageous to seed culture due to year round availability of explants.

To save the orchid species from extinction, several workers have used tissue culture techniques for mass propagation. The use of node explants from stem has proved successful in the propagation of orchids like Dendrobium\[34\], Vanda\[27\],
Vanilla planifolia[5, 25]. The resident axillary buds is the widely used stem node explants is a condensed shoot and its participation through induced mitotic activity and enhanced branching results in uniformity of the plants regenerated in vitro[30]. Shoot tips and nodal explants have been effectively used for the induction of shoot buds and PLBs of many orchids[12, 15, 23, 31, 36].

Transplantation and acclimatization processes continuous to be a major bottleneck in the micropropagation of many species including orchids. A substantial number of micropropagated plants do not survive transfer from in vitro conditions to greenhouse or field environment. The greenhouse and field have substantially lower relative humidity, high light level and septic environment that are stressful to micropropagated plants compared to in vitro conditions.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Species</th>
<th>Remarks</th>
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<tr>
<td>1</td>
<td>Acampae premorsa (Roxb.) Blatt. &amp;Mc Cann</td>
<td>Epiphyte</td>
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<td>2</td>
<td>Acampae rigida (Buch.-Ham ex J.E.Sm.)</td>
<td>Rare, Epiphyte</td>
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<td></td>
<td>P.F. Hunt</td>
<td></td>
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<tr>
<td>3</td>
<td>Acanthephippium bicolor (Lindl.)</td>
<td>Rare, Terrestrial</td>
</tr>
<tr>
<td>4</td>
<td>Aenhenrya rotundifolia (Blatt.). Sathish</td>
<td>Critically endangered,</td>
</tr>
<tr>
<td></td>
<td>and F. Rasm.</td>
<td>Terrestrial</td>
</tr>
<tr>
<td>5</td>
<td>Aerides ringens (Lindl.) Fischer</td>
<td>Rare, Epiphyte</td>
</tr>
<tr>
<td>6</td>
<td>Anoectochilus elatus Lindl.</td>
<td>Rare, Terrestrial</td>
</tr>
<tr>
<td>7</td>
<td>Aphyllorchis montana Rchb. f.</td>
<td>Rare, Terrestrial</td>
</tr>
<tr>
<td>8</td>
<td>Arundina graminifolia (D. Don) Hochr.</td>
<td>Rare, Terrestrial</td>
</tr>
<tr>
<td>9</td>
<td>Brachycorythis iantha (Wight) Summerh.</td>
<td>Rare, Terrestrial</td>
</tr>
<tr>
<td>10</td>
<td>Brachycorythis splendidia Summerh.</td>
<td>Rare, Terrestrial</td>
</tr>
<tr>
<td>11</td>
<td>Bulbophyllum aureum (J.D. Hook.) J.J. Sm.</td>
<td>Rare, Epiphyte</td>
</tr>
<tr>
<td>12</td>
<td>Bulbophyllum sterile (Lam.) Suresh</td>
<td>Rare, Epiphyte</td>
</tr>
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<td>13</td>
<td>Bulbophyllum tremulum Wight</td>
<td>Rare, Epiphyte</td>
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<td>14</td>
<td>Calanthe sylvatica (Thouars) Lindl.</td>
<td>Rare, Terrestrial</td>
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<td>15</td>
<td>Cheirostylis flabellata Wt.</td>
<td>Rare, Epiphyte</td>
</tr>
<tr>
<td>16</td>
<td>Chiloschista fasciata (F.v. Muell.) Seidenf. and Ormerod</td>
<td>Rare, Epiphyte</td>
</tr>
<tr>
<td>17</td>
<td>Cleissostoma tenuifolium (L.) Garay</td>
<td>Rare, Epiphyte</td>
</tr>
<tr>
<td>18</td>
<td>Coelogyne nervosa A. Rich.</td>
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<td>Cymbidium ensifolium (L.) Sw.</td>
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<td>Dendrobium diodon Rchb.f. subsp. Kodayarensis Gopalan &amp; Henry</td>
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<td>Dendrobium herbaceum (Lindl.)</td>
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<td><em>Eulophia epidendracea</em> (Koen.) Schltr.</td>
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<td><em>Pholidota imbricata</em> W. J. Hook.</td>
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<td><em>Polystachya concreta</em> (Jacq.) Garay</td>
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<td><em>Pteroceras leopardinum</em> (Par. &amp; Rchb.f.) Seidenf.</td>
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<td>68</td>
<td><em>Rhytionanthos indicum</em> Satish &amp; Garay, incd</td>
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<td><em>Robiquetia gracilis</em> (Lindl.) Garay</td>
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<td><em>Satyrium nepalense</em> D. Don</td>
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<td><em>Schoenorchis nivea</em> (Lindl.) Schltr.</td>
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<td><em>Sirhookera lanceolata</em> (Wight) Kuntze</td>
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<td><em>Sirhookera latifolia</em> (Wight) Kuntze</td>
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<td><em>Smithsonia straminea</em> Saldanha</td>
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<td><em>Taxine bicornis</em> (Lindl.) Rchb.f.</td>
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<td><em>Taprobana spathulata</em> (L.) Christ.</td>
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<td><em>Trias bonaccordensis</em> Sathish</td>
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<td><em>Trias stocksii</em> Benth ex J.D. Hook.</td>
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<td><em>Trichoglottis tenera</em> (Lindl.) Rchb.f.</td>
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<td>81</td>
<td><em>Vanda tessellata</em> (Roxb.) Hook. ex G. Don.</td>
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<td><em>Vanda testacea</em> (Lindl.) Rchb. f.</td>
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<td><em>Vanilla wightiana</em> Lindl. ex J. D. Hook.</td>
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<td><em>Xenikophyton smeeanum</em> (Rchb.f.) Garay</td>
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<td>85</td>
<td><em>Zeuxine flava</em> (Wall. ex Lindl.) Benth. ex J. D. Hook.</td>
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<td>86</td>
<td><em>Zeuxine longilabris</em> (Lindl.) Benth. ex J. D. Hook.</td>
<td>Rare, Terrestrial</td>
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References


For the conservation and sustainable utilization of any organism, proper identification and understanding are utmost essential. Taxonomy is the classification of organisms into groups based on similarities. Thus, taxonomy is a tool for proper identity. The term taxonomy was originated from two Latin terms Taxis (= order / arrangement) and Nomos (= law / science) and coined by A P de Candolle (1824-1873) in his publication Théorie élémentaire de la botanique (1813).

Nomenclature is the universally acceptable scientific naming of an organism.

- What is wrong with common names?
- Why we should go for a complex nomenclatural system?

Common names are generally applicable in only in a single language which is not at all universal.

In most parts of the world relatively a few species have common or vernacular names. Many of our wild plants/ insects /fishes do not have any common name.

Common names are applied indiscriminately to genera, species or varieties.

Often two or more unrelated plants are known by the same name and frequently even in one language a single species may have two or more common names applied either in the same or different localities.

There are different species with same common name, and causes severe confusion in identity. Some examples of such common names in Malayalam are:

- Pathiri - *Stereospermum suaveolens, Millingtonia hortensis*
- Analivegam - *Pittosporum neelgherrense, Alstonia venenata*
- Pathimukham - *Prunus cerasoides, Ceasalpinia sappan*
- Moovila - *Pseudarthria viscida, Uraria picta*
Another problem is different common names for the same species or its cultivars. For example, the vegetables cabbage, cauliflower, broccoli, kohl-rabi, and brussel sprouts, all come from the same original species. Breeders have produced five different vegetables by selecting for edible leaves in cabbage, edible flowers in cauliflower and broccoli, edible buds in Brussels sprouts and edible roots in kohl-rabi, and again this is possible only because of the genetic variation within the original species, *Brassica oleracea*.

1 What is taxonomic nomenclature . . .?

Classification and Nomenclature are two inseparable components with respect to Taxonomy. Classification is the establishment and definition of systematic groups. Nomenclature refers to the naming of various groups. In earlier days, Polynomial system was in practice. Polynomial is a plant name consisting of several words in a series revealing the diagnostic characters of the plant.

Example 1. *Sida rhombifolia* was known earlier (1692) as *Althaea maderaspatana subrotundo folio molli & hirsuto multipilis*.

Example 2. *Ranunculus bulbosus* was *Ranunculus foliis, ovatis serratis, scapo nudo unifloro* which means, *Ranunculus with ovate serrate leaves having a scape with a single bractless flower*.

The system of naming every organism in two parts with Latin words is called “Binomial System of Nomenclature”. According to this system, the first part is the generic name or epithet which represents the genus and the second part is the specific epithet of the species. Scientific name of a species consists of a binomial and an authority who proposed the name. The value of the binomial nomenclature system derives primarily from its economy, its widespread use, and the stability of names. Its advantages are: every species can be unambiguously identified with just two words and the same name can be used all over the world, in all languages, avoiding difficulties of translation.

Carl Linnaeus (1707-1778), a Swedish physician is recognized as the father of plant taxonomy. His work, *Species Plantarum* (May 1, 1753) is the starting point for modern taxonomy with a widely accepted nomenclature pattern. His most significant contribution was the consistent use of the binomial system. He has described 7,700 species of plants and 4,400 species of animals!!

2 Formation of Binominal System of Nomenclature

The first International Botanical Congress was held in Paris in 1864. In that gathering of botanists from different parts of the world, Alphonse De Candolle was
commissioned to formulate a set of laws ("lois") regarding the naming of plants. At the second congress, which was also in Paris (1867), the "Lois de la nomenclature botanique" were accepted, and translated into English as "Laws of Botanical Nomenclature" and adopted with a Historical Introduction and Commentary. The "laws" stated that nomenclature was to "start" when binomial naming was begun, i.e., in 1753. The 4th International Congress met at Cambridge (1930) approved the International Code of Botanical Nomenclature (ICBN) which is otherwise known as Cambridge Code. The aims of ICBN were to:

1. Establish a stable method of naming taxonomic groups
2. Avoid useless creation of names and
3. Ensure grammatical correctness, regularity, prevailing custom, respect for persons

After Cambridge Congress, 14 International Taxonomy Congresses were happened in various parts of the world. The last one (18th), was in Melbourne and the Melbourne Code 2011 made drastic changes to ICBN. Then onwards ICBN became ICN (International Code of Nomenclature for Algae, Fungi and Plants). The Major Amendments in ICN are:

1. Permits electronic-only publication of names of new taxa; no longer it will be a requirement to deposit hard copies.
2. Besides Latin, English also is allowed for description and no longer Latin description is a must.
3. Allows only 'one fungus one name' and 'one fossil one name'.
4. New fungal descriptions require the use of an identifier from a 'recognised repository'.

Some useful sites to clarify the nomenclatural doubts are: www.theplantlist.org and www.ipni.org, the International Plant Names Index.

Love taxonomy, practice it,
So that you could enjoy the fingerprint of an organism,
the signature of its CREATOR!!
1 Irrational numbers

Mathematics started as an attempt to analyze, understand and interpret the world through measurements. The results of such measurements are expressed in numbers and thus mathematics can be said to be the science of quantification. This was the predominant view of mathematics even as late as the eighteenth century as can be seen in the words of Leonhard Euler, the greatest mathematician of that age:

*Mathematics, in general, is the science of quantity; or, the science which investigates the means of measuring quantity*

The different kinds of numbers we now use were invented in the course of time, depending on the need at hand. During the nomadic or pastoral stage of human history, discrete counting—such as the number of people in a tribe, or number of cattle in a herd—was sufficient; and this resulted in the concept of what we now call natural numbers. Later during the period of agriculture, continuously varying quantities such as length, weight and time had to be measured. For such measurements, a unit has to be chosen and measurements may not always come out evenly as integral multiples of the unit. This necessitated the invention of fractions.

An interesting theoretical question at this point is this: having chosen a unit of length, for example, is every length a rational multiple of this unit? This question can be rephrased like this: given two lengths, is it possible to choose a unit such that both the given lengths are integral multiples of this unit? Pythagoras, the Greek philosopher of the fifth century BC, believed so but one his disciples, probably Hipparchus, proved him wrong by rigorously demonstrating that no unit of length gives both the side and diagonal of a square as natural numbers. Later Greek mathematicians called such pairs as *incommensurable* magnitudes.

The problem of measuring the diagonal of a square in terms of its side was addressed by the ancient Babylonians long before such theoretical considerations by
the Greeks. The problem is important because the easiest way to double the area of a square is to draw a square on the diagonal:

So, the question of expressing the diagonal of a square in terms of its side amounts to the calculation of the side of a square of double the area of a given square. In contrast to the theoretical discussions of this problem as done by the Greeks later, ancient Babylonians seem to have been more interested in computing approximate solutions. A Babylonian clay tablet dated to be around 2000 BC gives this in sexagesimal (base 60) notation as

\[ 1 + \frac{24}{60} + \frac{51}{60^2} + \frac{10}{60^3} \]

which translates to the current decimal notation as 1.4142129. The actual value correct to seven decimal places is 1.4142135.

It is worth investigating how they obtained such a high degree of accuracy. The answer can be found in another clay tablet, which says

*To find the diagonal of a tall slender rectangle, divide the square of the width by the height, take its half and add this to the height*

Using our algebraic notation, this means that in a rectangle of height \( a \) and width \( b \) the diagonal \( d \) is given by

\[ d \approx a + \frac{1}{2} \times \frac{b^2}{a} \]

provided \( b \) is small compared to \( a \):
We can easily see why this works. By Pythagoras Theorem, \( d = \sqrt{a^2 + b^2} \) and we know that

\[
\left( a + \frac{b^2}{2a} \right)^2 = a^2 + b^2 + \frac{b^4}{4a^2}
\]

And if \( a \) is large compared to \( b \), then \( \frac{b^4}{4a^2} \) is quite small, so that

\[
a + \frac{b^2}{2a} \approx \sqrt{a^2 + b^2}
\]

But such algebraic computations were developed only as late as the 16th century CE; so the Babylonian rationale behind this has to be sought elsewhere.

The geometric methods used by Babylonians to solve problems on areas (which later developed into algebraic methods of solving quadratic equations in the hands of Indian and Arabic mathematicians) suggests the following geometric method. The algebraic problem of computing \( \sqrt{a^2 + b^2} \) can be translated to the geometric problem of transforming the join of two squares into a single large square:

The Babylonian trick to do this is to first transform the smaller square into a rectangle with one side equal to that of the larger square:
The rectangle on the right is then vertically split into halves and one of the pieces is shifted to the top:

This makes a square of side $a + \frac{b^2}{2a}$, except for a missing square piece of side $\frac{b^2}{2a}$ at the top right corner.

The Babylonian method of computing square roots can be written

$$\sqrt{a^2 + x} \approx a + \frac{x}{2a}$$

where $x$ can be positive or negative. For example, using $2 = \frac{9}{4} - \frac{1}{4}$, we get

$$\sqrt{2} = \sqrt{\left(\frac{3}{2}\right)^2 - \frac{1}{4}} = \frac{3}{2} - \frac{1}{2} \times \frac{1}{4} \times \frac{3}{2} = \frac{17}{12}$$

and we find that

$$\left(\frac{17}{12}\right)^2 - 2 = \frac{1}{144}$$
An interesting feature of this method is that it can be recursively used to yield better approximations:

\[
\sqrt{a^2 + x} = \sqrt{\left(\frac{a + \frac{x}{2a}}{2}\right)^2 - \frac{x^2}{4a^2}} \approx \left(\frac{a + \frac{x}{2a}}{2}\right) - \frac{1}{2} \times \frac{x^2}{4a^2} \times \frac{1}{\left(\frac{a + \frac{x}{2a}}{2}\right)}
\]

Putting \(a = \frac{3}{4}\) and \(x = \frac{2}{9}\) in this equation, we get

\[
\sqrt{2} \approx 1 + \frac{1}{3} + \frac{1}{3 \times 4} - \frac{1}{3 \times 4 \times \frac{4}{9}} = \frac{577}{408}
\]

And we see that

\[(\frac{577}{408})^2 - 2 = \frac{1}{166464}\]

This second order approximation is seen in the *Baudhayanasulbasutra* written in India during the 8th century BC. The method was brought to its full generality during the first century CE by the Greek mathematician Heron. His discovery can be described in the current algebraic language as follows:

For any positive real number \(a\), if we start with any number \(x_0\) and recursively define

\[x_{n+1} = \frac{1}{2} \left( x_n + \frac{a}{x_n} \right)\]

then the sequence of numbers \(x_1, x_2, x_3, \ldots\) get closer and closer to \(a\)

Thus for \(a = 2\), starting with \(x_0 = 1\) and applying Heron’s formula, we get

\[
\begin{align*}
\frac{1}{2} (1 + 2 \times 1) &= \frac{3}{2} \\
\frac{1}{2} (\frac{3}{2} + 2 \times \frac{3}{2}) &= \frac{17}{12} \\
\frac{1}{2} \left(\frac{17}{12} + 2 \times \frac{12}{17}\right) &= \frac{577}{408}
\end{align*}
\]

so that the squares of the rational numbers

\[
1.5, \ 1.5, \ 1.6605555555555556, \ldots
\]

get closer and closer to \(2\).

Jumping ahead across several centuries, we find an interesting connection between Heron’s method and the Newton-Raphson method of finding approximate solutions of equations, developed in the 17th century.

To find an approximate solution of the equation \(f(x) = 0\), where \(f\) is a differentiable function, start with any real number \(x_0\) and recursively define

\[x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}\]
Taking \( f(x) = x^2 - a \), this gives
\[
x_{n+1} = x_n - \frac{x_n^2 - a}{2x_n} = \frac{x_n}{2} + \frac{a}{2x_n} = \frac{1}{2} \left( x_n + \frac{a}{x_n} \right)
\]
which is just Heron’s approximation.

The decimal representation of fractions, invented by Simon Stevin in the 16th century, gave a convenient way to express such approximations. For example, we find

\[
\begin{align*}
1.4^2 &= 1.96 < 2 & 1.5^2 &= 2.25 > 2 \\
1.41^2 &= 1.9881 < 2 & 1.42^2 &= 2.0164 > 2 \\
1.414^2 &= 1.999396 < 2 & 1.415^2 &= 2.002225 > 2 \\
1.4142^2 &= 1.9999616 < 2 & 1.4143^2 &= 2.0002449 > 2
\end{align*}
\]

In other words,

\[\text{the squares of the sequence of rational numbers}\]

\[1.4, 1.41, 1.414, 1.4142, \ldots\]

get closer and closer to 2

This statement we abbreviate as

\[\sqrt{2} = 1.4142 \ldots\]

It took a long time for mathematicians to admit the legitimacy of such irrational numbers. Thus we have the German mathematician Michael Stifel of the 16th century saying:

\[\text{It is rightly disputed whether irrational numbers are true numbers or false. Because in studying geometrical figures, where rational numbers desert us, irrationals take their place, and show precisely what rational numbers are unable to show ... we are moved and compelled to admit that they are correct}\]

More than a century later, we have this comment by the English mathematician John Wallis:

\[\text{Now, as for other incommensurable quantities, though this proportion cannot be accurately expressed in absolute numbers, yet by continued approximation it may; so as to approach nearer to it than any difference assignable}\]
2 Infinite series

Archimedes, the Greek mathematician and scientist of the second century BC, gave a method to compute the area of a parabolic segment and in the course of the proof, he shows that the sums

\[ 1, 1 + \frac{1}{2}, 1 + \frac{1}{2} + \frac{1}{4}, \ldots \]

get closer and closer to \(1\frac{1}{2}\). Such sums which can be continued indefinitely, but get closer and closer to a number reappear only during the Renaissance in Europe. For example, we have this from Nicole Oresme, a French philosopher of the 14th century:

*From a number, subtract a definite part; then remove that part of the remaining. If this is continued indefinitely, the number will be completely exhausted, neither more nor less.*

Denoting the original number as \(a\) and the part removed at every stage as \(\frac{1}{k}\), we have the following sequences of removed parts and remainders:

<table>
<thead>
<tr>
<th>Removed</th>
<th>(1 - (\frac{1}{k})) (\frac{1}{k})a</th>
<th>(1 - (\frac{1}{k}))^2 (\frac{1}{k})a</th>
<th>(\ldots)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Remainder</td>
<td>(1 - (\frac{1}{k})) a</td>
<td>(1 - (\frac{1}{k}))^2 a</td>
<td>(\ldots)</td>
</tr>
</tbody>
</table>

So in algebraic terms, Oresme’s proposition can be stated like this:

*The sums*

\[ \frac{1}{k}a, \frac{1}{k}a + \frac{1}{k} (1 - \frac{1}{k}) a, \frac{1}{k}a + \frac{1}{k} (1 - \frac{1}{k}) a + \frac{1}{k} (1 - \frac{1}{k})^2 a, \ldots \]

*get closer and closer to \(a\)*

In current terminology, we shorten this further as

\[ \frac{1}{k}a + \frac{1}{k} (1 - \frac{1}{k}) a + \frac{1}{k} (1 - \frac{1}{k})^2 a + \cdots = a \]

Oresme also proved that the sums

\[ 1 + \frac{1}{2}, 1 + \frac{1}{2} + \frac{1}{3}, 1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4}, \ldots \]

do not approach any number, even though the numbers added get smaller and smaller. His ingenious argument can be summarized into the following inequalities:

\[ 1 + \frac{1}{2} + (\frac{1}{3} + \frac{1}{4}) > 1\frac{1}{2} + (2 \times \frac{1}{4}) = 2 \]

\[ 1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + (\frac{1}{5} + \frac{1}{6} + \frac{1}{7} + \frac{1}{8}) > 2 + (4 \times \frac{1}{8}) = 2\frac{1}{2} \]

\[ 1 + \frac{1}{2} + \frac{1}{3} + \cdots + \frac{1}{8} + (\frac{1}{9} + \frac{1}{10} + \cdots + \frac{1}{16}) > 2\frac{1}{2} + (8 \times \frac{1}{16}) = 3 \]
By induction, we get the general inequality

\[ 1 + \frac{1}{2} + \frac{1}{3} + \cdots + \frac{1}{n} > 1 + \frac{n}{2} \]

Intuitively this means that by adding sufficiently many terms, the sum can be made as large as we please. For example,

\[ 1 + \frac{1}{2} + \frac{1}{3} + \cdots + \frac{1}{1998} > 1000 \]

It is interesting to contrast this with the fact that the sums

\[ 1 + \frac{1}{2^2}, 1 + \frac{1}{2^2} + \frac{1}{3^2}, 1 + \frac{1}{2^2} + \frac{1}{3^2} + \frac{1}{4^2}, \cdots \]

get closer and closer to \( \frac{1}{6}\pi^2 \), which in modern notation can be written

\[ 1 + \frac{1}{2^2} + \frac{1}{3^2} + \cdots = \frac{1}{6}\pi^2 \]

This was discovered by Euler in the 18\textsuperscript{th} century.

Such approximations through summation also arose in another context. In ancient astronomy, there was often the need to compute the length of a chord of a circle in terms of the arc length and this cannot be done using any of the usual arithmetic operations. In the second century CE, the Greek astronomer Claudius Ptolemy computed a table of chords of arcs differing by \( \frac{1}{2} \)\degree, using geometric techniques. In the 14\textsuperscript{th} century, Madhavan of Keralam gave this method to compute half the chord of double the arc:

\[ \text{Multiply the square of the arc by the the radius and take the result of repeating that. Divide by the squares of the successive even numbers increased by that number and multiplied by the square of the radius. Place the arc and the successive results so obtained one below the other and subtract each from the one above. These together give the half-chord} \]
Taking the radius of the circle as $r$, the arc length as $s$ and the chord length as $c$ as in the figure above, Madhavan’s method can be translated as follows. First compute the two rows of numbers:

\[
\begin{array}{c|c|c|c}
 & s & s \times s^2 & s \times s^2 \times s^2 \\
\hline
s & s^2 & s^2 & s^2 \\
\frac{s}{(2^2 + 2)r^2} & \frac{s^3}{(2^2 + 2)r^2} & \frac{s^5}{(2^2 + 2)r^2} \\
\frac{s^2}{(4^2 + 4)r^2} & \frac{s^4}{(4^2 + 4)r^2} & \frac{s^6}{(6^2 + 6)r^2} \\
\end{array}
\]

Successive subtractions as instructed gives

\[
\frac{1}{2}c = s - \left( \frac{s^3}{(2^2 + 2)r^2} - \left( \frac{s^5}{(2^2 + 2)(4^2 + 4)r^4} - \left( \frac{s^7}{(2^2 + 2)(4^2 + 4)(6^2 + 6)r^6} - \cdots \right) \right) \right)
\]

This can be stated in terms of trigonometry, by taking the corresponding arc length of unit radius as $x$:

\[
\sin x = x - \frac{1}{3!} x^3 + \frac{1}{5!} x^5 - \frac{1}{7!} x^7 + \cdots
\]

Two important consequences of this must be emphasized. The first is practical: it gives a purely numerical method for computing lengths of chords from arc lengths, as opposed to the geometric methods employed till then. The second is theoretical:
the geometrical definition of \( \sin x \) as the half-chord of arc length \( 2x \) in a circle of unit radius is meaningful only for \( 0 < x < \frac{\pi}{2} \), whereas Madhavan’s series converges (gets closer and closer to a number) for any real number \( x \); so, this series extends the definition of \( \sin \) to a function on the set of all real numbers.

A rigorous definition of convergence and limits of sequences was not made even as late as the 18th century. The French mathematician Augustin-Louis Cauchy made an attempt in the 19th century:

A series is an definite sequence of quantities,

\[ u_0, u_1, u_2, \ldots \]

which succeed each other according to a fixed law ... Let

\[ s_n = u_0 + u_1 + u_2 + \cdots + u_{n-1} \]

be the sum of the first \( n \) terms, where \( n \) is an arbitrary integer. If the sums \( s_n \) approaches a certain limit \( S \) indefinitely for increasing values of \( n \), then the series is said to be convergent, and the limit in question is called the sum of the series.

Cauchy also defined the idea of limits in a general way:

When the values successively attributed to the same variable approach a fixed value indefinitely, in such a way as to end up by differing from it as little as one could wish, this last value is called the limit of all the others.

The modern definition was first given by the Czech mathematician Bernhard Bolzano and later by the German mathematician Karl Weierstrass during the same century:

A sequence \( x_1, x_2, x_3, \ldots \) of numbers is said to converge to a limit \( a \) if for every \( \varepsilon > 0 \), there exists a natural number \( p \) such that \( |x_n - a| < \varepsilon \) for all \( n \geq p \)

This together with Cauchy’s definition gives a rigorous definition of the sum of an infinite series also.

3 Limits of functions

For an object dropped down from a height, it is known he distance \( s \) traveled (in meters) in time \( t \) (in seconds) is given by the equation

\[ s = 4.9t^2 \]

From this we see that in the first second, it falls 4.9 meters and in the second second, \((4.9 \times 4) - 4.9 = 14.7\) meters. Thus the distance traveled for the same interval of
time varies, and this means speed varies. The problem is how we can find speed at a particular instant.

This was the kind of problem which Isaac Newton of England considered in the 17th century, leading to the invention of differential calculus. Newton’s solution is to consider the average speeds for shorter and shorter time intervals. We see that the average speed during the 1 second from 1 to 2 seconds is 14.7 meters/second; that during the 0.5 second from 1.5 to 2 seconds is

\[
\frac{(4.9 \times 4) - (4.9 \times 1.5^2)}{0.5} = 17.15 \text{ meters/second}
\]

and so on. We can even make a table of average velocities for increasingly short time intervals ending or beginning at 2 seconds:

<table>
<thead>
<tr>
<th>Time interval</th>
<th>Average Speed</th>
<th>Time interval</th>
<th>Average Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9–2</td>
<td>19.11</td>
<td>2–2.1</td>
<td>20.09</td>
</tr>
<tr>
<td>1.99–2</td>
<td>19.551</td>
<td>2–2.01</td>
<td>19.649</td>
</tr>
<tr>
<td>1.999–2</td>
<td>19.5951</td>
<td>2–2.001</td>
<td>19.6049</td>
</tr>
<tr>
<td>1.9999–2</td>
<td>19.59951</td>
<td>2–2.0001</td>
<td>19.60049</td>
</tr>
</tbody>
</table>

We see that the average speeds get closer and closer to 19.6 meters/second and we define this as the instantaneous speed at 2 seconds. Thus the problem can be rephrased like this:

What happens to the fractions

\[
\frac{\text{distance difference}}{\text{time difference}}
\]

as time difference is made smaller and smaller?

Newton also considered the mathematical content of this physical problem:

For a function of \( f \) real numbers, what happens to the fractions

\[
\frac{f(x) - f(c)}{x - c}
\]

as \( x \) is given values closer and closer to \( c \)?

Later mathematicians also considered the more general problem:

For a function of \( f \) real numbers defined at points arbitrarily close to a real number \( c \), but not necessarily at \( c \), what happens to \( f(x) \) as \( x \) is given values closer and closer to \( c \)?
This led to the idea of the limit of a function at a point. It took several centuries to arrive at a rigorous definition of this. Newton himself stated it as follows:

Quantities, and the ratios of quantities, which in any finite time converge continually to equality, and before the end of that time approach nearer to each other than by any given difference, become ultimately equal

In the 18th century, the French mathematician Jean le d’Alembert tried to make this more precise:

One quantity is the limit of another, if the second can approach the first nearer than by any pre-assigned quantity

We have already seen how Cauchy attempted a definition of limit in the 19th century. Later in the century, Weierstrass gave the following definition:

A number $y_0$ is said to be the limit of the function $f(x)$ as $x$ tends to $x_0$ if for each $\epsilon > 0$, there exists $\delta > 0$ such that $|f(x) - y_0| < \epsilon$ for each $x$ with $|x - x_0| < \delta$

It is this definition with some minor modifications (we now refer to the function $f$, rather than $f(x)$) that we use today.

4 Conclusion

The foregoing discussion shows how the mathematical notion of limit originates from certain physical concepts and slowly develops in the course of time to a purely mathematical concept. This is the rule rather than the exception—all mathematical ideas, however abstract it maybe now, actually arises from certain physical problems and sometimes take centuries to evolve into a purely mathematical definition. Unfortunately this is turned upside down in the classrooms, where rigorous mathematical definitions are given first and some “applications” (if at all) are done later. This reduces mathematics to a mystical manipulation of symbols to most students. Tracing the historical evolution of the concepts will surely make mathematics more interesting and meaningful for the learners.
Finite Fields
A R Rajan
Department of Mathematics
University of Kerala, Thiruvananthapuram
Kerala, India - 695 581

1 Introduction

Fields provide a platform where all the usual arithemetic operations can be performed. Addition, subtraction, multiplication and division can be carried out in a field for every pair of elements except that division by zero is avoided. When we consider the number system, the set \( \mathbb{N} \) of all natural numbers admit addition for every pair but not subtraction. When we consider the set \( \mathbb{Z} \) of all integers we have addition, subtraction and multiplication but not division always. The set \( \mathbb{Q} \) of rational numbers admits all the four operations, of course avoiding division by zero.

2 Fields

A field can be defined as a system \((F, +, \cdot)\) where \((F, +)\) is an abelian group and \((F^*, \cdot)\) is also an abelian group where \(F^* = F \setminus \{0\}\). Further the distributive law for multiplication over addition holds. The natural examples of fields are:

i. the field \( \mathbb{Q} \) of rational numbers.

ii. the field \( \mathbb{R} \) of real numbers.

iii. the field \( \mathbb{C} \) of complex numbers.

All the above fields are infinite. Finite fields naturally occur as fields of residue classes of numbers taken modulo a prime number.

For a natural number \( n \) we denote \( \mathbb{Z}_n = \{0, 1, 2, \ldots, n - 1\} \). Defining addition mod \( n \), \( (\mathbb{Z}_n, +) \) is an abelian group. In \( \mathbb{Z}_n \), multiplication also can be defined mod \( n \) so that \( (\mathbb{Z}_n, +, \cdot) \) become a ring. In general \( \mathbb{Z}_n \) is not a field as certain non zero elements may not have multiplicative inverse. For example in \( \mathbb{Z}_6 \), 2, 3 and 4 have no multiplicative inverse.
When \( n \) is a prime number \( \mathbb{Z}_n \) becomes a field with respect to addition and multiplication \( \mod n \). Usually a prime number is denoted by \( p \) and we see that \( \mathbb{Z}_p \) is a field. This follows from the observation that if \( p \) is a prime and \( a < p \) and \( a \neq 0 \) then \( a \) and \( p \) are relatively prime. So \( an + pm = 1 \) for some integers \( n \) and \( m \). Choose some \( b < p \) and \( b > 0 \) such that \( n \equiv b(\mod p) \). Then \( ab = 1 \) in \( \mathbb{Z}_p \). Thus we get a class of finite fields as \( \mathbb{Z}_p \) for some prime \( p \).

The first question that arises is: Are they all the finite fields. The answer is ‘No’ and we proceed to describe methods of constructing other finite fields.

One general method in field theory for constructing larger field from a given field is known as extensions. Given a field \( F \), an extension of \( F \) is field \( K \) such that \( F \) is a subfield of \( K \). In practice this \( K \) is obtained by adjoining more elements to \( F \) and so the process is known as extension process.

As a simple case consider the field \( \mathbb{Q} \) of rational numbers. Consider the irrational number \( \sqrt{2} \). Let us extend \( \mathbb{Q} \) by adjoining \( \sqrt{2} \) to \( \mathbb{Q} \) and denote the new field by \( \mathbb{Q}(\sqrt{2}) \). The field operations require that together with \( \sqrt{2} \) several other elements also should belong to \( \mathbb{Q}(\sqrt{2}) \). What are these elements? For any \( a, b \in \mathbb{Q} \) we need that \( a\sqrt{2}, b + a\sqrt{2}, \frac{1}{\sqrt{2}}, \cdots \in \mathbb{Q}(\sqrt{2}) \). It can be observed that \( \{a + b\sqrt{2}: a, b \in \mathbb{Q}\} \) includes all the above elements. For example \( \frac{1}{\sqrt{2}} = \frac{1}{2}\sqrt{2} \). It follows that \( \mathbb{Q}(\sqrt{2}) = \{a + b\sqrt{2}: a, b \in \mathbb{Q}\} \) and that \( \mathbb{Q}(\sqrt{2}) \) is a field. Similarly we can extend \( \mathbb{Q}(\sqrt{2}) \) to \( \mathbb{Q}(\sqrt{2}, \sqrt{3}) \) etc. by adjoining more elements.

Similar procedure can be applied to finite fields also. For example consider the field \( \mathbb{Z}_3 = \{0, 1, 2\} \) of three elements where addition and multiplication are taken \( \mod 3 \). Clearly \( \sqrt{2} \notin \mathbb{Z}_3 \) as \( 1^2 \neq 2 \); \( 2^2 \neq 2 \). Consider \( \mathbb{Z}_3(\sqrt{2}) \). Now \( \mathbb{Z}_3(\sqrt{2}) = \{0, 1, 2, \sqrt{2}, 2\sqrt{2}, 1 + \sqrt{2}, 1 + 2\sqrt{2}, 2 + \sqrt{2}, 2 + 2\sqrt{2}\} \) and \( \mathbb{Z}_3(\sqrt{2}) \) has 9 elements. It can be seen that \( \mathbb{Z}_3(\sqrt{2}) \) is a field. For example here \( \frac{1}{1 + \sqrt{2}} = 2 + \sqrt{2} \). Now let us consider the question of order of a finite field. So far we have seen finite field of order \( p \), where \( p \) is a prime and of order 9, the field \( \mathbb{Z}_3(\sqrt{2}) \).

Let \( F \) be a field of order \( q \), which is an extension of \( \mathbb{Z}_p \). Then what are the possible values of \( q \)? A small amount of linear algebra will give easy answers here. It is easy to see that in this case \( F \) is a vector space over \( \mathbb{Z}_p \). Let \( n \) be the dimension of \( F \) over \( \mathbb{Z}_p \) and let \( \{\alpha_1, \alpha_2, \ldots, \alpha_n\} \) be a basis of \( F \) over \( \mathbb{Z}_p \). Then \( F = \{a_1\alpha_1 + a_2\alpha_2 + \cdots + a_n\alpha_n: a_i \in \mathbb{Z}_p\} \). So \( |F| = p^n \) and we have the following result.

**Theorem 2.1.** Let \( F \) be a finite field and \( F \) be an extension of \( \mathbb{Z}_p \). Then \( |F| = p^n \) for some natural number \( n \).

Two questions naturally arise now.

I. For any finite field \( F \) it is true that \( |F| = p^n \) for some prime \( p \).

II. For every prime \( p \) and every natural number \( n \), does there exist a field of order \( p^n \).
We proceed to show that both of the bove questions have answer “YES”. To answer the first question we consider an invariant associated with fields called characteristic of the field. For a finite field \( F \) the characteristics of \( F \) is defined as the smallest positive integer \( p \) such that \( 1 + 1 + \cdots + 1 = 0 \) where the sum is taken with \( p \) terms. Here \( 1 \) is the multiplicative identity in \( F \). Note that for \( \mathbb{Z}_2 = \{0, 1\} \), \( 1 + 1 = 0 \) and so characteristic of \( \mathbb{Z}_2 \) is 2. Similarly characteristic of \( \mathbb{Z}_p \) is \( p \). It is easy to observe that every finite field has a positive characteristic and that it is a prime number.

Note that for infinite fields \( 1 + 1 + \cdots + 1 \) added any number of times may not be zero. For example in \( \mathbb{Q} \) or \( \mathbb{R} \), \( 1 + 1 + \ldots \) never zero. In such cases we say that characteristic is zero.

Note let \( F \) be a finite field. Then \( F \) has characteristic \( p \) for a prime \( p \). In this case \( \mathbb{Z}_p \) can be realised as a subfield of \( F \). Thus \( F \) is an extension of \( \mathbb{Z}_p \). Thus \(| F | = p^n\) for some \( n \) and this answers Question I above.

Now we consider the problem regarding existence of finite field of order \( p^n \) for any prime \( p \) and any natural number \( n \).

First we observe that the general method of construction of extension fields by adjoining zeros of polynomials. Consider a field \( F \) and a polynomial \( f(x) \in F[x] \). Then \( f(x) \) may or may not have zeros in \( F \). There is a well known theorem in field extension referred as Kronecker’s theorem saying that given \( f(x) \in F[x] \) there is an extension field \( K \) of \( F \) such that \( f(x) \) has a zero in \( K \). Further it is known that corresponding to every field \( F \) there is an extension \( \overline{F} \) of \( F \) with the property that every polynomial \( f(x) \in F[x] \) factors as a product of linear polynomials in \( \overline{F}[x] \). This will mean that if \( f(x) \) is of degree \( n \) then \( f(x) \) has \( n \) zeros in \( \overline{F} \) where the zeros are counted with multiplicities and \( \overline{F} \) is called an algebraic closure of \( F \).

Now we construct a field of order \( p^n \) using zeros of a polynomial over \( \mathbb{Z}_p \). To locate such a polynomial we consider some of the relations in a finite field. Suppose that \( F \) is a field of \( p^n \) elements which is an extension of \( \mathbb{Z}_p \). Let \( q = p^n \). Then the multiplicative group of nonzero elements of \( F \) is of order \( q - 1 \). So \( a^{q-1} = 1 \) for all \( a \in F \setminus \{0\} \), and so \( a^q = a \) for all \( a \in F \). It follows that all elements of \( F \) are zeros of the polynomial \( x^q - x \in \mathbb{Z}_p[x] \). We use this polynomial in constructing a field of order \( q = p^n \), as given by the following theorem.

**Theorem 2.2.** Let \( p \) be a prime and \( n \) be a positive integer. Let \( \overline{\mathbb{Z}}_p \) be an algebraic closure of \( \mathbb{Z}_p \). Let \( q = p^n \) and \( f(x) = x^q - x \in \mathbb{Z}_p[x] \). Let \( F = \{ \alpha \in \overline{\mathbb{Z}}_p : f(\alpha) = 0 \} \). Then \( F \) is a subfield of \( \overline{\mathbb{Z}}_p \) and \( F \) is a field of order \( p^n \).

**Proof.** First note that \( f(x) \) has \( q = p^n \) distinct zeros in \( \overline{\mathbb{Z}}_p \). This is seen by taking the formal derivative \( f'(x) \) of \( f(x) \). Here \( f'(x) = qx^{q-1} - 1 = -1 \) in \( \mathbb{Z}_p[x] \). If \( f(x) \) has a zero \( \alpha \) of multiplicity more than one then \( f'(\alpha) \neq 0 \). In this case \( f'(\alpha) \) is never zero and all the zeros of \( f(x) \) are distinct. Thus \( f(x) \) has \( q \) distinct zeros and so \(| F | = q \).

To see that \( F \) is a subfield of \( \overline{\mathbb{Z}}_p \), observe the following for \( \alpha, \beta \in F \).
(α + β)^q = α^q + β^q = α + β
(α - β)^q = α^q - β^q = α - β
(αβ)^q = α^qβ^q = αβ
(\frac{1}{α})^q = \frac{1}{α^q} = \frac{1}{α} for α ≠ 0

Thus F is field of p^n elements.

3 Example

Here we consider constructing fields of order 4, 8 etc. Consider the polynomial
\[ p(x) = x^2 + x + 1 \in \mathbb{Z}_2[x] \]. Clearly p(x) has no zero in \( \mathbb{Z}_2 \). Let α be a zero of p(x) in \( \mathbb{Z}_2 \). Consider the field obtained by adjoining α to \( \mathbb{Z}_2 \). Since α^2 + α + 1 = 0, we see that α^2 = α + 1. So the field \( \mathbb{Z}_2(α) = \{0, 1, α, 1 + α\} \). The operations + and · are extended to \( \mathbb{Z}_2(α) \) from \( \mathbb{Z}_2 \) as follows:
\[
α + (1 + α) = 1; 1 + (1 + α) = α; α + α = 0; (1 + α) + (1 + α) = 0
\]
\[
α · (1 + α) = 1; α^2 = (1 + α); α^3 = 1; etc.
\]

Similarly a field of order 8 is constructed using the polynomial \( g(x) = x^3 + x + 1 \in \mathbb{Z}_2[x] \). Here g(x) has no zero in \( \mathbb{Z}_2 \); choose α \in \( \mathbb{Z}_2 \) such that g(α) = 0. It follows that
\[
F = \mathbb{Z}_2(α) = \{0, 1, α, α^2, 1 + α, α + α^2, 1 + α + α^2, 1 + α^2\}.
\]

Observe that α^3 = 1 + α, α^4 = α + α^2; α^5 = 1 + α + α^2; α^6 = 1 + α^2 and α^7 = 1. So the field F may also be represented as
\[
F = \{0, 1, α, α^2, α^3, α^4, α^5, α^6\}
\]

References


Recent Trends in Materials Research

Sam Solomon
Department of Physics
St. John’s College, Anchel, Kollam
Kerala, India - 695 581

1 Introduction

The field of materials science and engineering is often defined by the interrelationship between four topics: synthesis, structure, properties and performance. Crystalline materials have a very regular atomic arrangement whereas in non-crystalline or amorphous materials there is no long-range order. The crystals in which grain boundaries are absent are termed as single crystals and those possess grain boundaries are called as polycrystals. Polycrystalline materials consist of many grains and the size, shape and orientation of the grains play a key role in many of its macroscopic properties. The strength of the polycrystalline ceramics depends on the grain size. The particle size of the sample can be controlled using different types of synthesizing techniques. For example, nanometer scale materials can be prepared using the combustion methods while the micro scale materials can be synthesized using the solid state ceramic route.

To understand the behavior and properties of any material, it is essential to understand its structure. There are so many methods characterization of materials. These techniques can be categorized into six as mentioned below.

- Imaging using visible(or nearly visible) light
- Imaging using electrons[mainly scanning electron microscopy(SEM) and transmission electron microscopy(TEM)]
- Imaging using sensing[atomic force microscopy(AFM) and other scanned probes that “sense”a force or field]
- Scattering and diffraction(using X-rays, neutrons, electrons etc.)
- Spectroscopy and spectrometry(using X-rays for energy dispersive spectrometry(EDS) and wavelength dispersive spectroscopy(WDS), infrared(IR), etc.)
- Thermal analysis (measuring changes, e.g., enthalpy, as a function of temperature)

The suitability of a characterization technique depends on the type of information we hope to obtain and may also be dictated by the size of our sample, what part of the sample is important, and whether we can destroy the sample. The summary of the tools for the characterization of materials are given in Table 1.

<table>
<thead>
<tr>
<th>Chemical characteristic</th>
<th>Characterization tool</th>
</tr>
</thead>
</table>
| Composition             | X-ray diffraction(XRD)  
                          | X-ray fluorescence(XRF) 
                          | Neutron activation analysis(NAA)  
                          | Mass spectrometry(Mass Spec) |
| Elemental distribution or local Chemistry energy dispersive | Scanning electron microscope(SEM) with  
                          | X-ray spectroscopy,  
                          | Electron probe microanalysis(EPMA)  
                          | Transmission electron microscopy(TEM) with XEDS  
                          | TEM with electron energy-loss spectroscopy(EELS) |
| Surface/interface chemistry | X-ray photoelectron spectroscopy  
                          | Auger electron spectroscopy(AES)  
                          | Secondary ion mass spectroscopy(SIMS)  
                          | Rutherford backscattering spectrometry(RBS)  
                          | Ultraviolet photoelectron spectroscopy(UPS)  
                          | Raman spectroscopy |
| Phase changes (e.g. decomposition and dehydration) | Thermomechanical analysis(TMA)  
                          | Thermogravimetric analysis(TGA)  
                          | Differential thermal analysis(DTA)  
                          | Differential scanning calorimetry(DSC)  
                          | Mass Spec(MS) |
| Surface area/porosity | Small-angle neutron scattering(SANS)  
                          | Small-angle X-ray scattering(SAXS)  
                          | Mercury porosimetry |
### Table 1 (continued)

<table>
<thead>
<tr>
<th>Chemical characteristic</th>
<th>Characterization tool</th>
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<tr>
<td>Density/ homogeneity</td>
<td>VLM, SEM</td>
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<td>X-ray radiography/CT scan</td>
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<td>Ultrasound</td>
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<td></td>
<td>Die penetration</td>
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<tr>
<td>Particle/grain size, distribution, morphology and texture</td>
<td>VLM and quantitative stereology</td>
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<tr>
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<td>SEM and quantitative stereology</td>
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<td></td>
<td>Electron backscattering spectroscopy (EBSD)</td>
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<td></td>
<td>TEM, XRD</td>
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<tr>
<td>Phase identification/ molecular Structure</td>
<td>XRD</td>
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<td></td>
<td>Electron backscattering spectroscopy (EBSD)</td>
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<td>FTIR, Raman spectroscopy</td>
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<td>Neutron diffraction</td>
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<td></td>
<td>Mossbauer spectroscopy</td>
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<tr>
<td></td>
<td>Nuclear magnetic resonance (NMR)</td>
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<tr>
<td>Phase transitions (eg. structural transformations)</td>
<td>DTA</td>
</tr>
<tr>
<td></td>
<td>DSC, TMA</td>
</tr>
</tbody>
</table>

Since we cannot cover all the techniques, the discussion is limited to the key ones for the investigations on crystal structure and micro structure.

## 2 Analysis of crystal structure

Understanding the crystalline structure of materials is critical in understanding many of their properties like diffusion, deformation by slip or twinning, piezoelectricity, thermal conductivity, cleavage, ferromagnetism etc. X-ray diffraction analysis and vibrational spectroscopy are the two major techniques to analyze the crystal structure.
2.1 X-ray diffraction (XRD)

The atomic arrays in a crystal together will act just like the planes in a transmission grating. The X-rays falling on these arrays undergo diffraction according to Bragg’s law

\[ 2d \sin \theta = n\lambda \]

where \( d \) is interplanar spacing, \( \lambda \) is the X-ray wavelength and \( \theta \) is the Bragg angle.

Bragg made the first direct determination of a crystal structure using X-ray diffraction (XRD), which is still generally the most accurate method for characterizing crystal symmetry. Powder XRD is one of the most widely used techniques to characterize polycrystalline materials. The material is in the form of powder so that the grains will be present in all possible orientations so that all \( d \) spacings, or \( \lambda \) values, will appear in one pattern. Now the data are in the form of a plot (known as a diffractogram) of counts or intensity versus scattering angle (2\( \theta \)). One of the most useful sources of information for crystal structure data is the Powder Diffraction File (PDF) from the International Centre for Diffraction Data (ICDD). The PDF is a collection of single-phase X-ray powder diffraction patterns in the form of tables of interplanar spacings (\( d \)) and corresponding relative peak intensities. Reitveld analysis is one of the commonly used softwares for the for the structural analysis using XRD data.

![Fig 1. XRD apparatus showing the source sample and detector (Siemens D5005)](image)

The main components of an X-ray diffractometer include: X-ray source- Often CuK\( \alpha \), \( \lambda = 0.154060 \) nm because of its high intensity; sample- usually a powder, but it can be pressed or sintered; detector- there are two main types: proportional detectors use photoelectrons generated in Xenon and semiconductor detectors use electron-hole pairs created in p-n junctions formed in silicon. In the \( \theta/2\theta \) X-ray diffractometer, the sample and detector rotate relative to the X-ray source; when one moves through \( \theta \), the other moves through \( 2\theta \). Alternatively, the sample can be held fixed and the detector and source rotated in opposite directions. The conventional XRD geometry is often referred to as the Bragg-Brentano geometry.
different geometries and modifications are used for studying ceramics. Fig 1. shows an XRD apparatus showing the location of the source, sample and detector.

The incident X-rays get diffracted according to the Bragg’s law from the crystallites of finely powdered samples kept in the specimen holder. Samples are analyzed as powders with grains in random orientations to ensure that all crystallographic directions are “sampled” by the beam. When the Bragg condition for constructive interference is obtained, a “reflection” is produced, and the relative peak height is generally proportional to the number of grains in a preferred orientation. The X-ray spectra generated by this technique provide the structural fingerprint of the unknown crystalline materials. Mixtures of crystalline materials can also be analyzed and relative peak heights of multiple materials may be used to obtain semi-quantitative estimates of abundances. In addition, changes in peak position that represent either compositional variation (solid solution) or structure-state information (eg. order-disorder transitions) are readily detectable. The determination of the presence of impurities in a pure phase can also be done using X-ray diffraction studies. With modern X-ray optics and detectors, it is possible to detect impurities below 0.1 weight % which gives information for the optimization of the synthesis of the material, and for quality control.

2.1.1 Calculation of lattice parameters and theoretical density

Figure 2 is the XRD pattern of CaNb$_2$O$_6$ (CNO) polycrystal. The data obtained in Table 2 is plotted using origin software with 2θ values along the X axis and the corresponding intensity along the Y axis. All the major peaks are indexed on the basis of the most matching ICDD file 39-1392. Phase pure orthorhombic XRD pattern can be seen in the figure. For the orthorhombic crystal structure, the relationship between inter planar distance($d$), the Miller indices($h, k, l$) and the lattice parameters ($a, b, c$), is given by

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$  \hspace{1cm} (1)

- Step 1: Take a set of 3 reflections and their $h, k$ and $l$ values.
- Note the corresponding $d$ values from the XRD data.
- Substitute all the values in equation 1 to get three equations
- Solve these equations to get one set of $a, b$ and $c$ values.
- Repeat the same different sets of three 3 reflections each.
- Take the average of the obtained $a, b$ and $c$ values.

The cell volume of an orthorhombic structure is

$$V = abc$$  \hspace{1cm} (2)
Then the theoretical density of a poly crystal is given by

\[
\text{Theoretical density } \rho = \frac{\text{formula weight} \times \text{No: molecules per unit cell} \times 1.67 \times 10^{-24}}{\text{Cell Volume}}
\]

Fig 2. The XRD pattern of CaNb$_2$O$_6$ polycrystal

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</table>

2.1.2 Determination of particle size using XRD

The XRD data of nano crystalline CaHfO$_3$ is given in Table 3. The corresponding pattern is as shown in Fig 3. The structure is cubic and can be indexed according to the ICDD file.

![Fig 3. The XRD pattern of CaHfO$_3$ nanocrystal](image)

Particle size from the XRD pattern of any material can be calculated using Scherrer formulae

$$\text{Particle size} = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (3)

where $\lambda$ is the wave length of X-ray, $\beta$ is the full width half maximum and $\theta$ is the angle of diffraction.

From the data,

$$\lambda = 1.54060 \times 10^{-10} m, \quad \beta = 0.6203^\circ = 0.6203 \times \pi / 180 = 0.010826 rad, \quad \theta = 15.90805^\circ$$
Substituting these values in equation 3

\[
\text{Particle size} = \frac{0.9 \times 1.5406 \times 10^{-10}}{0.010826 \times \cos(15.9)} = 12.807 \text{nm}
\]

<table>
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</table>

2.2 Vibrational Spectroscopy

Electromagnetic spectroscopy involves the interaction of electromagnetic waves and matter. We can use all regions of the electromagnetic spectrum and each will give specific information about a material. Fourier Transform Infrared(FTIR) and FT Raman, the vibrational spectroscopy, both involve the scattering of light.

2.2.1 FTIR spectroscopy

Light is polychromatic and couples to vibrational modes in the solid through dipole moments, which are associated with the vibration. These vibrational modes cause a dip in the transmission spectra or a peak in the absorption spectra. The IR range is from 0.78 to 1000 µm (12.820 to 10 cm\(^{-1}\)). The region where most fundamental vibrational modes occur, which is the most useful for materials characterization, is between 2.5 and 25µm (4000-400 cm\(^{-1}\)). This is sometimes called the mid-IR region. The light source is a heated material (usually a conducting ceramic or a wire heater coated with ceramic) that emits a range of frequencies. An important variant is the FTIR spectrometer. The main advantages of FTIR are that it is much quicker because it measures all the frequencies simultaneously and it is more sensitive than dispersive IR spectrometers.

The key component of an FTIR is the interferometer, which can be understood by considering the Michelson interferometer shown in Figure 4. A parallel beam directed from the source is split at BS so that 50% of the light is transmitted and reflected back by mirror Mf, while the rest is reflected at Bs and then again at Mm.
2.2.2 FT Raman spectroscopy

In Raman spectroscopy, the light is nearly monochromatic and is usually in the visible range. The light source is a laser, e.g., a 50 mW, 785 nm diode laser. Raman spectroscopy has become a routine tool for exploring the structure and chemical properties of materials. It can provide more information than IR spectroscopy. There are three types of signal in a typical Raman experiment as illustrated in Figure 5. The scattering process can be anti-Stokes, Rayleigh, or Stokes. We are then interested in measuring the intensity and the Raman shift. In Rayleigh scattering, a molecule is excited by the incident photon to a virtual energy level. This energy level is caused by a distortion of the electron distribution of a covalent bond. The molecule returns to the vibrational ground state by emitting the same energy, $E_0 (E_0 = h\nu_0)$. Rayleigh scattering is an elastic process. Vibrational excitations can be created, which causes a decrease in the frequency (i.e., in energy) of the scattered light, or they can be annihilated, which causes an increase. The decrease in frequency is called Stokes scattering and the increase is anti-Stokes scattering. Stokes scattering is the normal Raman effect and Raman spectroscopy generally uses Stokes radiation.
2.2.3 Structural analysis using FTIR and FT Raman

The FTIR and FT Raman analysis are supporting to each other for almost all the materials. Factor group analysis is the base of these spectroscopic methods. On the basis of group theory we can predict the IR and Raman active modes of vibration of a particular composition. By comparing these modes of vibration with those of standard or reported materials the structure of the composition can be elucidated. Let us discuss this in the case of MgTiO$_3$ nano crystal.

Fig 6 shows the FT-IR spectra of (a) the as-prepared MgTiO$_3$, (b) the sample heated at 400$^\circ$C and (c) the sample heated at 800$^\circ$C, for 1 h. In Fig 6(a) and 6(b) very broad and intense absorption bands are observed in the region of the stretching
and bending vibration of the water molecules, indicating the presence of NH$_4^+$ ions, in addition to the water adsorbed during pelletization. The band at 3408 cm$^{-1}$ is due to the stretching vibrations of water molecules and that at 3149 and 2979 cm$^{-1}$ are due to the asymmetric and symmetric stretching vibrations of NH$_4^+$ ions. The band at 3408 cm$^{-1}$ is due to the stretching vibrations of water molecules and that at 3149 and 2979 cm$^{-1}$ are due to the asymmetric and symmetric stretching vibrations of NH$_4^+$ ions. The weak absorption band at 1765 cm$^{-1}$ may be a combination band. A substantial reduction in the intensity of the bands due to NH$_4^+$ ions is observed when the sample is heated up to 400$^\circ$C which in turn indicates the expulsion of more and more NH$_4^+$ ions, as the powder is heated. The reduction in the intensity of the and modes revealed three sharp bands at 2979, 2913 and 2848 cm$^{-1}$ which is the region of the stretching modes of CH$_3$ and CH$_2$ groups. The intensity of the band at 1377 cm$^{-1}$ has reduced and shifted to 1384 cm$^{-1}$, unveiling two bands, one at 1427 cm$^{-1}$ and another at 1042 cm$^{-1}$. The band at 1427 cm$^{-1}$ may be due to the CH$_3$/CH$_2$ group. The weak bands at 1042, 875 and 715 cm$^{-1}$ may be due to the vibrations of NO$_3^-$ ions.

In agreement with the earlier reports on MgTiO$_3$ prepared by the conventional method the XRD measurements made in the present study also show that nanocrystalline MgTiO$_3$ has a rhombohedral(hexagonal) structure with space group having two formula units per unit cell. The predicted ten Raman active and eight IR active modes of vibrations, excluding the acoustical modes, are distributed as

The IR and Raman spectra of the sample heated at 800 $^\circ$C for 1 h are shown in Fig. 6(c) and Fig. 7, respectively. The IR and Raman bands confirm the rhombohedral(hexagonal) structure of MgTiO$_3$ of the eight IR active modes, four are observed in the region 680- 420 cm$^{-1}$.

![Raman spectrum of MgTiO$_3$ nanoparticles](image)

**Fig 7. Raman spectrum of MgTiO$_3$ nanoparticles**

The remaining four IR bands occur below 400 cm$^{-1}$. The bands observed, in the present study, are at 667 cm$^{-1}$, 550 cm$^{-1}$, 454 cm$^{-1}$ and 422 cm$^{-1}$. The ten Raman active modes are observed at 715 cm$^{-1}$, 641 cm$^{-1}$, 486 cm$^{-1}$, 398 cm$^{-1}$,
The mode contributed by the vibrations of O atoms expected at 500 cm$^{-1}$ has merged with the intense mode at 486 cm$^{-1}$ which is contributed by the antisymmetric breathing and twisting vibrations of the O octahedra. The broad shoulder at 727 cm$^{-1}$ in the IR spectrum and the weak Raman bands at 257 cm$^{-1}$ and 207 cm$^{-1}$ are due to the additional phase MgTi$_2$O$_5$. Lattice vibrations are observed as weak to medium intense bands below 200 cm$^{-1}$.

3 Microstructure

There are many methods to study the microstructure (morphology, grain size etc.) of material surfaces as discussed in Table 1. Among them the Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) are discussed in this section.

3.1 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope (SEM) is one that uses electrons rather than light to form an image. There are many advantages for using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. The layout of the SEM is shown in Fig. 8. The SEM can have two imaging detectors, one for secondary electrons (SEs) and one for higher-energy backscattered electrons (BSEs). The SEM typically has a resolution in SE mode of 0.7 nm (at 25 kV) and 2.5 nm in BSE mode at 5 kV. SEs are low-energy electrons so they are very sensitive to surface topology. BSEs are higher-energy electrons and are sensitive to the atomic number of the scattering atom. The BSE electrons penetrate further into the sample and have further to come out after being scattered. Hence the BSE image can give excellent mass discrimination even at low voltages.

A major difficulty in studying ceramic surfaces is that many do not conduct electricity well. Thus techniques using electron beams can have limited application. To study surfaces in the SEM we may need to coat the sample with C or even Pt to prevent charge building up on the surface and thus deflecting the electron beam. Working at lower accelerating voltages can also reduce charging effects, but then the resolution is compromised.
Using SEM with a field-emission gun a much more precise EDS profile analysis can be performed providing chemical analysis at a spatial resolution of ~2 nm. The X-ray energy dispersive spectrometry (XEDS) spectrum is a plot of counts versus X-ray energy. The X-rays are produced as a result of electron transitions within the atoms in the sample. The transitions and, hence, the peaks are characteristic of specific atoms.

Fig. 9 (a), (b) and (c) show the SEM images of MgTiO$_3$, Ca$_{0.05}$Mg$_{0.95}$TiO$_3$ and Ca$_{0.6}$Mg$_{0.4}$TiO$_3$ ceramics, respectively. The images clearly show that the samples are well sintered with minimum porosity. The grain size is approximately 7 $\mu$m for all the compositions. More than 95% of theoretical densities are obtained for all the samples except CaTiO$_3$, for which the experimental density of 93% is obtained.
From the Fig. 9(b) and 9(c), it is easy to notice that there are two different distributions of phases and which are distributed randomly both at the grain boundaries and into grains. The EDS analyses of MgTiO$_3$ and Ca$_{0.6}$Mg$_{0.4}$TiO$_3$ samples are given in Fig. 10(a) and 10(b), respectively. These spectra show that all the constituent elements are present in the samples in the same stoichiometric concentrations.

3.2 Transmission Electron Microscopy (TEM)

The key requirement for using TEM is that we require the sample to be very thin. So the technique is destructive and specimen preparation can be time consuming.
Recent Trends in Materials Research/ S Solomon

Fig. 11 shows a state-of-the-art TEM with a field emission source. Because of the large range of signals generated by the incident electron beam, a TEM allows full characterization of a sample at high resolution.

![TEM Image](image)

**Fig 11. A TEM with key features labeled**

The conventional imaging modes in a TEM are bright-field (BF) imaging and dark-field (DF) imaging. In BF imaging the image is formed using only the direct beam. An aperture (the objective aperture) is used to exclude all the diffracted electrons from contributing to the image. In DF imaging the image is formed from one of the elastically scattered beams and the objective aperture blocks the direct beam and all the other scattered electrons. The resolution of a TEM is determined by the energy of the electrons (controlled by the accelerating voltage), the thickness of the specimen (we want to avoid multiple scattering within the sample), the distance between the sample and the objective lens, and the inherent quality of the lens (defined by its spherical aberration coefficient). At present, the best high resolution TEM (HRTEM) has a resolution of \( \sim 0.08 \) nm, but 0.05 nm should be achievable. For nanotechnology an HRTEM is an essential tool. Selected-area diffraction (SAD) involves selecting an area on the sample (actually an image of the area) with an aperture and then looking at the diffracting pattern from that area. The diameter of the area can be as small as 100 nm with a modern machine. From the positions of the spots in SAD we can obtain information about the structure and orientation of the sample. Fig. 12(a) and 12(b) show the TEM image and the SAED pattern of (Ca/Mg)TiO\(_3\) (CMT) nanopowder, respectively. The TEM studies on the powder morphology of the CMT nanopowder shows well faceted particles of sharp boundaries, of submicron size 20-40 nm, with a mean size of 30 nm. Individual crystallites in the agglomerates appear well bonded with few voids in between. The ring nature of the electron diffraction pattern is indicative of the polycrystalline nature of the
crystallites, but the spotty nature of the SAED pattern in Fig. 12(b) can be due to the fact that the finer crystallites having related orientations are agglomerated together resulting in a limited set of orientations.

**Fig 12. TEM micrographs of (a) CMT nanopowder in bright field and (b) corresponding electron diffraction data**

### 3.3 Atomic Force Microscopy (AFM)

The topic of scanned probe microscopy (SPM) includes several different techniques, which grew out of the development of scanning tunneling microscopy (STM) (for which Binnig and Rohrer shared the Nobel Prize in 1986). One of the most important SPM is the Atomic Force Microscope (AFM). In atomic force microscopy a tip, integrated to the end of a spring cantilever, is brought within the inter-atomic separations of a surface; such that the atoms of the tip and the surface are influenced by inter-atomic potentials. As the tip is raftered across the surface, it bounces up and down with the contours of the surface. By measuring the displacement of the tip (i.e. the deflection of the cantilever), one can theoretically map out the surface topography with atomic resolution.

The principal behind the operation of an AFM in the contact mode is shown in Figure 13. The AFM tip is first brought (manually) close to the sample surface, and then the scanner makes a final adjustment in tip-sample distance based on a setpoint determined by the user. The tip, now in contact with the sample surface through any adsorbed gas layer, is then scanned across the sample under the action of a piezoelectric actuator, either by moving the sample or the tip relative to the other.

A laser beam aimed at the back of the cantilever-tip assembly reflects off the cantilever surface to a split photodiode, which detects the small cantilever deflections. A feedback loop maintains constant tip-sample separation by moving the scanner in the $z$ direction to maintain the setpoint deflection. Without this feedback loop, the tip would “crash” into a sample with even small topographic features (although this phenomenon can happen even with careful AFM operation). By maintaining a constant tip-sample separation and using Hooke’s Law ($F = -kx$ where $F$ is force,
k is the spring constant, and x is the cantilever deflection), the force between the tip and the sample is calculated. Finally, the distance the scanner moves in the z direction is stored in the computer relative to spatial variation in the x-y plane to generate the topographic image of the sample surface.

![Diagram of laboratory setup of the 3000 SPM](Image)

Fig 13. Laboratory set up of the 3000 SPM (Courtsy digital instruments, Santa Barbara, CA)

![AFM images of BaWO4 thin film](Image)

Fig 14. The 2-dimensional and 3-dimensional AFM images of BaWO4 thin film

Fig 14 shows the 2-dimensional and 3-dimensional AFM images of BaWO4 thin film. The rms surface roughness (low spatial frequency) and the average grain size can be calculated from these AFM images.
4 Advanced fields in materials research

Advanced materials research includes the synthesis and characterization of new materials and modifications to existing materials to obtain superior performance in one or more characteristics that are critical for the application under consideration. Most of the research fields in materials science are interrelated and are given below.

4.1 Nanotechnology

Nanotechnology is the engineering of functional systems at the molecular scale (1-100nm). The key components of Nanotechnology are:

- Nano-measurement technology:
  for analyzing and evaluating nano-structures with a spatial resolution at nanometer level
- Nano-creation technology:
  to process, create and form nano-structures
- Nano-simulation technology:
  a large-scale, high-speed computing technology

4.2 Dielectric materials

A dielectric is a poor conductor of electricity but an efficient supporter of electrostatic field. These Materials include ceramics, mica, glass, plastics, oxides of various metals.

4.3 Optical materials

Atoms and their electronic configurations in the material interact with the photons to determine the material’s macroscopic optical properties such as transmission and refraction. These Materials include Glass, Crystalline materials, Polymers, Plastic materials.

4.4 Energy Materials (Essential to build a low - carbon society)

Materials used to fabricate energy devices like Lithium batteries, Solar cells, Fuel cells. Types of fuel cells: Alkaline fuel cell (AFC), Polymer electrolyte membrane fuel cell (PEFC), Phosphoric acid Fuel cell (PAFC), Molten carbonate fuel cell (MCFC), Solid Oxide Fuel cells (SOFC).
1 Introduction

After a long recess increasingly large countries have been showing interest in establishing or upgrading their civilian nuclear programme in the new century. Though countries like Iran and North Korea may have strategic interests, the rest of the countries like UAE, Turkey, Vietnam, Chile, Jordan and Nigeria have signed up hoping that they would stand to benefit from the unfolding nuclear resurgence. Protagonists of nuclear renaissance argue their case on the basis of global energy deficit, rising costs, plateauing or declining fossil fuel supplies, unreliability of overseas sourcing of fuel and increasing concerns over climate change (World Nuclear Association). As of 2012, thirty one countries possessed operational commercial-scale nuclear energy infrastructure. Apart from these states fifty other countries have expressed interest in joining the nuclear bandwagon. This is despite the three major nuclear accidents that occurred in the Three Mile Island (1979), Chernobyl (1986) and Fukushima (2011) and a host of near total misses and accidents occurred in several reactors worldwide.

The propaganda that nuclear power as “clean, affordable and plentiful” has been proved otherwise in no other country than US which has a long history of nuclear energy production. The first chairman of the US Atomic Energy Commission, Lewis Strauss, predicted in a 1954 speech that nuclear power would someday make electricity “too cheap to meter”[10]. Half century later, we have learned that nuclear power is, instead, too expensive to finance. By 1985, Forbes a business magazine had labelled U.S. nuclear industry as “the largest managerial disaster in business history, a disaster on a monumental scale”[5]. Between 1950 and 1990, U.S. taxpayers and utilities spent $492 billion on the “direct” costs of nuclear power. Yet, by the 1980s (30 years after the industry received its first taxpayer handout), nuclear reactors were only producing enough power to provide 11% of the country’s electricity. Between the early 1970s and mid - 1980s, inflation - adjusted capital costs of new
plants rose an average of 14 percent each year. Nuclear plants finished in the mid-1980s cost 20 times as much as reactors built in the early 1970s (a six-fold increase when adjusted for inflation). In 2002, the cost of each new reactor was set at $2.3 billion. By 2006, the cost had grown to nearly $4 billion[15]. In June 2008, staff at the Federal Energy Regulatory Commission estimated that building a new 1,000 megawatt (MW) reactor could cost up to $7.5 billion (Federal Energy Regulatory Commission 2008). At that cost, analysts at Moody’s calculate that reactor owners would have to sell power in the market at 15 cents per kWh (without transmission and distribution costs) in order to achieve a 10 percent return on the investment.

In 2005, Congress created a series of taxpayer-financed subsidies to support the construction of new nuclear reactors, including loan guarantees, extended liability insurance, and a tax credit for every kilowatt-hour of nuclear electricity generated. Altogether, the subsidies are valued at as much as 60 to 90 percent of the levelized cost of power from a new nuclear reactor - reaching as high as $13 billion for a single reactor. Some of the largest subsidies are: unlimited taxpayer-backed loan guarantees, covering up to 80 percent of the cost of a nuclear plant; an extension of the Price-Anderson Act, which limits nuclear industry liability in the case of a major accident; $5.7 billion in operating subsidies, such as a 1.8 cent tax credit for each kilowatt-hour of electricity produced from a new reactor during its first eight years of operation; $2 billion to insure companies against any costs caused by delays in licensing the first six new reactors; $1.3 billion for decommissioning old plants; $2.9 billion for research and development and $2 billion for uranium enrichment[9]. “The basic premise behind a nuclear renaissance is wrong whether one looks at it technically, economically, environmentally or socio-politically”, said Benjamin Sovakool in his work Contesting the Future of Nuclear Power: A Critical Global Assessment of Atomic Energy[16].

2 Nuclear accidents

The story of nuclearisation is the story of accidents, both major as well as minor. Data related to nuclear issues are classified information in all countries, whatever available in the public realm is either declassified or leaked. The impact of nuclear accidents has been a topic of debate practically since the first nuclear reactors were constructed in 1954. Accidents occur on account of human error, technical malfunction, absence of preventive mechanisms and sabotage. Worldwide there have been 99 accidents at nuclear power plants from 1952 to 2009. Fifty-seven accidents have occurred since the Chernobyl disaster, and 57% (56 out of 99) of all nuclear-related accidents have occurred in the USA. A nuclear meltdown is a severe nuclear reactor accident that results in reactor core damage from overheating. Nuclear meltdowns had occurred in the Lucens reactor, Switzerland, in 1969; at the Three Mile Island in Pennsylvania, in 1979; at Chernobyl in Ukraine in 1986 and in Fukushima in 2011. Not so severe meltdowns had happened in four other facilities in the US,
and also in Canada, UK, Scotland, France and Czechoslovakia. The incident was rated a five on the seven-point International Nuclear Event Scale: Accident with Wider Consequences. The accident at Three Mile Island in 1979 was caused by a combination of equipment failure and the inability of plant operators to understand the reactor’s condition at certain times during the event. A gradual loss of cooling water to the reactor’s heat-producing core led to partial melting of the fuel rod cladding and the uranium fuel, and the release of a small amount of radioactive material. The accident has triggered anti-nuclear protests by various civil society groups resulting in new regulations for the nuclear industry, and has been cited as a contributor to the decline of a new reactor construction program that was already underway in the 1970s[17].

On April 26th, 1986, reactor four at the nuclear power plant near Chernobyl, Ukraine exploded, releasing more than a hundred times the radiation of the bombs dropped on Hiroshima and Nagasaki. The cause of the accident was the result of a test run that went out of control causing explosion of reactor 4. The resulting fire sent a plume of highly radioactive fallout into the atmosphere and over an extensive geographical area, including parts of Soviet Union and Northern Europe. One of the major evacuation and resettlement programme was undertaken during 1986 - 2000 involving 3,50,400 people. The accident had long lasting impact on the flora, fauna and the ground water in the area cite IAEA2006. In Chernobyl, the number of additional cases of cancer and leukaemia caused by radiation is estimated to range from 34,000 to 1,40,000, leading to 1,60,00 to 7,30,00 fatalities. Some studies, including one published by the New York Academy of Sciences, put the number of fatalities at more than 10 times higher than the last figure[12].

3 Lessons learned from Fukushima

Nuclear power is an energy choice that gambles with disaster. The myth of safety and technological prowess that Japan claimed to possess have evaporated into thin air in Fukushima in March 2011 when twin natural calamities of an earthquake followed by a tsunami struck a 30 year old Pressurized Heavy Water Reactor throwing off its cooling system. The accumulation of heat in the reactor resulted in fuel melt down in three of the six reactors. Cooling of the spent fuel necessitated pumping of large quantities of water. This irradiated water later seeped into underground aquifers and ocean creating serious environmental and public health hazards. Although no fatalities due to short-term radiation exposure were reported, some 3,00,000 people were evacuated from the area; 15,884 (as of 10 February 2014) people died due to the earthquake and tsunami; and, as of August 2013, approximately 1,600 deaths were related to the evacuation or its consequences (such as living in temporary housing and hospital closures. The Fukushima Nuclear Accident Independent Investigation Commission found that the nuclear disaster was “manmade” and that its direct causes were all foreseeable. The report also found
that the plant was incapable of withstanding earthquakes and tsunamis. Tokyo Electric Power Company (TEPCO) which was running the utility, regulators like Nuclear and Industrial Safety Agency (NISA), Nuclear Safety Commission (NSC) and the government body promoting the nuclear power industry (METI), all failed to meet the most basic safety requirements, such as assessing the probability of damage, preparing for containing collateral damage from such a disaster, and developing evacuation plans. During the initial days of the accident, TEPCO had been playing down the intensity of the impact. The company was more concerned about its assets than the lives of people (Aldrich 2012). By the second week of the crisis, milk and vegetables in Fukushima and nearby prefectures were found to have higher - than - permissible concentrations of iodine - 131 and caesium - 137. Radiation from the reactors had spread hundreds of kilometres away. Tap water in Tokyo, 220 km away, was found to have been radioactively contaminated, and the government advised people not to give it to babies. People were evacuated from a zone with a 20-kilometre radius from the plant, while those living between a 20 km and 30 km radius were advised to leave[4].

TEPCO which runs the Fukushima nuclear plant is the largest electric utility in Japan and the 4th largest electric utility in the world. It had a questionable environmental/safety record in the past. On August 29, 2002, the government of Japan revealed that TEPCO was guilty of false reporting in routine governmental inspection of its nuclear plants and systematic concealment of plant safety incidents. All seventeen of its boiling-water reactors were shut down for inspection. Several of its top executives were stepped down as a result. The utility “eventually admitted to two hundred occasions over more than two decades between 1977 and 2002, involving the submission of false technical data to authorities”In 2007, however, the company announced to the public that an internal investigation had revealed a large number of unreported incidents. These included an unexpected unit criticality in 1978 and additional systematic false reporting, which had not been uncovered during the 2002 inquiry. Along with scandals at other Japanese electric companies, this failure to ensure corporate compliance resulted in strong public criticism of Japan’s electric power industry and the nation’s nuclear energy policy. Again, the company made no effort to identify those responsible. An earthquake in 2007 had paralyzed its Kashiwazaki-Kariwa nuclear plant - the world’s biggest resulting in an unprecedented radiation leak which the company did not acknowledge.

The operator of the Fukushima No 1 plant submitted a report to the country’s nuclear watchdog 10 days before the quake hit on March 11, admitting it had failed to inspect 33 pieces of equipment in its six reactors there. In June 2012 TEPCO revealed, that in 2006 and 2008 TEPCO - employees made two studies in which the effect of tsunami - waves higher than the “official”expected height of 5.7 meters was studied on the performance of the reactors. This was done after the large Indian Ocean tsunami in 2004. The conclusion from the simulation in 2006 was that a 13.5 meter wave would cause a complete loss of all power and would make it impossible
to inject water into reactor No.5. The cost to protect the plant for such an event was estimated to be about 25 million dollars. In 2008 the effect of a 10 meter high tsunami was calculated. TEPCO failed in both cases to take advantage of this knowledge, and nothing was done to prevent such an event to happen, because the study sessions were conducted only as training for junior employees, and the company did not really expect such large tsunamis.

Three years into the Fukushima nuclear power plant accident, not a single individual has been held criminally responsible for the disaster. This is in spite of the fact NAIIC (The National Diet of Japan Fukushima Nuclear Accident Independent Investigation Commission) stated on 5 July 2012 in its final report that, “The TEPCO Fukushima Nuclear Power Plant accident was the result of collusion between the government, the regulators and TEPCO, and the lack of governance by said parties”. They effectively betrayed the nation’s right to be safe from nuclear accidents. (Press Release by Aileen Mioko Smith of Green Action Japan, “Those Responsible for the Fukushima Daiichi Nuclear Power Plant Accident not Held Accountable: Japanese Government Pushing for Restart of Nuclear Power”, 11 March 2014 http://www.beyondnuclear.org/home/2014/3/11/those-responsible-for-the-fukushima-daiichi-nuclear-power-pl.html

India: “No look back on nuclear energy”

The report - Safety Evaluation of Indian Nuclear Power Plants Post - Fukushima Incident, is defensive and optimistic about India’s nuclear programme. The Report said that “adequate provisions exist at Indian nuclear power plants to handle station blackout situations and maintain continuous cooling of reactor cores for decay heat removal” (Nuclear Power Corporation of India). The owner and operator of India’s all 20 nuclear power plants is Nuclear Power Corporation of India Ltd (NPCIL). As nuclear power is a “holy cow”, no public scrutiny or resort to RTI could be possible. The Department of Atomic Energy has been getting liberal doses of fund and yet shows no public accountability. Since India maintains a concurrent nuclear weaponisation programme, its nuclear - related activities are shut out from the public. However, what comes out from the closet is bizarre. In the early 1980s numerous workers were exposed to radiation in Tarapur plant. In 1993, a fire broke out at Narora plant causing great concern. Due to faulty construction, the containment dome in Kaiga collapsed in 1994. In 1995, the Rajasthan Atomic Power Station leaked radioactive waste into a lake for two months. In 2003, six workers at the Kalpakkam reprocessing plant were exposed to excessive radiation doses - admittedly “the worst accident in radiation exposure in the history of nuclear India”. Oil leaks have also been common in Indian reactors. In 1988, the MAPS II was shut down due to an oil leak from the generator transformer. Another major issue that case intense concern is the frequent failure of safety devices. As evidenced in several previous nuclear accidents, a small event could cascade into a major accident. Absence of a truly independent regulatory mechanism in the nuclear industry is acutely felt in India[14]. The DAE refuses to acknowledge the thorny problem of
nuclear wastes, generated at every stage of the so-called “nuclear fuel cycle”, from uranium mining to reactor operation to spent-fuel storage or reprocessing.

It seems that India is absolutely unconcerned about any of the issues that happened in the recent past. Though it has been proved beyond doubt that nuclear programmes cannot survive without heavy state subsidy, investor guarantees and bailouts, how could it be made economically viable is a moot question. The profit over people attitude of the state was clearly discernible in the case of Bhopal gas tragedy. Thirty years down the line, justice for the victims still eludes. The nuclear apparatchiks in India live in ivory towers and ride on the same trodden path and commit the same mistakes that their counterparts do elsewhere. For them the nuclear renaissance is an achievable dream no matter what price the nation has to pay.

S. A. Bharadwaj of the NPCL writes: “One important mission of the Department of Atomic Energy is to harness nuclear energy as a safe, environmentally benign and economically viable source of electric power to meet the ever-increasing energy needs of the country. This is to be achieved through the concerted effort of operating existing Nuclear Power Plants (NPPs) in an efficient manner, implementing new power projects and developing/adopting new technologies for nuclear power production and fuel cycle processes for future deployment”. He further says that “nuclear power offers the most potent means for long-term energy security” of India[3]. The Integrated Energy Policy of India estimates the share of nuclear power in the total primary energy mix to be between 4.0 and 6.4% in various scenarios in the year 2031 - 32[13].

4 Conclusion

Nuclear discourse in almost every place in the world involves multiple interests, actors, and layers of engagement. Competition, conflict and cooperation are inevitable and often played out politically within the boundaries of nation states. The old development - security paradigm has lost its sheen when other challenging notions like sustainable development, environmental protection, public health etc. gained precedence. What peter Bradford said about US holds equally good for other states as well: The so - called US “nuclear renaissance” was in shambles well before the tragic events still unfolding in Japan . . . Most of the projects that were said to constitute the “renaissance” in 2008 have been canceled, suspended or greatly delayed[1].

References


1 Introduction

In the discipline of Political Science, both graduate and post-graduate students learn the Constitution of India as a compulsory paper in their course work. Except a few, the course content shows similarity across different universities in India. At the graduate level the course content begins with evolution of constitution making in India including the statutes and Government of India Acts introduced by the colonial government. It then proceeds to salient features of the constitution, preamble, fundamental rights, directive principles, powers and functions of three branches of government, centre-state relations, statutory bodies constituted by the constitution, and the syllabus ends with some units requiring some qualitative assessment of the general performance and challenges of the constitution. In Political Science the framework of the earlier syllabus of Indian Constitution was adopted from discipline of law by adding a tinge from Indian history. Legal experts cum political scientists such as D.D. Basu and M. V. Paylee were the leading authors of the books for the course. The content of the books mainly gives factual information regarding the constitutional provisions. At the post-graduate level also until very recently the prescribed books were the same. Even if some new writers found space in the reading lists such as Shibani Kinkar Chaube and Sobhanal Datta Gupta the students and the teachers tend to stick on the conventional authors based on a variety of reasons.

Proficient leaning based on systematic reading of literature was not yet a common norm. It is an irony that the major chunk of critical learning in social sciences, in which the central theme of study is society itself, still confines to a few centres of excellence. Why should not we seriously think about decentralisation and popularisation of critical and quality learning to widely dispersed colleges more democratically and judiciously? Though the public policy framework of higher education
is greatly inclined to encourage the creation of new centres of excellence and award new titles based on the performance for the existing ones, there are also moderate attempts to improve the quality of learning in all the existing institutions at different levels based on their need as well. I consider the opportunity to make a speech in the seminar organised by St Gregorios College, Kottarakara in association with its golden jubilee celebrations as part of such an effort.

For a long period of time there was a tendency among the teachers in Indian Constitution to strictly follow the stipulated framework provided in the conventional books. Many of us believe that teaching (even if it is in social science) is a non-political act in which the teacher is not expected to engage politics. Thus the constitution of India, which was widely projected as the will of the people formulated on the principle of common good and enshrining moral values and ethics, becomes the natural choice for those who adhere to this view. In addition to this, teaching Indian Constitution by focussing on facts and nurturing thin analysis was relatively a trouble-free task since the conventional syllabus demands for no higher reading. In fact we find it handy if the syllabus remains more or less the same even after periodical revisions.

In a large number of universities in India syllabus revision exercise rarely make any substantive change. Most of such efforts are limited to making changes in the titles and reordering the existing units and many participants in the syllabus workshop are found to be satisfied with this. It shows some disquieting implications. The revision of the syllabus does not incorporate properly the expansion of knowledge in the field of study. Many reasons are available for opposition to change the existing syllabus. One of such I heard in some of the syllabus revisions workshops is the inability of the students to follow the new syllabus! It was not clarified, who is really anxious about a change. As a result the knowledge about constitution remained stagnant and it became dreary for the aspiring students and teachers. Many other technical aspects of the syllabus revision exercise also greatly hamper the prospects of teaching and learning Constitution of India.

The aforesaid analysis indicates two sets of issues that confront a teacher in Political Science while teaching a course on the constitution. One is related to the prescribed syllabus and the second, the reign of a commonsense and the dominant ideology regarding our constitution that affects both the teachers and the students in the process of learning. This paper is written by focussing on the latter based on my experience of teaching Indian constitution and related topics for about a decade in different institutions.

2 Indian Constitution: ‘The Genesis’

The evolution of constitution is an important matter of learning it. It has significance more than simply following a tradition. It is useful to critically evaluate the debates in the Constituent Assembly and the constitutional reforms initiated by the colonial
rulers. But in the conventional teaching the debates in the assembly that gave shape to the constitution is given lesser importance than describing the major events and the summary of different constitutional reform packages introduced by the raj. Very rarely the conventional syllabus demands for a critical introspection into the social composition of the assembly, its representative character and mode of selection and the dominant value framework of the constitution makers. Evolution must also bring into account the variety of factors that influenced the constitution making, such as the historical context, the socio-political movements and the legacy of colonial modernity. Each of these requires a theoretical understanding as well. In the usual class room learning about the evolution of Indian Constitution many vital aspects of the process of constitution making are evading our attention.

The mainstream accounts consider the process of constitution making in India as the outcome of a successful national movement. Therefore, our emotional nationalism discourages a proper inquiry into the events and factors preceding the formation of Constituent Assembly of India and the specific nature of transfer of power from the British elites to the Indian elites through both negotiation and struggle. Many innovative assessments of national movement have come out in the past in the Indian historiography, but the mainstream teaching and our common reading pattern in the discipline hardly reorients our attention towards this critical literature.

Teachers who adopt the style of nationalist story telling about the pre-independent Indian history hardly inform the students about the real socio-political context, diverse political organisations that participated in the anti-colonial movement, the nature of struggles, the diverse demands and the ideology of the leadership in the formative years of Indian Constitution. As a result, mainstream teaching does not help the students to look into the process of interactive relation between the social structure and the constitution at the time of its making. A few questions would be helpful to the students to learn about this interaction. For instance, what was the social character (class, caste religious and gender) of the assembly? Did the assembly accommodate members from all the social groupings equally or proportionately? How did the inadequate representation of the disadvantageous sections of the population in the assembly affect their demands in the future democracy of the nation? What was the dominant ideology of the assembly members? Was it inclusive of the socio-cultural diversity of the population properly? Why some of the popular movements and certain political groupings did not participate in the constitution making process? What were the objections of Muslim League to Indian National Congress regarding the constitution making? What was the procedure of selection of the members of the Constituent Assembly? Was it based on adult suffrage or restricted franchise? Why the size of property holdings, personal income, tax payment and educational qualifications became the criterion of determining one’s voting rights? Was the Constitution of India strikingly different from the Government of India Act 1935? Why the constituent assembly members were more inclined towards constitutions of liberal democratic and capitalist countries of the West while adopting the
general framework of the Constitution of India?

Most often the commonly referred books keep a dubious silence on the largely unrepresentative character of the Constituent Assembly and the way of its election. The assembly was not elected by universal suffrage but was formed in 1946 as a result of indirect elections by the members of different provincial legislatures who themselves had been elected by a restricted electorate comprised of propertied classes and educated citizens. The voting right according the Government of India Act 1935 was restricted to 15 per cent of the total population and only 39 per cent of the adults. Why the mainstream academia in its enthusiastic accounts of the constituent assembly hides the shortage of democratic content of the Constituent Assembly? Why it was consistently reluctant to probe into the ways in which the members of the assembly upheld the interest of the property holders (bourgeoisie, landlords and the middle class) in various deliberations.

The lower class, women, minorities and lower castes were falling short of effective representation in the assembly even though social and ideological pluralism practiced by the Congress provided some accommodation to the moderate voices of the dissenting organisations and groups. Such a representation, except in the case of Ambedkar and a few, was proved not much effective and decisive to affect the course of deliberations in the assembly. After partition, the party-wise breakup shows that 80 per cent of the members were from the Congress. Why the Congress leadership agreed to accommodate representatives of the undemocratic princely rulers in the assembly after their merger with Indian union?

There were a small group of non-Congress members in the assembly from the Muslim League after partition and two socialist party members and a handful of independents. But, the Congress party which ruled the interim government and all the provincial governments possessing absolute majority in the assembly rendered rest of the membership further ineffective. Granville Austin in his book 'Indian Constitution: The Cornerstone of a Nation' gives the socio-economic profile of the constituent assembly as appendix. Though Austin takes a precaution in a footnote by saying that the social background of the members need not be the sole determinant of their views expressed in the assembly and it holds some truth, the careful neglect of the assembly to stipulate principle of economic distribution as constitutional mandate to the future governments exhibited its class character and lenience to the interest of the rich and the powerful who elected it. Austin like some other western scholars who studied about the constitution and its making need not be taken beyond criticism by their popularity alone. It seems that these liberal minded scholars described the constitution making in India, a non-western country as an exciting and revolutionary example mainly because from the western point of view such a development in the non-western social context was largely unprecedented. Therefore, they exaggerated the event of constitution making in an under developing nation against many of the shortcomings of the very process and the content of the constitutional text.
Those who evaluate the assembly debates and the constitution as revolutionary and robust hardly ask, why the framers of the constitution were more concerned about maintaining the standard of political democracy in the new nation and watered down the basic principles necessary for an economic democracy even though the poor, landless peasants and the workers constituted a big majority of the population? Like many other western capitalist nations where the constitutions were formed under the tutelage of liberal democratic and capitalist ideology, in India also the same was the dominant ideology of the majority of the constitution makers. It hardly envisaged the constitution as a legal document committed to principles of distribution and a political carrier of radical socialism. The socialist voices of K. T. Shah within the Congress and the two socialist party representatives and the mild socialism of Nehru were put down on several occasions in the assembly debates by the liberals and the conservatives.

Granville Austin reminds us about the oligarchy of leadership in the Constituent Assembly composed of Jawaharlal Nehru, Vallabhai Patel, Maulana Azad and Rajendra Prasad. Even though B R. Ambedkar was playing a crucial role in the assembly debates and he was treated as the architect of the draft constitution, compared with the former he did not have the clear backing of a party different from Congress in the Assembly and he was not part of the oligarchy. He was originally elected to the assembly as a candidate of his political party - Scheduled Caste Federation - from East Bengal and lost his constituency after partition. Later, Ambedkar was re-nominated from Bombay presidency in a Congress ticket. In addition, Ambedkar did not have any serious ideological objection to the liberal camp in the assembly except in matters related to reservation for Scheduled Castes. However, his proposal to include a list of basic economic rights as part of fundamental rights in the constitution was defeated in the assembly by others. S. Anand rightly states this in the following:

“When Ambedkar did make it to the Constituent Assembly, and even headed it, he could not have his way on most issues dear to him. His impassioned belief in separate electorates for dalits; his unique and original proposals to solve the communal deadlock through multi-member constituencies and cumulative voting within the framework of parliamentary democracy and to pre-empt the religious partition of India; his zeal for a uniform civil code among Hindus; his enthusiasm for a programme that ensured social and economic equality (not just political equality in terms of universal adult franchise); his advocacy of nationalisation of land and its redistribution as cooperative, collective farms - all these had no place in a Constituent Assembly dominated by conservative, feudal Hindus and a pusillanimous Nehru”(Anand 2009).

In addition, the oligarchy of leadership was effective to override ideological opposition by reminding the members about unity and integrity of India. In fact there
were occasions in which some liberal democratic principles were also greatly compromised in favour of strong centralised state. Somanath Lahiri, the only member of Communist Party in the pre-partition assembly from East Bengal who lost his seat after partition criticised the Assembly, especially Sardar Patel (Chairman of the Committee on Fundamental Rights) for holding the approach of a police constable in drafting the fundamental rights (See: Constituent Assembly Debates, Vol. 3)[12]. Why those who worried in the assembly about the possibility of economic rights creating a financial burden for the government in future hardly expressed any distress about the same through compensation for the landlords and zamindars and the extraordinary allowances (Privy Purse) to the erstwhile princely rulers provided by the constitution?

The political image of the Congress representing all sections of the Indian citizens is really a trap in our learning of the constitution. So the Constituent Assembly dominated by Congress is a reason for many of us following Granville Austin and others to treat it as a ‘microcosm of Indian society’. But, the Congress became a mass movement and socially and ideologically plural in membership only since late 1920’s and faced political challenges since 1930’s. In fact, the Congress governments came to power in several provinces were ruthless towards peasant and working class movements. Without looking into the actual history of the Congress in the pre-independence period how can we repeat the same lessons of our old school textbooks to students at the higher education level? Such a lopsided view prevents us to see that the Congress despite having a mass following carried with it always a political strategy vulnerable to the landlords and the industrial bourgeoisie. In all the critical moments the ruling class held sway over the organisation vis-a-vis the political decisions and policies and by using the strings of financial support to it. The changes in the organisation’s mobilization strategy due to the widely applauded Gandhian techniques since late 1920s neither curtailed the ruling class power nor it transformed the party exclusively into a mass party of the poor. The oscillating posture of the Congress between the rich and the poor was the reason for many of the radical left segments of its leadership and working class, peasant members to quit the organization from 1930s and to form socialist parties and the communist party during the anti-colonial movement. For a critical reading on the character of Indian national movement and its diverse streams the book, ‘Nationalist Movement in India: A Reader’ edited by Sekhar Bandyopadhyaya[4] would be highly useful.

At a time, when India was preceding to independence, the claim of the Congress as the one and unique representative of all sections of Indian population is false. The consolidation of Muslim minority behind the Muslim League, formation of political parties representing the lower castes and Scheduled Castes in different regions and the growing strength of socialist-communist parties and the right wing Hindu nationalist organisations affected negatively the capability of Congress for an inclusive representation of India within its own party structure. The strength of Congress to retain the nature of a catch-all movement was highly due to its permission of dual
membership for party workers. Even though the Congress demanded for a national constituent assembly since 1930s and urged for its election through universal adult franchise, why in 1940’s it was satisfied with an assembly elected on restricted suffrage as proposed by the Cabinet Mission Plan? Was the Congress deeply worrying about the opposition parties’ strength to cause damage to its dream of securing an absolute majority in an assembly elected by adult suffrage?

Congress understood the political advantage of indirect election to the Constituent Assembly from the existing provincial legislatures. The restricted franchise under the Government of India Act 1935 already provided it sweeping victory in the provincial elections. After a long period of their considerable support to the colonial rulers the landlords and the industrialists had begun to see Congress as their party for the future. It was reflected in the composition of provincial legislatures wherein the party could gain majority. Communist Party and sections of the Socialist Party had no conviction and hope of victory in such an undemocratic electoral process. They stood against an assembly which was elected exclusively by the propertied classes providing only an ineffective representation to the working class, peasants and the majority of poor in the proceedings of making the constitution. The effort of the Congress to pursue the agenda of the ruling class was unchallenged and it was free from facing an organisational opposition except from the Muslim League in the assembly. Though there were a minority of professed socialists in both Congress and the League the two organisations were vulnerable to ruling class domination. Therefore, the Muslim League hardly became a class-wise ideological critique of the congress.

The assembly had a strong contingent of legal experts also. This has a drawback which leaves our attention in the mainstream teaching. In fact, a large number of them were engaging in constitution making without any pressure from the people’s demands in real politics. However, their opinion was very decisive on several crucial debates in the Assembly. The movement dynamics of anti-colonialism, the class and mass struggles of various sorts and even the Gandhians made no direct impact in the content of the constitution. Did we inherit a legal framework that was in many

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1 There was an interesting development in 1947 budget of the interim government at the centre. Liyaqat Ali Khan, Finance Minister from League proposed for income tax of 25 per cent on business profits exceeding Rs. 100,000 per annum. The Congress leaders opposed this tooth and nail though Khan justified it on the basis of distributive principles and necessity of revenue mobilization. In fact the non-Muslim business men persuaded the Congress to oppose the Finance Minister since the tax proposals would affect them more negatively. Rajagopalachari and Sardar Patel went further by criticizing Khan for taxing them heavily in the budget. It should be a matter of our concern in teaching the political developments running parallel to the making of the constitution; why the Congress was much worrying about the tax burden of the businessmen and the Hindu rich? The party was catering to the needs of its fund raisers, the industrial bourgeoisie. Nehru, the socialist Prime Minister in the interim government also had once again made a volt-face against Khan’s budget proposals. However, the Congress and the League were equally persuaded by landlords since there was a strong contingent of landlords from the Muslim community also. (See for details, Raghabendra Chattopadhyaya, “Liyaquat Ali Khan’s Budget of 1947-48: Tryst with Destiny”, Social Scientist, Vol. 16, No. 6-7, 1988, pp. 77-89)
ways deprived of the impact of true mass politics of anti-colonial movement? There is also another reservation about the presence of legal experts in the Assembly. In fact, all of them were trained in Anglo-Saxon jurisprudence and law. This is cited as a reason why the Indian constitution and the judiciary while interpreting the constitutional provisions and addressing some extraordinary and new questions of justice in the post-independence are found to be very constrained by the cages of old conventions.

The conflict between the Congress and the League over separate electorate for Muslims was largely conceived as the biggest political conflict in the pre-partition period. Actually there was a plurality of struggles and multiple forces at tension with each other in the social terrain of pre-independent India. There is a tendency among the nationalist historians and their disciples in the academia to perceive the demand of Muslim League for separate electorate as anti-national and sectarian. Interestingly, such a view hides from the students of Indian constitution that the League and its liberal leaders raised a relevant point regarding the political safeguards for the minority religious groups against majoritarianism in a Hindu dominant independent India. Teaching on constitutional development in India used to generate a binary between the ‘separatist Muslims’ and the ‘nationalists’ by inculcating a Hinduised partisan approach to events and issues related to partition of India. This ‘we-they’ framework in our mainstream learning of the pre-partition political events tends to exonerate the nationalist Congress and prosecute the League. Many teachers used to express satisfaction over Indian leaders to get rid of the ‘League problem’ by way of agreeing to partition, and thus consider the total objection of post-partition assembly to separate electorate system as a real democratic success.

In fact, the demand for separate electorate was also raised by Ambedkar for Scheduled Castes. The post-partition assembly partially conceded to this by providing political reservation for SCs and STs in elections and public sector employment. Nothing like this as a sort of compensation or compromise was made available to Muslims even though a majority of the community were socially and economically deserved the status of backward class. The current demand for reservation for Muslims in India is partially a reminder of their unjust treatment by the Constituent Assembly. The political promise of the Congress to ensure representation for Muslims while fielding candidates in elections was not equivalent to mandatory reservation through constitution. Cultural rights in the constitution were not alleviating the problems of lack of representation and economic backwardness of Muslims. The growth of Hindu communalism and decline of Congress made their situation more vulnerable now. The assembly was also not really sensitive to issues of women reservation also. The ‘empowerment of the weaker sections’ was always considered as a tool ‘to build up a powerful state’, though the relation between the two notions stood contradictory to each other.

In the mainstream teaching and learning of constitution the text is widely perceived as a solution to the pressing problems of the day. A critical view suggests
that the constitution and its provisions produced problems and sometimes the doc-
ument as a whole became a problem from the vantage point of some sections of
the population. For example, as Pritam Singh argued the cultural language and
certain provisions in the constitution exhibited a Hindu Bias. In fact, many of the
teachers forget the fact that the framers of the constitution were pressurised by the
threat of a Hindu priest to go fast unto death to get a Hindu name for the coun-
try as ‘Bharat’in the first article of the constitution. Many of us also forget about
the presence of Hindu right wing members such as M. R. Jayakar, K.M. Munshi
and Syama Parsad Mukherjee and the soft Hindutva sentiments expressed by many
Congress members such as Sardar Pattel and Rajendra Prasad in the assembly de-
liberations. In his writings on constitutional principles of Indian secularism, James
Chiriyankandath remarks:

“It was scarcely surprising that the form of secularism that found expres-
sion in the Constitution was ambiguous. Leaders like Deputy Prime Min-
ister Sardar Patel, Rajendra Prasad, the President of the Constituent
Assembly, and K.M. Munshi, Patel’s right-hand man in the Assembly,
were sensitive, if not openly sympathetic, to the majoritarian Hindu sen-
timents voiced by a number of Congressmen in the Constituent Assem-
by. They knew that their predilections were widely shared, especially
among upper caste Hindi-speaking members from the United Provinces
(U.P.), the Central Provinces (C.P.) and Berar, Bihar and Punjab”

Do we rightly know about some events in the assembly for example, P.S. Desh-
mukh, a Congress member from Central Province moving an amendment demanding
citizen status only to Hindus and Sikhs with the support of a few? Even though the
amendment was defeated, its reminiscence still seduces the Hindu fundamentalists
in contemporary Indian politics.

Under the pressure of the Hindu right wing members enjoying the support of
Hindu traditionalists of the Congress the provisions such as cow protection was
included in the directive principles. The Constituent Assembly as a whole was not
resistant to all forms of fundamentalist demands from Hindus, Sikhs and Muslims by
following a principle of accommodation and recognition for religions. For example,
only some lady representatives (Rajkumari Amrita Kaur) raised problems regarding
the impact of the right to religious practices and the right to personal laws upon
women’s rights. The assembly might have been moderate to arrive at the end level
conclusions in making final provisions, but equally important that the assembly did
not produce any radical conclusion in the form of a constitutional text which would
be diametrically opposite to the prevailing modes of class, patriarchal, caste and
religious power structure of the day.

Why should we sideline objective and scientific assessment of the assembly and
the making of constitution and force our critical stamina to be subsumed under an
imported commonsense? Why should we repeat to the students that the constitution
is a divine gift and a true reflection of the will of the people? Does it deserve the
status of a sacrosanct document to evade democratic criticism in social science class rooms? Should it be praised as if it flows from the supreme wisdom of our national leaders? For many students particularly at the graduate level criticism of the constitution is an unfair practice. Only after their exposure to better academic environments in their future studies they start to learn the elements of critical learning and theoretical thinking. For many who stop higher education after the B. A. course carries with them the uncritical knowledge about constitution which serves the interest of the establishment. Mostly, they would be willing to briefly point out the ‘limitations’ of the constitution while writing answers in the examinations. Why don’t they explicitly state the ‘drawbacks’ of the constitution? Why do we fail to recognize the distinction between two modes of our relation to Indian constitution by splitting our own self into one based on our identity as the learner and the other based on our identity as the citizens? Why should we strictly adhere to the same rules of the citizens when we study the Constitution of India as students?

Enlisting the relevant literature related to study of Indian Constitution is a critical challenge for the teachers in the concerned discipline. Preparation of a reading list for the course necessitates serious reading from the teacher. It demands for both historical understanding and theoretical learning of the expansion of knowledge about Indian Constitution. Unfortunately most of our mundane syllabus revision exercise gives little attention to incorporate a well planned reading list even though it is the linchpin of a course. Most of our syllabi do not give the reading list unit-wise. It is necessary for focussed reading for the students as well as for the teachers.

Shortage of standard text books was taken seriously by the academia in India only recently. At the national level such efforts were taken by some Political Scientists. The best examples are ‘India’s Living Constitution’, ‘Politics and Ethics of Indian Constitution’, ‘Contemporary India: Economy, Society, Politics’, ‘Oxford Companion to Politics in India’ and ‘Routledge Handbook of Indian Politics’. In some universities teachers have replaced the text books of the old genre with these new ones. The scholarly articles included in the last three books give a good review of the existing literature on different topics more comprehensively and thus sets a new practice for textbook writing. However, in the mainstream we pay no heed to the fact that preparation of standard text book require much precaution and care more than that we need to maintain in writing a research article or a book. Do our prolific text book writers and the usual titles one finds in the shelves of our bookshops related to Constitution of India mind this academic task well?

3 Constitution: An Ensemble of Enduring Social Conflicts

There is a problem in learning the constitution while we perceive it as a treaty of social consensus instead of an ensemble of social conflicts of the period of its formulation and now. In the assembly all the members were not holding the same
ideology and political view though a majority were from the same political fold. There were socialists, liberals, conservatives and even reactionaries. The ideological plurality would likely increase if we include the members of the assembly from non-Congress parties and the nominees of the princely rulers.

The Congress was not a well-knit political organisation. The leadership practiced a strategy to absorb support from different sections of the population based on a single point agenda of political freedom from the British rule. This led to coexistence of different ideological groupings and movements of different sections of the society under the loosely held political banner. Regarding the socio-economic agenda of the constitution and the future state the Congress did not presume a uniform view. It was entirely difficult for a party like Congress to bring about a constitution representing the interest of the poor and the disadvantageous sections of the population against the interest of the ruling class.

The Congress did not formulate a draft constitution carrying the vision of the party prior to the formation of the Constituent Assembly to bring some clarity in the deliberations. Such a task was quite uneasy for the Congress because of the acute differences within the party. There was little consensus within the party regarding the stand to be taken towards land reforms, industrial legislations and even about state’s role in development and planning. Neither the Motilal Nehru report nor the Karachi resolution of the Congress reflected any consensus. As stated earlier the party sought for the support of the masses to lead the national movement, and at the same time, rendered its organisational set-up and ideology vulnerable to accommodate the ruling classes and the conservatives. The mass following of the party was not a compulsion for the Congress to act as a mass party. It is also illogical to conclude that the Congress equally appealed to the poor and the rich in the Constituent Assembly. On many socio-economic questions the Congress organisation seemed to be nurturing the interest of the ruling classes rather than rising up with the aspirations of the masses. The assembly was more so in this respect. There are plenty of examples available from the assembly debates and the provisions enacted in the constitution to show the bias of the assembly dominated by the Congress to the ruling class. The right to private property is a case in point.

The constitution made the property right as a fundamental right and majority of members in the assembly strongly demanded for monetary compensation to the property holders in case of acquisition of private property by the state either for distribution to the landless (through land reforms) or for other public purposes. The economic rights (livelihood rights) such as right to minimum wage, basic health, education and decent conditions of work, which were the pertinent demands of the majority of people, were not enforced as fundamental rights in the constitution. The enforcement of property rights in the list of fundamental rights and the relegation of economic rights of the poor into the non-justiciable directive principles of state policy was really a ruling class project that worked through the Constituent Assembly elected by the propertied class. A number of scholars have pointed out the ways
in which the Constitution of India provided the rules and legal provisions for a capitalist economic order in independent India[5, 8, 20]. There was also significant amount of tension between different sections within the ruling class coalition, for instance the landlords and the bourgeoisie. Decline of the Congress dominance in the party system since 1967 election was a consequence of its inability to maintain the mediatory role in the conflicting class interest of the agrarian and industrial classes. To grasp the real impact and the nature of constitution we will have to take into account certain events and issues in the post-independent Indian politics also. The books - “India since Independence: Making Sense of Indian Politics” by Krishna Ananth, “Politics of India since Independence” by Paul R. Brass, “India since Independence” by Bipan Chandra et al. and “India: Government and Politics in a Developing Nation” by Robert L. Hardgrave and Stanley Kochanek - would be quite helpful for reading.

We may be aware of the head on conflicts between the right to wage and the profit of the capital, and the contradictory demands raised by the landlords and the landless peasants in the Indian economy. Viewed against these class conflicts what was the intension behind the constitution to give extreme weight to right to property? Did it help distribution or possession and accumulation of property concentrated in fewer hands? The major constitutional cases that we teach the students by presenting them as a conflict between the fundamental rights and the directive principles, about separation of power, the limitation of amendment power of the Parliament and the problem of judicial review were in fact regarding the controversial right to private property. But in the usual class room teachings a critical introspection into the basic reasons of the constitutional cases popularly known as Sajjan Singh, Golak Nath, Keshavanada Bharati and Minerva Mills are missing because of the relative neglect of theoretical training in Marxism for students in the Political Science in general. A systematic study of the Constitution of India is dependent on the strength of the political theory courses in the curriculum. Theory is both indispensible and can be an outcome of critical learning. Really, are we teaching the students to learn the constitution as a social construct? Are we learning about the interaction between the constitution and the society without having a theory of it?

4 Constitution and Its Politics: The Conclusion

In the introduction to ‘Politics and Ethics of Indian Constitution’ Rajeev Bhargava points out six limitations of the constitution viz., the over centralised idea of national unity in the constitution, the neglect to gender justice, no provision for a minimal representation to minorities in the legislature as a political safeguard, fundamental rights constrained by several restrictions which eventually creates ‘rightless people’ instead of ‘empowered citizens’, relegation of socio-economic rights into non-enforceable directive principles rather than making them an integral part of
the fundamental rights when the majority of Indians were poor and socially backward, and the lack of giving an idea about the institutional mechanism to realize the concept of social justice. The limitations stem from the nature of membership in the assembly and the dominance of the ruling classes and their intelligentsia in the mainstream national movement that brought about political independence in the form of transfer of power from colonial elites to the Indian elites rather than in the form of a mass revolution by transferring power to the powerless.

The ruling class character of Indian constitution cannot be exempted from responsibility for the pitiable condition of the poor and the deprived sections of the Indian society in contemporary India. However, in the class room lectures on Indian Constitution the audience are introduced to the ruling ideas only. We repeat the chanting that the constitution was quite fair, but it was failed by the unruly political leaders. The students who internalised similar narratives from the mainstream media and popular discussions take hold this view voluntarily as a part of their commonsense and start to demand for a strong state, presidential system of government, ruthless law and order mechanism, undemocratic discipline, chosen political leaders and even the abolition of political parties to resolve the problem. In fact, teaching and learning fail to grasp the critical mission of higher education and we are forced to satisfy with abstract solutions instead of seeking for concrete corrective measures and democratic political alternatives.

We know that the old practices of teaching constitution at secondary education confined the subject within the scope of civics. Learning the constitution in a limited length in the school text books was considered as helpful to transform the students as ‘future citizens of India’. Students and teachers are supposed to be role models for the rest of the society, the ordinary citizens who engage in politics without any primary reading of the constitution. (Hardly have we asked why the makers of the constitution drafted it in the form of lengthy and incomprehensible text for the common people!) Education was considered by the conventional intelligentsia as a process through which we mould the uncritical self in the students. Should they suppose that uncritical self is a precondition for model citizenship? Questions are very rarely raised about the ultimate consequence of such a harmless study to the pressing problems of inequality and lack of freedom and dignity to a sizeable number of our fellow citizens. There was no much concern about the state of detachment of social science learning from the liberating ideologies that inspired the masses to radically alter their course of living through permanent struggles and confrontations with structures of authority. In our class rooms why should we refrigerate our study of the constitution by guarding it always from the heat of many forms of social struggles? The ‘normal’ classroom teaching proves directly and indirectly helpful for the perpetuation of the iniquitous social structure and for retaining the power of the ruling classes. The legitimacy of constitution must be explored seriously in the classroom teaching to fasten our learning as a critical component to the process of radical social change, and also to reform the constitution.
References


Endosulfan Toxicity to a Freshwater Fish

Tresa Radhakrsihnan¹, Shirly Vardhanan², R.V. Vimal Raj³
Shibu Vardhanan⁴

¹,²,³Department of Aquatic Biology and Fisheries
University of Kerala, Thiruvananthapuram, Kerala, India - 695 581
⁴Department Zoology
University of Calicut, Calicut, Kerala.

1 Introduction

Among the eight planets of the solar system the ‘Earth’ is unique in being endowed with a large quantity of water. Water is the most abundant substance on the earth’s surface, it covers nearly 3/4 of the surface area of the planet. Water is just another compound of hydrogen and oxygen and the universal solvent to the chemist. To the physicist it is a marvelous state of matter that possess unique physical qualities but for which this frigid fluid matter would have been a burden rather than a boon to earth. And to the layman it is a liquid indispensable for his day to day activities. To the biologist it is water that upholds their identity, for life originated in water, water sustains life and today it is the medium that possess perhaps the severest of challenges to life on earth.

Out of the total water, the Ocean, the ice caps and the glaciers together comprise 99.35% of earth’s water. The remaining less than 1% (petit portion of water) are apportioned to the rivers, lakes, streams, streamlets, brook, brooklets, springs, pools, swamps, bogs, the rain, snow and the ice on mountain slopes, the moisture in the soil and ground water. Water covers almost 75% of the earth’s surface of which only 0.6% of the water comes under fresh water that also in three forms namely (i) water vapor, (ii) ground water and (iii) inland surface water. Yet, it is this unimaginably petit quantity of this liquid that is the most dear and inevitable for life on earth, in spite of the fact that the salty ocean and seas, estuaries and brackish waters and other inland water bodies on earth support a bewildering kaleidoscopic variety of life forms.

Water medium, no doubt is an excellent mega ecosystem that harbors innumerable kinds of micro as well as macro ecosystems. Water is a polar liquid which
has the properties of cohesion, surface tension, transparency, viscosity, buoyancy, density and pressure and it is also called as a universal solvent. Man’s interest on waters on around him is as old as mankind. From the moment one cautiously began to use the natural waters around us for our own purposes, we began to collect and organize facts about various water bodies that dot and cut the face of the earth. In his book ‘Historia Animalium’ Aristotle recognized that nature had made inland waters different not only from sea but also from one another. Knowledge on the organisms and its external influences which directly and indirectly affect them is called ecology. A suitable environment is necessary for any organism and life sustenance depends on the inter relation between organisms with their surroundings or environment. What is an environment? The term environment means “space on, below, above or within or in between the earth’s surface.

The earth is mainly divided into (i) Lithosphere - 25% (ii) Hydrosphere - 75%. The hydrosphere receives various pollutants from very many sources and deterioration of water quality is a major threat all over the world and in India also, however, Kerala is no exception. The environmental pollution and its abatement is a hot subject and restoration activities are initiated in major water bodies in advanced countries. India and Kerala are far behind along this line. In this contest we should seriously discuss and debate on pollution problems, their abatement and remedial measures. Pollution means “an act of making dirty, defiling, contaminating, profaning, and corrupting”. Pollutants are anything produced by man and can be considered some time to be a pollutant. The effect of pollutant on organism may be either acute or chronic. The toxic effect of pollutants on organisms can be studied both quantitatively and qualitatively.

Toxicology is a branch of science which deals with poisons and their effects on biota. Aquatic toxicology is a qualitative and quantitative study of the adverse effects of the toxins, toxicants, pollutants, contaminants, xenobiotics and other anthropogenic materials on aquatic organisms. Aquatic toxicology can be defined as the study of the effect of chemicals and other foreign agents on aquatic organisms with special emphasis on adverse or harmful effects. Toxicity tests are used to evaluate the concentration of the chemical and the duration of exposure required to produce the criterion effect. The effects of a chemical may be of such minor significance that the aquatic organisms is able to carry on its functions in a normal manner and that only under conditions of additional stress (eg. change in pH, DO, salinity, temperature). Effect may also result from the interaction of small amounts of some chemicals and larger amounts of other chemicals without the additional stress. Aquatic toxicity tests are used to detect and evaluate the potential toxicological effects of chemicals on aquatic organisms (Tresa Fernandez and Jones, 1989). Since these effects are not necessarily harmful, a principal function of the test is to identify chemicals that can have adverse effects on aquatic organisms. These tests provide a data base that can be used to assess the risk associated with a situation
in which the chemical agent, the organism and the exposure conditions are defined. A toxic test is performed to measure the degree of response produced by a specific level of stimulus (test chemical concentration). Aquatic toxicology is also concerned with the concentration or quantities of chemicals that can be expected to occur in the aquatic environment in water, sediment or food. Therefore, it includes the study of the transport, distribution, transformation and ultimate fate of chemicals in the aquatic environment.

The co-development with the commencement of the Industrial Revolution resulted in indiscriminate use of broad spectrum of xenobiotics including heavy metals, pesticides and weedicides in the agricultural field. Environmental contamination due to these chemicals is beyond the threshold level of “Mother Nature”, the land, air and the water around us carry large quantities of residues of these toxicants. The aquatic environment is the ultimate sink for contaminants and pollutants, through runoff and leaching. The adversity of any chemical compound manufactured on an industrial scale is sure to reach the aquatic realm sooner or later. A large variety of contaminants are drained into water bodies where fish encounter them and develop various metabolic abnormalities. They accumulate in fish and affect human health too via ecological cycling and biological magnification. Measuring the impact of pollution to the environment is a difficult task because of the lack of cutting edge parameters. Monitoring of the lethal potentials through biological responses other than death–bio indicators or biomarkers or ‘bio signatures’ as it is now popular among environmental scientists–for assessing the biological and ecological significance of environmental contaminants is a complementary approach to chemical monitoring. Organisms respond to environmental contaminants in some measurable and often predictable ways. Such responses may be perceived and assayed at several levels of biological organization; from the biomolecular level to the organismic level. Such assays might provide not only evidences of exposure to a broad spectrum of anthropogenic chemicals, but also might serve as a temporally integrated measure of bioavailable contaminant level in the environment. Poikilotherms in general are very intimately associated with their external environment. The physiology of aquatic poikilotherms such as fish is very sensitive even to minor changes in the milieu in which they live. Blood being the only tissue that has intimate contact with all organs and tissues of an animal, changes in the quality of the environment would be reliably indicated by changes in circulating blood.

Exposure of living beings to sub lethal levels of environmental pollutants has been shown to trigger several defense mechanisms at the cellular and molecular levels. ‘Heat Shock Response’ is a fundamental aspect in cellular physiology in which exposure to stressors results in dramatic redirection of metabolism so that a suite of new proteins is rapidly synthesized and the synthesis of some native proteins is augmented and of some others is suppressed. Many of the chemical toxicants are known to induce the typical heat shock response as an evolutionarily conserved cel-
lular mechanism to cope up with the adverse effects of a variety of external stressors, which acts through a specific set of proteins, called ‘heat shock proteins’ (HSPs) or molecular chaperones, exhibiting wide-ranging cellular functions, including protection from stress-induced injury by a variety of agents (Radhakrishnan and Tresa Radhakrishnan, 2007). Among the HSPs, HSP70 is suggested to protect cells from the injury inflicted by a variety of stressors by preventing misfolding or aggregation of misfolded protein, proteolytic degradation of unstable proteins or catalyzing proper degradation of unstable proteins or catalyzing proper folding of nascent polypeptides to their native functional state.

Endosulfan is a persistent, semi-volatile pesticide that has been detected in nearly all environmental compartments, including water and even in areas where it is not used (e.g., the Arctic and National Parks). In India, endosulfan is classified as an “extremely hazardous” pesticide affecting the central nervous system, reproductive system and immune system of vertebrates, including humans.

This paper will focus on the following,

1. Determination of the tolerance of a fish or the lethal concentration to endosulfan \( \text{LC}_{50} \) at different time intervals, 24 h, 48 h, 72 h, 96 h (Litchfield and Wilcoxon, 1949).

2. Determination of the effect of sub lethal concentration of endosulfan on the peripheral hematological make-up of the fish.

3. Study on the stress protein profiles of the eye lens, brain, gill and muscle at different time intervals of exposure and subsequent recovery after transferring the exposed fish to toxicant-free water to evaluate the recovery response.

## 2 Test Fish

The test organism selected for the present study is the slender barb or slender rasbora, *Rasbora daniconius* (Hamilton, 1822), popularly known as *Thuppal Kudiyan* in the Malayalam language. It is widely distributed in inland waters of Asia and Sri Lanka, inhabiting small streams and ponds neighbouring paddy fields. It is a non-edible, ornamental freshwater fish, available throughout the year, easily maintainable under ordinary laboratory conditions and it satisfies all conditions of an ideal aquatic animal model.

Specimens of *R. daniconius* for the study were collected from small streams nearby the Vellayani Lake, the major freshwater lake of Kerala, situated 14 km away from Thiruvananthapuram City, between 8° 24' 09.20'' & 8° 25' 32.63'' N lat.; 76°59' 48.34'' & 76°59' 39.96'' E long. Specimens were collected using mosquito net. Healthy specimens of more or less uniform size were immediately transferred into large polythene buckets containing water from the same habitat and transported to
the laboratory ensuring minimum stress during transportation. In the lab, healthy and active individuals were stocked in glass aquarium tanks (90 cm x 45 cm x 45 cm) holding filtered well-water, and kept under aeration. A four days acclimatisation period was provided prior to each experiment.

3 The Toxicant

The pesticide selected for the present study, endosulfan (Trade name - Hildan, Technical grade powder of 94% purity), was procured from the Hindustan Insecticide Ltd., Cochin, strictly for research purpose.

4 Static Toxicity Tests

Static toxicity tests were conducted using laboratory acclimatised fish and as per EPA protocol. Healthy fish of almost the same size (TL = 97.8 ± 7.8 mm; Weight = 95.4 ± 16.1 mg) were used for the definitive toxicity tests. Separate tanks were maintained for the hauler (equal volume of emulsified water as in the highest concentration) and control. The number of fish introduced into each experimental, hauler and control tank was ten. The test solutions, emulsified water in the hauler and water in the control tank were renewed every 24 h by slowly siphoning out about 3/4 of the contents of each tank and then filling it by siphoning in the respective solution. A 5 mm bore polythene tube was used for siphoning. The excretory materials and other debris, if any, were siphoned out every day. Sublethal pesticide concentration fixed was 1/5 of the 96 h, LC$_{50}$ i.e. 0.9 ppb. Physicochemical characteristics of dilution water used for LC$_{50}$ experiments were monitored regularly (Shibu Vardhanan, 1998).

5 Haematological Studies

Fishes were exposed to sublethal concentration of endosulfan in rectangular glass tanks (30 cm x 23 cm x 23 cm). Blood samples were collected at 24, 48, 72 and 96 h post-exposure and subsequent recovery at 24, 72, 48 and 96 h after 96 h exposure. The peripheral haematological parameters–total erythrocyte count (TEC), total leucocyte count (TLC), total platelet count (TPC), haemoglobin content (Hb), haematocrit (Ht) and erythrocyte sedimentation rate (ESR)–were estimated of ten each of exposed and control fishes following standard methods. From the values of TEC, Hb and Ht, the erythrocyte constants–mean corpuscular volume (MCV), mean corpuscular haemoglobin (MCH) and mean corpuscular haemoglobin concentration (MCHC) and the erythrocyte indices–volume index (VI), colour index (CI) and saturation index (SI)–were calculated.
6 Analysis of Protein Profiles

The protein profiles of eye lens, brain, gill and muscles of pesticide exposed, hauler and control fish were studied during both exposure and post-exposure recovery phase. After 4 days of gut evacuation, 75 healthy fish were subjected to protein profile analyses along with 10 each in control and hauler groups. Fishes were exposed to sublethal concentration of endosulfan in rectangular glass tanks (30 cm x 23 cm x 23 cm). Simultaneously two groups of ten fish each were maintained in toxicant-free water as control and hauler group throughout the experiment. Tissue samples were collected at 2, 4, 8, 12, 24, 48, 72, 96 h, and 7 days post-exposure and subsequent recovery at 24, 48, 96 h and 7 and 15 days after 96 h exposure. Test organisms were carefully observed for any behaviour progression during and post exposure recovery phase. The digested tissue samples were subjected to discontinuous 1-D SDS-PAGE analysis using Promega protocols, USA, in a 20 well, maxi-size electrophoresis unit (GENI, Bangalore, India) with 1 mm spacer. The gel concentration of the stacking and separating gels were 5 and 12.5%, respectively. Equal volumes of digested samples (90 \( \mu l \) for muscle, 75 \( \mu l \) each for eye lens, brain and gill) along with two separate standards (Sigma, USA and Fermentas, EU) were loaded. Electrophoresis was performed at constant current of 15 mA in stacking gel and 30 mA in separating gel. The electrophoresis runs terminated as the bromophenol dye front reached 1 cm above the bottom margin of the gel. The gels were transferred to fixative (70% acetic acid + 30% ethanol) for 15 min., then stained with Coomassie blue stain (Brilliant blue R-250, 0.125%; Sigma, USA and Fermentas, EU) and subsequently the protein bands were differentiated using acetic-methanol-water (10:20:70). Destained gels were stored for 48 h in 15% glycerol and subsequently transferred to pure glycerol. Stained gels were documented using Molecular Image Gel Doc (BIO-RAD GS 800, USA). Acquired gel images were subjected to further analysis using Quantity One 4.7 software. The molecular weight, rf value, peak density and line comparisons were performed.

7 Static Toxicity Tests

Fish exposed to different concentrations of endosulfan showed heavy mucus secretion, and behavioural changes like rapid opercular movement, erratic swimming, convulsion, jerky movement, positioning in the air-water interface and finally loss of equilibrium. Exposed fish struggled hard to breathe, and engulfed atmospheric air. These behavioural changes were time and concentration dependent. In higher concentrations, the behavioural changes were fast, and animals succumbed, with thick mucus covering over the whole body surface, especially in the oral region along with a red tint on mouth, opercular area and eyes. The 96 h LC\(_{50}\) value calculated as per the graphic interpolation method (Litchfield
and Wilcoxon, 1948) was 4.5 ppb. 1/5 of 96 h LC$_{50}$ value, i.e. 0.9 ppb, was selected as the sub lethal concentration for further studies like haematological and stress protein response.

8 Haematology

Mean TEC of the control fish was 2.39 x $10^6$ mm$^{-3}$, with a range from 2.30 to 2.60. Exposure to endosulfan caused an apparent progressive increase in TEC up to 96 h. During recovery, TEC was higher than that of the control fish. Mean TLC of the control fish was 90.31 x $10^3$ mm$^{-3}$, ranging from 73.13 to 106.25. Exposure to endosulfan caused significant progressive increase in TEC up to 96 h. During recovery, TLC was much higher than that of control. Mean TPC of the control fish was 46.08 x $10^4$ mm$^{-3}$, with a range from 37.63 to 49.00. Exposure resulted in progressive increase in TPC up to 72 h post-exposure, but at 96 h post-exposure, TPC decreased and reached 57.30. In recovering fish, TPC remained high, mostly higher than in exposed fish. Mean Hb of control fish was 8.1 g%, with a range from 7.5 to 9.0. In exposed fishes, Hb registered marginal increase at 24 h(8.4) and remained the same at 48 h. At 72 h, though it increased to 9.1, at 96 h, Hb decreased to 8.7. In recovering fish, Hb was marginally higher than in control. Mean Ht of control fish was 29.8%, with a range from 27.8 to 31.8. Ht of exposed fishes increased progressively up to 72 h post-exposure. But in the 96 h exposed fishes, Ht decreased(31.8). During recovery, Ht was somewhat equal to that of the control. Mean ESR of control fish was 1.2 mm h$^{-1}$, with a range from 0.6 to 1.8. ESR during 24 h recovery(1.9) was noticeably higher than that at 96 h post-exposure(1.5). Then the value showed a decreasing trend at 48 h(1.6) and 72 h(1.5) recovery. ESR at 96 h recovery recorded 1.6. Mean MCV of control fish was 125.0 µm$^3$ with a range from 115.4 to 133.0. Exposure to endosulfan caused decrease in MCV at 24 h(116.7) and thereafter, showed an increasing trend at 48 h(121.8) and 72 h(26.4). But at 96 h post-exposure, MCV decreased to 120.9. During recovery, MCV was lower than of control and exposed fishes. Mean MCH of control fish was 33.9 pg, ranging from 30.1 to 39.1. MCH recorded at 24 h and 48 h were 32.6 and 32.1, respectively. Thereafter, it got elevated to 36.0 at 72 h post-exposure but then decreased at 96 h(33.1). During recovery, MCH increased progressively from 24 h(30.0) to 72 h(32.1) through 48 h(31.4). However, at 96 h recovery, MCH decreased to 31.1. Mean MCHC of control fish was 27.1%, with a range from 25.3 to 30.3. MCHC of exposed fish registered the same value at 24 h and 72 h(28.2). At 48 h of exposure, it was 26.6 and at 96 h, 27.6. At 24 h recovery, MCHC was 27.0. At 48 h and 72 h recovery it increased to 28.1 and 28.4, respectively, and at 96 h of exposure, it decreased to 27.6.

VI of endosulfan exposed fishes was lower than that of control fish except at 72 h post-exposure when it was very marginally higher(1.01). All through during
recovery, VI was noticeably lower than unity. CI was less than unity in exposed fish, except at 72 h post exposure when it recorded 1.06. All through recovery, CI registered less than unity and it was as low as 0.89 at 24 h recovery. During exposure, SI of fishes showed the same trend as for CI. During recovery, SI was 1.00 at 24 h, 1.04 at 48 h and 1.05 at 72 h. At 96 h recovery, SI recorded 0.99.

In the peripheral blood of *R. daniconius*, five types of leucocytes were met with: lymphocyte, neutrophil, monocyte, macrophage and plasmacyte. In control fish, lymphocytes constituted 81.2% of the circulating leucocytes; 16% were neutrophils and 2.5%, monocytes. Macrophages comprised 0.3% of the circulating leucocytes, whereas, plasmacytes were not encountered in the peripheral blood of control fishes. Exposure to endosulfan essentially caused drastic decrease in the circulating lymphocyte population (lymphocytopenia). During recovery, however, relative percentage of lymphocytes recouped. Neutrophils registered an opposite trend; drastic increase during exposure (neutrophilia) and recoupment to near normalcy during recovery. Monocytes showed a tendency to remain higher than of control both during exposure and recovery. Relative percentage of this cell type was very high (25%) at 24 h recovery. Macrophages, after an initial slight increase to 1% at 24 h and 48 h post-exposure, disappeared from the circulating blood of exposed fish. During most part of recovery, except at 48 h, macrophages were absent in the circulating blood of the fish. Plasmacytes also showed almost a similar trend as of macrophages; these cells appeared in the blood of fish at 24 h and 48 h post-exposure, but later disappeared at 72 h and 96 h post-exposure so also during recovery. In the peripheral blood of exposed and recovering fishes, haemoblasts were met with very frequently.

To sum up, though there were noticeable changes in the peripheral haemogram of *R. daniconius* exposed to sub lethal concentration of endosulfan, statistically significant changes occurred only in TLC and TPC. Lymphocytopenia, with simultaneous neutrophilia, were very marked during exposure, suggesting a non-specific immune response of inflammatory nature, wherein there was general increase in the circulating phagocytic elements, possibly to eliminate particulate toxic metabolites induced by the pesticide.

### 9 Stress Protein Profiles

The results showed that the protein profile was unique to each tissue analysed. Exposure of fish to sublethal concentration of endosulfan elicited an array of new proteins along with the augmentation of the synthesis of some existing proteins in the brain, eye, gill and muscle tissues. Suppression of several native proteins was noticed in the tissues at both exposure and recovery phases. The existing and elicited proteins belonged to five protein families: high molecular weight proteins (HMWP), HSP80, HSP70, HSP60 and low molecular weight proteins (LMWP). Very low molecular weight proteins (VLMWP) were not detected in any of the four tissues selected
Eighteen proteins with apparent molecular weights ranging from 33 to 332 kDa were distinguishable in the protein profile of the brain of control fish. The relative quantity of each band widely differed from protein to protein and the maximum value was noted in 36 kDa protein (31.46%) and the minimum (1.34%) was expressed by 33 kDa. Similarly, relative quantity of 46 kDa protein in control was represented by 16.1%. LMWPs were relatively less in the brain tissue of control fish. The protein profile of the brain of test organisms exposed in “vehicle” control was almost similar to that of the control.

The endosulfan-exposed fish brain showed rigorous changes in the protein profile during exposure and also during recovery period. Rapid expression of stress response was observed in the early hours of exposure that is 2 h. Induction of three HMWPs (148, 271 and 396 kDa) was observed and the relative quantity increased at 4 h post-exposure. The intensity of HMWP, HSP80, HSP70 and HSP60 increased at 12, 24, 48, 72, 96 h and 7 days post-exposure. Though the intensity of HSP70 family protein 69 kDa and HSP60 family proteins 64 and 58 kDa were reduced at the 7th day of exposure, these fractions persisted throughout the recovery period.

A gradual increase in the relative quantity of expression of three different proteins of 35, 45 and 52 kDa was observed all through the exposure period and the same proteins were expressed during recovery as well. Six LMWPs (14, 16, 18, 20, 26 and 30 kDa) were newly induced at 8, 12, 24, 48, 72 and 96 h post-exposure but their expression was very feeble at the 7th day of exposure. On the 7th day of exposure, the protein profile of brain showed reduction in the relative quantity of several proteins, except 35, 45 and 52 kDa. During recovery, two characteristic proteins, such as 18 kDa and 16 kDa, were expressed at 4, 48, 96 h, 7 days and 15 days recovery.

Fish eye was found to have the maximum number of proteins among the tissues studied for stress protein profile. There were 35 distinct proteins in control fish eye with apparent molecular weight range from 15 to 332 kDa. Among these proteins, the highest relative quantity was shown by 20 kDa protein and only two proteins (14 and 11 kDa) were able to filter through this protein. The relative quantity of the individual proteins decreased with increasing molecular weight. The exposed fish eye showed characteristic changes in the protein profile during exposure and also during recovery period. The relative quantity analysis of eye proteins showed gradual succession of increase during exposure period. But the trend was reversed during recovery. HMWPs (101 kDa), HSP80 (84 kDa), HSP70 (72 & 74 kDa), HSP60 (55 kDa), and LMWPs (47, 37, 20 and 14 kDa) showed increase in the relative quantity during exposure and remained unchanged during recovery period. A low molecular protein of 11 kDa was newly elicited during 2 h of exposure; it was expressed at 4th h of recovery also.

Gill tissue had the least member of proteins among the tissues studied for stress protein profiles. There were 16 distinct proteins in control fish, ranging from 14 to
68 kDa. HMWPs were totally absent in the gill tissues and 14 kDa protein was strongly induced. Exposed fish gill showed characteristic changes in the protein profile. In the exposed gill, three HMWPs, one HSP70(74 kDa), two HSP60 and one LMWP were expressed from 2 h post-exposure onwards. Two proteins in the HSP60(55 and 52 kDa) and LMWP of 14 kDa were expressed at 4 h post-exposure. The relative quantity assessment data showed that synthesis of HMWPs(105, 169, and 360 kDa), HSP70(74 kDa) and LMWPs(19, 23, 27, 29 kDa) was augmented from 8 h of exposure and continued throughout the experiment including 15 days recovery period. The 15th day recovery gill tissue showed slow recovery by way of disappearance of HMWPs(216, 246, 304, 315 kDa) and of LMWPs(18, 20 and 26 kDa).

Twenty different proteins were identified in control fish muscle with a molecular weight range from 11 to 348 kDa. The LMWP of 11 kDa showed the highest relative quantity and the same was four times higher than 53 kDa, which was the next abundant fraction.

The protein profile of exposed muscle tissue had a unique pattern compared to that of the other tissues selected in the present study. The relative quantity of 11 kDa protein at 2 h exposure was 7.05, whereas in the control and in the vehicle control, its expression was 20.62 and 21.22, respectively. The relative quantity of 11 kDa protein showed almost three times inhibition in the early hour (2 h) of exposure. Similarly, elicitation of 82, 91 and 97 kDa proteins was very feeble at 2 h of exposure; they reappeared during 4, 8 and 12 h of exposure. The relative quantity of 33 kDa protein in control fish was 3.09 and 0.31, 0.34, 0.34, 0.28, respectively for 2, 4, 8, 12 h exposure; this fragment was restored during 15th day of recovery by 6.81. The intensity and relative quantity of 36 kDa protein gradually increased with exposure period and the maximum was noticed during 7th day of exposure followed by a gradual decrease during the recovery period.

To sum up, exposure to sub lethal concentration of endosulfan had strong sub cellular impact on R. daniconius, as revealed by the stress protein profiles of the brain, eye lens, gill and muscle tissues of the exposed fish, such as high expression of HMWP and low induction of LMWP in all tissues and the poor subcellular restoration even after 15 days of recovery. Since pesticides have the ability to generate reactive oxygen species(ROS), the poor recovery response may be due to impairment of antioxidant defense systems or an insufficient capacity to repair oxidative damage. More studies are warranted in this direction to better understand pesticide toxicity to vertebrates.

References


Climate Change Impacts and Implications in Kerala

M K P Roy
Director, Centre for Community Health Research(CCHR)
Sadanathil bungalow, Vettikavala, Kottarakara, Kollam
Kerala, India - 691 538.
E-mail: roycchr@sify.com, http://www.cchrindia.org
Tel: 91-474-2403358, 91-9847282833

1 Introduction

The climate of a place is defined as the average weather that is experienced over a period of time. The factors that contribute to weather are the rainfall, sunshine, wind, humidity and temperature. Climate is usually described in terms of the mean and variability of temperature, precipitation and wind over a period of time, ranging from months to millions of years with a minimum of 30 years. Climate change is currently evidenced as severe storms, floods and droughts. Substantial reduction of tropical forests and grassland; decrease in the availability of water in the rivers/groundwater level/dug wells; decline in yields of food grains; rise in sea level leading to erosion of coastal areas; increased incidence of water borne disease, and vector-borne disease such as malaria.

The amount of CO₂ in the atmosphere till 1950 has never exceeded 300 ppm. But the atmospheric concentration of CO₂ in 2005 was 370 ppm. Sea temperatures have risen by an average of 0.5°C over the last 40 years. Global surface temperatures have risen about 0.7°C in the past 100 years. Further, the global mean sea level has risen between 10 and 25 cm (average 13 cm) during the last 100 years. In the Arctic region 20,000 square kilometers of fresh water ice have melted.

Climate models predict an increase in average surface air temperature of about 2.5°C by the year 2100. The sea level will rise by approximately 49cm over the next 100 years, with a range of uncertainty of 20-86cm. Increase in global temperature can alter local climate conditions, affecting forests, crop yields and water supplies. It may also affect human health, animals and many types of ecosystems[1].
2 Impacts and implications in Kerala

Kerala is a small strip of land lying at the south-west tip of India. It lies to the north of the equator between $8^\circ 18'$ and $12^\circ 48'$ north latitude and $74^\circ 52'$ and $77^\circ 24'$ east longitude. Kerala extends over an area of 38,863 sq.km which is only 1.03 percent of the total area of India. It has a total coastline of 580 km. Its width varies greatly from west to east. It is about 120 kilometers at its maximum and just 30 kilometers at its minimum.

Although Kerala lies close to the equator, its proximity with the sea and the presence of the fort like Western Ghats, provides it with an equable climate which varies little from season to season. The temperature varies from $28^\circ$ to $32^\circ$ C. Southwest monsoon and Northeast monsoon are the main rainy seasons. Owing to its diversity in geographical features, the climatic condition in Kerala is diverse. It can be divided into 4 seasons: winter, summer, South - West monsoon and North - East monsoon.

2.1 Temperature

Temperature data for seven IMD (India Meteorological Department) stations of Kerala were collected from National Data Centre of IMD, Pune from 1956 to 2004 (49 years) showed that there was an increase in maximum temperature over Kerala by $0.64^\circ$ C during the period of 49 years. It was further observed a clear upward trend in surface air temperature of Kerala.

2.2 Rainfall pattern

Kerala showed decreasing trend in monsoon rainfall for the period 1901-2007. After 1999, rainfall was below long term average rainfall (except in 2006). Another study showed that Kerala experienced decline in annual monsoon rainfall during the recent past decades (1961 and 2003). Rainfall data for the IMD stations of the State of Kerala for the period from 1871 to 2008 (140 years) revealed a declining trend in annual and southwest monsoon rainfall during the past 60 years.

2.3 Lowering of water tables

It was observed by the Central Groundwater Board that lowering of water tables in certain regions of Kerala reported to be critical and alarming.

2.4 Rise in sea level

Observations based on tide gauge measurements along the Indian coast, for a period of 20 years indicated that the sea level along the Indian coast has been rising at the rate of about 1.3mm/year on an average. The mean sea level rise trends in Kochi (Kerala), based on 54 years of available data is 1.75mm per year. Estimation
of inundation of coastal areas due to sea level rise was made for one location (Kochi) along the west coast of India. The estimate shows that the inundation area will be about 169 km$^2$ of the coastal region surrounding Kochi for a 1.0 m rise in sea level. It has also been observed that overexploitation of ground water in certain stretches of Kerala coast has contributed to the entry of salinity into the coastal aquifers from the sea.

### 2.5 Salinity intrusion

The potential impacts of global climate change in coastal Kerala are salinity intrusion into aquifers and rise in salinity of wetlands[3]. Studies indicate that fall in rainfall and sea level rise, along with other factors have resulted in salinity intrusion affecting ground water resources in the coastal districts of the state.

### 2.6 Sunstroke and Sunburn

Sunstroke is a form of hyperthermia, an abnormally elevated body temperature with accompanying physical and neurological symptoms, resulting from exposure to high temperature. Sunburn is literally a burn on the skin. It is a burn from UV radiation. The consequence of this burn is inflammation of the skin—reddening of skin with some blisters. Skin damage and loss may take place. Several cases of sunstroke and sunburn reported from Kerala during every extreme summer.

### 2.7 Water-borne diseases

In 2008, World Health Organisation (WHO) reported that an outbreak of chikungunya in Kerala during 2006 and 2007 was mainly due to climate change. It was further observed that during that period, over 100 people died, while more than 100,000 were affected by the mosquito-borne disease in the coastal state. There are other reasons of the spread of the disease but climate change cannot be denied as a prime reason. Due to change in climate, it becomes more conducive for mosquitoes to spread to new areas and affect people. Chikungunya is a viral disease that spreads through the bite of infected mosquitoes. It is characterised by severe, sometimes persistent joint pain, as well as fever and rash. Malaria is a climate-sensitive disease and its transmission dynamics are greatly affected by climatic conditions. The development of the parasite takes place in a mosquito. Global warming is a major cause of surge in chikungunya, dengue and malaria in Kerala. According the report of WHO in 2008, these vector borne diseases will intensify with climate change and more people and new areas will fall prey to it.

### 2.8 Decline of agricultural crops

Kerala state was facing serious crisis in major areas of food security, agriculture and marine resources due to climate change. The agriculture sector in Kerala was badly
affected due to continuous rain. The untimely rain in Kerala, which hit the entire Kerala during pre-monsoon in 2008 and caused crop damage and flooding. It was estimated that farmers could not harvest paddy worth about Rs. 128 crores (1280 million rupees) due to unexpected flooding in the Kuttanad fields during the same period.

The thermo-sensitive crops like black pepper, cardamom, tea, coffee and cocoa will be badly affected as temperature range (the difference between maximum and minimum temperatures) is likely to increase and rainfall is likely to decline. Heavy pre-monsoon showers periodically hit pepper production in Kerala, the main producer of the commodity in India. Increase in maximum temperature of 1-3°C during summer 2004 adversely affected thermo-sensitive crops like black pepper and cocoa in Kerala[2]. Records show that almost all the plantation crops suffered to a great extent in 1983 and 2004 due to disastrous summer droughts. Climate change and unseasonal rain in November and January over the period 2009 and 2010 had been dampened the prospects of mango farmers in Palakkad district of Kerala.

References


Abstract

Medicinal plants are renowned for its therapeutic properties. *Adhatoda* is one among those plants which is proved to be the one of the effective medicine against the ailment of many of the respiratory disorders. Hence an attempt is made to study the antimicrobial property of this plants and activity against respiratory tract infection causing pathogens. The result of antibacterial activity analysis proved that the extract from this plant can be used as an alternative medicine.

Keywords: *Adhatoda*, Antimicrobial Assay, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, agar-well diffusion.

1 Introduction

Medicinal plants have always been considered a healthy source of life with many therapeutic applications. Therapeutic attribute of medicinal plants is due to the presence of a group of bioactive compounds[12].

*Adhatoda* (Adalotaka) belongs to Family Acanthaceae. Two major species are important medicinally viz., *Adhatoda vasica* (*Justicia adhatoda* or, Valiya adalodakam) and *Adhatoda beddomei* (Cheriya adalodakam).

*Adathoda vasica* is native to Asia, leaves are large and dark green with characteristic odour tastes bitter Cattle do not eat this plant because of unpleasant smell of the leaf. Leaf extract is good for Asthma and cough. A good medicine to stop internal and external bleedings. Active ingredient medicine for fever, expectorant, antispasmodic and good blood purifier. Leaves of the plant contain two major alkaloids called vasicine, and vasicinone, which is having bronchodilator and antihistaminic effects. Alkaloids exist in combination with adhatodic acid[1, 10].
Adathoda beddomei (Clarke) is a plant common in India. The leaves are white-green and smaller. Medicinally useful for pitta, kapha, cough, bronchitis, asthma, inflammation, hemorrhage, hemorrhoids, diseases of the eyes, and bleeding diarrhoea. The leaves, roots, flowers and stem bark of this plant are used in medicinal applications. It has been used as an antispasmodic, bronchodilator, and mucolytic agent in asthma and other respiratory conditions. It has oxytocic properties and can be abortifacient [3].

Dasaraju, and Liu [5] reported that respiratory pathogen are ranked quite high as a causative agents for increasing mortality rate in developing countries. It is the need of the time to look for an effective alternate medicine for healthcare needs since the Antibiotic resistance producing bacteria are becoming an emerging threat. The is aimed us to is to screen antimicrobial properties of two Adhatoda plants against respiratory infection causing organisms.

![A. vasica - Vialiya adalodakam and A. beddomei - Cheria adalodakam](image)

Fig. 1

## 2 Materials and Methods

Two plant varieties under Acanthaceae family, considered for the study are namely Adhatoda vasica and Adhatoda beddomei. The locally available plant samples were collected.

### 2.1 Antimicrobial Assay

Clean dry plant samples were collected in cotton bags. The materials were grinded to fine powder with the help of mixer grinder. 10 gm of powered materials were soaked in 30 ml of 70% methanol and were kept at 30°C for 12 hours on a rotary shaker. After 12 hours the previous portion of added methanol was evaporated so to make the same volume methanol was added and then it was placed on a rotary shaker for another 12 hours at 30°C. After that it was filtered through Whatman No. 1 filter
paper. The filtrate was centrifuged at 2000 rpm for 10 min. The supernatant was collected and the supernatant was allowed to evaporate until completely dry. The extracts were kept sterile bottles under refrigerated condition until use. Then 30 mg of dry extract was resuspened in 1 ml of 70 % methanol. The final concentration of the extract was 30 mg/ml.

2.2 Microorganisms used
Pathogens that are known to cause various respiratory diseases were chosen to test the antimicrobial activity of the plants extracts *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Pseudomonas aeruginosa*. Pathogenic bacterial samples were collected from the MTCC collection Chandigarh.

2.3 In vitro Antibacterial Study
The modified agar-well diffusion method of Cheesbrough[2] and Black[4] was employed to study the antibacterial activity of the plant extracts. The wells were then added with 50 µl each the plant extract, methanol (negative control) and chloramphenicol (positive control). Plates were incubated for 24 hours at 37°C. After 24 hours the plates were examined and the result were recorded.

3 Result
3.1 Antimicrobial Bioassay
The methanolic extracts of leaves of *Adhatoda vasica* and *Adhatoda beddomei* were subjected to screening of antibacterial activity against respiratory disease causing pathogens viz *Staphylococcus aureus* and *Klebsiella pneumoniae* and *Pseudomonas aeruginosa*. *Adhatoda vasica* leaf extract showed maximum antimicrobial activity against *S. aureus* (22±0.5), *P. aeruginosa*, *Adhatoda beddomei* leaf extract showed maximum antimicrobial activity against *S. aureus* (20±0.2), *P. aeruginosa* (14±0.2), *K. pneumonia* (18±0.7) Table(1) and Fig(2).

Table I shows the zones of inhibition obtained by Agar well diffusion method for the leaf samples studied, the positive and negative control.

<table>
<thead>
<tr>
<th>Bacteria</th>
<th>Zone of inhibition (mm)</th>
<th>A. vasica</th>
<th>A. beddomei</th>
<th>Chloramphenicol (+ve control)</th>
<th>Methanol (-ve control)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Staphylococcus aureus</em></td>
<td></td>
<td>22±0.5</td>
<td>20±0.2</td>
<td>25±0.9</td>
<td>8±0.7</td>
</tr>
<tr>
<td><em>Klebsiella pneumoniae</em></td>
<td></td>
<td>20±0.3</td>
<td>18±0.7</td>
<td>27±0.6</td>
<td>6±0.5</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em></td>
<td></td>
<td>16±0.2</td>
<td>14±0.2</td>
<td>25±0.7</td>
<td>4±0.5</td>
</tr>
</tbody>
</table>
4 Discussion

Nascimento et al.[7] and Rajput et al.[11] reported the efficacy of various plant extract as antimicrobials. The results of the agar-well diffusion method showed that the crude methanolic extract of the leaf exhibits an antimicrobial activity against the tested organisms *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Pseudomonas aeruginosa*. Both the leaf extracts showed a maximal activity against *Staphylococcus aureus*.

![Zone of inhibition against *S. aureus* against *A. vasica*](image1.png)

![Zone of inhibition against *S. aureus* against *A. beddomei*](image2.png)

![Zone of inhibition against *K. pneumoniae* against *A. vasica*](image3.png)

![Zone of inhibition against *K. pneumoniae* against *A. beddomei*](image4.png)

![Zone of inhibition against *Pseudomonas aeruginosa* in *A. vasica*](image5.png)

![Zone of inhibition against *P. aeruginosa* in *A. beddomei*](image6.png)
Despite advances in antimicrobial therapy, *S. aureus* remains a major multidrug resistant bacteria causing nosocomial infecton. Hence the extract could be used as an alternative for antibiotics against drug resistant bacteria. The result is accordance with the findings of Muroi[8] where MRS resistant *Staphylococcus* were sensitive to plant extacts on antimicrobial assay. These findings also support the traditional knowledge of local users about their selection of plant samples as antimicrobial agents and the use of these plants for antibacterial activity Dhuley[6]. The result of the study opened a gate way for the future investigations involving the isolation of the active compounds and invivo etc.

References


Facile Seed Mediated Cum Capping Strategy for the Preparation of Silver Nano Particles and Anti Bacterial Activity Studies

Sivakala S
Department of Chemistry
S.N. College, Kollam
Kerala, India

Abstract

Significant efforts have been made for the synthesis and characterization of stable dispersion of silver, gold and other noble metals because their importance in the field of catalysis, photography, electronics, photonics, optoelectronics, biological labeling, imaging and sensing. In the present work, we propose to use a seed-mediated strategy for the preparation of silver nanoparticles using a renewable resource based low cost surfactant, 3-pentadecyl phenyl phosphate derived from cashew nut shell liquid, a byproduct obtained from cashew industry. Here silver nanoparticles are produced by the reduction of silver nitrate in presence of surfactant micelle at room temperature using ascorbic acid as the reducing agent. Effect of concentration of surfactant, amount of seed on the particle size, shape were studied. Surface plasmon resonance energy of the particles was measured using UV-Visible spectroscopy. Crystalline structure of the silver nanoparticles was studied by XRD. Morphology of the particles was observed through scanning electron microscopy, transmission electron microscopy and atomic force microscopy. Additionally, the antibacterial activity of the nanoparticle dispersion was measured by Kirby-Bauer and Stokes’ methods. The nanoparticles of silver showed high antimicrobial and bactericidal activity against bacteria such as Escherichia Coli. This method is well documented and standard zones of inhibition have been determined for susceptible and resistant values.

Keywords: silver nano particles, seed mediated method, anti bacterial activity.

1 Introduction

Noble metal nanoparticles have been the subjects of focused research interests in recent years due to their unique electronic, optical, mechanical, magnetic and chem-
ical properties that are attributing from their small sizes and large specific surface area. Silver nanoparticles have been also found to exhibit interesting antibacterial activities. Antibacterial activity of the silver-containing materials can be used, for example, in medicine to reduce infections as well as to prevent bacteria colonization on prostheses, catheters, vascular graft, dental materials and human skin arising from the large surface to volume ratio\cite{1}. Silver-containing materials can be employed to eliminate microorganisms on textile fabrics and can also be used for water treatment. The surface of a metal is like plasma, having free electrons in the conduction band with positively charged nuclei. Their antibacterial activity involves inactivating the essential respiratory enzymes and proteins responsible for RNA and DNA replication and disrupts ion transport processes\cite{2, 3, 4, 5}. It is reasonable to state that the binding of the particles to the cell membrane depends on the surface area available for interaction. Though silver will indiscriminately form complexes with several different amino acids and thereby inhibit protein function. Also literature showed that silver nano particles can exhibit shape dependent antimicrobial property. Sukedh Pal et al. investigated the antibacterial properties of different shapes nanoparticle against the gram negative bacterium Escherichia coli, both in liquid systems and on agar plates\cite{6}. Therefore, development of synthetic strategy for the preparation of uniform small size silver particle is receiving importance. Several strategies are reported for the synthesis of silver nanoparticles: electrochemical method, thermal decomposition, laser ablation microwave irradiation and sonochemical synthesis. The seed-mediated approach has become increasingly popular recently in the production of ordered morphologies of gold and silver particles in aqueous surfactant solutions. These seed particles can be capped with a variety of surface groups like surfactant, block copolymers etc. that could be present during the reaction. It is then placed in a reaction system containing weak reducing agent and which is usually ascorbic acid which itself, at room temperature is not capable of reducing the metal salt to elemental metal. But up on addition of the seeds, the reaction is thought to take place on the seed surface and be autocatalytic to produce larger particles. In a seed-growth method, small metal nanoparticles are prepared first and later used as seeds(nucleation centers) for a systematic growth of large sized nanoparticles. Such methods have been successfully applied for shape-controlled synthesis of Au, Ag, Ir, Pd, and Pt NP\cite{7, 8, 9, 10}. However, finding a suitable growth condition that inhibits additional nucleation generally limits the application of such methods. The secondary nucleation mostly leads to anisotropic growth which can be controlled by a selective adsorption of surfactant ions on specific crystal planes. The direction of the crystal growth governs by electrostatic interactions, polarity of the surfactant head group which plays an important role in an effective capping process. Assemblies of surfactants or synthetic amphiphiles have been utilized as surface stabilizers and/or templates in the synthesis of metal nanoparticles. These moieties, by their binding to the nanoparticle surface, decrease the surface energy, control the growth and shape of the particles, and act as a stabilizer against
coagulation. Neutral surfactants such as alkanethiols, alkylphosphines, and amines are used as stabilizers in the synthesis of different nanoparticles[11, 12, 13, 14, 15]. However, taking advantage of high surface area of the nanoparticles, it is possible to study the assemblies of surfactants on these active surfaces.

In the present work, we propose to use seed-mediated strategy for the preparation of silver nanoparticles using a renewable resource based low cost surfactant, 3-pentadecyl phenyl phosphate derived from cashew nut shell liquid, a byproduct obtained from cashew industry. Critical micelle concentration of the surfactant was measured by light scattering method. Here silver nanoparticles are produced by the reduction of silver nitrate in presence of surfactant micelle at room temperature using ascorbic acid as the reducing agent. Optimisation of the reaction conditions like seed concentration, silver nitrate concentration and amount of surfactant for tuning the shape of the silver particles from nanospheres to nanorods. Here, the amphiphilic surfactant 3-PDPPA can act as structure-directing agent cum capping agent. Effect of concentration of surfactant, amount of seed on the particle size, shape were studied. Surface plasmon resonance energy of the particles was measured using UV-Visible spectroscopy. The interaction between the capping agent and the silver particles were manifested from FTIR. Crystalline structure of the silver nanoparticles was studied by XRD. Morphology of the particles was observed through polarized light microscopy, scanning electron microscopy, transmission electron microscopy and atomic force microscopy.

Additionally, the antibacterial activity of the nanoparticle dispersion was measured by Kirby-Bauer method. The nanoparticles of silver showed high antimicrobial and bactericidal activity against bacteria such as Escherichia Coli. The Kirby-Bauer and Stokes’ methods are usually used for antimicrobial susceptibility testing, with the Kirby-Bauer method being recommended by the National Committee for Clinical Laboratory Standards (NCCLS, 03). This method is well documented and standard zones of inhibition have been determined for susceptible and resistant values. The antibacterial characteristics of silver nanoparticles produced have been demonstrated by directly exposing bacteria to colloid silver particles.

2 Experimental

Seed of silver nanoparticles were prepared by the reduction of silver salt using strong reducing agent, sodium borohydride in presence of sodium citrate as a capping agent which will prevent the aggregation of silver nanoparticles. Reduction was performed in aqueous media at room temperature. Particle size of the seed was measured using dynamic light scattering method and observed in between 4 to 5 nm. Nanostructured silver particles were prepared by a seed mediated growth process in the presence of an amphiphilic surfactant, 3-PDPPA as capping agent. Here, the amphiphilic surfactant, 3-PDPPA is acting a dual role of controlling the aggregation of nanoparticles as well as structure-directing agent. It is reported in literature that the shape of the micelle
can act as structure directing agent during the growth of the nanoparticle. Here, the silver Nps are formed by the reduction of silver salt in presence of weak reducing agent, ascorbic acid. The newly formed silver nanoparticles will adhere within the seed surface which may act as the nucleating centre for the secondary growth of silver particles.

3 Results and discussion

The optical properties of the silver nanoparticles were measured by performing UV-Visible spectroscopy. The UV-Visible spectra of Ag Nps with different concentration of PDPPA are shown in Fig1. The nature and shape of the peak could be qualitatively related to the nature of nanoparticle. Smaller and uniform sized particles with narrow particle distribution exhibited sharp well defined absorbance in the UV spectra while nanoparticles with wide range of distribution or aggregation showed broad absorbance.

![Fig 1. Effect of concentration of 3-PDPPA on the optical properties of Ag Nps](image)

Another interesting observation made is that when the concentration of PDPPA decreased to $10^{-5}$ M concentration, it exhibited optical absorption maxima at 435 nm with orange color. Slowly within 10 minutes, the orange color becomes green color with two plasmonic peaks appearing at 421 nm and 651 nm as given in Fig 2. The snapshots showing the color change is given at the inset. Under TEM, the orange color is observed as spherical particles and it became rod shaped particle when changed into green color. The two peaks observed in the UV-Vis spectrum corresponds to the longitudinal and transverse plasmon peaks exhibited by silver nanobars/nanorods. The intensity of the longitudinal mode is observed to be higher compared to transverse mode and the same observation strengthened by the observations made by other researchers. The observed color change could be explained
by two possible growth mechanism. In one mechanism, the surfactant forms a soft template in which the template has a certain dependence on the surfactant concentration and the ionic strength of the solution. By introducing the seed to the growth solution, the surfactant capped seed become the part of the soft template and the growth starts by diffusing the silver atoms into the template. The other possible mechanism is that the surfactant capped seed starts growing and the new atoms join the nanocrystal lattice. They are protected by the surfactant monomers coming from the solution. Particle size distribution curve measured using dynamic light scattering is given in Fig 3. With increasing concentration of PDPPA in the system, particle size increased from 37 nm (10⁻⁴ M) to 79 nm (10⁻³ M).

Fig 2. Effect of time on the optical property of Ag Nps (10⁻⁵ M PDPPA, 0.6ml seed)

Fig 3. Particle size distribution of Ag Nps using dynamic light scattering method
4 Crystalline structure and morphology of silver NPs

Crystalline structure of Ag Nps was studied by performing X-ray diffraction technique. XRD is a useful technique for studying the crystalline phase, crystallinity and crystalline size of nano materials. Understanding the crystallographic structure of silver Nps is crucial to know their stability and the reasons for their spontaneous growth during the formation of Ag Nps in solution. The representative X-ray diffractograms of Ag Nps having two different shapes like nanospheres, nanobars are given in Fig 4. Fig 4 a shows the diffractogram of the nanobar AgNps. It exhibited sharp maxima at at $2\theta = 38.09^\circ$ ($d$ spacing = 2.36Å) indicates (111) plane, $2\theta = 44.29^\circ$ ($d$ spacing = 2.04Å) indicates(200) plane, $2\theta = 64.50^\circ$ ($d$ spacing = 1.44Å) indicates(220) plane and $2\theta = 77.42^\circ$($d$ spacing = 1.23Å) indicates(311) plane. Lot of studies have been envisaged with a large agreement pointing to a face centred cubic lattice(fcc) with atomically flat surface parallel to the (111) plane. This confirms the formation of face centred cubic crystallites of AgNP (JCPDS file no: 893722).

![Fig 4. XRD of AgNps having shapes like nanospheres, nanorods](image)

5 Morphology

Morphology of the formed silver nanoparticles is characterized by observation under scanning electron microscopy(SEM), Transmission electron microscopy(TEM), and atomic force microscopy(AFM). Experiments were performed with different concentration of silver nitrate, surfactant(PDPPA) concentration and amount of ascorbic acid. It exhibited different morphologies like nanospheres, nanocubes, nanorods, nanobars and nanosheets. Details of the morphological observation are given in Fig 5. Fig 6 shows the TEM images of the sample prepared with $10^{-3}$M PDPPA.
and 0.05 ml of 10Mm AgNO₃ showed the formation of nanospheres, nanocubes and truncated cubes. Fig 7 Shows the TEM images of AgNps prepared using different concentration of surfactant and it exhibited morphology like nanospheres, nanocubes, nanobars, hexagonal crystallites and truncated cubes. Figure shows the AFM images of AgNps having spherical shape. The AFM profile is also given.

Fig 5. SEM images of AgNps having shapes like nanosphere, nonorods and nanobars

Fig 6. HRTEM images of AgNps having different shapes

Fig 7. AFM image and profile of the of AgNPs
6 Antimicrobial activity of silver nanoparticles

Antimicrobial susceptibility of silver nanoparticles was tested against E.coli culture in LB agar plate. Fig 8 shows inhibition zone which clearly indicates antibacterial activity of Ag Nps against E.coli. Experiments were performed as per Kirby Bauer diffusion method was used as antimicrobial susceptibility testing method. Disposable plates inoculated with tested E-coli bacterial at a concentration of $10^5$ CFU/ml (colony forming unit) were used for the test. Zone of inhibition was measured after 24 hrs on incubation at 37°C. The comparative stability disc containing E-coli was made. Figure shows plates to which a bacterial suspension was applied. The presence of Ag Nps at a certain inhibited bacterial growth by more than 90%. Decrease particle size showed a lower susceptibility. However, it is necessary to determine minimum inhibitory concentration leading to inhibition of bacterial growth.

![Fig 8. Snap shot antibacterial activity of AgNps was tested against E.coli culture in LB agar and broth.](image)

Further antimicrobial acceptability of Ag Nps was studied by optical density measurement. Studies conducted in LB broth which showed 80% increase in O.D (initial OD: 0.531; final OD: 2.719) for control without silver Nps and 71% increase in OD (initial OD: 0.73; final OD: 2.53) for test with silver Nps after 24 hrs at 600 nm which supports the antibacterial effect of Ag Nps. Then this E-coli inoculated and standard LB broth systems were fluorescent stained with Propidium iodide (specific for dead cells) and SYBR green (specific for live cells). Fluorescent photographic images were taken after incubation and the representative photographs are given in Figure 9 and 10, respectively. We got 100% increase in number of dead cells and 83% decrease in number of live cells in test solution (with silver Nps) with respect to the control (without silver Nps). The mechanism of the bactericidal effect of silver colloid particles against bacteria is not very well known. Silver Nps may attach to the surface of the cell membrane and disturb its power functions such as permeability and respiration[16, 17, 18]. It is reasonable to state that the binding of the particles to the cell membrane depends on the surface area available for interaction.
Smaller particles, larger surface will be area available for interaction will give more bactericidal effect.

![Fig 9. Fluorescent micrograph of Propidium iodide stained E. coli dead cells in control without AgNps and test with AgNps](image1)

![Fig 10. Fluorescent micrograph of SYBR green stained E. coli live cells in control without AgNps and test with AgNps](image2)

7 Summary

Silver nanoparticles of different shapes and sizes prepared using this surfactant molecule as capping agent and ascorbic acid as reducing agent. Summary and conclusion of the important observation is given below. The UV-visible spectra of Ag NPs in aqueous solution showed an absorption peak at 393 nm corresponds to the surface plasmon resonance of AgNS. With aging there appears a shoulder peak at 498 nm indicating the longitudinal vibration of Ag nano bars. The effect of concentration of surfactant and the amount of seed on the particle size of AgNPs were studied using dynamic light scattering method. The results indicates a decrease in particle size with increase in the concentration of surfactant which may be due to the decrease in hydrodynamic diameter of the surfactant micelle. Also it is observed that on increasing the amount of seed ,the particle size decreases. Morphological observations of the AgNPs using PLM, SEM, AFM and TEM revealed the formation of surfactant micelle which act as template for the formation of AgNS and AgNWs. The topographical studies through AFM analysis indicates the formation of AgNS and AgNWs. SEM and TEM showed the presence of Ag NS. The formation of the bilayer of the surfactant on the AgNPs were studied by taking XRD of the samples.
before and after centrifugation. Before centrifugation the diffractogram appeared as diffused halo with no distinct peak maxima suggesting the formed AgNP were fully covered with surfactant micelle. After centrifugation the diffractogram showed distinct peaks corresponding to the crystalline planes of the AgNPs.

References

Some Notes on the Navier-Stokes Equations in Unbounded Channel Domains

Manil T. Mohan
School of Mathematics
Indian Institute of Science Education and Research (IISER)
Thiruvananthapuram
Kerala, India 695 016
Email: manil@iisertvm.ac.in

Abstract

In this paper we will give some notes on the solvability of viscous flow in unbounded channels with multiple outlets in both 2-D and 3-D domains.

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Keywords: Navier-Stokes equations, viscous flow in channels

1 Introduction

Mathematical theory of viscous incompressible flow through unbounded channel has many applications such as hydraulics in water resources, hydraulic machinery, oil transport networks, fluid in engines etc. Well-posedness theorem is an essential step for applications in optimal control theory (Sritharan [16]), convergence of numerical algorithms and nonlinear filtering (Sritharan [15]). Solvability theory of generalized solutions to Navier-Stokes equations was pioneered by Leray [12], Hopf [7] and Ladyzhenskaya [8], [9]. Steady state flow through channels of various kinds has been studied by a number of authors including Amick [1], [2], Amick and Frankel [3], Ladyzhenskaya and Solonnikov [10], [11]. In [1], Amick discussed the steady flow of viscous incompressible fluid in channels and pipes in two and three dimensions which are cylindrical outside some compact set. The paper by Heywood [5] highlighted the question of uniqueness of Navier-Stokes equations for certain unbounded domains modeling channels, tubes, or conduits of some kind and the importance

1This note has been extracted from the original work, “Stochastic Navier-Stokes Equations in Unbounded Channel Domains” of the author with Utpal Manna and S. S. Sritharan, which is under review for a journal publication.
of prescribing flux or the overall pressure difference. In [3], Amick and Fraenkel studied steady state solutions of the Navier-Stokes equations in various types of two-dimensional channel domains. In [6], Heywood constructed classical solutions of the Navier-Stokes equations for both stationary and non-stationary boundary value problems in arbitrary three-dimensional domains with smooth boundaries. The time-dependent flow through the three-dimensional channels with outlets diverging at infinity has been studied by Ladyzhenskaya and Solonnikov [10] and Solonnikov [13]. The paper by Solonnikov [13] presents solvability of boundary value problems for the Stokes and Navier-Stokes equations in noncompact domains with several outlets to infinity. Babin [4] considered the Navier-Stokes system in an unbounded planar channel-like domain and proved that when the external force decays at infinity, the semigroup generated by the system has a global attractor and its Hausdorff dimension is finite using weighted Sobolev estimates.

2 The Admissible Channel Domain

In this section following Sritharan [14] we define the class of channel domains that will be analyzed.

**Definition 2.1.** (Admissible channel domain) A simply connected open set $\Theta \subset \mathbb{R}^2$ with $C^\infty$ boundary $\partial \Theta$ consisting of two disconnected components $\partial \Theta_1$ and $\partial \Theta_2$ is called an admissible channel domain (see Figure 1), if it is the union of three disjoint sets $\Theta_0 \cup O_1 \cup O_2$ defined in the following way. Let $O_1$ and $O_2$ be two semi-infinite strips of width $d_1$ and $d_2$ respectively. These two straight channels are smoothly (not necessarily coaxially) joined by a bounded domain $\Theta_0$ such that $\partial \Theta_1 \cup \partial \Theta_2 = \partial \Theta \in C^\infty$.

![Figure 1: admissible channel domain](image)

Now let us consider the problem of accelerating a viscous incompressible fluid from rest to a given flux rate through an admissible channel domain. The mathematical problem is to find the velocity field $u$ and pressure field $p$ such that

$$(u, p) : \Theta \times [0, T] \to \mathbb{R}^2 \times \mathbb{R},$$

the momentum equation

$$u_t + u \cdot \nabla u = -\nabla p + \nu \Delta u \quad \text{in} \quad \Theta \times (0, T),$$

(1)
the incompressibility condition
\[ \nabla \cdot u = 0 \text{ in } \Theta \times (0, T), \tag{2} \]
the non-slip boundary condition on the channel walls
\[ u(x, t) = 0 \text{ on } \partial \Theta \times [0, T], \tag{3} \]
the initial condition
\[ u(x, 0) = 0, \ x \in \Theta, \tag{4} \]
and the flux condition
\[ \int_{\Gamma} u \cdot ndS = \mathcal{F}(t), \text{ for all } t \in [0, T] \text{ with } \mathcal{F}(0) = 0, \tag{5} \]
are satisfied. Here \( \nu > 0 \) is the co-efficient of kinematic viscosity and \( \Gamma \) is any cross-sectional curve cutting the channel. The solvability results of (1)-(5) can be found in Sritharan [14].

### 3 The Multi-Channel Domain

The paper by Sritharan [14] addressed the following two important cases which were not considered in the earlier works:

(i) time-dependent flow through two and three dimensional channels with finite cross section;

(ii) time-dependent flow through two-dimensional channels with outlets diverge at infinity

and provided a unique solvability theorem for the two-dimensional case of the problem type (i). The problem of type (ii) may possibly be resolved by suitably choosing a conformal mapping (see Amick and Franekel [3] for similar ideas in the case of steady flows) to straighten the diverging outlets.

Let us consider the unbounded multi-channel domains, with several outlets as shown in the figure (see Figure 2). Let the outlets of the multi-channel domain be named as \( O_1, O_2, \ldots, O_N \) and outside a compact region let the outlets be of constant widths \( d_1, d_2, \ldots, d_N \). The idea of the proof is to construct a basic vector field through each of these outlets with the flux \( \mathcal{F}_i(t) \) such that \( \sum_{i=1}^{N} \mathcal{F}_i(t) = 0 \) (see Sritharan [14]). The methodology of proof can be understood by considering a channel with two outlets having a unit width connected in a smooth way \( \Theta = O_1 \cup O_2 \cup \Theta_0 \) (see Figure 3).

Let us now discuss the problems of type (i) and type (ii) and examine the difficulties that arise in proving solvability. The time-dependent Navier-Stokes problem
is usually treated using the method of Hopf [7] which relies on $L^2$-energy estimates. The traditional methods of solvability fail in the absence of an energy inequality. For channels of finite cross section, as pointed out in Srinathran [14], in order for the net flux to be nontrivial, the velocity field should not decay to zero at infinity (upstream and downstream). Such velocity fields would then have infinite energy.

If the net flux of the velocity field $u$ is $\mathcal{F}(t)$, then across any cross section $\Gamma$, we have

$$\int_{\Gamma} u \cdot n \, dS = \mathcal{F}(t),$$

where $n$ is the normal to the curve $\Gamma$ and $dS$ is the length element.

(i) **Channels with finite cross section:**

In this case, the velocity $|u(x,t)| \rightarrow 0$ as $|x| \rightarrow \infty$. Let us take the 2-D case with the outlet $O_2 = \{(x,y) \in (0,\infty) \times (0,1)\}$. On the contrary to $|u(x,t)| \rightarrow 0$, let us assume that $|u(x,t)| \rightarrow 0$, as $|x| \rightarrow \infty$. We know that $\mathcal{F}(t) = \int_{\Gamma} u \cdot n \, dS = \int_{0}^{1} u \cdot n \, dy$.

Let us consider the two cross sections $\Gamma_1$ and $\Gamma_2$ across the outlet $O_2$ (see Figure 4). Let $\mathcal{O}$ be the region between the two cross sections $\Gamma_1$ and $\Gamma_2$. The normals at each cross section be $n_1$ and $n_2$ with the corresponding flux $\mathcal{F}_1(t)$ and $\mathcal{F}_2(t)$ (but note that $n_2 = -n_1$). Then by using Green’s formula, we have

$$\int_{\mathcal{O}} \nabla \cdot u \, d\mathcal{O} = \mathcal{F}_1(t) - \mathcal{F}_2(t).$$

Figure 2: multi-channel domain

![Figure 2: multi-channel domain](image)

Figure 3: channel with two outlets having unit width

![Figure 3: channel with two outlets having unit width](image)
\[
\int_{\partial \Omega} \text{div} \, \mathbf{u} \, d\mathbf{s} = \int_{\partial \Omega} \mathbf{u} \cdot d\mathbf{s} = \int_{\Gamma_1} \mathbf{u} \cdot \mathbf{n}_1 dS + \int_{\Gamma_2} \mathbf{u} \cdot \mathbf{n}_2 dS
\]
\[
= \int_{\Gamma_1} \mathbf{u} \cdot \mathbf{n}_1 dS - \int_{\Gamma_2} \mathbf{u} \cdot \mathbf{n}_1 dS = \mathcal{F}_1(t) - \mathcal{F}_2(t).
\]

**Figure 4:** The channel $\Omega_2$ with cross sections $\Gamma_1$ and $\Gamma_2$

Since we are considering the incompressible flow, by using the divergence free condition, $\int_{\partial \Omega} \text{div} \, \mathbf{u} \, d\mathbf{s} = 0$ and hence we have $\mathcal{F}_1(t) = \mathcal{F}_2(t)$ for all time $t \in [0, T]$. That is, the flux across any cross section is same throughout the channel. Hence, if $|\mathbf{u}(x,t)| \to 0$ as $|x| \to \infty$, then $\mathcal{F}(t) \to 0$ as $|x| \to \infty$, i.e., $\mathcal{F}(t) \equiv 0$ throughout the channel for all time $t \in [0, T]$. Hence for the flux to be non-zero in a finite cross sectional channel we need the condition that $|\mathbf{u}(x,t)| \nrightarrow 0$ as $|x| \to \infty$. The same implication hold in three dimensional case also. As a consequence, both in 2-D and 3-D channels with finite cross section, if $\mathcal{F}(t) > 0$ and finite, then $|\mathbf{u}(x,t)| \nrightarrow 0$ as $|x| \to \infty$.

Next, we will observe that for the channels with finite cross section (both in 2-D and 3-D) the flow possesses infinite energy. From above, we have $|\mathbf{u}(x,t)| \nrightarrow 0$ as $|x| \to \infty$. Then there are two possibilities, namely

1. $\mathbf{u}(x,t)$ converges to a non-zero finite value as $|x| \to \infty$,
2. $\mathbf{u}(x,t)$ oscillates finitely between two non-zero values (or diverges finitely).

In both cases $\mathbf{u}(x,t)$ is bounded and for each fixed time $t \in (0, T]$, $\mathbf{u}(x,t)$ will have a lower/upper bound depending on $\mathbf{u}(x,t)$ positive/negative as $|x| \to \infty$. Since we are considering unit width case, then $0 \leq y \leq 1$ and $|x| \to \infty$ implies $x \to \infty$. Then for a fixed $t \in (0, T]$, for a sufficiently large $b$ and for all $|x| > b$, there exists a lower/upper bound $a > 0$ such that $|\mathbf{u}(x,t)| > a$. Hence the $L^2$-energy estimate is given by

\[
\int_0^1 \int_0^\infty |\mathbf{u}(x,y,t)|^2 \, dy \, dx = \int_0^1 \int_0^b |\mathbf{u}(x,y,t)|^2 \, dy \, dx + \int_0^1 \int_b^\infty |\mathbf{u}(x,y,t)|^2 \, dy \, dx \geq a^2 \int_0^1 \int_b^\infty dy \, dx = \infty,
\]

for $|x| \to \infty$. 

(6)
In the 3-D case, for the channels with unit width, the $L^2$-energy estimate for almost all time $t \in (0, T]$ is given by

$$\int_{r=0}^{1/2} \int_{\theta=0}^{2\pi} \int_{z=0}^{\infty} |u(r, \theta, z)|^2 r dr d\theta dz \geq \int_{r=0}^{1/2} \int_{\theta=0}^{2\pi} \int_{z=b}^{\infty} a^2 r dr d\theta dz = \infty,$$  \hspace{1cm} (7)

for all $|z| > b$. Hence both in 2-D and 3-D channel flow with finite cross section, the flow possesses infinite energy.

(ii) **Channels with outlets diverge at infinity:**

Let us consider the radial flow across the channels with outlets that diverge at infinity with the diverging angle be $\theta$ (see Figure 5). In the two dimensional case,

$$\text{Figure 5: The 2 - D channel with outlets diverge at infinity}$$

for $\mathcal{F}(t)$ to be finite, $u(r, \theta) \to 0$ as $r \to \infty$ for all $t \in [0, T]$. If not, $u(r, \theta) \to 0$ as $r \to \infty$, then as in the previous case, for each fixed time $t \in (0, T)$, there exists a positive number $a > 0$ such that $|u(r, \theta)| > a$ for all $r > r_0$, where $r_0$ is a positive real number. Hence

$$\mathcal{F}(t) = \int_{\Gamma} u \cdot n dS = \int_{0}^{\theta_0} u(r, \theta) r d\theta \geq ar \int_{0}^{\theta_0} d\theta = r a \theta_0 \to \infty \text{ as } r \to \infty.$$  

Therefore if $|u(r, \theta)| \to 0$ as $r \to \infty$, then $\mathcal{F}(t) \to \infty$. Hence for the flux $\mathcal{F}(t)$ to be finite, we have $u(r, \theta) \to 0$ as $r \to \infty$ for all $t \in [0, T]$.

Let the decay rate of $u(r, \theta)$ be in the order of $\frac{1}{r^\beta}$, i.e., $u(r, \theta) = C \frac{1}{r^\beta}$, where $C$ is a constant independent of $r$. The flux across any cross section $\Gamma$ in $O_2$ is given by

$$\mathcal{F}(t) = \int_{\Gamma} u \cdot n dS = \int_{0}^{\theta_0} u(r, \theta) r d\theta = C \frac{1}{r^\beta-1} \theta_0.$$  

Hence for the flux $\mathcal{F}(t)$ to be non-zero and finite as $r \to \infty$, $\beta$ should be equal to 1. Therefore the decay rate of $u(r, \theta)$ is $\frac{1}{r}$ and hence $u(r, \theta) \to 0$ as $r \to \infty$ for all $t \in [0, T]$ in the 2-D case.

The $L^2$-energy estimate in the sector $(r_0, R) \times (0, \theta_0)$ is given by

$$\int_{0}^{\theta_0} \int_{r_0}^{R} |u(r, \theta)|^2 r dr d\theta = C^2 \int_{0}^{\theta_0} \int_{r_0}^{R} \frac{1}{r^2} r dr d\theta = C^2 \theta_0 \ln \left( \frac{R}{r_0} \right) \to \infty \text{ as } R \to \infty,$$  

where $C$ is a constant independent of $r$. Hence the flow possesses infinite energy in the two dimensional flow.
In the three dimensional case, (see Ladyzhenskaya and Solonnikov [11], and Solonnikov [13]) if $u(r, \theta, \phi) \to 0$ as $r \to \infty$, then as in the 2-D finite cross sectional channel case, there exists a number $a > 0$ such that $|u(r, \theta, \phi)| > a$ for all $r > r_0$, where $r_0$ is any positive real number (see Figure 6). Then in any cross section $\Gamma$, the flux is given by

$$\mathcal{F}(t) = \int_{\Gamma} u \cdot ndS = \int_{\theta=0}^{\theta_0} \int_{\phi=0}^{2\pi} u(r, \theta, \phi)r^2 \sin \theta d\theta d\phi \geq ar^2 \int_{\theta=0}^{\theta_0} \int_{\phi=0}^{2\pi} \sin \theta d\theta d\phi = 2\pi ar^2 (1 - \cos \theta_0) \to \infty \text{ as } r \to \infty.$$ 

Hence for the flux $\mathcal{F}(t)$ to be finite, $u(r, \theta, \phi) \to 0$ as $r \to \infty$ for all time $t \in [0, T]$. Now in the three dimensional case also let us assume that the decay rate of $u(r, \theta, \phi)$ be $\frac{1}{r^\beta}$, i.e., $u(r, \theta, \phi) \propto \frac{1}{r^\beta}$. Then the flux across any cross section $\Gamma$ is given by

$$\mathcal{F}(t) = \int_{\Gamma} u \cdot ndS = \int_{\theta=0}^{\theta_0} \int_{\phi=0}^{2\pi} u(r, \theta, \phi)r^2 \sin \theta d\theta d\phi = \frac{2\pi C}{r^{\beta-2}} (1 - \cos \theta_0),$$

where $C$ is a constant independent of $r$. Hence for $\mathcal{F}(t)$ to be non-zero and finite as $r \to \infty$, $\beta$ should be equal to 2. Therefore the decay rate of $u(r, \theta, \phi)$ is $\frac{1}{r^2}$ and hence $u(r, \theta, \phi) \propto \frac{1}{r^2}$ for all $t \in [0, T]$ in the 3-D case.

Let us consider the sector $(r_0, R) \times (0, \theta_0) \times (0, 2\pi)$, the $L^2$-energy estimate in this sector is given by

$$\int_{0}^{\theta_0} \int_{0}^{2\pi} \int_{r_0}^{R} |u(r, \theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi = C^2 \int_{0}^{\theta_0} \int_{0}^{2\pi} \int_{r_0}^{R} \frac{1}{r^2} r^2 \sin \theta dr d\theta d\phi = 2\pi C^2 \int_{0}^{\theta_0} \int_{0}^{R} \frac{1}{r^2} \sin \theta dr d\theta = 2\pi C^2 (1 - \cos \theta_0) \left( \frac{1}{r_0^2} \right) \to 2\pi C^2 (1 - \cos \theta_0) \frac{1}{r_0} < \infty \text{ as } R \to \infty.$$ 

Hence the flow possesses a finite energy in the three dimensional case.

We can summarize the results obtained above as
I. Channels with finite cross section.

1. For both two dimensional and three dimensional channels with finite cross section if the far field velocity goes to zero, i.e., \(|u(x, t)| \to 0\) as \(|x| \to \infty\), then the flux across any cross section will be equal to zero, i.e., \(\mathcal{F}(t) \equiv 0\) for all \(t \in [0, T]\). Since the flux across any cross section is non-zero and finite, as a consequence the far field velocity does not decay to zero, i.e., \(|u(x, t)| \to 0\) as \(|x| \to \infty\).

2. Since the far field velocity is non-zero, the flow possesses infinite energy for both two dimensional and three dimensional channels with finite cross section (see (6) and (7)).

II. Channels with outlets diverging at infinity.

1. In the two dimensional case, since the flux across any cross sectional channel is non-zero and finite, the far field velocity vanishes, i.e., \(|u(r, \theta)| \to 0\) as \(r \to \infty\) (otherwise the flux will be infinity) and in this case, the flow possesses infinite energy for all time \(t \in [0, T]\).

2. In three dimensional case also the far field velocity vanishes, i.e., \(|u(r, \theta, \phi)| \to 0\) as \(r \to \infty\) but in this case, the flow possesses finite energy for all time \(t \in [0, T]\).

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Synthesis and Structural Study of Nanostructured Calcium Carbonate

A Devarajan
Department of Physics
St. Gregorios College, Kottarakara
Kollam, Kerala, India - 691 531
e-mail: devan2012@gmail.com

Abstract
Calcium Carbonate (CaCO₃) in the nanometer size regime have been synthesized using chemical roots in ethanol - water medium. Nanoparticles of different average gain sizes were synthesized by changing the composition of the reaction medium. Different techniques like X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and High Resolution Transmission Electron Microscopy (HRTEM) are used to carry out structural characterisation of the Nanoparticles.

Keywords: Vaterite phase of CaCO₃, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and High Resolution Transmission Electron Microscopy (HRTEM).

1 Introduction

The words nanoparticle and nanotechnology are relatively new. However, nanoparticles themselves had been studied long before the words were coined. The existence of functional devices and structures of nanometer dimensions dates back to the existence of life on earth. The abalone, a mollusk, constructs very strong shells having iridescent inner surfaces by organizing calcium carbonate into strong nanostructured bricks held together by glue made of a carbohydrate-protein mix. The shells represent a natural demonstration that a structure made from nanoparticles can be much stronger and harder. It is not known when humans first began to understand the uses of nanosized materials. It is seen that in the fourth century A.D Roman glass makers were fabricating glasses containing nanosized metals. The great varieties of beautiful colors of the windows of medieval cathedrals are due to the presence of metal nanoparticles in the glass. Silver nanoparticles, sensitive to
light were employed in photographic emulsions developed in the eighteenth century. In 1857 Michael Faraday explained how metal particles affect the color of church windows. Though Faraday never measured the average size of the particles of gold, this was the first observation that the properties of small particles can differ from those of the bulk material[1, 2, 3].

Nanocrystalline materials are single phase or multi phase polycrystals, the crystal size of which is of the order of a few nanometers(typically 1 to 100 nm) in atleast one dimension. Nanostructured materials are also referred to as nanocrystalline materials, nanophase materials and nanomaterials. The structures of nanophase materials on a variety of length scales have an important impact on their unusual physical and chemical properties. Nanostructured materials are broadly classified into four categories - zero dimensional, one dimensional, two dimensional and three dimensional - according to the number of dimensions in which the crystallite sizes are confined to or spatially modulated in the nanometer range.

Controlled chemical precipitation is one of the simple, convenient and commonly employed techniques for the preparation of nanostructured materials. Wet chemical nanoparticle preparation is a “bottom-up method”which basically relies on the chemical reduction of metal salts, electrochemical pathways, or the controlled de-
composition of metastable organometallic compounds in solution. Control over the growth of the primarily formed nanoclusters and their agglomeration is effected by the use of a variety of stabilizers, in the form of donor ligands, polymers and surfactants\[4, 5\]. The particle size can be controlled by lowering the solvent temperature and thereby controlling the kinetics of precipitation. One of the methods is to increase the viscosity of the medium by the addition of ethylene glycol so as to control the diffusion constant.

2 Synthesis of Nanostructured Calcium Carbonate

In the present work, nanostructured calcium carbonate samples were synthesized through a controlled chemical precipitation reaction in ethanol-water medium. Calcium chloride (CaCl\(_2\)) and ammonium carbonate ((NH\(_4\))\(_2\)CO\(_3\)) were used as the starting materials. All the chemicals used were of analytical grade and were used without further purification. Freshly prepared, 0.5 molar aqueous solutions of CaCl\(_2\) and (NH\(_4\))\(_2\)CO\(_3\) were simultaneously dropped at a slow and steady rate (40 ml/hr) into a 50:50 mixture of ethanol and water kept under vigorous stirring with a magnetic stirrer. The reaction was carried out at room temperature. The insolubility of CaCO\(_3\) precipitated in the reaction medium promoted the formation of a number of nuclei. Further growth of the nuclei formed is prevented by the presence of ethanol molecules. The OH groups of ethanol molecules form bonds with the surfaces of the CaCO\(_3\) nuclei and thus prevent further growth\[6\]. The electric field of -OH group in alcohols can, to an extent, change the surface free energy of the metastable phase of CaCO\(_3\). Thus, the role of ethanol is to control the precipitation reaction in such a way that more number of small crystallites is formed while their subsequent growth is prevented. The particles of CaCO\(_3\) were separated and washed thoroughly using an ultrasonic disintegrator in distilled water and finally in acetone. The precipitate was then dried at 343 K and was ground using an agate mortar and pestle to obtain calcium carbonate in the form of a fine powder. Samples with different average grain sizes were synthesized by changing the composition of the reaction medium. Table 2.1 gives the composition of the reaction medium along with sample codes.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Composition of reaction medium (Water to ethanol ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>50:50</td>
</tr>
<tr>
<td>C2</td>
<td>60:40</td>
</tr>
</tbody>
</table>

Sample codes together with the composition of reaction medium
3 X-ray Diffraction Analysis

In the context of nanocrystalline materials the most important parameter that influences the physical and chemical properties is the average grain size. X-ray diffraction is the most convenient indirect method for the determination of average grain size of nanocrystalline samples. Simultaneous use of X-ray diffraction technique and High Resolution Microscopy is ideal for the size determination and structural characterization of nanocrystalline samples.

![Figure 3.1(a) X-ray diffraction pattern of the as prepared nanostructured CaCO\textsubscript{3} sample C1 with average grain size 18 nm.](image)

In the present study, X-ray diffraction (XRD) pattern of the samples were recorded using a Philips PW 1870 series X-ray diffractometer using Cu - K\(\alpha\) (\(\lambda = 1.540598\,\text{\AA}\)) radiation. The diffraction patterns were recorded at 40kV and 30mA in the range 20\(^{0}\) < 2\(\theta\) <70\(^{0}\) and at a scanning speed of 4\(^{0}\)/min at steps of 0.02\(^{0}\). The X-ray diffraction patterns of the as prepared nanostructured CaCO\textsubscript{3} samples are given in Figs. 3.1(a) and 3.1(b).
3.1 Determination of crystalline phases present

The inter planar spacing (d-values) and the relative intensities (I/I0) of the diffraction peaks in the X-ray diffraction pattern of all the samples are listed in Table 3.1. The d-values and the corresponding relative intensities were compared with the ICDD values(Table 3.2) for calcite, vaterite and aragonite phases of CaCO3 to determine the crystalline phases present. The samples were predominantly of vaterite phase with hexagonal structure. The lattice parameters, for the nano-structured samples were estimated from the X-ray diffraction patterns and are listed in Table 3.3 together with the ICDD values for vaterite phase[7]. The calculated values are in good agreement with the standard values. Further, in the diffraction pattern of samples C1 and C2 the maximum intensity peak corresponding to the stable calcite phase(d=3.035 Å) is present as a very low intensity peak. This indicates the presence of a small percentage of calcite phase in the samples. Further, no peaks corresponding to the aragonite phase of calcium carbonate are observed in the XRD patterns of the samples indicating the complete absence of this phase in the as-prepared samples.
Table 3.1: d-values and relative intensities of the X-ray diffraction peaks of the as-prepared samples C1, C2

<table>
<thead>
<tr>
<th>Sample C1</th>
<th>Sample C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inter planar spacing d(Å)</td>
<td>Sample C1</td>
</tr>
<tr>
<td>4.268</td>
<td>36</td>
</tr>
<tr>
<td>3.615</td>
<td>69</td>
</tr>
<tr>
<td>3.200</td>
<td>100</td>
</tr>
<tr>
<td>3.055</td>
<td>16</td>
</tr>
<tr>
<td>2.751</td>
<td>94</td>
</tr>
<tr>
<td>2.331</td>
<td>13</td>
</tr>
<tr>
<td>2.130</td>
<td>12</td>
</tr>
<tr>
<td>2.077</td>
<td>62</td>
</tr>
<tr>
<td>2.068</td>
<td>52</td>
</tr>
<tr>
<td>1.865</td>
<td>22</td>
</tr>
<tr>
<td>1.828</td>
<td>41</td>
</tr>
<tr>
<td>1.652</td>
<td>19</td>
</tr>
<tr>
<td>1.547</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3.2: ICDD-PDF data for bulk calcium carbonate of vaterite, calcite and aragonite phases

<table>
<thead>
<tr>
<th>ICDD-PDF No.33-268</th>
<th>Vaterite/Hexagonal</th>
<th>d(Å)</th>
<th>Int.(I/I₀)</th>
<th>hkl</th>
<th>d(Å)</th>
<th>Int.(I/I₀)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.226</td>
<td>25</td>
<td>004</td>
<td>3.860</td>
<td>12</td>
<td>012</td>
<td>4.212</td>
<td>3</td>
</tr>
<tr>
<td>3.573</td>
<td>60</td>
<td>110</td>
<td>3.035</td>
<td>100</td>
<td>104</td>
<td>3.984</td>
<td>1</td>
</tr>
<tr>
<td>3.294</td>
<td>100</td>
<td>112</td>
<td>2.845</td>
<td>3</td>
<td>006</td>
<td>3.397</td>
<td>100</td>
</tr>
<tr>
<td>2.730</td>
<td>90</td>
<td>114</td>
<td>2.495</td>
<td>14</td>
<td>110</td>
<td>3.274</td>
<td>50</td>
</tr>
<tr>
<td>2.318</td>
<td>5</td>
<td>211</td>
<td>2.285</td>
<td>18</td>
<td>113</td>
<td>2.872</td>
<td>6</td>
</tr>
<tr>
<td>2.282</td>
<td>2</td>
<td>205</td>
<td>2.095</td>
<td>18</td>
<td>202</td>
<td>2.733</td>
<td>9</td>
</tr>
<tr>
<td>2.212</td>
<td>5</td>
<td>106</td>
<td>1.927</td>
<td>5</td>
<td>024</td>
<td>2.702</td>
<td>60</td>
</tr>
<tr>
<td>2.161</td>
<td>2</td>
<td>213</td>
<td>1.913</td>
<td>17</td>
<td>018</td>
<td>2.481</td>
<td>40</td>
</tr>
<tr>
<td>2.113</td>
<td>20</td>
<td>088</td>
<td>1.875</td>
<td>17</td>
<td>116</td>
<td>2.411</td>
<td>14</td>
</tr>
<tr>
<td>2.064</td>
<td>60</td>
<td>300</td>
<td>1.626</td>
<td>4</td>
<td>211</td>
<td>2.373</td>
<td>45</td>
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<tr>
<td>1.854</td>
<td>30</td>
<td>304</td>
<td>1.604</td>
<td>8</td>
<td>122</td>
<td>2.342</td>
<td>25</td>
</tr>
<tr>
<td>1.820</td>
<td>70</td>
<td>118</td>
<td>1.587</td>
<td>2</td>
<td>101</td>
<td>2.330</td>
<td>25</td>
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</tbody>
</table>
Table 3.2: ICDD-PDF data for bulk calcium... (continued)

<table>
<thead>
<tr>
<th>ICDD-PDF</th>
<th>ICDD-PDF No.5-586</th>
<th>ICDD-PDF No.41-1475</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaterite/Hexagonal</td>
<td>Calcite/Rhombohedral</td>
<td>Aragonite/Orthorhombic</td>
</tr>
<tr>
<td>d(A)</td>
<td>Int.(I/I₀)</td>
<td>hkl</td>
</tr>
<tr>
<td>1.788</td>
<td>5</td>
<td>220</td>
</tr>
<tr>
<td>1.750</td>
<td>2</td>
<td>222</td>
</tr>
<tr>
<td>1.646</td>
<td>30</td>
<td>224</td>
</tr>
<tr>
<td>1.544</td>
<td>5</td>
<td>401</td>
</tr>
<tr>
<td>1.510</td>
<td>1</td>
<td>226</td>
</tr>
<tr>
<td>1.477</td>
<td>10</td>
<td>308</td>
</tr>
<tr>
<td>1.413</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>1.366</td>
<td>10</td>
<td>228</td>
</tr>
<tr>
<td>1.351</td>
<td>1</td>
<td>410</td>
</tr>
<tr>
<td>1.355</td>
<td>1</td>
<td>412</td>
</tr>
<tr>
<td>1.311</td>
<td>20</td>
<td>1112</td>
</tr>
<tr>
<td>1.286</td>
<td>20</td>
<td>414</td>
</tr>
<tr>
<td>1.190</td>
<td>5</td>
<td>330</td>
</tr>
<tr>
<td>1.630</td>
<td>5</td>
<td>3012</td>
</tr>
<tr>
<td>1.146</td>
<td>10</td>
<td>334</td>
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<tr>
<td>1.138</td>
<td>10</td>
<td>418</td>
</tr>
<tr>
<td>1.109</td>
<td>10</td>
<td>2212</td>
</tr>
<tr>
<td>1.057</td>
<td>5</td>
<td>16</td>
</tr>
</tbody>
</table>

Table 3.3: Lattice parameters evaluated from X-ray diffraction data of nanostructured CaCO₃ samples C1, C2, C3 and C4

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>a=b(Å)</th>
<th>cÅ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>7.20358</td>
<td>17.02271</td>
</tr>
<tr>
<td>C2</td>
<td>7.20199</td>
<td>17.06355</td>
</tr>
<tr>
<td>ICDD values</td>
<td></td>
<td></td>
</tr>
<tr>
<td>for vaterite phase</td>
<td>7.14730</td>
<td>16.91700</td>
</tr>
</tbody>
</table>

3.2 Determination of average grain size of nanostructured CaCO₃ samples

The X-ray diffraction peaks of a nanocrystalline sample will be broadened in comparison with those corresponding to coarse-grained and single crystalline samples.
with same average chemical composition and crystal structure, due to the finite
grain size. The average grain size of a fine grained polycrystalline sample can be
estimated from the line broadening of the X-ray diffraction peaks using Scherrer
equation
\[
D = \frac{0.9\lambda}{B \cos \theta}
\]
where \(D\) is the average grain size, \(k = 0.09\) is the shape factor lying between 0.95
and 1.15 depending on the shape of the grains, \(\lambda\) is the wavelength of the X-rays
used, \(B\) is the Full Width at Half Maximum (FWHM) of the X-ray diffraction peaks
measured in radians and \(\theta\) the Bragg angle [8, 9, 10].

The average grain sizes of the nanocrystalline CaCO\textsubscript{3} samples determined from
the line broadening of the X-ray diffraction pattern using Scherrer equation are
listed in Table 3.4. It can be noted that that there is an increase in the average
grain size with decrease in the fraction of alcohol in the reaction mixture. This is
in agreement with the earlier observation that the concentration of -OH group in
the reaction medium plays an important role in controlling the reaction kinetics and
hence the grain size of the sample formed [11].

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Phases present</th>
<th>Average grain size D estimated from Scherrer equation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Vaterite</td>
<td>17</td>
</tr>
<tr>
<td>C2</td>
<td>Vaterite</td>
<td>24</td>
</tr>
</tbody>
</table>

3.3 HRTEM and SEM Analysis of Nanostructured Calcium Carbonate Samples

The microstructure of nanocrystalline CaCO\textsubscript{3} sample was examined by high resolu-
tion transmission microscopy (HRTM) using a JEOL 3010 HRTEM operating at
300 kV. Solutions of the sample were drop-coated on carbon coated copper grid
and the solvent was allowed to evaporate at ambient conditions. Imaging of the lattice
planes is essential to distinguish individual grains. Figs. 3.1 shows the HRTM mi-
crographs of the as-prepared sample C1. Different lattice planes are visible. Single
grains of size approximately 10 to 15 nm are visible in Figure. . The fringes from
the (004), (114), (211), (300) and (220) planes are visible in the HRTEM images.
These planes correspond to the hexagonal structure of the vaterite phase of CaCO\textsubscript{3}. 
The average grain sizes observed from the micrographs ranges between 10 to 15 nm is slightly differs from the grain size obtained from XRD analysis (Table 3.4).

Scanning electron micrographs of the powder sample C1 were recorded using a Hitachi Model S 2400 SEM and the micrographs are given in Figure 3.2. Even though the individual grains are not resolved, the arborescent nature of the surface morphology of the agglomerates of nanoparticles is clear from Figure.

4 Conclusion

Nanostructured calcium carbonate samples were synthesized through an arrested chemical precipitation reaction in ethanol-water medium. CaCO3 Samples having different average grain sizes were synthesized by changing the proportions of ethanol
and water in the reaction medium. XRD analysis revealed that the as prepared samples were of the meta stable vaterite phase with diminutive percentages of stable calcite phase. The predominance of the meta stable vaterite phase over stable calcite phase is due to the significant contribution of the interfacial energy to the total free energy of the system. The average grain sizes of the samples were estimated from the broadening of the XRD peaks using Scherrer equation.

The surface morphology of the agglomerates of the vaterite phase of calcium carbonate can be clearly seen in the Scanning Electron Micrograph(SEM) of the as prepared sample. The microstructures of nanocrystalline CaCO$_3$ sample(sample C1) was examined by the HRTEM. The fringes from the (004), (114), (211), (300) and (220) planes can be visibly seen in the HRTEM images. These planes correspond to the hexagonal structure of the vaterite phase of CaCO$_3$. The average grain sizes observed from the micrographs ranges between 5nm to 15 nm.

References


Dielectric Studies of Nano Crystalline NdTiNbO$_6$

Ceramic Through Combustion Technique

Fergy John$^1$, J. K. Thomas$^2$, Sam Solomon$^3$

$^1$Department of Physics, St. Gregorios College, Kottarakara, 691531
$^2$Department of Physics, Mar Ivanios College, Thiruvananthapuram 695015
$^3$Department of Physics, St. John’s College, Anchal, 691306

Abstract

Solution combustion technique is used for the preparation of Nano crystalline NdTiNbO$_6$(NTN). XRD analysis reveals that sample has orthorhombic aeschnite structure. The crystalline size is calculated using scherrer formula. The variation of ac conductivity, dielectric loss, dielectric constant with radio frequencies are studied. Nano crystalline NdTiNbO$_6$ shows very attractive characteristics for the use in communication systems and impedance studies shows that it can be useful in Solid Oxide Fuel Cells

Keywords: Combustion technique, Nano ceramic, X-ray diffraction, dielectric response.

1 Introduction

With the development of new technologies, such as mobile communication, personal computers and the internet need for miniaturization of electronic materials and high-performance electro ceramics. Niobium and tantalum compounds have been used successfully in a variety of different applications in the electronic and electro-optic markets, including dielectric ceramics. Niobium based ceramics are frequently used as additives and main components to increase the capacitance of multilayer ceramic capacitors.

Many niobium based dielectric resonator materials also have been reported which find application in the microwave field. Sebastian et al. have reported the microwave dielectric properties of microsized RETiNbO$_6$ (RE= Ce, Pr, Nd, Sm, Eu, Gd, Tb, Y and Yb) ceramics by solid state ceramic route[1]. Hydrothermally synthesized RETiNbO$_6$ have reported by Komkov et al[2]. Sam Solomon et al have reported that the addition of ZnO reduced the sintering temperature in micro sized...
NdTiNbO$_6$[3]. Solid state ceramic route has very long calcination time and repeated grinding steps to obtain pure phase. There are number of methods to prepare nano sized particles, such as chemical vapour deposition[4], sputtering[5], wet chemical method[6], sol-gel[7], precipitation[8], combustion[9], microwave hydrothermal method[10], etc. Among these techniques, combustion method is taking as a leading role in the synthesis of nano-sized particles.

Here, we report the preparation, and impedance spectroscopic studies of nano-sized NdTiNbO$_6$(NTN) by solution combustion method for the first time.

2 Experimental

NdTiNbO$_6$(NTN) is prepared by solution combustion technique[11, 12] using the corresponding metal nitrate(oxidizing agent) and suitable fuel(reducing agent). Calculations are based on the principles used in propellant chemistry, keeping fuel to oxidant ratio unity in order to produce maximum energy. In this synthesis, high-purity Niobium penta chloride(NbCl$_5$, 99.9%), Titanium isopropoxide(Ti[OCH(CH$_3$)$_2$]$_4$, 98%) and Neodymium oxide(Nd$_2$O$_3$, 99.99%) are used as cation sources and oxidant agents, and urea(NH$_2$CONH$_2$)is used as fuel reagent(reducing agent). Neodymium oxide is dissolved in conc. nitric acid to provide a better homogeneity of neodymium ions. We have used NbCl$_5$ as niobium source in oxalic acid solution without any heat treatment. Citric acid is used as complexing agent to get precursor complex. Stoichiometric amount of oxidizing agents and reducing agent in a minimum volume of deionized water to obtain transparent aqueous solutions in a glass beaker is heated using a hot plate at 250$^\circ$C in a ventilated fume hood forms a viscous gel. The gel thus formed undergoes dehydration on further heating and self-ignites with the evolution of huge quantity of gases. Hence the residual ash that is formed after combustion has a fluffy nature. This ash is further heated up to 600$^\circ$C to get the pure phase nano powder.

3 Characterization

The XRD (Model: Philips PW1710 diffractometer) is used to determine the formation of the desired phase, for the powder. The crystallite size is calculated from X-ray line broadening by the Scherrer equation:

$$D = \frac{0.89\lambda}{\beta_{hkl} \cos \theta_{hkl}}$$  \hspace{1cm} (1)

where, $D$ is the crystal size in nm, $\lambda$ is the CuK$_{\alpha1}$ wavelength (1.5406 Å), $\beta$ is the half width of the peak in rad, and $\theta$ is the corresponding diffraction angle[13].

The prepared powder is mixed with one drop of 1 wt% solution of polyvinyl alcohol and uniaxially pressed at room temperature for 1 min at the pressure 190 MPa. The sintering of the pressed pellet is done with the help of furnace. The
density of the sintered pellet is measured. The Dielectric constant, conductance, the tangent loss and Complex impedance measurements are done on the polished pellet samples as a function of frequency(100 kHz) using an LCR meter(HIOKI, model 3532).

4 Results and discussion

The XRD pattern of NTN as prepared is shown in fig 1. All the peaks are indexed using JCPDF data file 52-1130. The compound has orthorhombic aeschnite structure with space group $P_{nma}$[13]. The average particle size, calculated using the Scherrer formula from all crystal plane of NTN is 27nm.

Fig 1 XRD pattern of NTN as prepared

Due to fine nature of Nano-sized NTN, it has high surface area and surface energy which leads to its excellent sintering characteristics. Nano sized NTN sintered at 1250°C only for 2 hrs which is relatively shorter time and temperature as compared to the conventional NTN.

The variation of the dielectric constant($\epsilon$), ac conductance (G) and loss factor($\tan \delta$) with radio frequency range are obtained for the sintered sample. Dielectric constant decreases initially with the increase in frequency and it reached a constant value 50.5 at higher frequency range shown in fig 2. This is due to Maxwell-Wagner interfacial polarization[14]. The decrease in dielectric constant is due to the delay in polarization with the application of the electric field because of inertia. When frequency increases, those with large relaxation time cease respond and results the decrease of dielectric constant. And at low frequency range the variation of ac conductance is very less and almost constant up to 1MHz, and then increases according to the increase in frequency. Thus this material can be useful for capacitive applications in communication systems.
The variation of tan δ in RF region is shown in Fig 3. Loss reached a minimum value and almost constant as frequency increases in accordance with Koops phenomenological model[15]. It means that, material has low loss in RF range because of the relaxation frequency of the sample is out of this frequency range. Therefore, dissipation of electrical energy is low at this range. The studies of the variation of ac conductance, dielectric loss and dielectric constant, shows that the nano sized NTN can be effectively useful for communication systems[1].
Fig 4 Real part of impedance with radio frequency at different temperatures

Fig 5 shows the variation of imaginary part of impedance ($Z''$) as a function of frequency at different temperatures. It shows asymmetric peaks and the peak maximum occur at $f_z$ called peak frequency. As the temperature increases, $f_z$ shift towards higher frequencies. This is due to non-Debye type of relaxation behavior in the system. Fig 6 shows the Arrhenius plot of $f_z$ and the activation energy is calculated from its slope to be 0.214eV. This low value of activation energy implies that the sample has higher ionic conductivity.

Fig 5 Imaginary part of impedance of NTN with radio frequency at different temperatures
Fig. 6 Arrhenius plot of NTN

Fig. 7 shows the impedance plot (Cole-Cole plot) of the sample at different temperatures. The semicircle arcs are found to be depressed with their centers lying below the real axis. This indicates the poly dispersive nature of the sample. The high frequency semicircle is due to the bulk property due to interior grain and the low frequency semicircle is due to the presence of grain boundary. As temperature increases the radius of semicircle decreases which indicates activated conduction mechanism.

Fig 7 Complex impedance plot (cole-cole plot) of NTN

5 Conclusion

Solution combustion method can be efficiently used to prepare NTN in nano scale without any calcination with low sintering temperature, better electrical and dielectric properties. NTN nano powder, due to its excellent sintering characteristics, is useful in ceramics at comparatively lower temperatures. XRD analysis reveals that sample has orthorhombic aeschnite structure. The crystalline size is estimated from
XRD pattern as 27nm. The variation of ac conductivity, dielectric loss gave the evidence that sample can be used as capacitive application in communication systems. The dielectric constant was estimated in RF region as 50.5. An analysis of the real and imaginary part of impedance is performed; it is found that they are frequency and temperature dependent. Cole-cole plot reveals that both the grain and grain boundary resistance decreases with increase in temperature. Ionic conductivity of the sample is high at high temperatures and therefore it can be used as electrolyte in solid oxide fuel cell (SOFC).

References


XRD and FTIR Characterization of ZnS Nanoparticles Synthesised by Novel Aqueous Chemical Method

Ansu P Joseph¹, A Devarajan²

¹,²Department of Physics
St. Gregorios College
Kottarakara, Kerala, India-691 531
e-mail: devan2012@gmail.com

Abstract

ZnS nanoparticles have been prepared using glycerol both as capping agent and stabilizer. The obtained ZnS nanoparticles are studied by X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The mean particle size of the different ZnS nanoparticles prepared is found to be 2.8 nm to 32.3 nm. The XRD analysis confirms the cubic (hexagonal for the annealed sample) and crystalline nature of the synthesized sample which is in good agreement with JCPDS patterns. FTIR spectra were recorded and different modes are assigned.

Keywords: Nanoparticles, ZnS, XRD, FTIR

1 Introduction

Nanosized inorganic semiconducting materials have been generating an extensive interest in recent years owing to their structure, chemical and physical properties, which are different from those of the bulk materials. ZnS has a wide band gap of 3.5 - 3.8 eV at room temperature and the band gap can be tuned in the UV region. It is an important inorganic material for a variety of applications including photoconductors, solar cells, field effect transistors, sensors, transducers, optical coatings and light-emitting materials [1, 2, 3, 4]. It has been investigated extensively, because of its potential optical applications [5, 6, 7]. ZnS doped with various transition metal ions such as manganese is an efficient light emitting material [8, 9, 10]. Nanostructured materials have been synthesized by many simple methods such as wet chemical method [11, 12], solid-state reaction method [13], etc. We report a simple and
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Economical method for the preparation of ZnS nanoparticles using glycerol as a capping agent. The ZnS nanoparticles were characterized using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy.

2 Experimental

In this method, nanoparticles of ZnS were prepared by arrested chemical precipitation method using Glycerol as encapsulating agent. Hydrogen sulphide (gas) was periodically passed into a solution of 200 ml (0.5 m) zinc chloride and 10 ml glycerol in continuous stirring. Magnetic stirrer was employed to maintain homogeneity of the nanosized crystals. The kinetic control of H₂S passing was also maintained at a constant rate.

\[ \text{ZnCl}_2 + \text{H}_2\text{S} \rightarrow \text{ZnS} + 2\text{HCl} \]

The nanoparticles are separated from the reaction medium by centrifugation, washing in de-ionized water several times and finally in acetone. It was then dried at 100°C and was taken to be the first sample at room temperature (Z1). The sample at 100°C was annealed to 200°C, 400°C and 600°C tagged as Z2, Z3, Z4 and subjected to experimental investigation. Annealing schemes and sample codes are given in the Table 1.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Annealing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td>As prepared heated at 100°C</td>
</tr>
<tr>
<td>Z2</td>
<td>Annealed at 200°C</td>
</tr>
<tr>
<td>Z3</td>
<td>Annealed at 400°C</td>
</tr>
<tr>
<td>Z4</td>
<td>Annealed at 600°C</td>
</tr>
</tbody>
</table>

Table 1: Annealing schemes and sample codes

The ZnS samples were characterized by X-ray powder diffraction (XRD). The XRD analysis is carried out on Bruker D8 Advance model X-ray diffractometer applying Cu-Kα radiations of wavelength 1.5406 Å. The XRD patterns of the samples are analyzed by peak fitting program in Origin 6.1 software. The FTIR spectra of the samples are recorded in Thermo Nicolet, Avatar 370 FTIR spectrometer in the spectral range 400-4000 cm⁻¹. The resolution was kept at 4 cm⁻¹. KBr pellet method is employed and the ratio of the sample to KBr is made very low as 1:100 so that the powder sample is uniformly dispersed in the pellet.
3 Result And Discussion

X-ray diffraction patterns of the nanostructured Zinc Sulphide (sample Z1) annealed at 100°C in $2\theta$ values and d-values are given in the Fig 1 and Fig 2 respectively.

![X-ray diffraction pattern of nano structured Zinc Sulphide annealed at 100°C](image1)

**Fig 1** X-ray diffraction pattern of nano structured Zinc Sulphide annealed at 100°C

![X-ray diffraction pattern of nano structured Zinc Sulphide annealed at 100°C in d-values](image2)

**Fig 2** X-ray diffraction pattern of nano structured Zinc Sulphide annealed at 100°C in d-values

The peaks are well defined and broad, which point towards the high crystalline nature of the sample. The broadness of the diffraction peaks, according to the Scherrer equation, is an indication towards the nano sized grains of the sample Z1. The d-values and h k l planes of the three well defined peaks of sample Z1 are in
well agreement with the standard values in the literature (JCPDS Card No: 80-0020 with cell constant $a = 5.3450 \, \text{Å}$) of cubic phase of Zinc Sulphide[14, 15]. No peaks from any other impurities such as ZnO or other compounds are detected.

<table>
<thead>
<tr>
<th>$2\theta$ values (Degrees)</th>
<th>Intensity (Arb. units)</th>
<th>h k l plane</th>
<th>d-values ($\text{Å} , \text{U}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.236</td>
<td>100.0873</td>
<td>1 1 1</td>
<td>3.05218</td>
</tr>
<tr>
<td>48.425</td>
<td>27.334</td>
<td>2 2 0</td>
<td>1.87446</td>
</tr>
<tr>
<td>57.722</td>
<td>17.001</td>
<td>3 1 1</td>
<td>1.59952</td>
</tr>
</tbody>
</table>

Table 2 Observed $2\theta$ values, d-values, h k l planes and intensity of the diffraction Peaks of the sample Z1

<table>
<thead>
<tr>
<th>$2\theta$ values (Degrees)</th>
<th>Intensity (Arb. units)</th>
<th>h k l plane</th>
<th>d-values ($\text{Å} , \text{U}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.909</td>
<td>999</td>
<td>1 1 1</td>
<td>3.0859</td>
</tr>
<tr>
<td>33.503</td>
<td>88</td>
<td>2 0 0</td>
<td>2.6725</td>
</tr>
<tr>
<td>48.110</td>
<td>496</td>
<td>2 2 0</td>
<td>1.8897</td>
</tr>
<tr>
<td>57.105</td>
<td>288</td>
<td>3 1 1</td>
<td>1.6115</td>
</tr>
<tr>
<td>59.897</td>
<td>17</td>
<td>2 2 2</td>
<td>1.5429</td>
</tr>
<tr>
<td>70.462</td>
<td>55</td>
<td>4 0 0</td>
<td>1.3362</td>
</tr>
</tbody>
</table>

Table 3 JCPDS Card No: 80-0020 for the CUBIC structure of ZnS

X-ray diffraction patterns of the nanostructured Zinc Sulphide particles Z2 and Z3 annealed at 200°C and 400°C respectively are shown in the Fig 3. The samples Z2 and Z3 are also found to be cubic in structure according to JCPDS Card No. 80-0020. We can also observe a significant grain growth from sample Z1 to Z3.
Fig 3 X-ray diffraction pattern of nano structured Zinc Sulphide annealed at 200°C and 400°C in $2\theta$ values

X-ray diffraction patterns of the nanostructured Zinc Sulphide (sample Z4) annealed at 600°C in $2\theta$ values and d-values are given in the Fig 5 and Fig 6 respectively. The observed d-values and lattice parameters of sample Z4 coincides with the standard JCPDS file values (JCPDS Card No: 80-0007) for hexagonal phase of ZnS. From the sharp peaks in the X-ray pattern of Z4 sample it is clear that the particle size has increased significantly at higher temperature.

Fig 5 X-ray diffraction pattern of nano structured Zinc Sulphide annealed at 600°C
Fig 6 X-ray diffraction pattern of nano structured Zinc Sulphide annealed at 600°C in d-values

Table 4 Observed 2θ values, d-values, h k l planes and intensity of the diffraction Peaks of the sample Z4

<table>
<thead>
<tr>
<th>2θ values (Degrees)</th>
<th>Intensity (Arb. units)</th>
<th>h  k  l plane</th>
<th>d-values (Å U)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.488</td>
<td>62</td>
<td>1 0 1</td>
<td>2.83453</td>
</tr>
<tr>
<td>34.133</td>
<td>43</td>
<td>0 0 2</td>
<td>2.62018</td>
</tr>
<tr>
<td>36.024</td>
<td>100</td>
<td>1 0 0</td>
<td>2.49111</td>
</tr>
<tr>
<td>47.306</td>
<td>18</td>
<td>1 1 0</td>
<td>1.91999</td>
</tr>
<tr>
<td>56.345</td>
<td>26</td>
<td>2 0 0</td>
<td>1.63154</td>
</tr>
<tr>
<td>62.597</td>
<td>19</td>
<td>0 0 4</td>
<td>1.48277</td>
</tr>
<tr>
<td>66.044</td>
<td>3</td>
<td>1 0 4</td>
<td>1.41232</td>
</tr>
<tr>
<td>67.622</td>
<td>16</td>
<td>1 0 4</td>
<td>1.38349</td>
</tr>
</tbody>
</table>
Table 5 JCPDS Card No: 80 - 0007 for Hexagonal structure of ZnS

<table>
<thead>
<tr>
<th>2θ values (Degrees)</th>
<th>Intensity (Arb. units)</th>
<th>h k l plane</th>
<th>d-values (Å U)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.241</td>
<td>999</td>
<td>1 0 0</td>
<td>3.2709</td>
</tr>
<tr>
<td>28.832</td>
<td>613</td>
<td>0 0 2</td>
<td>3.0940</td>
</tr>
<tr>
<td>30.896</td>
<td>949</td>
<td>1 0 1</td>
<td>2.8918</td>
</tr>
<tr>
<td>40.082</td>
<td>324</td>
<td>1 0 2</td>
<td>2.2477</td>
</tr>
<tr>
<td>48.143</td>
<td>601</td>
<td>1 1 0</td>
<td>1.8885</td>
</tr>
<tr>
<td>52.398</td>
<td>578</td>
<td>1 0 3</td>
<td>1.7447</td>
</tr>
<tr>
<td>56.196</td>
<td>85</td>
<td>2 0 0</td>
<td>1.6354</td>
</tr>
<tr>
<td>57.091</td>
<td>355</td>
<td>1 1 2</td>
<td>1.6119</td>
</tr>
<tr>
<td>58.307</td>
<td>109</td>
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<td>1.5811</td>
</tr>
<tr>
<td>59.725</td>
<td>11</td>
<td>0 0 4</td>
<td>1.5470</td>
</tr>
<tr>
<td>64.38</td>
<td>55</td>
<td>2 0 2</td>
<td>1.4459</td>
</tr>
<tr>
<td>66.844</td>
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<td>1 0 4</td>
<td>1.3984</td>
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<tr>
<td>73.892</td>
<td>146</td>
<td>2 0 3</td>
<td>1.2815</td>
</tr>
</tbody>
</table>

The particle sizes of the ZnS sample were evaluated from Scherre formular[16]

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

where \( D \) is the particle size, \( \lambda \) is the X-ray wavelength, \( \theta \) is the Bragg angle, \( \beta \) is the full width at half maximum in radians and \( K = 1 \) (since grain shape is assumed to be spherical).

XRD pattern of the sample Z1 fitted with FWHM for the prominent diffraction peaks is given in the Fig 1. The full width at half maximum in degrees is first
converted to radians and then by using the Scherrer formula, the grain size was calculated. The average grain size for the sample evaluated is 2.8 nm for the as prepared sample Z1. The cell parameter for the cubic structure of ZnS was evaluated using the formula

\[\sin^2 \theta = \frac{\lambda^2}{4a^2} \left[ h^2 + k^2 + l^2 \right]\]

The cell parameter \(a = 5.297 \text{ Å} \) well agrees with the JCPDS value (Card No. 80-0020). The grain size and the cell parameters for the cubic structure of samples Z2 and Z3 were also determined by using the formula and are tabulated in Table 6. Grain growth is observed for the annealed samples Z2 and Z3. The annealing temperatures for these samples favored the crystallization of the amorphous atoms surrounding the corresponding grain. The sample Z4 annealed at 600°C found to be hexagonal structure which is in agreement with the standard JCPDS value (Card No. 80-0007). The unit cell parameters of hexagonal structure of ZnS were calculated using the formula,

\[\sin^2 \theta_{hkl} = \frac{\lambda^2}{4a^2(h^2 + k^2)} + \frac{\lambda^2}{4c^2l^2}\]

The cell parameters \(a = b = 3.543 \text{ Å} \) and \(c = 6.012 \text{ Å} \) and this value agrees with the standard value (Table 6).

### Table 6 The sample code, particle size and lattice parameters of the as prepared and annealed samples of ZnS

<table>
<thead>
<tr>
<th>Samples</th>
<th>FWHM (rad)</th>
<th>Average grain size (nm)</th>
<th>Calculated value of cell parameter (Å)</th>
<th>JCPDS values of Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td>0.05532</td>
<td>2.8</td>
<td>a=5.297</td>
<td>a = 5.345, Cubic</td>
</tr>
<tr>
<td>Z2</td>
<td>0.03062</td>
<td>13.3</td>
<td>a=5.356</td>
<td>a = 5.345, Cubic</td>
</tr>
<tr>
<td>Z3</td>
<td>0.00603</td>
<td>27.3</td>
<td>a=5.326</td>
<td>a = 5.345, Cubic</td>
</tr>
<tr>
<td>Z4</td>
<td>0.00527</td>
<td>32.3</td>
<td>a=3.543</td>
<td>a = b = 3.777</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b=3.543</td>
<td>c=6.188</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=6.012</td>
<td>Hexagonal</td>
</tr>
</tbody>
</table>

The optical properties of the ZnS samples were carried out using FTIR spectroscopy. The FTIR spectra of the samples Z1, Z2, Z3 and Z4 in the mid IR region (400-4000 cm\(^{-1}\)) are given in the figures 7-10. Prominent absorption peaks for the as prepared sample Z1 and for the annealed sample Z2, Z3, Z4 are given in the table 7. The different absorption peaks for these samples were assigned in the table.
Absorbed water is usually present in the samples prepared using wet chemical precipitation method. This water also may absorb radiation from the incident light. Therefore absorption bands corresponding to this structural water are also expected in the FTIR spectra of the samples. The structural water which has bond structure with sulphide and zinc atoms inside the molecule will be eliminated at higher temperatures. The peaks located at 3402 cm$^{-1}$, 3420 cm$^{-1}$, 3490 cm$^{-1}$, and 3434 cm$^{-1}$ for samples Z1, Z2, Z3 and Z4 respectively corresponds to the O - H symmetric stretching mode of water molecule. The intensity of the symmetric stretching vibration of absorbed water molecule is found to decline as the annealing temperature increases. Heat treatment at different range of temperatures leads to significant reduction in intensity caused by removal of absorbed water molecules present in the samples.

The peaks detected at 1618 cm$^{-1}$ for Z1 sample and at 1622 cm$^{-1}$ for Z2 sample represents the bending mode of water molecule. Intensity of these peaks goes on decreasing from Z1 to Z4 sample.

The absorption peaks originates at 466 cm$^{-1}$ Z3 and at 448 cm$^{-1}$ for Z4 corresponds to the lattice mode of vibration of Zinc Sulphide. This band is found to be more intense in Z4 than in samples Z3, Z2, Z1. Thus the samples at higher temperature clearly elucidate the nano crystallization of pure phase of ZnS.

Thus the FTIR spectra are powerful tool for the analysis of materials to find even a small trace of the elements present in the material. The absorbed water in the sample and their elimination from the sample on annealing is visibly seen from the FTIR studies.

Fig 7 FTIR spectra of the sample Z1
Fig 8 FTIR spectra of the sample Z2

Fig 9 FTIR spectra of the sample Z3

Fig 10 FTIR spectra of the sample Z4
Table 7 FTIR bands of nanosized ZnS samples Z1, Z2, Z3 and Z4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td>O - H stretching mode of water molecule</td>
</tr>
<tr>
<td>Z2</td>
<td>Bending mode of water molecule</td>
</tr>
<tr>
<td>Z3</td>
<td>Negligibly low intensities</td>
</tr>
<tr>
<td>Z4</td>
<td>Negligibly low intensities</td>
</tr>
<tr>
<td></td>
<td>Lattice mode vibration of Zn and S</td>
</tr>
</tbody>
</table>

4 Conclusion

Zinc Sulphide nanoparticles were prepared by chemical precipitation method using Glycerol as encapsulating agent. Nanoparticles of different grain sizes were prepared by annealing the as prepared sample at different temperatures. The crystal structure and the particle size were determined from the XRD patterns of the samples. The Origin 6.1 software was used for the peak fitting and evaluation of the FWHM. ZnS nanoparticles of grain size around 2 nm to 24 nm were prepared. It was found that the grain size increases with temperature. Using the standard JCPDS data sheet, it was concluded that the ZnS has a cubic structure at lower temperature and then turns into hexagonal structure at higher degrees of heating.

The FTIR spectra of the samples were recorded and the different absorption bands in the spectra are analyzed and assigned. Even though the presence of water molecule is not detected in the XRD patterns, FTIR spectra clearly shows the presence of absorbed water in the sample and their removal from the annealed samples. The FTIR spectroscopy is a very sensitive spectroscopic characterization technique useful in the analysis of nanostructured materials.

Acknowledgment

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References


Chemical synthesis and FTIR Characterisation of NiO Nanoparticle

Sharon Thankachan1, A Devarajan2
1,2Department of Physics
St. Gregorios College
Kottarakara
Kollam, Kerala, India-691 531
e-mail: devan2012@gmail.com

Abstract
Nickel Oxide (NiO) nanoparticles have been prepared by chemical precipitation route using EDTA as stabilizer. Nanoparticles of different grain size were prepared by annealing the as prepared sample at different temperatures. The samples are studied by X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The mean particle size of the different NiO nanoparticles prepared is $\sim 5$ nm and $\sim 22$ nm for the as-prepared and annealed samples. The $hkl$ planes of the maximum intensity peaks of the samples are in well agreement with the standard JCPDS values of cubic structure of nickel oxide. FTIR spectra were recorded and different modes are assigned.

Keywords: Nanoparticles, NiO, XRD, FTIR spectra.

1 Introduction

The research in the area of nanostructured metal oxides, gradually to be interesting for their remarkable properties in electronic, magnetic, optical, thermal and mechanical fields[1, 2]. Out of these, NiO (Nickel oxide) nanoparticles, as an important metal oxide with a wide band gap, acts as a P-type semiconductor[3], drawn much attention due to its broad range of high technology application. It can be used in smart windows[4], electrochemical super capacitor[5, 6], as a transparent P-type semiconducting layer[7, 8] and as an antiferromagnetic film[9]. It can also been extensively used in dye sensitized photocathodes[10, 11]. Another important application of NiO is in battery systems[12]. In the present study, nanoparticles of NiO were synthesized by chemical precipitation method. The as-prepared sample and the annealed samples of different grain size were characterized by X-ray diffraction and FTIR method.
2 Experimental

Nanoparticles of nickel oxide were prepared by chemical precipitation method using Nickel nitrate(S) and Ammonium carbonate(S) as the source materials. Solutions of 0.5N Nickel nitrate and ammonium carbonate were prepared in de-ionized water. EDTA(0.1 N) in de-ionized water is prepared as the stabilizer and capping agent. The nickel nitrate solution from the dropping funnel was added drop wise at constant rate to the beaker containing ammonium carbonate and EDTA, under vigorous stirring using a magnetic stirrer. By employing a magnetic stirrer the homogeneity of the nanosized crystals formed were maintained. The precipitate was collected in beaker. The preparation was repeated for 200 ml stock solutions. The precipitate was then decanted and was repeatedly washed 5 times using de-ionized water and centrifuged to collect the precipitate. Finally the precipitate was washed using acetone to remove any trace of organic impurities. The precipitate was then dried overnight in an oven at 100°C and the sample is designated as N1. Then the sample is divided into three parts and annealed at 200°C, 400°C and 600°C in a muffle furnace and is coded as N2, N3 and N4 respectively. The sample code annealing temperature and average grain size of the samples are given in Table 1. The NiO samples were characterized by X-ray powder diffraction (XRD). The XRD analysis was carried out on Bruker D8 Advance model X-ray diffractometer applying Cu-Kα radiations of wavelength 1.5406Å. The XRD patterns of the samples are analyzed by peak fitting program in Origin 6.1. The FTIR spectra of the samples were reordered by KBr pellet method in a Thermo Nicolet, Avatar 370 FTIR spectrometer in the spectral range 400-4000cm⁻¹.

Table 1 Sample code, annealing temperature and grain size.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Annealing temperature</th>
<th>Grain size</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>100°C</td>
<td>Amorphous</td>
</tr>
<tr>
<td>N2</td>
<td>200°C</td>
<td>Amorphous</td>
</tr>
<tr>
<td>N3</td>
<td>400°C</td>
<td>~5 nm</td>
</tr>
<tr>
<td>N4</td>
<td>600°C</td>
<td>~22 nm</td>
</tr>
</tbody>
</table>

3 Results and discussion

The XRD patterns of the NiO nanoparticles are shown in figures. X-ray diffraction patterns of the nanostructured Nickel Carbonate (sample N1 and sample N2) an-
nealed at 100°C and 200°C are given in the figures 1. The XRD patterns of the samples N1 and N2 are broad and diffused. This may be a sign of amorphous nature of the as prepared sample N1. The XRD pattern of the sample annealed at 200°C (sample N2) seems to be more crystalline, yet the peaks are not profound and analysis of the sample is not carried out. XRD pattern of the sample annealed at 400°C (sample N3) and 600°C is shown in the figure 2. All the reflection peaks with relative intensities of different planes, indexed in the figure, specify the presence of NiO. The sharpness and the intensity of the peaks indicate the well crystalline nature of the prepared sample. The h k l planes of the maximum intensity peaks of the samples N3 are in well agreement with the standard JCPDS values (No 78-0643) of cubic structure of nickel oxide. The 2θ values, intensity and the h k l planes of the XRD peaks for the samples are given in Table 2. The standard JCPDS card No. 78-0643 for the cubic phase of NiO is tabulated in Table 3.

Table 2. The peak position (2θ), Intensity and h k l reflection planes of the XRD peaks of the samples N3 and N4

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>2θ values (Degrees)</th>
<th>Intensity (%)</th>
<th>h k l values</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3</td>
<td>36.949</td>
<td>61.09</td>
<td>1 1 1</td>
</tr>
<tr>
<td></td>
<td>42.13</td>
<td>99.78</td>
<td>2 0 0</td>
</tr>
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<td></td>
<td>62.703</td>
<td>45.78</td>
<td>2 2 0</td>
</tr>
<tr>
<td>N4</td>
<td>37.057</td>
<td>62.77</td>
<td>1 1 1</td>
</tr>
<tr>
<td></td>
<td>43.114</td>
<td>99.88</td>
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<tr>
<td></td>
<td>62.728</td>
<td>44.49</td>
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</tr>
</tbody>
</table>

Table 3 Standard JCPDS data card No. 78-0643 for cubic phase of NiO

<table>
<thead>
<tr>
<th>2θ values (Degrees)</th>
<th>Intensity (%)</th>
<th>h k l values</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.264</td>
<td>67.5</td>
<td>1 1 1</td>
</tr>
<tr>
<td>43.297</td>
<td>99.9</td>
<td>2 0 0</td>
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<tr>
<td>62.895</td>
<td>43.4</td>
<td>2 2 0</td>
</tr>
<tr>
<td>75.435</td>
<td>14.3</td>
<td>3 1 1</td>
</tr>
<tr>
<td>79.430</td>
<td>10</td>
<td>2 2 2</td>
</tr>
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</table>
Figure 1 X-ray diffraction pattern of nano structured Nickel Carbonate samples N1 and N2 annealed at 100°C and 200°C.

Figure 2 X-ray diffraction pattern of nano structured Nickel Carbonate samples N3 and N4 annealed at 400°C and 600°C.

The grain size of the NiO nanoparticles were evaluated from the Debye-Scherrer formula\[13\]

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where D = particle size, \( \lambda \) = the X-ray wavelength, \( \theta \) = the Bragg angle, \( \beta \) = Full width at half maximum in radians and \( K = 1 \) (since grain shape is assumed to be spherical).

The grain size calculated for the sample N3 by Scherrer equation is \( \sim 5 \) nm. Grain growth is recorded for the sample N4, which is annealed at 600°C, and has a grain size \( \sim 22 \) nm. On annealing the atoms in the amorphous region surrounding the nanoparticles gets sufficient energy to adhere to the grain or the grain growth crop up.
4 FTIR study of nanoparticles of NiO

FTIR spectra of the nanostructured NiO samples in the mid IR region (400 - 4000 cm⁻¹) are given in the Fig 3 and Fig 4. The peaks located at 3415 cm⁻¹, 3412 cm⁻¹, 3450 cm⁻¹ and 3451 cm⁻¹ for samples N1, N2, N3 and N4 respectively corresponds to the O - H stretching mode of water molecule. The intensity of these symmetric stretching vibrations of absorbed water molecule is found to decline as the annealing temperature increases. Heat treatment at different range of temperatures leads to significant reduction in intensity caused by removal of absorbed water molecules present in the samples.

![Figure 3 FTIR spectra of the nanostructured NiO samples N1 and N2](image)

The very intense and broad peak observed around 1455 cm⁻¹ for N1 and N2 are the asymmetric stretching of carbonate ion (ν3). But the intensity of this broad peak decreases significantly from N1 to N2 and vanishes in N3 and N4. Therefore, it is clear that as the annealing temperature increases Nickel Carbonate is gradually
converted to Nickel Oxide. The bands originated at 837 cm\(^{-1}\) and 835 cm\(^{-1}\) for the samples N1 and N2 are assigned to \(\nu_2\) symmetric bending of carbonate ion and the peaks at 724 cm\(^{-1}\) and 729 cm\(^{-1}\) are the in-plane bending of carbonate ion (\(\nu_4\)). The absorption peaks observed at 1628 cm\(^{-1}\), 1384 cm\(^{-1}\) and 1621 cm\(^{-1}\), 1417 cm\(^{-1}\) in the samples N3 and N4 respectively has very low intensity and hence not assigned.

![Figure 4 FTIR spectra of the nanostructured NiO samples N3 and N4](image)

The absorption peaks originates at 436 cm\(^{-1}\) for N3 and at 428 cm\(^{-1}\) for N4 corresponds to the lattice mode of vibration of Nickel Oxide. This band is found to be more intense in N4 than in sample N3 for the samples at higher temperature, clearly elucidate the nano crystallization of pure phase of NiO. The assignment of absorption peaks are given in Table 4.
5 Conclusion

Nickel Carbonate nanoparticles are synthesized by chemical precipitation method using EDTA as stabilizer. Nanoparticles of different grain sizes were prepared by annealing the as prepared sample. The crystal structure and the particle size were determined from the XRD patterns of the samples. The Origin 6.1 software is used for the peak fitting and evaluation of the FWHM. NiO Nanoparticles of grain size around 5nm and 22nm were prepared. By search match program it was observed that the prepared sample has a cubic structure of NiO. The FTIR spectra of the samples were recorded and the different absorption bands in the spectra are analyzed and assigned. Even though the presence of water molecule and carbonate ion is not detected in the XRD patterns, FTIR spectra clearly shows the presence of absorbed water and carbonate ions in the sample N1 and N2, and their removal from the annealed samples.

Acknowledgment

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References


Ecology of Mysids (Crustacea: Mysida) from the Cochin Backwater

Biju A.1, Panampunnayil S. U.2, Sreejai R3

1,3 P G & Research Department of Zoology
St. Stephen’s College, Pathanapuram, Kerala, India - 689 695
e-mail: bijuanio75@gmail.com
2CSIR - National Institute of Oceanography
Regional Centre, Dr Salim Ali Road, Ernakulam North P.O.
Cochin - 18, Kerala, India.

Abstract

Ecology of crustacean mysids from a tropical estuary (Cochin backwater) was studied based on samples collected over a period of one year. Four species of mysids belonging to three genera were reported: Mesopodopsis orientalis, Mesopodopsis zeylanica, Rhopalophthalmus indicus and Kochimysis pillaii, among which Mesopodopsis zeylanica was the most dominant species. The wide range of fluctuation in mysids population density was considered to be mainly due to their heterogeneous distribution. All species except Kochimysis pillaii, occurred throughout the year and showed seasonality in their abundance. Rhopalophthalmus indicus peak abundance was observed during the pre-monsoon while Mesopodopsis zeylanica and Mesopodopsis orientalis abundance were occurred during monsoon period. In addition to reproduction, geographical conditions of particular stations affecting the population density of mysids. Mesopodopsis orientalis and Rhopalophthalmus indicus showed swarming behavior.

Keywords: Crustacea, mysids, diversity, Cochin estuary, India.

1 Introduction

Estuarine ecosystems rank amongst the most productive biomes of the world and serve as important life-support systems by providing nursery and feeding habitats for fish, crustaceans and birds[1, 6, 8]. Mysid crustaceans are one of the major components of estuarine and coastal zooplankton communities and play a key role in structuring estuarine communities [21]. Their ecological importance, in particular their role in food chains as a link between the benthic and the pelagic system, is becoming increasingly apparent[29]. In general, mysids are omnivores, feeding on detritus, zooplankton and phytoplankton, and as such form a link between microbial
producers and secondary consumers[34] and are responsible for the remineralization of a large portion of the refractile detritus[9]. Mysids have been recorded in the gut contents of marine and estuarine fishes[5, 19, 32] as well as of birds[23], thus playing a part in energy transfer to higher trophic levels[20]. Mysid related fisheries based on several mixed groups of species are present in regions of China, Korea, and southeastern countries[?], where they are used for making shrimp paste, sauces and preserved food for human consumption. In some areas of India (Chilka Lake and Konkan region), mysids have been harvested for human consumption, but they are not commercially exploited. Compared to other estuaries in India, the mysid fauna of the Cochin backwater remains the least explored population. Considering its ecological importance, the present study aims to elucidate the distribution and ecology of mysids in the Cochin backwaters.

2 Materials and Methods

2.1 Study area

Cochin backwater is part of a long chain of lakes and canals, parallel to the coast, extending between 9°40′12″ to 10°10′46″N and 76°09′52″ to 76°23′57″E. The total area of the backwater is about 157 km², with depths ranging from 2 to 8m. A large number of rivers discharge into it, and it opens into the Arabian Sea through one major and several minor outlets.

![Fig. 1 Map showing the study area and sampling locations(S1-S3), in the Cochin backwater](image)

Of the three sampling stations (Fig 1), Fortkochi (S1, harbour entrance) maintains a marine condition throughout the year. Bolghatty (S2), situated in the northern limb
of Cochin backwater, is free from sudden tidal variations and has an intermediate condition with regard to salinity. Thevara (S3), in the southern branch, experiences the maximum tidal variation due to a shipping channel. The distance between stations is $\sim 7$ km on average.

### 2.2 Sampling procedure and data analysis

Samples were collected as a part of the studies on “Ecosystem Modeling of Cochin backwaters” in the period March 2003 - February 2004. Weekly samples were taken for one full year cycle covering pre-monsoon (February - May), monsoon (June - September) and post-monsoon (October - January). Zooplankton was collected before dawn from surface waters using a Working Party (WP) net (mesh size 0.2 mm, mouth area $0.6 \text{ m}^2$) fitted with a flow meter to estimate the volume of water filtered. The net was hauled for 10 min. at the surface using a small boat at a speed of approximately 2 knots. Samples were preserved in 4% formaldehyde. At each station, surface water samples were collected using a clean plastic bucket and measured temperature, salinity (Digi Autosalinometer), dissolved oxygen (Winkler methods), pH (pH meter), and chlorophyll $a$.

Multiple regression analysis (SPSS-10) was employed to assess the predictability of population density on the physico-chemical variables. The model used for the purpose was,

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_5x_5$$

where $Y =$ population density, $x_1 =$ chlorophyll, $x_2 =$ dissolved oxygen, $x_3 =$ salinity, $x_4 =$ pH, $x_5 =$ water temperature. The significance of the fitted regression was tested using ANOVA. Statistical package SPSS V10 was used for analysis.

### 3 Results

#### 3.1 Mysid fauna in the Cochin backwater

Four species of mysids belonging to three genera, *Mesopodopsis orientalis* Tattal-sall, *M. zeylanica* (Nouvel), *Rhopalophthalinus indicus* Pillai and *Kochimysis pillaii* Panampunnayil and Biju, were recorded from the study area during the period of study. Population densities of mysids in the backwaters were highly inconsistent. All the four mysid species were present at Bolghatty (S2), three species (*M. orientalis*, *M. zeylanica* and *R. indicus*) were found at Thevara (S3), while two species (*M. orientalis* and *M. zeylanica*) were recorded at Fortkochi (S1). Invariably numerical abundance of all species was high at Bolghatty (S2) followed by Thevara (S3) and Fortkochi (S1) (Table 1).
Table 1: **Annual population density (ind./ 1000 m$^3$) at different stations and total percentage composition of mysids from the Cochin backwaters.**

<table>
<thead>
<tr>
<th>Mysid species</th>
<th>Fortkochi (S1)</th>
<th>Bolghatty (S2)</th>
<th>Thevara (S3)</th>
<th>Total percentage composition</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Mesopodopsis orientalis</em></td>
<td>2,129</td>
<td>7,086</td>
<td>5,277</td>
<td>26.10</td>
</tr>
<tr>
<td><em>Mesopodopsis zeylanica</em></td>
<td>4,139</td>
<td>14,151</td>
<td>8,273</td>
<td>47.80</td>
</tr>
<tr>
<td><em>Rhopalophthalmus indicus</em></td>
<td>-</td>
<td>12,928</td>
<td>1,310</td>
<td>25.60</td>
</tr>
<tr>
<td><em>Kochimysis pillaii</em></td>
<td>-</td>
<td>320</td>
<td>-</td>
<td>0.58</td>
</tr>
</tbody>
</table>

### 3.2 *Mesopodopsis zeylanica*

#### 3.2.1 Distribution and ecology

*Mesopodopsis zeylanica* thrived in the estuary throughout the year and was the dominant mysid species (47.80% of the total population) in the Cochin estuary. Although density fluctuated greatly at each sampling station, there was showed more or less a similar trend in the timing of their annual peaks (Fig. 2).

![Fig 2. Seasonal changes in the abundance of *Mesopodopsis zeylanica* collected from the Cochin backwater.](image)

The highest population density was observed at S2 (14,151 indi./1000 m$^3$) followed by S3 (8,273 indi./1000 m$^3$) and S1 with the lowest density (4,139 indi./1000 m$^3$). There was a clear seasonal variation: during the pre-monsoon period (February-May)
19.9% of *M. zeylanica* occurred with an average density of $89 \pm 168.3$ indi./1000 m$^3$ at S1, $220 \pm 309.7$ indi. 1000 m$^3$ at S2 and $150 \pm 221$ indi./1000 m$^3$ at S3.

In the present study, *Mesopodopsis zeylanica* most occurred along with *R. indicus* and *M. orientalis*. This species is a euryhaline (0 - 32.5) and eurythermal species($27.2 - 33.5 ^\circ C$). The dissolved oxygen and pH in which *M. zeylanica* occurred were 138.4 to 379 µM and 6.3 to 8.7 respectively.

### 3.2.2 Relation with environmental parameters

The fitted multiple regression model for the data was found to be

$$Y = 607.04 - 6.435x_1 - 6.530x_2 - 30.562x_3 + 16.515x + 4 + 1.121x_5$$

The fitted regression was significant as it could be seen from the Table 2. The only significant variable in the regression is salinity($p < 0.05$), which is having negative impact on population density. Only 12.6% of the variability in the data is explained by the fitted model.

<table>
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<th>F</th>
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<tr>
<td>Total</td>
<td>11389609</td>
<td>116</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.3 *Mesopodopsis orientalis*

#### 3.3.1 Distribution and ecology

*M. orientalis* was present in the estuary throughout the year. Although density fluctuated greatly at each sampling stations, they showed a more or less similar trend in their annual peak(Fig. 3). The highest population density was observed at station S2(7086 ind./1000 m$^3$), followed by S3(5277 ind./1000 m$^3$), and S1 with the lowest density(2129 ind./1000 m$^3$). Compared to other seasons, the highest abundance of *M. orientalis* occurred in the monsoon period(67.7% of the total sampled population), with an average density of $161 \pm 231.4$ ind./1000 m$^3$. This species occurred in wide range of salinity(0 - 34.6 psu) and temperature(27.2 - 32.8°C). Dissolved oxygen and pH ranged between 138.4 - 336.6 µM and 6.8 - 8.3 respectively. It is a euryhaline species and some time occurred in swarms/aggregations.
3.3.2 Relation with environmental parameters

The fitted multiple regression model for the data was found to be

\[ Y = 1309.398 - 25.678x_1 - 3.525x_2 - 41.648x_3 - 13.128x_4 + 1.269x_5 \]

In this regression model, the variables, dissolved oxygen, salinity, pH and water temperature are having negative impact on population density of *Mesopodopsis orientalis*. Only chlorophyll showed to have a positive impact. The fitted regression model for the data is significant and it could be seen from the ANOVA. Even though the fitted regression is significant (Table 3) it explains only 13.5% of the variability in the data.

Table 3: ANOVA for environmental parameters with population density of *M. orientalis*

<table>
<thead>
<tr>
<th>Source</th>
<th>SS</th>
<th>df</th>
<th>MSS</th>
<th>F</th>
<th>P-value</th>
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<td>199148.451</td>
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<td>p &lt; 0.01</td>
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<tr>
<td>Residual</td>
<td>6364132</td>
<td>111</td>
<td>29.62</td>
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</tr>
<tr>
<td>Total</td>
<td>7359874</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.4 *Rhopalophthalmus indicus*

3.4.1 Distribution and ecology

The distribution of *R. indicus* fluctuated greatly in each sampling stations (Fig. 4). The highest population density was observed at S2 (1298 ind./1000m$^3$), while marked reduction in S3 (1310 ind./1000m$^3$) and completely absent in S1. *R. indicus* occurred throughout the study period. There was a clear seasonal variation in the distribution of *R. indicus* during the present study. Compared to that of other seasons, the high abundance of *R. indicus* occurred in pre-monsoon period (February- May)(65.9% of the total population) with an average density of 779.6 ± 552.5 ind./1000m$^3$ at S2 and 73.6 ± 97.2 ind./1000m$^3$ at S3.

![Fig 4. Seasonal changes in the abundance of Rhopalophthalmus indicus collected from the Cochin backwater.](image)

This species is observed in temperature and salinity range of 28 - 33.5°C and 1.84 - 29.16 psu respectively. Polyspecific /monospecific swarms or grouping of *R. indicus* were observed at the sampling stations.

3.4.2 Relation with environmental parameters

*R. indicus* thrives in the estuary throughout the year and tolerates temperature and salinity of 28-32.5°C and 1.84 - 29.16 psd respectively. The fitted multiple regression model for the data was found to be

$$Y = -1322.681 + 63.631x_1 + 6.856x_2 - 135.959x_3 + 56.304x_4 + 0.644x_5$$

Statistical analysis revealed that pH did not have much influence on population density of *R. indicus*, while chlorophyll a, dissolved oxygen salinity and water temperature, had apparently some influence on their distribution. The fitted regression model for the data was significant as can be seen from the ANOVA(Table 4)
Table 4: ANOVA for environmental parameters with population density of *Rhopalophthalmus indicus*

<table>
<thead>
<tr>
<th>Source</th>
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<th>F</th>
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<td>p &lt; 0.01</td>
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<tr>
<td>Residual</td>
<td>5293379</td>
<td>111</td>
<td>47688.095</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1022673</td>
<td>116</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.5 *Kochimysis pillaii*

3.5.1 Distribution and ecology

This species contributed only 0.59% to the total population and was observed only at S2 during pre-monsoon period. In this season, they contributed 1.5% with an average density of 29.1 ± 42.1 ind./1000 m³. Seasonal distribution were plotted in Fig 5. *K. pillaii* preferred temperature and salinity ranging from 25.02 to 32.47°C and 30 to 32.5 psu respectively. This species was observed along with *R. indicus*.

![Fig 5. Seasonal changes in the abundance of *Kochimysis pillaii* collected from the Cochin backwater.](image)

3.5.2 Relation with environmental parameters

The fitted model for the data is

\[ Y = -4.629 + 0.684x_1 + 0.302x_2 - 3.937x_3 + 1.681x_4 - 0.00649x_5 \]
The fitted model is significant ($P<0.01$) as it is evident from the Table 5. The fitted regression only addresses 16.2% of variability in the data. Significant variations in the prediction equations were pH and salinity, pH is having negative impact while sanity is having a positive impact.

Table 5: ANOVA for environmental parameters with population density of *Kochimysis pillaii*

<table>
<thead>
<tr>
<th>Source</th>
<th>SS</th>
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<th>MSS</th>
<th>F</th>
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<tr>
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<td>4256.534</td>
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<td>851.307</td>
<td>4.305</td>
<td>$p &lt; 0.01$</td>
</tr>
<tr>
<td>Residual</td>
<td>21950.252</td>
<td>111</td>
<td>197.750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>26206.786</td>
<td>116</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4 Discussion

Four species of mysids were collected from the Cochin backwater, of which *Mesopodopsis orientalis* has previously been recorded from various localities in India[2, 3, 10, 11, 25, 30] Malaysia[13, 14] Indonesia[14] and Thailand[24, 25, 14]. This species is one of the most important components of the shallow-water crustacean community[13] and dense shoals of this species are exploited for human consumption in coastal areas of India and Thailand[4, 19, 26]. *M. orientalis* are also a food source of dolphin and sea horses[27].

*Mesopodopsis zeylanica* are limited in their distribution with records only in India and Ceylon(Sri Lanka)[13], and the other two species(*R. indicus* and *K. pillaii*) are endemic to Indian waters. The density fluctuation did not show a fully synchronous pattern between the sampling stations. This probably indicates a heterogeneous distribution of the mysids. All species except *K. pillaii*, occurred throughout the year and showed seasonality in their abundance. For example *R. indicus* peak abundance was observed during the pre-monsoon while *M. zeylanica* and *M. orientalis* abundance were occurred during monsoon period.

The fitted regression equation is significant for the data, it explains only little amount of variability in the data except for *R. indicus*. This may be due to the fact that there are other important variables, which control the population density of mysids in the Cochin Backwaters. According to Heubauch[15] reproduction was the principal factor affecting the seasonal and geographical abundance. But the present data reveals that, in addition to reproduction other factors play an important role in species abundance. This may be coinciding with the geographical conditions of particular stations. Comparatively high abundance of *R. indicus* occurred in
pre-monsoon seasons and its total absence in the Fort Cochin station during pre-
monsoon is a matter of concern. This may be due the effect of tidal current of
that particular area. Many workers described the influence of tidal current on the
distribution of zooplankton and mysids[15, 16, 17, 23, 29, 35, 36]. The abundance of
*M. zeylanica* and *M. orientalis* of Fort Cochin station was very low when compared
to that of other two stations.

In the present study two species, *M. orientalis* and *R. indicus* showed swarming
behavior. Mauchline[19] suggests a number of advantages associated with swarming
behavior including protection of individuals and population against predators and
facilitation of breeding. Mysids decrease predation risk by forming swarms. Mysids
in swarm have not been observed to be consumed by fish[7, 12]. Whereas those
removed by a net and artificially displaced from their swarm have been attacked
and eaten by predator[12]. Modline[22] reported that swarming by itself might deter
predation. According to Ritz[28], the swarm represents a strategy for conserving
energy and maximize food capture, his work clearly confirms the energetic benefits
of being a larger social group rather than a smaller one or remaining solitary. Most
of the swarms were observed during night. In general, mysids are attracted to
weak source of light but avoid bright light. Bright light often inhibits the swarming
behavior[31] and may damage their large sensitive eyes[18].

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*Mesopodopsis orientalis*(Crustacea: Mysida) in a tropical mangrove ecosystem


A Study on Physico-Chemical Aspects of Kallada River at Parappar Dam Site, Kerala

Elizabeth John¹, Vidhu Mohan C.K.²
¹Department of Zoology, St. Gregorios College
Kottarakkara, Kollam, Kerala, India - 691 531
e-mail: elizabethmoji@gmail.com
²Research & P. G Department of Zoology
Catholicate College, Pathanamthitta
Kerala, India

Abstract

The present investigation was conducted to evaluate physic chemical nature of River Kallada near Parappar dam site where irrigation project and eco-tourism are factors of major concern. Pappar dam onwards the river flow north-west till it debouches into the Ashtamudi estuary. Three sampling sites were selected downstream to Parappar dam till the region of ‘Look Out’ reservoir. Temperature, Appearance, TDS, PH, total hardness, dissolved oxygen and dissolved CO₂ were analysed. The study revealed slight variations in the quality of water analyzed but not to the pollution level.

Keywords: River Kallada, Parappar Dam, Water Quality, Physical parameters, Chemical parameters

1 Introduction

Water is the most ubiquitous material in nature and is most vital and fascinating of all God’s creation. Water resources are said to be polluted when, because of man’s action in adding or causing the addition of matter to the water or altering the physical, chemical, or biological characteristics of water are changed to such an extent that its utility for a reasonable purpose or its environmental value is demonstrably depreciated. Most of the rivers are deteriorating gradually and maintenance of the quality of river water will be severe problem in the years to come[3].

There are several reports on the pollution of different fresh water bodies and studies on physical and chemical parameters of several drinking water samples from surface waters[7, 8, 9, 17]. The construction of dam results drastic changes in aquatic environment, one difference is that lake level fluctuations may be much larger than
are normal in a natural lake[6]. The chemical quality of the various water sources in the Neyyar River Basin (NRB) in Kerala has been assessed and evaluated[11]. Construction of dam, irrigation project and ecotourism cause many environmental problems. The present investigation was conducted to study the physico chemical nature of river Kallada near the dam site where irrigation project and ecotourism are factors of major concern.

2 Materials and Methods

2.1 Study Area

The river is formed by the confluence of three small streams - the Kulathupuzha, the Chendurni and the Palaruvi at Parappar(Themala) on the upper forest catchment. Thenmala dam onwards the river flow north - west and the west ward where it is joined by an important tributary the Chitar river. Thereafter the river follows a meandering course through gentle to moderately undulated terrain and flows in a south westerly course till it debouches in to the Ashtamudi estuary. Thenmala region of river Kallada from dam site towards 4 KM downstream.

<table>
<thead>
<tr>
<th>Site</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Site I</td>
<td>Parappar Dam Site</td>
</tr>
<tr>
<td>Site II</td>
<td>River Downstream to Parappar dam (2Km from Dam Site)</td>
</tr>
<tr>
<td>Site III</td>
<td>River Upstream to Look out (4Km from Dam Site)</td>
</tr>
</tbody>
</table>

2.2 Collection of water samples

Samples from the sampling sites were collected in 3 litre polyethylene sampling bottles (previously washed thoroughly with clean distilled water followed by rinsing with water from sampling sites). Sampling were conducted from September 2012 to February 2013.

2.3 Water analysis

Temperature, transparency, pH in site, dissolved oxygen fixed with manganous sulphate and alkaline iodide at the site of collection. All water samples were then transported to the laboratory and stored at 4°C in refrigerator and physico chemical parameters were analysed within 24 hours. The following physico chemical aspects of water were were analysed.

1. Temperature
2. Appearance
3. Total Dissolved Solids (TDS)
4. pH
5. Total hardness
6. Dissolved Oxygen
7. Dissolved CO₂
The analytical methods adopted in the analysis were as per the standard methods[1, 19].

3 Results and Discussion

The present study reports on various physico chemical parameters of water in the different areas of Kallada River from Parappar dam site to Upstream of Look out reservoir(Table 1, 2, 3).

Temperature is an important factor in monitoring the quality of water in the fact that it affects the chemical and biological reactions in water. The elevated temperature change in water accelerates chemical reactions, reduces solubility of gases and may cause death in extreme cases, but with lower ranges it may ultimately influence the movement, migration and even behavior of organisms. However in the present study, water temperature in the sampling points in the river was within the permissible limits. Highest value was noticed during Jan - Feb 2013. From Sep to Nov 2012 the temperature was low. The increase of temperature in water samples during this time may be attributed to rise in atmospheric temperature and increase in day length during the season[15].

Appearance is one of the most obvious indicators of water pollution and the discharge of highly colored effluents containing dyes can damage the receiving bodies[16]. This in turn may interfere with the penetration of sunlight essential for photosynthesis. During monsoon high turbulence of rain water and seepage mixing along the river was evident from the brown colored water samples from all the three sites during Nov - Dec 2012 period.

TDS include salts, organic and gaseous impurities. Water with high TDS is not suitable for drinking purpose as it causes gastro - intestinal irritation[14]. In the present study, TDS detected was very high during Jan - Feb 2013 period. This may be due to the low amount of water due to high temperature and lack of rain. Which results more concentrated water. The present study is in tune with the earlier reports[2] in the evaluation of the quality of water bodies due to high concentration.

pH is a valuable parameter which guides not only the acid alkaline balance of the water but also serves as an important index for the degree of pollution[4]. It is a well known fact that pH may adversely affect biota as it influence the toxicity of certain substances. The increase in pH is not a common occurrence but may be attributed to anthropogenic eutrophication in the study area[5]. In this study pH was in the permissible level for all samples except one which showed comparatively high value at Site I. The lowering of pH at site II may be due to the presence of more CO₂ and also the presence of household waste and other pollutants. The pH showed a drastic rise at site III, this can be explained by considering the huge amount of water and sedimentation at the reservoir site. pH range of similar pattern was noticed in the limnological studies[15].

Total hardness is an important water quality parameter attributed to presence
Table 1 Temperature, Appearance and TDS in station I, station II and station III during the period Sep 2012 - Feb 2013

<table>
<thead>
<tr>
<th>Month</th>
<th>Temperature(°C)</th>
<th>Appearance</th>
<th>TDS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SI</td>
<td>SII</td>
<td>SIII</td>
</tr>
<tr>
<td>Sep-Oct 2012</td>
<td>28±1</td>
<td>28.6±1</td>
<td>28.1±1</td>
</tr>
<tr>
<td>Nov-Dec 2012</td>
<td>29±1</td>
<td>29.4±1</td>
<td>29.2±1</td>
</tr>
<tr>
<td>Jan-Feb 2013</td>
<td>30±1</td>
<td>29.6±1</td>
<td>29.9±1</td>
</tr>
</tbody>
</table>

of carbonates, bicarbonates and hydroxides. In this study, total hardness, couldn’t show a uniformity in the selected sites. This may be due to hardness imparted by different ionic constituents in the different samples. Hardness was high during Jan - Feb 2013 at three sites low during Sep - Oct 2012 and moderate during Nov - Dec 2013. This owes to the dilution of water in the canal during rain and the dilution of water during the flow. This pattern of total hardness was noticed in River Bandi[19] in Rajasthan due to textile effluent discharge.

One of the deleterious effects of the textile process effluents is that it will deplete the dissolved oxygen in the receiving water body. Organic matter such starch, dextrin and inorganic chemicals like sulfite, hydrosulphide and nitrite will exert an immediate oxygen demand[19]. In this study, DO in the upstream remained at an appreciable level in all the seasons considered at three sites. Low oxygen content i.e, below the permissible limit in the rest of the water samples attributes to the oxygen demand created by different pollutants in the effluent. DO was high in Nov - Dec 2012 and low in other two time period in all sampling points in the river. This may be due to high flow of water during the first study period and the drastic increase in the second time period may be due to the presence of phytoplankton, more water plants and pollutants. The lowering of this amount at the third stage may be due to the high amount of water and sedimentation. The present results were in conformity with the seasonal wise studies conducted in the Rivers of Malawi[18].

CO₂ is produced as a result of respiration of aquatic organisms. Normally about 0.5 mg/l of CO₂ is present in a simple solution. This amount of CO₂ referred to have free CO₂. The CO₂ concentration was comparatively high in all samples, even though slight variation can be explained on the basis of rain and impact of human population in that specific sample. The high value was recorded in SIII. This may be due to the decomposition of organic matter in the water[10]. The minimum value of was recorded in SI. Low level of CO₂ might be either due to consumption in carbon assimilation or its complete conservation into carbonic acid[12, 13].
### Table 2 pH and dissolved oxygen in station I, station II and station III during the period Sep 2012 - Feb 2013

<table>
<thead>
<tr>
<th>Month</th>
<th>pH</th>
<th>Dissolved Oxygen (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S I</td>
<td>S II</td>
</tr>
<tr>
<td>Sep- Oct</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>7±0.5</td>
<td>6.7±0.5</td>
</tr>
<tr>
<td>Nov- Dec</td>
<td></td>
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<tr>
<td>2012</td>
<td>7±0.4</td>
<td>6.5±0.5</td>
</tr>
<tr>
<td>Jan-Feb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2013</td>
<td>7.7±0.7</td>
<td>6.8±0.5</td>
</tr>
</tbody>
</table>

### Table 3 Hardness and dissolved CO$_2$ in SI, SII and SIII during the period Sep 2012 to Feb 2013

<table>
<thead>
<tr>
<th>Month</th>
<th>Hardness (mg/L)</th>
<th>Dissolved CO$_2$ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S I</td>
<td>S II</td>
</tr>
<tr>
<td>Sep- Oct</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>7±2</td>
<td>8±2</td>
</tr>
<tr>
<td>Nov- Dec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>10±1</td>
<td>12±1</td>
</tr>
<tr>
<td>Jan-Feb</td>
<td></td>
<td></td>
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<tr>
<td>2013</td>
<td>15±2</td>
<td>18±2</td>
</tr>
</tbody>
</table>

### 4 Conclusion

The present study explains the various physico-chemical parameters in different localities of the river Kallada from Parappar Dam site to Lookout reservoir. The results of the study describe the inter-relation between various physico-chemical factors. That is the rise in temperature during Jan-Feb duration showed increased level of hardness, TDS and drastic change in pH. The study confirms that the river Kallada in the tested sites are not polluted in terms of physico-chemical result obtained from water samples during the six month (Sep 2012 to Feb 2013).

### References


Abstract

Marine plankton pigment concentration estimated as total chlorophyll or chlorophyll a is used as an indicator for determining the biological product or simply trophic state of water. In the study trophic state evaluation was carried out using acetone extraction and spectrophotometry methods of plankton pigment estimation. This ecosystem was monitored for a year extending from January to December 2011. The evaluation of trophic state was based on the subsurface representation of chlorophyll a in phytoplankton and the zooplankton grazing from the quantification of detrital chlorophyll/phaeophytin. Different areas of the coastal waters extending from Vizhinjam to Calicut was monitored for chlorophyll pigment concentration and was recorded > 7.0 mg.m$^{-3}$ throughout the study, and expressed the trophic state as eutrophic. Trophic level changes were observed seasonally during the monitoring period.

Keywords: Plankton pigment, trophic state, southwest coast

1 Introduction

Recently plankton pigment concentrations in natural water bodies are used as indicators of trophic state or biological production influenced by nutrient characters[1]. In the coastal regions of southwest India, monsoon plays a critical role in environmental feature changes such as sea water temperature, salinity, dissolved oxygen and nutrient generation which become responsible for the production of both phytoplankton and zooplankton which in turn has a great bearing on fish yield. Zooplankton are considered as the primary consumers in a food chain and play an important role in the study of faunal biodiversity of aquatic ecosystems[2]. The aim of this study is to describe the variations of phytoplankton pigments and its detrital form in evaluating the trophic state of south west coast of India.
2 Materials and methods

Figure 1. Area of investigation along southwest coast of India

For the present study sampling was carried out from January to December 2011. Predetermined four stations Vizhinjam, Neendakara, Cochin and Calicut situated along southwest India were selected for the study (Fig.1). Sub surface water samples were collected using teflon coated Niskin samplers of 1L capacity operated on board fishing vessels. chlorophyll a concentrations was determined using Whatman 47mm $\phi$ GF/C fiber (0.7 $\mu$m pore size). The contents were extracted in 90% acetone, centrifuged, refrigerated in dark for 20 to 24 hrs and the light absorbance at 647nm was recorded in a spectrophotometer (Shimadzu UV 1800), as per the standard protocol[3]. Phaeophytin or chlorophyll degradation was determined by adding two drops of dilute hydrochloric acid to the cuvette and mixing thoroughly and re-measuring the extinction at 665 and 750 nm. The water samples collected for plankton pigment extraction were filtered and the filter paper soaked in 90% acetone was transported to the laboratory for further analysis. The values for chlorophyll a (total chlorophyll) and phaeophytin (detrital chlorophyll) were expressed in mg. m$^{-3}$. 
3 Results

The variations in plankton pigment range along southwest coast of India are presented in Fig 2. Total chlorophyll ranged from 8.67 to 11.81 mg m\(^{-3}\) with a peak during pre-monsoon at Vizhinjam (13.82 mg m\(^{-3}\)). At Neendakara the pigment concentration ranged from 8.67 to 11.81 mg m\(^{-3}\)). A decreasing trend in chlorophyll was observed during monsoon (8.67 mg m\(^{-3}\)). Phaeophytin showed a peak concentration (2.07 mg m\(^{-3}\)) during post monsoon which indicates the maximum microzooplankton grazing strength. Compared to other three sampling stations at Cochin, it was high at post-monsoon (22.17 mg m\(^{-3}\)) and an average low concentration during pre-monsoon (19.02 mg m\(^{-3}\)), indicating the enhanced primary production and consumption. However, the phaeophytin value showed its maximum during monsoon (5.63 mg m\(^{-3}\)) and a concentration of 3.81 mg m\(^{-3}\) in pre-monsoon. The zooplankton grazing strength could be assumed at its peak during monsoon. Pigment concentration along Calicut showed an almost similar trend of values recorded at Vizhinjam. The chlorophyll content at Calicut ranged between 7.69 and 12.04 mg m\(^{-3}\) having a peak during post monsoon.

![Figure 2. Chlorophyll pigment concentration along southwest coast of India](image)

Phaeophytin values ranged from 1.03 to 2.86 mg m\(^{-3}\) and exhibited a peak during post monsoon (Fig 2). A mean chlorophyll a concentration of > 8.0 mg m\(^{-3}\) was observed throughout the study, suggesting the eutrophic state prevailing along the southwest coast of India.
Figure 2. Phaeophytin pigment concentration along southwest coast of India

The phaeophytin value showed its maximum during monsoon with 5.63mg.m\(^{-3}\) and a minimum of 3.81mg.m\(^{-3}\) in post-monsoon. Productivity based grazing was also a major factor noticed in the study by means of phaeophytin values.

4 Discussion

Naturally occurring seasonal nutrient enrichment in the waters along the west coast resulted by the upwelling during the southwest monsoon period trigger high primary production and the stock of phytoplankton in terms of Chlorophyll \(a\)[4].

Trophic state determination along southwest coast of India was tabulated according to a comparison trophic delineation table structured from earlier related publications presented in Table 1.

Unlike the nutrient distribution by pollutant inflow[8], total chlorophyll was high at Cochin indicating the eutrophic state and a well balanced ecosystem is maintained by means of zooplankton grazing revealed through phaeophytin or detrital chlorophyll values. Based on the chlorophyll content, the trophic state along southwest coast of India is eutrophic ascertained by various pollution inflows. The results of this study lead to infer that zooplankton grazing is an important component in balancing the trophic state and averting the chances of harmful algal blooms.
Table 1 Comparison of trophic state of the present study with similar earlier findings

<table>
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<tr>
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<th></th>
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<td></td>
<td>&lt;0.1</td>
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<td>Oligo-Mesotrophic</td>
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<td>Meso-Eutrophic</td>
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<td>1.5-2.5</td>
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<tr>
<td>Eutrophic</td>
<td>2.5-10</td>
<td>&gt;5.0</td>
<td>2.5-5.0</td>
<td>8.67 - 22.17</td>
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<td>Hypertrophic</td>
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<td>&gt;10</td>
<td>&gt;5.0</td>
<td></td>
</tr>
</tbody>
</table>

Acknowledgement

We are grateful for the assistance in the field from the Masters and Crew members of fishing crafts accessed at each sampling stations.

References


On Wild Animal - Human Interaction at Kuryanayam in Kumaramkudy Forest Range, Kerala

Rani S Dharan
Department of Zoology
St. Gregorios College, Kottarakara
Kollam, Kerala, India - 691 531

Abstract

A study on man, plant and animal interaction was conducted at Kuryanayam in kumaramkudy range, Kerala. The cultivations that were done in the encroached area led to man-animal conflict. Major animals and birds invading the study area were boar, mongoose, ibex, varanus, polecat monkey, hornbill peafowl, kite, wildfowl etc.

Keywords: Kuryanayam, encroached area, boar, hornbill.

1 Introduction

Living organisms on the earth are mutually interdependent for their sustenance, growth and development. It is important to know how and to what extent various kinds of interdependent relationships keep balance in nature and how this balance is disturbed by continuous and deliberate actions of man. But this relationship is hardly realized by man who has been through the ages the principal agent of change. The need for conservation of India’s natural habitats and thereby protecting various plants and animal forms are stressed by many investigators. At present India has about 350 species of wild mammals in different forest habitats, but it is unfortunate to note that 81 species among them were and/or facing threatened extinction[1, 5]. The forest of Kerala has been classified into specific types based on diversity composition of species[3]. An extent of about 3,000 km² was under reserve forest at the time of independence. However, large extent of forest area was converted for other land use during the last four decades. Currently, only nine percent of the total area of the state is under forest cover.

Mammalian fauna of Kerala forest comprises of 40 species of large and medium and a number of small sized mammals belonging to the order Chiroptera, Rodentia and Insectivora. Detailed field observations dealing with the population of mammalian fauna have been made only in silent valley National Park[1, 9], Periyar Tiger
Reserve[9], Parambikulam wild life sanctuary and Wynad wildlife sanctuary[2]. Further a few field observations on species specific projects in Kerala have also been reported[4, 6, 7, 8].

2 Study Area

The area selected for this study was Kuryanayam in kumaramkudy forest range, have a more or less seasonal climate with a distinct summer and winter season. Temperature is found to be ranging between 18°C - 34°C March and April are appeared to be comparatively more warmer. Average rainfall available for the area is 2171mm/annual(Meteorological Deptartment, Govt. of India). The whole area was divided into 16 plots by random selection(lottery method) and each plot was visited 4 times a month, on a weekly basis. Data were collected by studying the nature of the crops damaged, and the intensity of attack. The animals were identified by interviewing the plot owners, local people and also the pug marks.

3 Observation and Results

Major cultivations in various plots were plantain, tapioca, colacasia, rubber, vanilla, yam, amorphophalus, cumbumcumber, betel, ginger, snake-guard, coconut trees etc. The first seven plots(Plt 1 to Plot 7) and Plot 16 were near to the forest and Plot 8 were more or less equal distance towards road and forest boarder, but Plot 9, Plot 10, Plot 11 were close the road. The next four plots(Plot 12, Plot 13, Plot 14, Plot 15) were somewhat away from the road. Mode of interaction and type of invading animals in all the sixteen plots are given in Table 1 and Table 2.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Invading Animals</th>
<th>Interaction</th>
<th>Measures adopted to curb the menace</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Boar</td>
<td>Uprooted and ate tapiocca, yam, Plantain, Colacassia, dismantle pepper and betel twiners</td>
<td>Kaval maadam, Fire crackers</td>
</tr>
<tr>
<td>2</td>
<td>Monkey</td>
<td>Consume jackfruits, tamarind, pea, guava, break rubber seeds</td>
<td>Spraying chilli powder</td>
</tr>
<tr>
<td>3</td>
<td>Mongoose</td>
<td>Coughed hen</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Hornbill</td>
<td>Consume pepper, Shysigium jambos</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Toddy cat</td>
<td>Uprooted and ate coffee, Pineapple</td>
<td>Kaval maadam</td>
</tr>
</tbody>
</table>
Table 1 Interactions Performed by Invading Animals

<table>
<thead>
<tr>
<th>Sl. No.</th>
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<th>Measures adopted to curb the menace</th>
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<tbody>
<tr>
<td>6</td>
<td>Varanus</td>
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</tr>
<tr>
<td>7</td>
<td>Sambar Deer</td>
<td>Ate pea</td>
<td>Driven away</td>
</tr>
<tr>
<td>8</td>
<td>Flying fox</td>
<td>Consume jackfruits, Plantain</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Pea fowl</td>
<td>Consume flowers, budsof cucumber, amaranthus</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Kite</td>
<td>Caught chicken</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Jackal</td>
<td>Competitor of boar using a particular discharge</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>King cobra</td>
<td>No Significant Interaction</td>
<td>Locals tried to handle it with rodes</td>
</tr>
<tr>
<td>13</td>
<td>Wildfowl</td>
<td>No Significant Interaction</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Vulture</td>
<td>No Significant Interaction</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Wild cock</td>
<td>Consume flowers and budsof cucumber, amaranthus</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Lynx</td>
<td>Caught hen</td>
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</table>

Table 2 Animals invaded in 16 plots

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Invaded Animals</th>
<th>Bear</th>
<th>Monkey</th>
<th>Hog</th>
<th>Deer</th>
<th>Turkey</th>
<th>Vulture</th>
<th>Sambar</th>
<th>Jackal</th>
<th>Kite</th>
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<th>Wild fowl</th>
<th>Wild cock</th>
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4 Conclusion

Major animals and birds invading the area are boar, mongoose, ibex, varanus, polecat monkey, hornbill peafowl, kite, wildfowl etc. For preventing the invasions land owners deploy various measures like traps with crackers, domestication of dog, kavalmadam etc. Human beings and domesticated dogs also become their targets in some instances. Intensity of invasions greatly depends on the diligence of the landowners. Seasons are also playing a key role in regulating the rate of invasions. In this viewpoint Karkkidakam has a significant role, as it is the breeding period of boar. Among the invading animals, boar occupies the topmost position and plot number 16 is more susceptible.

References


Role of Germline Polymorphism

**XRCC3 Thr241Met** in Familial and Sporadic Breast Cancer Susceptibility

Volga S Syamala¹, Ravindran Ankathil²

¹Department of Zoology
St. Gregorios College, Kottarakara, Kerala, India - 691 531
²Division of Cancer Research, Regional Cancer Centre
Thiruvananthapuram, Kerala, India

Abstract

This study evaluated the influence of XRCC3-Thr241Met in familial and sporadic breast cancer predisposition. 140 familial breast cancer patients, 219 sporadic breast cancer patients and 367 females without cancer as control group were genotyped using PCR-RFLP method. Carriers of at least one 241Met allele showed a significant association with familial breast cancer (OR=1.9; 95%CI=1.26-2.79) but not with sporadic breast cancer (OR=1.1; 95%CI=0.77-1.58). There was no statistically significant association between this polymorphism and overall survival. Considering the increased OR among familial breast cancer patients with the 241Met allele, it can be conjectured that XRCC3-Thr241Met may be a risk predisposing factor for familial breast cancer in this south Indian population.

1 Introduction

The genes involved in DNA damage repair and maintenance of genome integrity play a crucial role in protecting against mutations that lead to cancer and inheritance of genetic variants of these genes results in altered DNA repair capacity and cancer risk. These genes are highly important in the current scenario as we are exposed to a plethora of chemical and physical carcinogens which create such DNA mutations. Worldwide, breast cancer is the most frequently diagnosed cancer among women. The strongest risk factors for breast cancer include family history of the disease, indicating a genetic basis of the disease. But, germline mutations in the two known major susceptibility genes BRCA1 and BRCA2 are thought to account for less than 20-30% of the excess familial risk of breast cancer[13], suggesting that other breast cancer susceptibility genes remain to be identified. With this background it has been anticipated that the remaining familial aggregation may be largely ‘polygenic’, i.e. due to a large number of alleles each contributing a small effect.
Single nucleotide polymorphisms (SNPs) in genes involved in DNA damage repair can affect repair efficiency, which in turn can confer predisposition to breast cancer. A common SNP C to T substitution, results in a threonine (T) to methionine (M) amino acid change at codon 241 in the XRCC3 gene. A plethora of studies including a meta-analysis are available regarding the role of XRCC3 Thr241Met in breast cancer susceptibility, but the results are inconsistent [4, 6, 8, 11]. Furthermore, studies by Figueiredo et al. (2004) and Han et al. (2004) showed that this germline polymorphism also contribute to familial breast cancer. In this scenario, it was of interest to undertake this case control study to investigate the influence of XRCC3 Thr241Met in familial and sporadic breast cancer susceptibility risk in a South Indian population.

2 Subjects & Methodology

2.1 Study subjects

The cases included in this study were breast cancer patients randomly selected from the out patient clinic of Regional Cancer Centre, Thiruvananthapuram, South India, during the period from May 2000 to April 2006. The familial and sporadic breast cancer patients were identified based on a face to face interview followed by detailed pedigree analysis. The familial breast cancer cases were selected based on IARC selection criteria (1989).

The control subjects without any history of any type of personal or family histories of cancer were identified from out patient department of a near by hospital, as the institution where the study has been carried out caters to the treatment of cancer patients only.

Altogether there were 726 females as study subjects including 359 breast cancer patients (219 sporadic and 140 familial) of 20-79 years and 367 controls. The study protocol used in this study was approved by the Institution Review Board and Ethics committee of the institution.

2.2 Genotype Analysis

For genotype analysis, 2 ml blood samples were collected from each study subject after obtaining a written informed consent and preserved in ACD solution at −80°C until further analysis. DNA was extracted from the blood using a standard phenol-chloroform extraction method.
Fig 1 Ethidium bromide stained Poly Acrylamide Gel and corresponding Electropherograms showing XRCC3 polymorphisms

Genotyping of XRCC3 Thr241Met was performed using PCR-RFLP method with slight modification of the protocol used by Tuimala et al. (2002). PCR primers were F: 5’ gct cgc ctg gtg gtc atc gac tcg 3’ and R: 5’ aag agc aca gtc cag gtc agc tg 3’. After PCR amplification, restriction digestion was performed using 10U of the Nla III restriction endonucleases (New England Biolabs, Beverly, MA) at 37°C overnight. The digested PCR product was then resolved by electrophoresis on a 2% agarose gel. An uncut 336 bp band showed the presence of 241Thr genotype, two bands of 231 and 105 bp fragments represented 241Met genotype while the heterozygous individuals were identified by the presence of 3 bands representing 336, 231 and 105 bp fragments. Any sample with ambiguous result (due to low PCR yield) was reanalyzed, and a random selection of 10% of all samples was repeated. No discrepancies were discovered upon replicate testing.

2.3 Statistical Analysis

The association between XRCC3 Thr241Met polymorphism with familial or sporadic breast cancer susceptibility risk and disease characteristics was examined using conditional logistic regression analyses adjusted to age to calculate the ORs and 95%CIs.

3 Results

The present study examined the impact of germline polymorphism of XRCC3 Thr241Met in familial and sporadic breast cancer susceptibility risk. The age of the study subjects ranged from 20 to 79 with a mean age of 46.51 ± 10.23 among breast cancer patients and 46.22 ± 10.27 among controls.
3.1 Genotype frequencies

The genotype frequencies for XRCC3 Thr241Met among familial and sporadic breast cancer patients and control subjects are represented in Tables 1 and 2.

**Table 1: ORs for XRCC3 Thr241Met and familial breast cancer**

(* P value < 0.05 statistically significant association)

<table>
<thead>
<tr>
<th>Genotype</th>
<th>Controls N=367(%)</th>
<th>Familial patients N=140(%)</th>
<th>OR (95% CI)</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thr/Thr</td>
<td>251 (68.4%)</td>
<td>75 (53.6%)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Thr/Met</td>
<td>104 (28.3%)</td>
<td>51 (36.4%)</td>
<td>1.6 (1.08-2.51)</td>
<td>0.022*</td>
</tr>
<tr>
<td>Met/Met</td>
<td>12 (03.3%)</td>
<td>14 (10.0%)</td>
<td>3.9 (1.73-8.80)</td>
<td>0.001*</td>
</tr>
<tr>
<td>Thr/Met or Met/Met</td>
<td>116 (31.6%)</td>
<td>65 (46.4%)</td>
<td>1.9 (1.26-2.79)</td>
<td>0.002*</td>
</tr>
</tbody>
</table>

**Table 2: ORs for XRCC3 Thr241Met and sporadic breast cancer**

(* P value < 0.05 statistically significant association)

<table>
<thead>
<tr>
<th>Genotype</th>
<th>Controls N=367(%)</th>
<th>Sporadic patients N=219 (%)</th>
<th>OR (95% CI)</th>
<th>P value</th>
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<tr>
<td>Thr/Thr</td>
<td>251 (68.4%)</td>
<td>145 (66.2%)</td>
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<tr>
<td>Thr/Met</td>
<td>104 (28.3%)</td>
<td>67 (30.6%)</td>
<td>1.1 (0.77-1.61)</td>
<td>0.56*</td>
</tr>
<tr>
<td>Met/Met</td>
<td>12 (03.3%)</td>
<td>7 (03.2%)</td>
<td>1.0 (0.39-2.62)</td>
<td>0.98*</td>
</tr>
<tr>
<td>Thr/Met or Met/Met</td>
<td>116 (31.6%)</td>
<td>74 (33.8%)</td>
<td>1.1 (0.77-1.58)</td>
<td>0.59*</td>
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3.2 Breast cancer risk

Conditional logistic regression analysis adjusted for age was used to analyze the role of these variants in the risk for familial and sporadic breast cancer. The results showed that the presence of at least one methionine allele increased familial breast cancer risk (Table 1) while such risk association was absent for sporadic breast cancer (Table 2). The heterozygous genotype increased the familial breast cancer risk to 1.6 fold (95% CI=1.08 - 2.51) while the risk due to homozygous variant genotype was 3.9 (95% CI=1.73 - 8.80).

4 Discussion

DNA double strand breaks (DSBs) are the most detrimental form of DNA damage, and are frequently induced by carcinogens such as ionizing radiation. They lead to chromosomal breakage and rearrangement - events that may result in apoptosis or tumorigenesis[10]. Eukaryotic cells have developed two pathways to repair DNA DSBs - the homologous recombination (HR) and the non-homologous end-joining (NHEJ) pathways. In HR, RAD51-related proteins RAD51B-D, XRCC2 and XRCC3 are also involved in HR, and there is a direct interaction between XRCC3 and RAD51[9]. The 241Met variant of XRCC3 gene involved in DNA double strand break repair has been associated with higher levels of bulky DNA adducts, mitotic defects and lower DNA repair capacities of X-ray-induced DNA damage[12].

In this case-control study carried out in a south Indian population, we investigated the impact of XRCC3 Thr241Met in sporadic and familial breast cancer risk. One meta-analysis of 48 case-control studies[6] showed that there were significant differences in terms of the variant XRCC3 241Met allele frequency between the two major ethnicities (European, 36.1%; 95% CI=34.8-37.5; Asian, 8.22%; 95% CI=3.00-13.4; P<0.0001). The present study results shows that the frequency of 241Met is found more frequently in this South Indian population compared to other Asian populations previously studied.

Our results demonstrated a strong risk association for familial breast cancer susceptibility in XRCC3 241Met genotype carriers (OR=1.9; 95% CI=1.26 - 2.79). But there was no statistically significant association between this polymorphism and sporadic breast cancer risk (OR=1.1; 95% CI=0.77 - 1.58). Our result is consistent with report by Han et al.(2004). This previous study observed that 241Met allele carriers have an increased risk for familial breast cancer (OR=1.47; 1.20-2.70) but not for sporadic breast cancer (OR=0.95; 95% CI=0.78 - 1.15). Quite contrarily, a study by[1] in Portuguese population observed an increased risk association of XRCC3 241Met polymorphism with sporadic breast cancer (OR=2.21; 95% CI=1.42 - 3.44), but not with familial breast cancer (OR=1.16; 95% CI=0.71 - 1.89). Simi-
larly in the study[2] in a group of Brazilian patients, an increased risk association of Thr241Met genotype with an OR 2.07 (95% CI=0.85 - 5.06) was observed in sporadic breast cancer, but there was no statistically significant association with familial breast cancer (OR=1.57; 95% CI=0.57 - 4.35). But in this study, the lack of statistically significant association may also be attributable to insufficient sample size to demonstrate any true association if present. Figueiredo[3] also observed no evidence of interaction between family history and XRCC3- Thr241Met among Caucasian women. With individuals of Thr241Thr genotype and negative family history as reference group, the ORs for familial breast cancer cases with Thr241Thr genotype was 2.70(95% CI=1.34 - 5.46) while that for Thr241Met and Met241Met were 2.26(95% CI=1.24 - 4.12) and 4.77(95% CI=1.55 - 14.70) respectively(P = 0.82).

The variance in results of association of XRCC3 polymorphism in different case-control studies may be attributed to variation in genetic/ethnic origin and different carcinogenic exposures of the studied populations. However, these studies altogether suggest that, the risk for breast cancer due to this polymorphism depends not only on one’s family history but also on cumulative effects of other shared genes and environmental factors.

In conclusion, our findings support the hypothesis that XRCC3 Thr241Met may be related to familial and not sporadic breast cancer susceptibility. This study provides further support on the influence of SNPs of low penetrance genes in familial breast cancer susceptibility. Further studies assessing the interactive influence of various candidate gene polymorphisms in breast cancer susceptibility may be an important goal to get a clear picture on the role of low penetrance genes in familial breast cancer.

Acknowledgements

We are grateful to the participants of the study and their families without whose cooperation this study would not have been possible. We also thank the staff members of various clinical departments of Regional Cancer Centre, Thiruvananthapuram for their help in identification of patients and providing necessary data for the study.

References


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