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*Research Frontiers  
In Sciences  
Vol. II*

*Associate Editors*

Dr. (Smt.) Shakun Mishra

Dr. Purushottam R. More

Dr. Prashant Kumar Gangwar

Dr. (Smt.) Pratibha S. Desai

*Editors-in-Chief*

Dr. Sagar A. Vhanalakar

Dr. Sharadrao A. Vhanalakar



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# **RESEARCH FRONTIERS IN SCIENCES Vol. II**

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Presently, she is Fellow/Life Member of 10 National and International research societies such as Society of Life Sciences, Satna (M. P.), Indian Hydrobiology, Chennai and I.A.A.T., etc. She received some prestigious awards like F.I.C.C.E. in 2004, F.S.L.Sc. in 2005 and F.E.S. in 2013. She is completed one M.R.P. funded by U.G.C. and Ex-Chairman of BOS in subject of Botany, Soil Sc., Seed Tech. and Horticulture in D.A.V.V.Indore and also same in Central University Bhopal. *Typhonium flagelliforme* (Lodd.) Blume(Araceae), is reported by Mishra for the first time for Burhanpur District from Madhya Pradesh forms an addition to the Araceae, Flora of Madhya Pradesh.



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Dr. Purushottam More is presently working as Head, Department of Zoology, Kai. Rasika Mahavidyalaya, Deoni. Dist. Latur. Dr. More completed his Ph. D. from Dr. Babasaheb Ambedkar Marathwada University, Aurangabad in August, 2014. His topic of research for Doctoral degree was “comparative study of induced breeding by the application of pituitary extract and ovaprim in *catla catla*”. His area of research is fish biology, aquatic toxicology and limnology.

Dr. P. R. More published 13 research article in various national and international reputed journals. Apart from his research contribution he attended and presented research papers in more than 40 national and international symposia, conference and workshops. Presently, Dr. More is life member of an international organization namely ‘Association of Zoologist’. Dr. More headed various student and social related activities under National Service Scheme (NSS) in Latur District. He also actively participated in programmes run by renowned Pani Foundation. Dr. More was awarded by “Jal Ratna Award” by Pani Foundation for his social contribution.



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Dr. Prashant Kumar Gangwar is a renowned educationalist, environment activist, researcher & civil engineer. He holds a bachelors (B. Tech) degree in Civil engineering, Masters (M. Tech.) in Construction engineering as well as Ph. D. in Civil engineering. He worked with various educational institutions in Rajasthan and Uttar Pradesh. He is having more than 50 international paper published in various journals as well as he is serving as a reviewer and editor in many international journal's board. He is also nominated as a member in different international professional organizations around the globe including China, United Kingdom, United States etc. He is currently working as a Vice President of "Wings for Wild "(A Non Government Trust) which mainly work in the field of wild life conservation.



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Dr. Desai received 'Excellent Research Paper' Award at MSSTEA Annual National Conference for two times. She is working as a course coordinator for YCMOU (Open University on Maharashtra) from last 12 years in education faculty. She contributed actively in curriculum framing for B. Ed. (Shivaji University, Kolhapur). She is members of many scientific professional bodies and societies. She delivered more than 20 invited talks on various subjects including Science, Mathematics, and Education etc. Apart from academic record, Dr. Desai also worked as examiner for various science exhibitions and other examinations carried out by district and state level bodies.



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The main area of his research is thin film solar cell. He is actively engaged in research. Dr. Sharadrao Vhanalakar has published more than 100 research papers in various international journals having more than 400 citations and 'h' index is near to 16. He is awarded by prestigious 'Raman Post-Doc Research Fellowship in USA' by University Grants Commission, New Delhi in year 2016. He is recipient of 'Young Scientist Award' by Department of Science and Technology, Government of India in 2014. He is working as a principal investigator of one research project funded by Department of Science and Technology, Government of India.

## Content

Sr. No.	TITLE OF BOOK CHAPTER	Author(s)
1	NEW APPROACH FOR SUSTAINABLE DEVELOPMENT BY MATERIAL SCIENCE	Prashant Kumar Gangwar
2	RESONANCE RAMAN STUDY OF NANOSTRUCTURED ZNS	S. Saravana Kumar
3	THERMAL EVOLUTION OF ALUMINIUM DOPED NI-CU-ZN NANO FERRITES	B. L. Shinde
4	A BRIEF REVIEW ON METHODS INVOLVED IN COUMARIN SYNTHESIS	R. V. Kupwade
5	STUDIES ON EFFECTS OF ORGANIC FERTILIZERS ON THE SEED GERMINATION OF CHICK PEA ( <i>CICER ARIETINUM</i> L.)	Ugandhar.T, Venkateshwarlu M., Anitha Devi. U., and Srilatha.T.
6	GREEN CHEMISTRY FOR HUMAN WELFARE AND ENVIRONMENT	Ch. Srinivasa Prasadacharyulu
7	GROUNDWATER QUALITY & ITS SUITABILITY FOR WATER SUPPLY AND IRRIGATION IN VILLAGES AROUND GORAMBE, MAHARASHTRA	K. Bandivadekar and K. D. Shirke
8	INFLUENCE OF VERMIWASH ON GERMINATION AND GROWTH OF RICE ( <i>ORYZA SATIVA</i> ) VARIETY BHOGAVATI	Shrutika A. Patil, A. R. Kasarkar, S. S. Wadkar, S. B. Kubal, S. P. Salokhe
9	PROCESSING AND HEALTH BENEFITS OF FISH	Savita Hulamani
10	CAUSES, EFFECTS AND CONTROL MEASURES OF EUTROPHICATION	P. M. Kahate
11	MANGO PEELS - A POTENTIAL SOURCE OF NUTRIENTS IN THE FOOD	Nisha and Vibha Bhatnagar
12	PLANT TISSUE, ORGAN AND CELL CULTURE FOR ALKALOID PRODUCTION: A MINI REVIEW	Jitendriya Panigrahi, Dipika Rathod and Illa C. Patel
13	STUDENTS AWARENESS PROGRAMME FOR SUSTAINABLE DEVELOPMENT OF ENVIRONMENT	Pratibha S. Desai
14	SOME MATHEMATICAL TECHNIQUES USEFUL IN GRADING WATER QUALITY	Faizanul Mukhtar, Hamida Chisti, Nawaz Ahmad Mir, Shabir Ahmad Mir
15	A STUDY OF FECUNDITY	Purushottam R. More and Ashok S. Munde

## **PREFACE**

*We are delighted to publish about our book entitled "Research Frontiers in Sciences Vol. II". This book is the compilation of esteemed articles of acknowledged experts in the various fields of science providing a sufficient depth of the subject to satisfy the need of a level which will be comprehensive and interesting. It is an assemblage of up to date information of rapid advances and developments taking place in the field of science. With its application oriented and interdisciplinary approach, we hope that the students, teachers, researchers, scientists and policy makers in India and abroad will find this book much more useful.*

*The articles in the book have been contributed by eminent scientists, academicians. Our special thanks and appreciation goes to experts and research workers whose contributions have enriched this book. We thank our publisher Bhumi Publishing, Nigave Khalasa for taking pains in bringing out the book.*

*Finally, we will always remain a debtor to all our well-wishers for their blessings, without which this book would not have come into existence.*

**- Editorial Team**

# **NEW APPROACH FOR SUSTAINABLE DEVELOPMENT BY MATERIAL SCIENCE**

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## **Abstract:**

Materials Science or Materials Engineering is the examination investigation of the considerable number of materials we see around us consistently. From simple accomplishments, we consider given like the can holding our carbonated drink or the pen we create with, to materials squeezing the points of confinement of development, for example, those utilized in aviation, sports gadgets or prescription.

The field of materials is massive and assorted. Truly, it started with the development of man himself, and materials offered name to the periods of human advancement. Today, the field sensibly includes the desolate miner and the progressed instrumented scan for oil; it spreads from the irate fire of the oxygen steelmaking heater to the peaceful cold electrodeposition of copper; from the gigantic moving factory creating steel rails to the specialist pounding out a cup or a bit of gems; from the littlest chip of an electronic gadget to the biggest building made by man; from the regular paper-pack to the titanium shell of a space send; from the clearest glass to carbon dark; from fluid mercury to the hardest precious stone; from superconductors to protectors; from the room-temperature throwing plastics to infusible refractories (with the exception of they can be liquefied today); from milady's loading to the activist's bomb; from the perspiring metalworker to the isolated considering researcher who once stressed over the idea of issue and now attempts to figure the contrast between materials.

Materials independent from anyone else do nothing; yet without materials man can do nothing. Nature itself is a self-requested structure which created through time by the use of similar properties of nuclear chain of command that man manages in his basic developments.

Materials Engineers or analysts take a gander at all of the different gatherings of metals, amalgams and materials, polymers, pottery and composites. They set up pristine materials for fresh out of the box new applications, improve existing materials to offer better productivity and take a gander at techniques in which different materials can be utilized together.

## **Introduction:**

The field of Materials Science, which incorporates the science, building and development of materials, is an interdisciplinary area including the structure and homes of issue with application to the plan, headway and production of veritable things.

To set up the spic and span things and developments that will make our lives a lot more secure, less demanding, increasingly pleasurable and progressively economical we have to fathom approaches to make best utilization of the materials we right now have, and the most ideal approaches to set up pristine materials that will fulfill the requirements of things to come. Materials Science incorporates the exploration investigation of the structure, homes and conduct everything being equal, the progression of systems to deliver accommodating things from them, and research contemplate into reusing and eco-accommodating transfer.

A system for deciding the break profundity depends on the skin result, the marvel where a high-recurrence turning existing is limited to the surface region of a conductor. This makes it conceivable to decide the territory of a little zone with an essential meter, given that a lift in crack profundity proposes a lift in existing course, and this thusly triggers a lift in voltage drop.

Estimation with time at that point empowers the opportunity to inability to be approximated; fix works can be influenced before disappointment happens. For this situation, a comprehension of microstructure, the materials exploration of tiredness, and the examination investigation of break improvement have really caused a simple screening technique for tremendous budgetary hugeness.

### **Historical Perspective:**

Materials are so vital in the advancement of progress that we partner Ages with them. In the beginning of human life on Earth, the Stone Age, individuals utilized just characteristic materials, similar to stone, dirt, skins, and wood. At the point when individuals discovered copper and how to make it harder by alloying, the Bronze Age began around 3000 BC. The utilization of iron and steel, a more grounded material that gave favorable position in wars began at around 1200 BC. The following enormous advance was the disclosure of a modest procedure to make steel around 1850, which empowered the railways and the working of the cutting edge foundation of the mechanical world.

### **Materials Science and Engineering:**

Comprehension of how materials act as they do, and why they contrast in properties was just conceivable with the atomistic comprehension permitted by quantum mechanics, that initially clarified molecules and after that solids beginning during the 1930s. The mix of physical science, science, and the attention on the connection between the properties of a material and its microstructure is the area of Materials Science. The improvement of this science permitted planning materials and gave a learning base to the building applications (Materials Engineering).

### **Structure:**

- At the atomic level: arrangement of atoms in different ways.
- At the microscopic level: arrangement of small grains of material that can be identified by microscopy.

### **Properties:**

Properties are the manner in which the material reacts to the earth. For example, the mechanical, electrical and attractive properties are the reactions to mechanical, electrical and attractive powers, separately. Other essential properties are warm (transmission of warmth, heat limit), optical (retention, transmission and dispersing of light), and the synthetic dependability in contact with the earth (like consumption obstruction).

Preparing of materials is the use of warmth (heat treatment), mechanical powers, and so on to influence their microstructure and, consequently, their properties.

### **Why Study Materials Science and Engineering?**

To have the capacity to choose a material for a given utilize dependent on contemplations of expense and execution.

- To comprehend the points of confinement of materials and the difference in their properties with use.
- To have the capacity to make another material that will have some attractive properties.

All building orders need to think about materials. Indeed, even the most "unimportant", like programming or framework building rely upon the advancement of new materials, which thus adjust the financial matters, similar to programming equipment exchange offs. Expanding uses of framework designing are in materials fabricating (mechanical building) and complex natural frameworks

### **Classification of Materials:**

In the same way as other different things, materials are characterized in gatherings, so our mind can deal with the multifaceted nature. One could characterize them as indicated by structure, or properties, or use. The one that we will utilize is as per the way the molecules are bound together:

#### **Metals:**

Valence electrons are confined from orbitals, and spread in an 'electron ocean' that "sticks" the particles together. Metals are normally solid, lead power and warmth well and are murky to light (sparkly whenever cleaned). Models: aluminum, steel, metal, gold.

#### **Semiconductors:**

The holding is covalent (electrons are shared between molecules). Their electrical properties depend amazingly emphatically on moment extents of contaminants. They are obscure to noticeable light however straightforward to the infrared. Models: Si, Ge, GaAs.

#### **Ceramics:**

Molecules carry on for the most part like either positive or negative particles, and are bound by Coulomb powers between them. They are generally blends of metals or semiconductors with oxygen, nitrogen or carbon (oxides, nitrides, and carbides). Models: glass, porcelain, numerous minerals.

#### **Polymers:**

Are bound by covalent powers and furthermore by feeble van der Waals powers, and typically dependent on H, C and other non-metallic components. They disintegrate at moderate temperatures (100 – 400 C), and are lightweight. Different properties shift extraordinarily. Models: plastics (nylon, Teflon, polyester) and elastic.

Different classes are not founded on holding. A specific microstructure recognizes composites, made of various materials in cozy contact (precedent: fiberglass, solid, wood) to accomplish explicit properties. Biomaterials can be any kind of material that is biocompatible and utilized, for example, to supplant human body parts.

### **Advanced Materials:**

Materials utilized in "High-Tec" applications, typically intended for most extreme execution, and regularly costly. Models are titanium amalgams for supersonic planes, attractive combinations for PC circles, extraordinary pottery for the warmth shield of the space transport, and so forth

### **Modern Material's Needs:**

Engine effectiveness increments at high temperatures: requires high temperature auxiliary materials

- Use of atomic vitality requires taking care of issue with deposits, or advances in atomic waste handling.
- Hypersonic flight requires materials that are light, solid and oppose high temperatures.
- Optical interchanges require optical strands that assimilate light insignificantly.
- Civil engineering– materials for unbreakable windows.
- Structures: materials that are solid like metals and oppose consumption like plastics

**Conclusion:**

This study & use of materials science and designing has created an image of noteworthy complexities. From one perspective, the examination has uncovered a field of incredible essentialness—quickly developing logical disclosures, shocking new abilities for comprehension and expectation, and applications that are fundamental for the wellbeing of each U.S. industry. Then again, a few alarming advancements have become known. In spite of developing open doors in the field, a lack of taught work force is predicted. Confinements on assets are compelling advancement. Furthermore, our national exertion needs more noteworthy concentration and coordination so as to address the difficulty of global challenge.

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# RESONANCE RAMAN STUDY OF NANOSTRUCTURED ZnS

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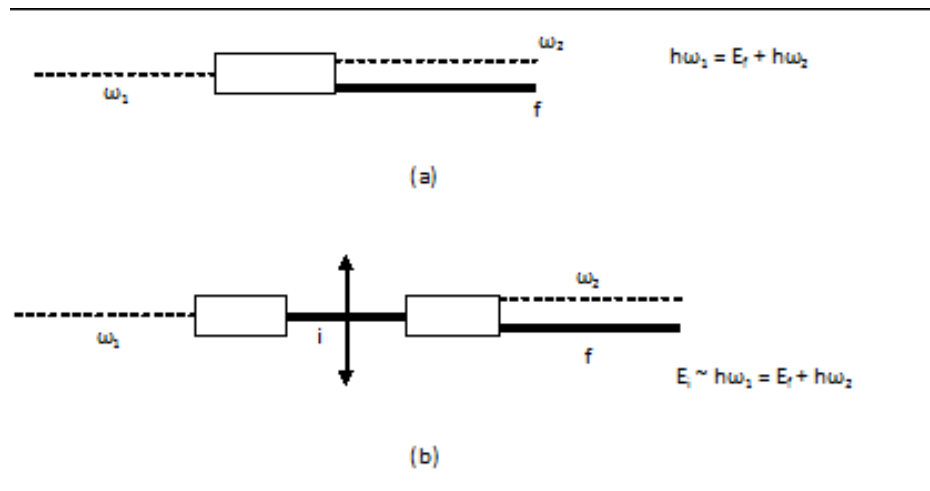
## Introduction:

Raman scattering studies, in general, yield information on low energy excitations of molecules, liquids, and solids. Such information contained in the frequency shift and polarization of the scattered photon, is in general restricted to states which are typically up to  $5 \times 10^{-2}$  eV from the ground state of the material. Usually Raman spectra, being independent of the electronic structure of the material and the laser energy used to excite the spectra, only involve phonons explicitly. Furthermore, the Raman scattering signal is weak. However, the scattering efficiency gets enhanced when the laser energy matches the energy between optically allowed electronic transitions in the material, and this intensity enhancement process is called resonance Raman scattering [1]. The resonance Raman intensity depends on the density of electronic states (DOS) available for the optical transitions, and this property is very important for nanostructured materials. Graphical representations of ordinary Raman and Resonance Raman processes are shown in the figure 1[1].

The wide band gap II-VI semiconductors and especially, the nanostructures of these materials have been investigated intensely during the last several years [2-9]. Most of the interest in these materials was focused on the size dependence of the optical and vibrational properties as well as on the electron-phonon coupling. Resonance Raman spectroscopy is one of the powerful tools to probe not only the vibrational frequencies of the lattice but also the modulation of electronic properties of crystallites by the displacement of the nuclear cores [10-11]. It is known that the resonance enhancement of Raman cross section in semiconductors is due to the exciton-phonon coupling [1]. Different vibrational modes, due to the presence or absence of an accompanying electric field, modulate the electronic properties and thereby modulate the electron – phonon coupling on different length scales. In a bulk polar solid, the optical modes split into two distinct branches: the LO and the TO modes. Both modes distort the unit cell in the same way, which can be visualized as the central atom of a tetrahedron moving relative to the four other atoms (figure2). When there is a difference in effective charge of the two atoms, a local polarization is generated. The modes differ in the alignment of this charge displacement between different unit cells. Thus the polarization fields that result from excitation along either of the mode coordinates are different. The polarization field induced by the LO mode is curl-less, has a finite divergence, and generates a macroscopic electric field which exhibits long-range coupling to the motion of the electrons. The TO mode, on the other hand, produces a polarization field which is divergence-less and has net curl. Therefore, no macroscopic electric field is produced, and the electron–phonon coupling is relatively of short range.

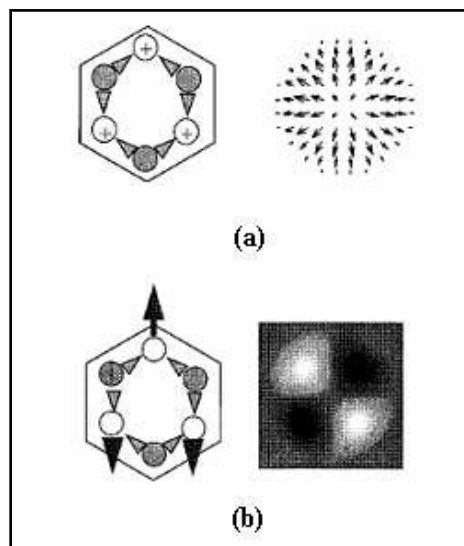
Grain size dependence of electron-LO phonon coupling in nanostructured materials has kindled great interest during the last decade [12-18]. Decreasing, increasing and constant exciton-phonon coupling strength have been found as the nanocrystals size is reduced. Theoretically, Schmitt-Rink et al. [12] predicted that the exciton-LO phonon coupling mediated by Frohlich interaction decreases with decrease in grain size. Klein et al. [13] have presented resonance Raman data of CdSe nanocrystals for sizes ranging from 1.9 to 4 nm and observed that the electron – phonon coupling strength is independent of size. They also developed a theory which states that the electron – vibration coupling is not a function of size for nanocrystals in the 1.5 to 10 nm regime. But Efros et al. [14], Marini et al. [15] and Nomura and Kobayashi [16] have shown that the Huang – Rhys parameter, which

measures the strength of the Frohlich interaction, increases with decrease in the nanocrystals size in the limit of small mean particle radius less than 10 nm.



**Figure 1: Graphical representations of (a) ordinary Raman and (b) Resonance Raman process. ----- Photon ———> electron; □ electron – phonon interaction; ===== General excitation of the material system**

A series of experimental studies in CdSe, CdS and InP nanocrystals indicated that the electron – LO phonon coupling diminishes with decrease in the nanocrystal size. Alivisatos et al. [17] reported a decrease in the exciton-phonon coupling strength of CdSe nanocrystals when compared to that of bulk. In the case of resonance Raman spectra CdS nanocrystals, a decrease in coupling strength with decrease in size was observed by Shiang et al. [11].



**Figure 2: Graphical representation of the LO and TO mode displacements for one section of a plane in a zinc-blende lattice (a) LO mode and (b) TO mode.**

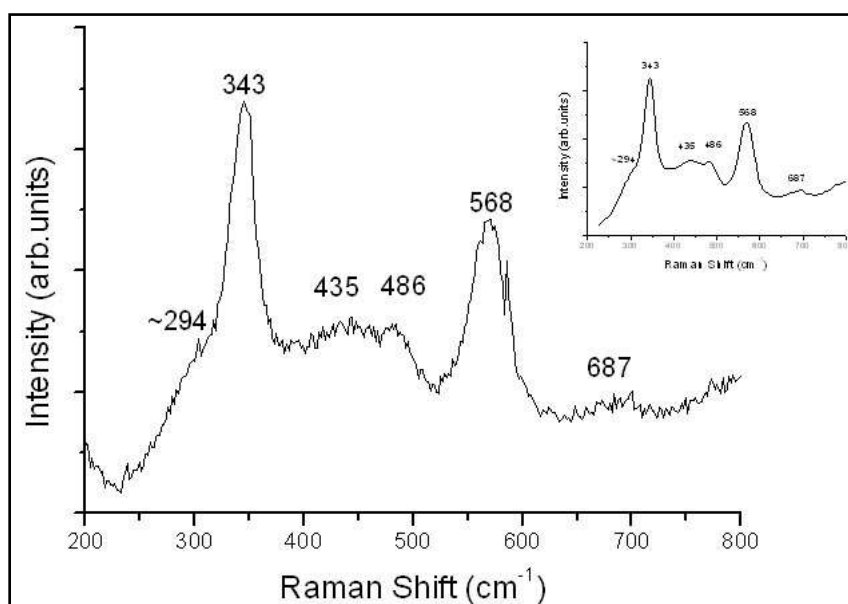
Scamarcio et al. [18] observed an increase in the coupling strength with decrease in the size of  $\text{CdS}_x\text{Se}_{1-x}$  nanocrystals embedded in a glass slab. Thus measurements of the exciton-phonon coupling strength as a function of nanocrystals size have produced widely varying results. In nanoparticles, the exciton-phonon coupling strength is determined by both quantum confinement and the surface characteristics [19-20]. The electron-phonon coupling in nanoparticles is weakened with decrease in size due to the decrease in the density of states for both the electrons and phonons and also due to the increased overlap between the electron and hole wave functions with decrease in size [19, 21]. But the trapping of electrons or holes at the surface states of nanoparticles will cause an increase in the exciton-phonon coupling [19, 22]. These two factors may compete with each other and determine the overall size dependence of the exciton - phonon coupling strength.

### **Study of Exciton – Phonon Coupling Strength in ZnS Nanoparticles:**

Raman spectrum of the unimplanted ZnS nanoparticles recorded using UV excitation (325 nm) is shown in figure 3. The spectrum show Raman peaks at 294, 343, 435, 486, 568 and 687  $\text{cm}^{-1}$ . Only a few reports on the resonance Raman studies of bulk ZnS and no reports on that of nanoparticles of ZnS are available in the literature. Brafman and Mitra [23] and Nilsen [24] have reported the Raman spectra of bulk hexagonal and cubic phases of ZnS. They observed LO, 2TO and 2LO modes for bulk cubic ZnS at 352, 542 and 704  $\text{cm}^{-1}$  respectively. Compared with the bulk Raman spectra of cubic ZnS, the LO and 2LO Raman peaks of nanoparticles of ZnS in the present study are shifted to lower frequencies and the 2TO peak is shifted to higher frequency. This type of shifting of Raman peaks of nanoparticles is accountable on the basis of confinement of optical phonons as discussed in chapter 4. The phonon dispersion data for ZnS shows the zone boundary at 333 and 306  $\text{cm}^{-1}$  for LO and TO modes respectively [25]. Thus for scattering satisfying the condition  $k \neq 0$  in the case of nanoparticles of ZnS, LO frequency should be lower than 352  $\text{cm}^{-1}$  (bulk value) but more than 333  $\text{cm}^{-1}$  while TO frequency should be more than 276  $\text{cm}^{-1}$  but lower than 306  $\text{cm}^{-1}$  which is consistent with the present observation. The intensity of TO mode of bulk samples of ZnS is reported to be very weak compared to the LO phonon mode (reported intensity ratio of LO to the TO mode for bulk cubic ZnS is 15) [23]. This condition may be true for nanoparticles samples of ZnS and hence the non observation of TO mode in the present study may be a result of weak scattering. Yang et al. [26] observed a red shift of the frequency by approximately 2  $\text{cm}^{-1}$  for both the TO and LO modes of ZnS nanocrystals of grain size 20 to 25 nm doped with Mn ions. The frequency shift (red shift) of LO Raman line in the present study is 9  $\text{cm}^{-1}$  and the blue shift of 2TO Raman line is 16  $\text{cm}^{-1}$ . The larger shift of Raman peak in the present study compared to the reported value should be a cumulative effect of the shift due to phonon confinement effect and tensile strain.

Now, we discuss the possible origin of the peaks observed at 294, 435 and 586  $\text{cm}^{-1}$ . The peak observed at 294  $\text{cm}^{-1}$  lies between the TO and LO modes of bulk cubic ZnS. When the electromagnetic radiation propagates through nanostructures of polar materials, the polarization of the nanostructure entities in the electric field of the radiation results in the excitation of electric dipoles vibrating at specific frequencies. These vibrations, not present in bulk material give rise to new optical phonon modes located in the frequency gap between the bulk TO and LO optical phonons in binary compounds. The new optical modes, called as surface modes, have been calculated for small ionic crystals of different morphologies by Fuchs and Kliewer [27-28] and have been observed in the Raman spectra of nanoparticles of II – VI and III – V compounds. Several authors [29-32] report that surface phonon modes can be observed in the Raman spectra, if the sizes of the crystallites are so small that the surface to volume ratio is high. Ruppin and Englman [29] have discussed the possibility of observing surface phonons by light scattering in small crystallites of spherical, cylindrical or slab like geometries. Scott and Damen [30] observed surface phonons in small crystallites of CdS in a polycrystalline film using Raman scattering. One of the important characteristics of surface phonon modes is that they lie in between the frequencies of bulk TO and LO phonon modes. Thus, the peak

observed at  $294\text{ cm}^{-1}$  in the present study can be ascribed to surface phonon mode. Nilsen [24] and Zhang et al. [33] reported the observation of combinational bands in the Raman spectra of bulk cubic ZnS and ZnS nanowires respectively. The combinational bands involve two phonons so that the scattering process need not originate near the Brillouin zone center as in the case of one phonon scattering. The chances of the observation of combinational modes are more in the case of nanoparticles since phonon scattering will not be limited to the center of Brillouin zone but the phonons near the zone boundary will also participate in the scattering process. The peaks observed at  $436$  and  $485\text{ cm}^{-1}$  can be attributed to the (LO+TA) and (2TO-TA) combinational modes respectively.



**Figure 3: Raman spectrum of unimplanted nanostructured ZnS samples recorded using UV excitation. Inset : 5 Point FFT smoothing of the spectrum to observe peak positions clearly**

The interesting observation in the resonance Raman spectrum of the present sample is the observation of 2TO mode, which is not reported elsewhere in the resonance Raman study of the bulk ZnS. Scott et al. [34] reported the resonance enhancement of LO phonon mode in ZnS using a 325 He-Cd laser line excitation for the first time. Subsequently, Iida et al. [35] and Uchiki [36] et al. reported the enhancement of 2LO modes of ZnS. Kani et al. [37] and Moon et al. [38] reported the temperature dependence of the resonance enhancement of LO mode of ZnS. But, in all these reported works, resonance enhancement of TO mode is not observed and only the resonance enhancement of nLO phonon, where n is the order of Raman line, is observed. It is known that the resonance enhancement of Raman cross section in semiconductors is due to the exciton-phonon coupling. Exciton-phonon coupling in semiconducting materials is governed by two mechanisms: the Frohlich potential and the deformation potential. Kaminow and Johnston [39] suggested that the TO Raman scattering cross section is mainly determined by the deformation potential that involves the short range interaction between the lattice displacement and the electrons and the LO Raman scattering is determined by Frohlich potential that involves interaction between by the macroscopic electric field associated with the LO phonons and the electronic charge density. Chamberlain et al. [40] and Scott et al. [34] reported that the TO cross section increase more rapidly with frequency than that for LO, for excitation energies far below the band gap of the material. When the excitation energy is just nearer to the band gap of the material (under resonant conditions), the TO cross section displays less pronounced enhancement than that of LO, and the scattering cross section for TO disappears entirely for the excitation energies above the band gap (off-

resonant conditions). Resonant Raman studies of ZnS reported in the literature are performed in bulk ZnS. The band gap of bulk ZnS is 3.69 eV [41] which is near to the energy used for excitation (3.84 eV) in the resonance Raman studies reported for bulk ZnS. Thus, the resonant enhancement of nLO modes is observed, (and 2TO mode is not observed) in bulk ZnS. Hence the observation of 2TO mode in the present sample can be attributed to the deformation potential mediated exciton-phonon coupling which enhances the TO scattering cross section under off-resonant conditions. The low value of deformation potential, reported for 1TO mode of cubic ZnS (25 eV) compared to that for 2TO mode (2470 eV) [25] may be correlated to the low intensity of 1TO mode in the spectrum.

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# THERMAL EVOLUTION OF ALUMINIUM DOPED Ni–Cu–Zn NANO FERRITES

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## **Abstract:**

Aluminium Doped Ni–Cu–Zn nano ferrites were synthesized by wet chemical co-precipitation method, in oxygen atmosphere, from corresponding analytical grade metal sulphates. The dried precursor metal hydroxides were characterized by thermo gravimetric analysis (TGA). Precursor metal hydroxides were dehydrated completely in the range of temperatures 351 to 448 K, and the oxidation takes place in the temperature range 623–667 K and converted in to nano ferrites. The precursor metal hydroxides were calcinated at 973 K. The structural morphology, crystallinity investigated by X-ray diffraction, scanning electron microscopy. X-ray diffraction pattern confirm all composition with single phase cubic spinel structure.

**Keywords:** Wet chemical method, Ni–Cu–Zn ferrites, Thermal analysis

## **Introduction:**

Ferro spinels are mixed metal oxides with ferric oxides as a main component, having chemical formula  $MFe_2O_4$  (where, M = Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, etc.) The ferro spinels are technologically important material due to their interesting electrical and magnetic applications in various fields of science, such as information storage systems, magnetic nano devices, semiconductors, pigments, catalysts, refractories, high density information storage, ferro-fluide's color imaging, bimolecular separation, medical diagnosis, drug delivery etc.[1,2]

Wet chemical co-precipitation method used to synthesize homogeneous and fine ferrite powder with high surface areas resulting improvised magmatic and catalytic properties [3,4]. The ferrite particles in nano range with significant change in physical properties provide more advantages over bulk ferrite [5]. The structural magnetic and catalytic activity of ferro-spinel compounds particularly depends upon the distribution of cation among the tetrahedral and octahedral site of spinal structure [6,7].

Cu–Zn and Ni–Cu–Zn have been reported useful in multilayer chip inductors [8-10].  $Al^{3+}$  substituted Ni ferrites have high electrical resistivity [11].

In this chapter thermal take account of study of Aluminium doped  $Ni_{0.2}Cu_{0.2}Zn_{0.6}Fe_{2-x}Al_xO_4$  system with  $x = 0.0$  in step of 0.2 compositions prepared by wet chemical co-precipitation method.

## **Experimental:**

Analytical grade corresponding metal sulphates are used in stoichiometric proportion to prepare desired Aluminium Doped Ni–Cu–Zn mixed metal hydroxides by wet chemical co-precipitation method. [12] The metal sulphates in stoichiometric proportion dissolved in deionized water to yield clear solution; the initial pH of mixed solution was 3. 2M NaOH solution used as precipitant, in oxygen atmosphere at 60 °C, temperature, dark brownish precipitate of precursor metal hydroxides were obtained at pH ≈12. The precursor precipitate was filtered, washed with deionized water till free from sodium sulphates and dried in inert atmosphere.

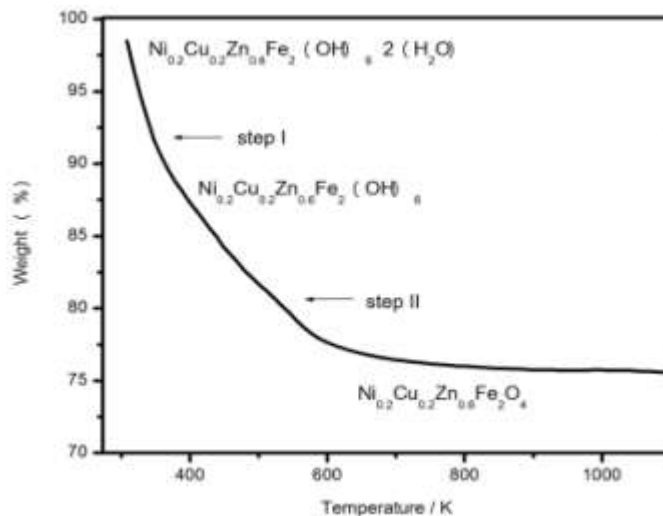
### Characterization:

It seems that the systematic study of nature of solid state thermal influence reaction and phase evolution is important for determination of stoichiometry and phase purity. TG analysis of precursor metal hydroxides were carried on SDT Q600 V20.9 Build 20, instrument in air atmosphere at heating rate  $10^{\circ}\text{C} / \text{min}$  within temperature range  $0^{\circ}\text{C}$  to  $1000^{\circ}\text{C}$ . The calcinated ferrite samples were characterized by X-ray Diffraction technique, X-ray patterns were recorded at room temperature in the  $2\theta$  range,  $20^{\circ}$  to  $80^{\circ}$  using Cu-K $\alpha$  radiation ( $\lambda=1.5404 \text{ \AA}$ ). The microstructures of the prepared samples were studied by Scanning Electron Microscopy (SEM).

### Results and discussion:

#### Thermogravimetric analysis:

The solid precursor metal hydroxides  $\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Al}_x(\text{OH})_6.n(\text{H}_2\text{O})$  prepared by wet chemical coprecipitation method. The mass loss calculated from TGA analysis of each precursor metal hydroxide to fix  $n\text{H}_2\text{O}$  [13]. Table 1 illustrates comparison between total mass loss % obtained by theoretical calculations and observed mass loss % of precursor metal hydroxide samples. The observed mass loss % is in good agreement with theoretical mass loss %. Thus the compositions of  $n\text{H}_2\text{O}$  proposed in precursor metal hydroxides are confirmed.



**Figure 1: TG curve of  $\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_2(\text{OH})_6.2(\text{H}_2\text{O})$  ( $x=0.0$ )**

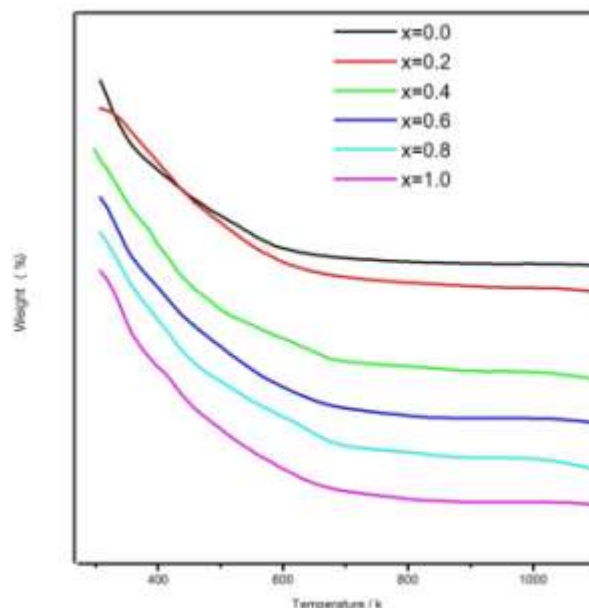
Figures (1-2) shows TG curves of weight % versus temperature. From the fig.1; the initial mass loss in TG curve corresponds to dehydration step (step I) in temperature range 303 - 448 K, which shows loss of water of crystallization from precursor metal hydroxides to form an anhydrous metal hydroxides. While second part of TG curve (step II) in temperature range 450 - 666 K corresponds to the oxidation of anhydrous metal hydroxides to corresponding ferro spinels.

TGA curves figures 1 and 2 shows single step dehydration of precursor metal hydroxides with general formula,  $\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Al}_x(\text{OH})_6.n(\text{H}_2\text{O})$  where,  $x= 0.0, 0.2, 0.4, 0.6, 0.8$  and  $1.0$ , to form anhydrous metal hydroxide having general formula  $\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Al}_x(\text{OH})_6$ .

The mass loss % observed and theoretical is tabulated in table 1; indicate both theoretical and observed values are closely agree to each other, confirms molecular formulae of each precursor metal hydroxide compositions.

**Table 1: Mass loss % values obtained by TGA (Observed) and theoretical**

X	Proposed formulae	Total mass loss %	
		TGA (Obs.)	Theoretical
0.0	$\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_2(\text{OH})_6 \cdot 2(\text{H}_2\text{O})$	24.95	25.71
0.2	$\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{1.8}\text{Al}_{0.2}(\text{OH})_6 \cdot 2(\text{H}_2\text{O})$	24.26	27.60
0.4	$\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{1.6}\text{Al}_{0.4}(\text{OH})_6 \cdot 3(\text{H}_2\text{O})$	30.72	30.41
0.6	$\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{1.4}\text{Al}_{0.6}(\text{OH})_6 \cdot 3(\text{H}_2\text{O})$	32.04	30.61
0.8	$\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{1.2}\text{Al}_{0.8}(\text{OH})_6 \cdot 3(\text{H}_2\text{O})$	32.74	31.10
1.0	$\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{1.0}\text{Al}_{1.0}(\text{OH})_6 \cdot 3(\text{H}_2\text{O})$	32.26	32.18



**Figure 2: TG curves of  $\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Al}_x(\text{OH})_6 \cdot n(\text{H}_2\text{O})$**

Table 2 indicates stepwise mass loss % during dehydration by TGA (observed) and are in good agreement with theoretical mass loss %. This supports the  $n\text{H}_2\text{O}$  values given in general formula of precursor metal hydroxides. The second step shows oxidation of anhydrous metal hydroxides to form ferrites. Also values of mass loss % during second step (oxidation) by TGA (observed) and are in good agreement with mass loss % by theoretical calculations. The dehydration of precursor metal hydroxide to form anhydrous metal hydroxide (step I) and oxidation of metal hydroxide to form ferrite (step II) are given by general reactions as follows:

Onset and termination temperatures during dehydration and oxidation steps of precursor metal hydroxides observed from TGA were given in Table 3. It is observed that, precursor metal hydroxides were dehydrated completely in the range of temperatures 351 to 448 K.

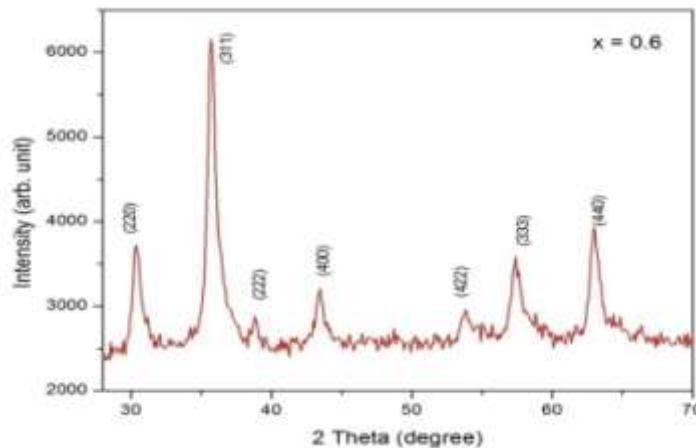
**Table 3: Onset and termination temperatures during dehydration and oxidation steps by TGA**

x	Dehydration		Oxidation	
	Step I / K		(Step II) / K	
	Onset	Termination	Onset	Termination
0.0	303.00	351.18	351.18	623.00
0.2	303.00	433.97	433.97	627.87
0.4	304.00	427.32	427.32	658.79
0.6	303.00	448.00	448.00	652.70
0.8	303.00	437.48	437.48	665.90
1.0	303.00	438.49	438.49	663.24

The complete oxidation of anhydrous metal hydroxides to form nano ferrites having general formula:  $Ni_{0.2}Cu_{0.2}Zn_{0.6}Fe_{2-x}Al_xO_4$ , where, x= 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0. It is observed that the oxidation of anhydrous metal hydroxides takes place in the temperature range 623-667 K. Therefore all precursor metal hydroxides calcinated at 973 k for 4 hour to obtain nano ferries.

**X-ray diffraction analysis:**

The typical XRD pattern of the calcinated nano ferrite is shown in Fig. 3. The XRD pattern clearly indicates that the samples are belongs to single phase spinel structure and no impurity peaks observed.

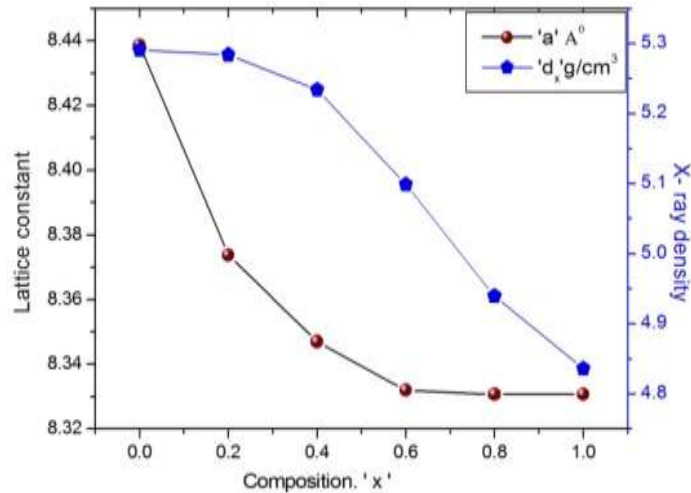


**Figure 3: Typical XRD patterns of sample (x=0.6)**

The lattice parameter ‘a’ was calculated using the following equation: [14]

$$a = d\sqrt{(h^2 + k^2 + l^2)} \quad (1)$$

Where, *d* is the inter-planer spacing and (*hkl*) is the index of the XRD reflection peak.



**Figure 4: Variation of experimental lattice constant and X-ray density with Al<sup>3+</sup> substitution of Ni<sub>0.2</sub>Cu<sub>0.2</sub>Zn<sub>0.6</sub>Fe<sub>2-x</sub>Al<sub>x</sub>O<sub>4</sub>**

Calculated values of lattice constants graphically represented in fig.4 indicate that lattice constant ‘a’ decreased from 8.4387 to 8.3307 Å with an increase in Al<sup>3+</sup> content (x). The decrease in the lattice constant is related to the difference in ionic radii of Fe<sup>3+</sup> and Al<sup>3+</sup>. In the present ferrite system Fe<sup>3+</sup> ions (0.67Å) ions are replaced by the relatively small Al<sup>3+</sup> ions (0.50 Å). [15]

The X-ray density (dx) of all the samples of the series was obtained by the following relation:

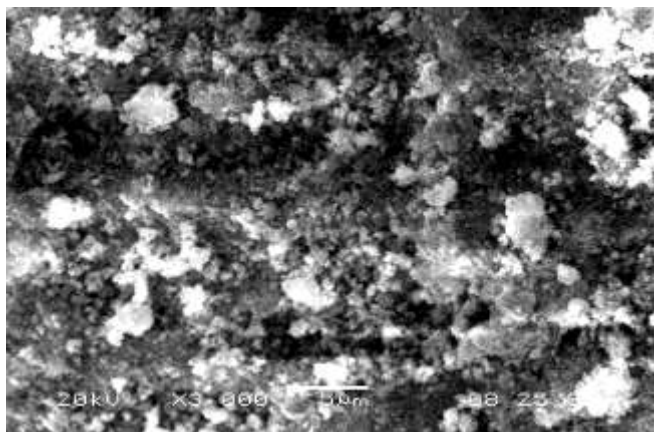
$$dx = \frac{8M}{Na^3} \quad (2)$$

where ‘8’ is the number of molecules per unit cell, ‘M’ is the molecular weight of sample, ‘N’ is the Avogadro’s number and ‘a’ is lattice constant.

It is observed from Fig. 4 that, the X-ray density decreased from 5.291 to 4.836 g/cm<sup>3</sup> with increase in Al<sup>3+</sup> content (x). This behaviour of X-ray density is related to the molecular weight (M) and lattice constant (a).

**Scanning electron microscopy (SEM):**

Fig. 5 shows typical scanning electron micrographs (SEM) of nano ferrite (x=0.6). Each ferrite sample is characterized by a typical porous structure. It is illustrated from the SEM images that the prepared ferrite samples are amorphous and porous in nature. The uniform nature of the ferrite particle is shown with some agglomeration.



**Figure 5: Typical SEM micrograph of sample (x=0.6)**

### Conclusion:

Aluminium doped  $\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Al}_x\text{O}_4$  system with  $x = 0.0$  in step of 0.2 compositions prepared by wet chemical co-precipitation method. Precursor metal hydroxides were dehydrated completely in the range of temperatures 351 to 448 K.  $\text{Al}^{3+}$  substituted Ni-Cu-Zn ferrites formed by oxidation of homogeneous solid mixture of hydroxides of  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ . The ferrites are formed in the temperature range 623-667 K. All precursor metal hydroxides calcinated at 973 k for 4 hour to obtain nano ferrites. The XRD pattern clearly indicates that ferrites formed after sintering are belongs to single phase spinel structure. It can be illustrated from the SEM images that the prepared ferrite samples are amorphous and porous in nature and were well distributed and slightly agglomerated.

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## A BRIEF REVIEW ON METHODS INVOLVED IN COUMARIN SYNTHESIS

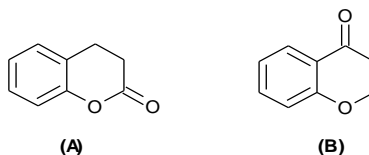
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### Introduction:

Benzopyrones constitute a class of heterocyclic compounds which are obtained by fusion of pyrone ring with benzene nucleus. Depending upon the position of carbonyl group in the pyran ring, two different types of benzopyrones are known; i) benzo- $\alpha$ -pyrones, coumarins, wherein carbonyl group is present at position-2 in pyran ring (**Fig. 1A**) and, ii) benzo- $\gamma$ -pyrones, chromones, wherein carbonyl group is present at position-4 in the pyran ring (**Fig. 1B**). Thus, chemically coumarin is 2H-1-benzopyran-2-one.



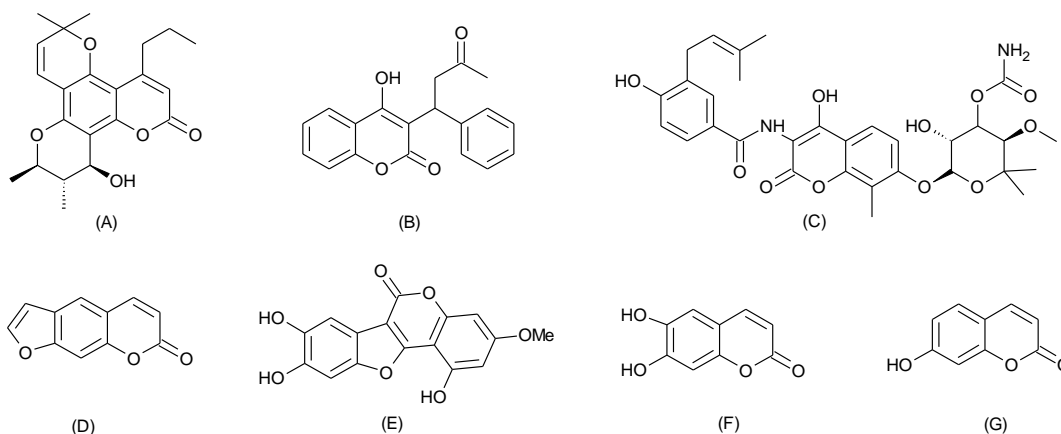
**Figure 1: Structures of  $\alpha$ -pyrone and  $\gamma$ -pyrone**

Among these coumarin constitutes a core unit of diverse natural products that exhibit a range of biological activities [1]. Coumarin was first isolated in 1820 from tonka beans [2]. Large number of coumarin derivatives are distributed in high concentration in Tonka bean, lavender, licorice, woodruff, apricots, cherries, strawberries, sweet clover, cassia leaf oil, cinnamon bark oil and bison grass having vanilla like flavor.

Calanolide-A (**Fig. 2A**) is a natural coumarin derivative isolated from *Calophyllum lanigerum*. It is *non-nucleoside reverse transcriptase inhibitor (NNRTI)* and is known to exhibit anti-HIV activity [3,4]. Warfarin (**Fig. 2B**) is known to exhibit anticoagulant property and it is used to prevent clotting of blood in the veins and heart [5]. Novobiocin (**Fig. 2C**), a 3-benzamidocoumarin derivative which possesses strong antibiotic activity by inhibiting DNA gyrase, and has potential as an anticancer agent [6]. Psoralens (**Fig. 2D**) are the naturally occurring compounds having furan ring fused to coumarin. Citrus fruits, clove and common fig are the main sources for their isolation and they are mainly used in the treatment of psoriasis [7]. Wedelolactone (**Fig. 2E**) is another naturally occurring furan ring fused coumarin and is used as a venomous snake-bite antidote [8]. A natural coumarin analogue, Esculetin, 6,7-dihydroxycoumarin (**Fig. 2F**) has antioxidant, antiproliferative, and anti-inflammatory activities [9] while Umbelliferone, 7-hydroxycoumarin (**Fig. 2G**) is encountered in several plants with notable antimycobacterial [10] and anticancer [11] activities.

Coumarins in general have effective healing action against edema and are able to subsidize swelling. Therefore they are also used in the treatment of lymph edema, elephantiasis and other high protein edema conditions [12]. Several synthetic compounds which enclose coumarin moiety are well known for their odour, availability and stability. They are commonly used in perfume, soaps, detergents [13], optical brightening agents [14] and in the synthesis of insecticides. Furthermore, the pharmacological, biochemical and therapeutic properties of simple

coumarins can be altered by the incorporation of particular group as a fused component or through their structural modifications.



**Figure 2: Naturally occurring coumarin derivatives**

### Literature survey:

Varied biological activities of coumarins have led many researchers to develop simple and general methods for their synthesis. Numerous synthetic methods involving the well known reactions like Knoevenagel condensation, Wittig reactions, Perkin reaction, Reformatsky reaction, Pechmann reaction, etc. have been designed for the synthesis of coumarin. These methods have been summarized below.

### Knoevenagel condensation:

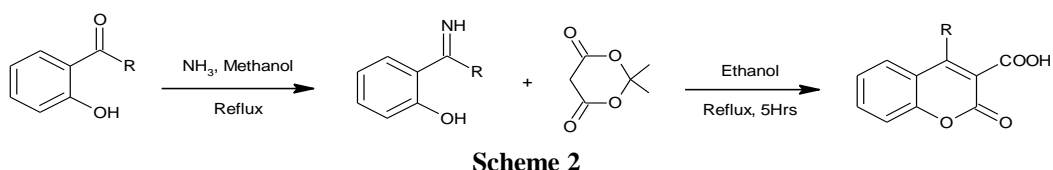
The simplest route towards the synthesis of coumarins involves a base catalyzed reaction of *o*-hydroxy benzaldehyde with diethyl malonate, ethyl acetoacetate, ethyl cyanoacetate, etc. The reaction follows Knoevenagel condensation-intramolecular cyclization path and furnishes 3-acetyl, 3-carboxy or 3-cyano coumarin respectively (Scheme 1) [15].



**Scheme 1**

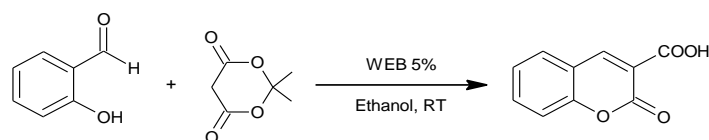
This reaction has been effectively used by various researchers and wide array of catalysts have been screened for the synthesis of coumarin and its derivatives. Ranu *et al.* [16] have developed an environmental friendly and high-yielding synthesis of substituted coumarins using basic ionic liquid, 1-butyl-3-methylimidazolium hydroxide {[Bmim]OH} as the catalyst as well as reaction medium. Other basic catalysts like NaOMe/[bmim]PF<sub>6</sub> [17], task-specific ionic liquid *viz.* imidazolium based phosphinite (IL-OPPh<sub>2</sub>) [18], K<sub>2</sub>CO<sub>3</sub> [19], silica-immobilized piperazine [20], have also been reported. An unprecedented metal salt *viz.* ZrCl<sub>4</sub>, has also been reported in the synthesis of coumarin derivatives [21].

In all the aforementioned methods, the active methylene compound employed has been diethyl malonate, ethyl acetoacetate or ethyl cyanoacetate. There are a few reports wherein Meldrum's acid has been used as an active methylene compound. For instance, Song and coworkers have reported a synthesis of coumarin 3-carboxylic acid by condensation of salicylaldehyde and Meldrum's acid in alcoholic ammonia under reflux condition [22]. This protocol also works for less reactive *ortho*-hydroxy aromatic ketones wherein ketones were reacted with alcoholic ammonia to form intermediate kitimines, which undergo condensation with Meldrum's acid to furnish coumarin-3-carboxylic acid (**Scheme 2**).



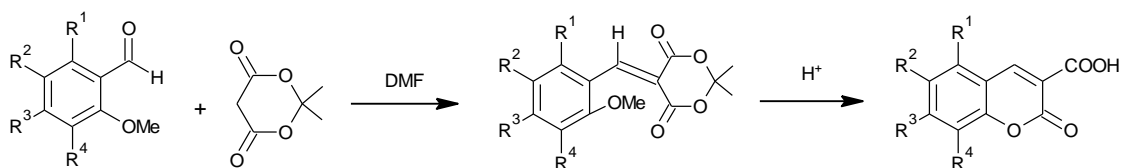
Scheme 2

Undale *et al.* [23] have reported potassium phosphate catalyzed synthesis of 3-carboxy coumarins under ambient condition. In another report Bandagar *et al.* [24] have mentioned the use of natural kaolinitic clay as the catalyst for microwave assisted synthesis of coumarin 3-carboxylic acids under solvent free condition. Most recently, an environmentally benign synthesis of 3-carboxy coumarins has been reported by using water extract of banana peel (WEB) as the catalyst. In the developed protocol to a stirred solution of *ortho*-hydroxy benzaldehyde and Meldrum's acid in ethanol was added WEB and the mixture upon stirring together at ambient temperature was shown to furnish coumarin-3-carboxylic acid (**Scheme 3**) [25].



Scheme 3

In all the aforementioned methods, *ortho*-hydroxy benzaldehyde has been employed as the starting material. However, Armstrong *et al.* have reported sulfuric acid catalyzed atwo-step synthesis of coumarin-3-carboxylic acids by the reaction of 2-methoxybenzaldehyde with Meldrum's acid in DMF as the reaction medium (**Scheme 4**) [26].

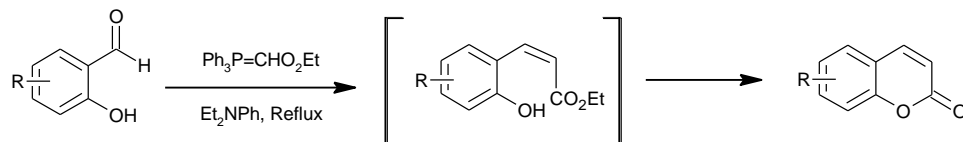


Scheme 4

#### Wittig reaction:

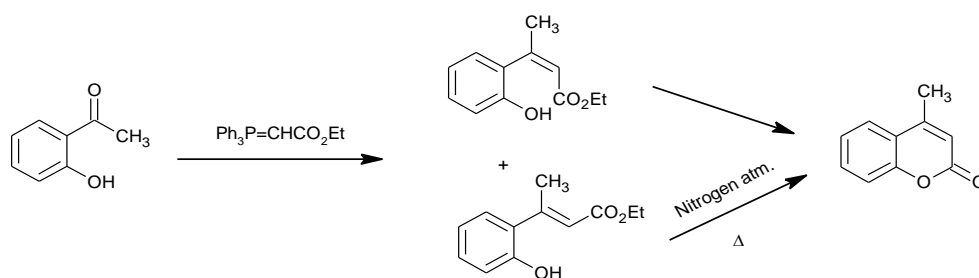
Harayama and co-workers have reported a simple preparation route for the synthesis of coumarins using carbethoxymethylene-triphenylphosphorane (Ph<sub>3</sub>P=CHCO<sub>2</sub>Et) and salicylaldehyde as the substrates. The reaction follows, Wittig olefination-intramolecular cyclization pathway. The success of this protocol depends upon the geometry of alkene intermediate resulted during olefination. It has been demonstrated that, the presence of electron-

donating group at C<sub>4</sub> and C<sub>6</sub> position on salicylaldehyde favors the formation of *cis*-cinnamate to offer cyclized product, coumarin, in excellent yields. On the other hand, the presences of electron-withdrawing groups at these positions yield *trans*-cinnamate which undergoes cyclization with difficulty and thus lowers the yield of final product (**Scheme 5**)[27].



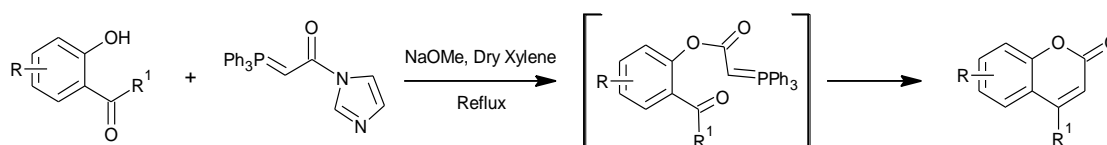
Scheme 5

Mali *et al.* reported the synthesis of coumarins by Wittig reaction of *ortho*-hydroxy acetophenones and carbethoxymethylenetriphenylphosphorane ( $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$ ). They have reported that after initial olefination, apart from coumarin, uncyclized ester also results. However, this ester can be made to undergo lactonization by heating the reaction mixture in nitrogen atmosphere for longer time. This improves the overall yield of the reaction (**Scheme 6**)[28].



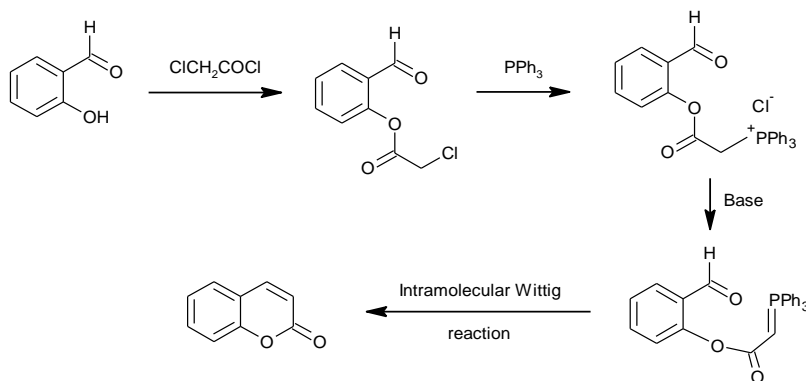
Scheme 6

Upadhyay and co-workers have also employed intramolecular Wittig olefination-cyclization route for the synthesis of coumarins. The noteworthy feature of this protocol involves the use of triphenyl ( $\alpha$ -carboxymethylene) phosphorane imidazolide in initial Wittig olefination (**Scheme 7**)[29].



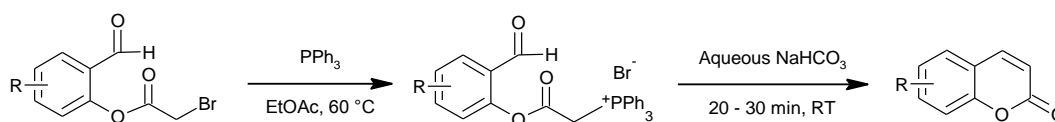
Scheme 7

Desai and co-workers have reported another approach for the synthesis of coumarins using salicylaldehyde, chloroacetyl chloride and triphenylphosphine as the reactants. Coumarin is presumably produced by intramolecular Wittig reaction (**Scheme 8**)[30].



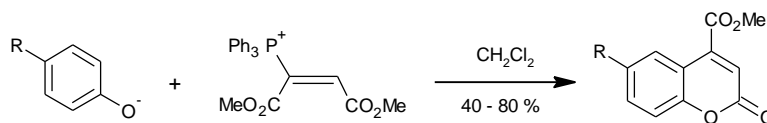
Scheme 8

Recently Belavagi and co-workers have reported a simple, efficient and green protocol for synthesis of coumarins through intramolecular Wittig reaction. Wittig salt was prepared by reaction of 2-formylphenyl-2-bromoacetate and triphenylphosphine, which is then subjected to intramolecular Wittig reaction to afford coumarin (Scheme 9)[31].



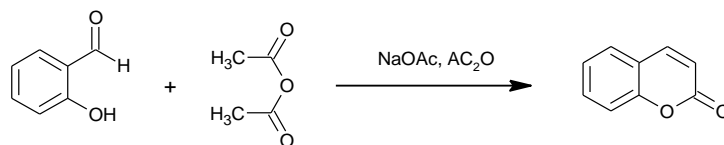
Scheme 9

In an innovative approach, Yavari *et al.* reported a protocol for the synthesis of 4-carboxymethylcoumarins. This protocol involves formation of a reactive intermediate by addition of triphenylphosphine to dimethylacetylene dicarboxylate (DMAD) which subsequently undergoes aromatic electrophilic substitution with conjugate base of a substituted phenol to yield 4-carboxymethylcoumarin (Scheme 10)[32].



Scheme 10

#### Perkin reaction:

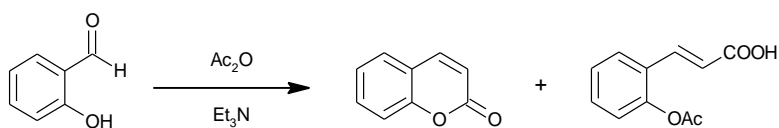


Scheme 11

Perkin in 1868 reported the synthesis of coumarins by heating together a mixture of *ortho*-hydroxy benzaldehyde and acetic anhydride in the presence of anhydrous sodium acetate. Reaction proceeds *via* formation of *ortho*-hydroxy cinnamic acid as an intermediate which then undergoes cyclization to yield coumarin (Scheme 11)[33]. *Prima facie*, although the protocol appears straightforward, *trans* geometry of cinnamic acid formed as the

intermediate lowers the yield of the final product considerably (50–55 %). This problem was successfully addressed by Yanagisawa and Kondoby using iodine as the catalyst in this condensation reaction [34].

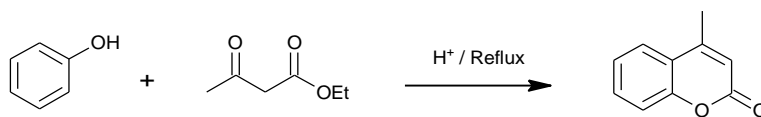
The reaction of *ortho*-hydroxy benzaldehyde with acetic anhydride in the presence of triethylamine as the catalyst is also reported to furnish coumarin. The main drawback associated with the protocol is the formation of *ortho*-acetyloxy cinnamic acid as the by product (**Scheme 12**)[35].



**Scheme 12**

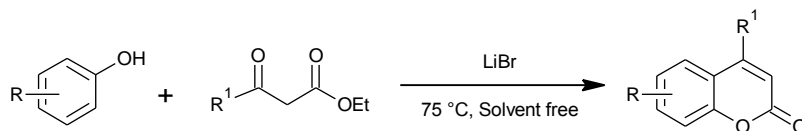
### Pechmann reaction:

Von Pechmann in 1883 reported that, heating together a mixture of phenol and ethyl acetoacetate or malic acid in the presence of concentrated sulfuric acid furnishes coumarin in excellent yield (**Scheme 13**)[36].



**Scheme 13**

Several modifications, mainly concerned with selection of the catalyst (homogeneous and heterogeneous acid catalysts), the reaction medium (ILs, PEGs, etc.) as well as the mode of heating (thermal, MW, etc.) have been reported in recent years to make the protocol high yielding and environmental benign. For instance, lithium bromide has been demonstrated to be a mild and efficient Lewis acid catalyst in solvent free synthesis of coumarin *via* Pechmann reaction (**Scheme 14**)[37].



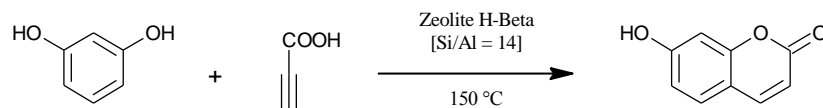
**Scheme 14**

Kad *et. al.* have reported microwave-assisted Pechmann reaction of substituted phenol and methyl acetoacetate for the synthesis of substituted Coumarins [38]. In another microwave assisted approach, Vahid *et al.* have reported the use of iron trifluoride as the catalyst in the synthesis of coumarins (**Scheme 15**)[39].



**Scheme 15**

The synthesis of coumarin derivatives using equimolar amounts of resorcinol and propiolic acid in the presence of Zeolite H-beta [ $\text{Si}/\text{Al} = 14$ ] as a catalyst was achieved by Bekkum *et al.* (**Scheme 16**)[40].

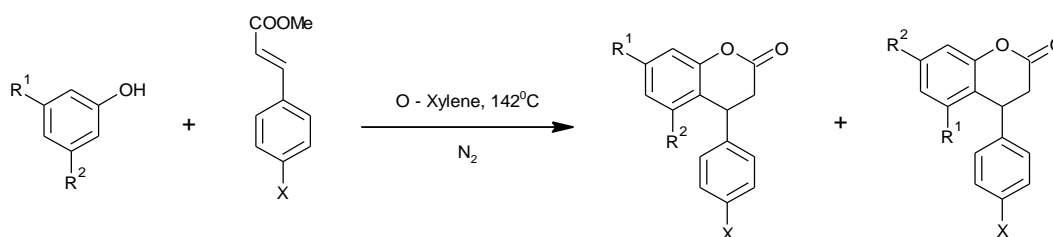


Scheme 16

Varieties of ionic liquids are also successfully employed for efficient synthesis of coumarin derivatives through Pechmann reaction [41].

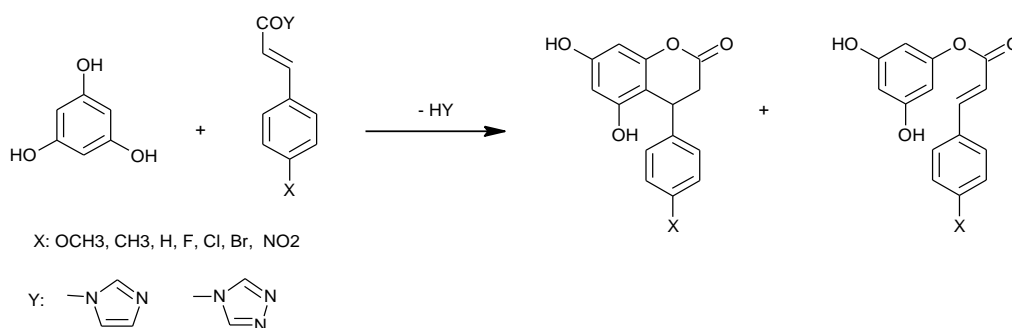
### Michael Reaction:

Speranza *et al.* introduced Michael addition reaction based approach for the synthesis of chroman-2-ones. He has described the synthesis of 4-arylchroman-2-ones by condensation of phenols with cinnamic acids (or alkyl cinnamates) under catalyst-free condition. Formation of isomeric mixture of products that precludes the isolation of desired product is the main drawback of the developed protocol (Scheme 17)[42].



Scheme 17

Speranza *et al.* have reported another mild protocol for the synthesis of chroman-2-ones by the reaction of dihydric or trihydric phenols with *in situ* generated *N*-cinnamoylazoles using DBU as the catalyst. The mechanism of these protocols involve initial esterification followed by cyclization through intramolecular conjugate addition (Scheme 18)[43].

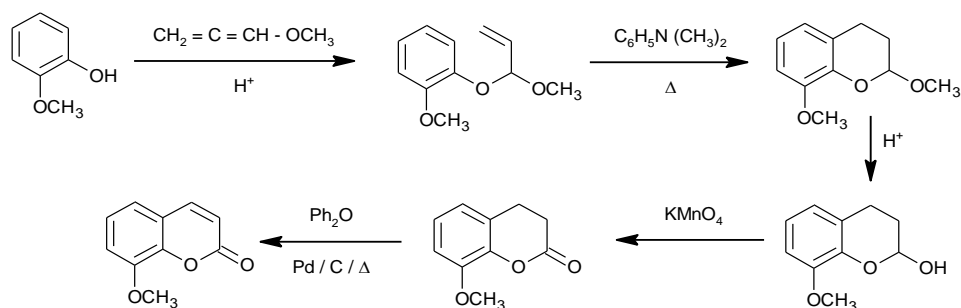


Scheme 18

### Claisen rearrangement:

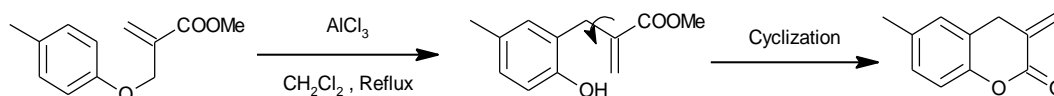
Rapoport *et al.* have reported Claisen rearrangement based approach for the synthesis of coumarins. In this method allyl or propargyl aryl ether having allylic or propargylic  $\alpha$ -carbon is oxygenated was prepared which subsequently undergoes cyclization *via* Claisen rearrangement. The intermediate alkoxychroman thus formed is then

subjected to oxidation affording corresponding coumarin. This method has been suitable in the cases where difficulties are encountered with the Pechmann synthesis of coumarin derivatives (Scheme 19)[44].



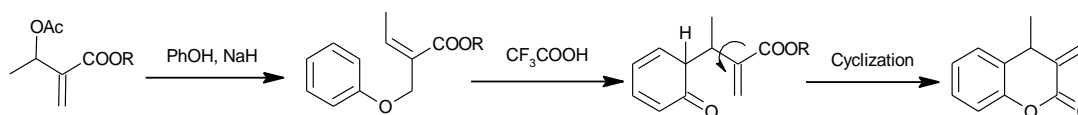
Scheme 19

Sunitha *et al.* reported Claisen rearrangement based anhydrous aluminum chloride catalyzed path for the synthesis of 3-methylenecoumarin using methyl ( $\alpha$ -aryloxymethyl) acrylate as the starting material (Scheme 20)[45].



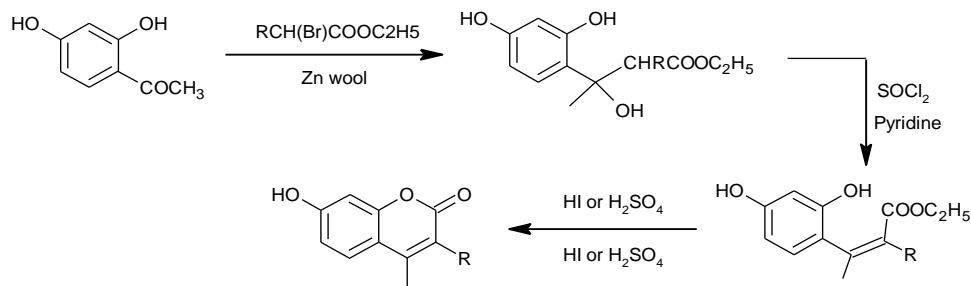
Scheme 20

As an extension to this, Drewes *et al.* reported one-pot synthesis of 4-methyl-3-methylene-3,4-dihydrocoumarins by the reaction between phenol and alkyl 3-acetoxy-2-methylene butanoate using trifluoroacetic acid as the catalyst (Scheme 21)[46]. The necessary precursor was prepared by acetylation of Baylis-Hillman product.



Scheme 21

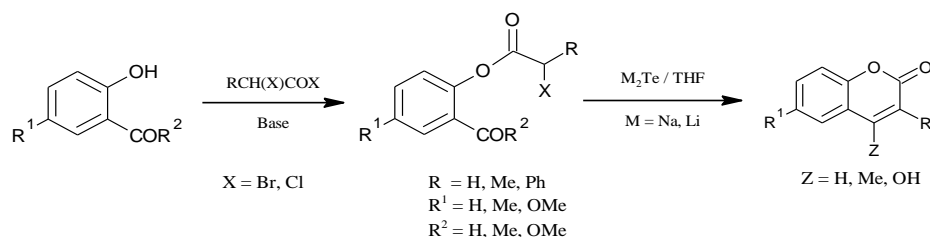
### Reformatsky Reaction:



Scheme 22

Chakravarti and Mujumdar have reported Reformatsky reaction based approach for the synthesis coumarins. The protocol involves Reformatsky reaction of *o*-hydroxy (or alkoxy) aryl alkyl ketones with  $\alpha$ -haloester. Resultant  $\beta$ -hydroxy ester on dehydration furnishes conjugated ester as an intermediate which upon heating with con.  $H_2SO_4$  or HI furnishes otherwise difficult to prepare 3,4-dialkyl coumarins (**Scheme 22**)[47].

Dittmer *et al.* reported modified Reformatsky reaction based protocol for the synthesis of coumarins. In this method, aryl esters of salicylaldehyde, *o*-hydroxy acetophenone as well as methyl salicylate are known to undergo cyclization in the presence of sodium or lithium tellurium to furnish coumarin derivatives in excellent yield. This synthesis of necessary aryl esters was achieved by base catalyzed reaction of salicylaldehyde, *o*-hydroxy acetophenone or methyl salicylate with  $\alpha$ -halo acyl halides (**Scheme 23**)[48].



**Scheme 23**

### Summery:

After the literature survey it is surmised that, simplest method for the synthesis of Coumarins is Knoevenagel condensation which involves base catalyzed reaction of salicylaldehydes with active methylene compounds. However other protocols mostly involve specialized reaction condition or reagents. In Knoevenagel condensation reaction most frequently used active methylene compounds are alkyl cyano acetates, alkyl acetoacetate or Meldrum's acid and the reaction is known to follow Knoevenagel condensation intramolecular cyclization path.

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# STUDIES ON EFFECTS OF ORGANIC FERTILIZERS ON THE SEED GERMINATION OF CHICK PEA (*CICER ARIETINUM* L.)

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## Abstract:

An experiment was carried out in the Govt. Degree College at Mahabubabad during the season, 2018 (Sept to Oct) to evaluate the seed germination and seedling growth of Chick Pea as affected by different organic fertilizers. There were five treatments viz. trichocompost, vermicompost, kitchen waste compost, cow dung based bioslurry and control (soil). Treatments significantly influenced the germination and seedling growth. The results showed germination percentage and co-efficient of germination were significantly higher in trichocompost which was identical with vermicompost and cowdung based bioslurry but different from kitchen waste compost and control, Similarly the seedling growth characters like root length, shoot length, number of leaves, number of roots, fresh and dry weight of 10 seedlings and effectiveness against damping off disease were significantly highest in the treatment media of trichocompost which reflected on higher vigour index in the same treatment. However, there was no significant variation among the treatments in respect of root and shoot length ratio. The results suggest that trichocompost and vermicompost are suitable for raising healthy seedlings in organic chick pea production

## Introduction:

Legumes are one of the most important groups of crop plants and have been the subject of efforts to improve desirable traits including their *in vitro* culture response. Since legumes are notoriously recalcitrant to regenerate from tissue culture, much effort has been devoted to developing and optimizing efficient *in vitro* regeneration systems to facilitate a variety of technologies [1]. The ability to regenerate plants from cultured cells, tissues or organs constitutes the basis of producing transgenic crops. Successful regeneration of legume species has been greatly aided by species-specific determination of critical parameters, such as explants source, genotype and media constituents [2].

Chickpea (*Cicer arietinum* L.), commonly called gram, Bengal gram, or garbanzo bean, is the most important food grain legume of South Asia and the third most important in the world after common bean (*Phaseolus vulgaris* L.) and field pea (*Pisum sativum* L.). Chickpea is a diploid with  $2n=2x=16$  chromosomes and a genome size of approximately 750 Mbp. Chickpea is one of the first grain crops cultivated by man and has been uncovered in Middle Eastern archaeological sites dated to the eighth millennium BC. Two distinct market type classes, desi and kabuli, are recognized in chickpea. The desi types that account for about 85% of chickpea area usually have small, angular shaped, dark-colored seeds with a rough surface, pink flower, anthocyanin pigmentation on the stems, and either semi-erect or semi-spreading growth habit. The kabuli types, which cover the remaining 15% area, usually have large “rams head”-shaped smooth surface seeds, lack of anthocyanin pigmentation, and semi-spreading growth habit. It has become increasingly clear during the last few decades that meeting the food needs of the world's

growing population depends, to a large extent, on the conservation and use of the world's remaining plant genetic resources. Conservation without use has little point and use will not come without evaluation. Genetic resources encompass all forms of the cultivated species, as well as their related wild species. That is a general concept to which chickpea is no exception. In reviewing genetic resources and their multifaceted applications in chickpea genetic improvement, we have placed more emphasis on the wild genetic resources of the cultivated chickpea, while providing a brief overview of resources available in the cultivated species.

In India, the total food production in 1999-2000 was about 209 million tones, out of this only 13.4 million tones was contributed by pulses. The production of cereals increased by 460 per cent since 1950-51 the production of pulses has increased only 178 per cent. There is a shortage of pulses in the country. The price has increased considerably and the consumer is hard hit to buy his requirements. Thus, the availability of pulse per capita per day has proportionately declined from 71 g (1955) to 36.9 g (1998) against the minimum requirement of 70 g per capita per day. There is not much possibility of the import of pulses in the country. The production of pulses has to be increased internally to meet the demand.

### Classification:

The Indian grams have been classified into two broader groups:

#### 1. **Desi or Brown Gram (*Cicer arietinum* L.):**

In this group the color of the seed ranges from yellow to dark brown. Seed size is usually small. It is the most widely grown group. Plants are small with good branching ability. Chromosomes number is  $2n = 14, 16$ .

#### 2. **Kabuli or White Gram (*Cicer kabulium*):**

In this group the color of the seed is usually white. Grains are bold and attractive. Yield potential of this group is poor as compared to desi or brown gram. Plants are generally taller than the desi gram and stand more or less erect. The chromosome number is  $2n = 16$ .

### Material and Methods:

The experiment was conducted at the Department of Botany Govt. Degree College Mahabubabad during the period of 1<sup>st</sup> Nov to 15<sup>th</sup> Dec in 2018. The experiment was laid out in a randomized complete block design with three replicates. This experiment included five different treatments like Trichoderm compost, Humas compost, Vermicompost, Kitchen Waste Compost, Cow dung based Bioslurry, and Soil (control). They were analyzed following proper methods just after have been received. Plastic pots (Jugs) measuring 15 cm x 12cm x 7 cm (1260 cm<sup>3</sup>) were used for raising the seedlings. 10 pots were used for each of treatment and thus fifty pots for each replication. Sterilized soils were mixed with individual organic fertilizer at the ratio of 50:50 (Soil: Fertilizers by volume) for potting. Ten (10) seeds were sown in each pot. The speed of emergence was determined by counting the number of seeds emerged at twenty four (24) hours interval immediately after sowing. The criterion used for seed germination was taken as emergence of 2 mm radicle at the time of observation [3]. Germination counts were recorded until 36 days after sowing. The germination percentage of the seeds was finally determined for each of the treatments. Co-efficient of germination was calculated using the following formulae [4].

Coefficient of Germination,  $CG = (A_1 + A_2 + \dots + A_x) / (A_1 T_1 + A_2 T_2 + \dots + A_x T_x) 100$ . Where, CG = Co-efficient of Germination (%), A = Number of seeds germinated, T = time corresponding to A, X = number of days to final count. For determination of seedling vigour index 10 seedlings were randomly selected from each treatment and their individual shoot and root length were measured. The vigour of the seedlings was determined by following the formula of Abdul-Baki and Anderson [5]. Vigor index = [mean of root length (cm) + mean of shoot length (cm)] × percentage of seed germinations. After 36 days, the growth parameters were estimated after

uprooting and cleaning the seedlings. Different parameters were recorded with appropriate measures. The fresh weight and dry weight (in grams per 10 seedlings) was measured with a digital weighing balance. Damping off disease incidence of infected seedlings was recorded and calculated by using the following formula, % Disease incidence = (Number of infected seedling) x 100/Number of inspected seedling. Percentage data were transformed to square root and were analyzed including other data by using MSTAT-C program

### Results and Analysis:

The analyzed report of different compost materials is furnished in Table 1 and it revealed that trichoderm compost contained more nutrients which were followed by vermicompost.



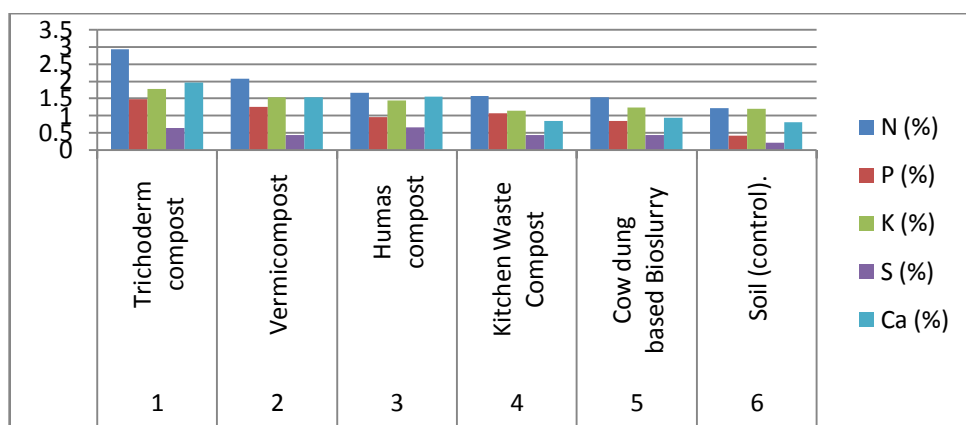
**Photographs showing the organic fertilizers induced seed germination in Chick pea seeds  
Germinated in the Jugs**

The seed germination percentage was significantly ( $P=0.05$ ) affected by different types of organic fertilizer and ranged from 96.0 to 65.0 (Table 2). The highest seed germination was recorded in trichoderm compost which was statistically similar to vermicompost and the least performance was observed in case of kitchen waste compost which was identical with control (soil). Significant variation was also observed in case of co-efficient of germination (%). Trichocompost gave the best performance in co-efficient of germination velocity (15.0) which was statistically similar with vermicompost and cow-dung based bioslurry while poor performance (9.0) was observed in case of kitchen waste compost even less than the control. The longest root (18.0 cm) was found in trichocompost which was

followed by vermicompost and the shortest root (14.0 cm) was appeared in case of kitchen waste compost. The shoot length (18.0 cm) was found in trichocompost which was followed by vermicompost and the shortest shoot (10.0 cm) was appeared in case of kitchen waste compost. The number of leaves after six weeks were recorded 32 leaves was found in trichoderm compost which was followed vermicompost and the less number of leaves developed on control soil.

**Table 1: Result of the chemical analysis (Nutrient content) of different kinds of compost on Seed germination of Chickpea (*Cicer arietinum* L.)**

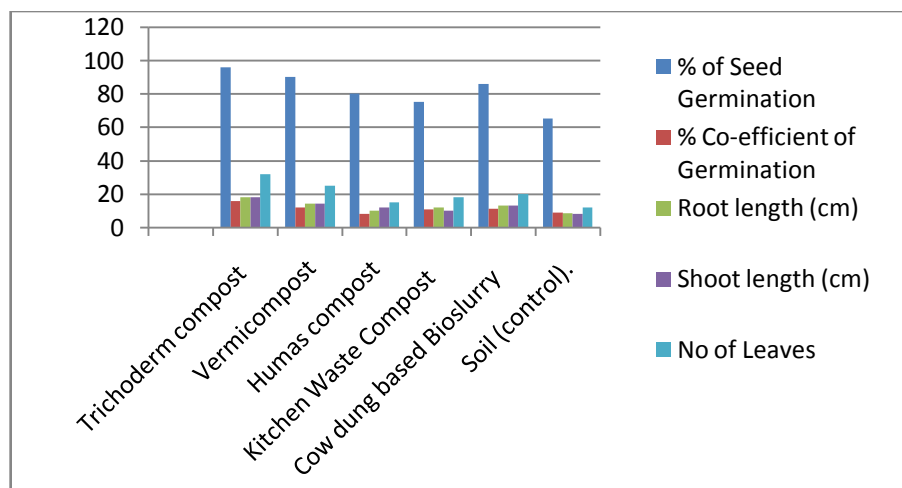
Sr. No.	Types of compost	N (%)	P (%)	K (%)	S (%)	Ca (%)	Zn (ppm)
1	Trichoderm compost	2.93	1.49	1.78	0.64	1.96	188.0
2	Vermicompost	2.08	1.26	1.53	0.44	1.54	136.0
3	Humas compost	1.67	0.97	1.45	0.67	1.56	113.0
4	Kitchen Waste Compost	1.57	1.08	1.15	0.45	0.85	136.0
5	Cow dung based Bioslurry	1.54	0.86	1.24	0.45	0.95	125.0
6	Soil (control).	1.23	0.43	1.20	0.23	0.82	124.0



**Graph 1: Result of the chemical analysis of different kinds of compost on Seed germination of Chickpea**

**Table 2: Effect of organic fertilizers on germination and seedling growth of Chickpea (*Cicer arietinum* L.)**

Types of compost	% of Seed Germination	% Co-efficient of Germination	Root length (cm)	Shoot length (cm)	No of Leaves
Trichoderm compost	96.0	15.8	18.0	18.0	32
Vermicompost	90.0	11.9	14.0	14.0	25
Humas compost	80.0	8.0	10.0	12.0	15
Kitchen Waste Compost	75.0	10.7	12.0	10.0	18
Cow dung based Bioslurry	86.0	11.0	13.0	13.0	20
Soil (control).	65.0	9.0	8.5	8.0	12



**Graph 2: Effect of organic fertilizers on germination and seedling growth of Chickpea (*Cicer arietinum* L.)**

### Discussion:

Trichocompost gave the best performance might be due to the synergistic effect of compost and trichoderma in increasing the root surface area per unit of soil volume, water use efficiency and photosynthetic activity of seedlings in addition of higher nutrient contents in trichocompost which had been reflected in sample analysis. It also gave the better performance against damping off disease which is in agreement with the findings of Islam *et al.*, [6] and Manoranjitham *et al.*, [7]. In most cases, the performance of trichocompost was followed by vermicompost. This finding was supported by many investigators [8, 9], who reported that worm worked waste and their excretory products (vermicast) can induce excellent seed germination and enhanced rate of tomato seedling growth. However, kitchen waste compost gave the poor performance could be due to presence of heavy metal like lead and copper which was observed by Jaja and Odoemena [10].

### Conclusions:

1. The results reveal that aspects of plant nutrition in organic farming will gain increasing interest and concern, respectively.
2. Crop quality and promotion of natural plant health by nutrient induced resistance mechanisms are supposed to be of major relevance for organic farmers.
3. The efficacy of precision agriculture technologies to improve the N supply and to reduce N losses to the environment needs to be verified under practical conditions

***ORGANIC FARMING IS THE ONLY OPTION WE HAVE LEFT TO LIVE HEALTHY LIFE***

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# GREEN CHEMISTRY FOR HUMAN WELFARE AND ENVIRONMENT

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## **Introduction:**

Nature has provided us with everything in a benign balanced ratio that is necessary to maintain the normal and healthy life of human being. Early human being used natural resources to satisfy their needs for air, water, food and shelter. With the dawn of the industrial revolution, human beings for better than ever to satisfy their age-old needs of air, water, food and shelter. However to maintain our current standard of healthy living and improve our quality of life, society has come to depend on the products of the “ Chemical Industry”. Chemistry is here to develop, maintain, control and protect the life of living organisms including human being or to cause environmental problems. Chemistry has an unique role to play in achieving a sustainable civilization on earth. Chemistry plays an integral part of our lives and is all round us in the air we breath , the food we eat , clothes we wear , house we live and even our own body system.

As human populations increasing day to day, urban metroplexes, deforestation and unwanted land usage changes continue to grow and increasing man made pollution and degradation of air, soil and water quality have become a severe and critical global problem. Anthropogenic or human-induced harmful pollutants have over-loaded in the environment. By the late nineteenth and twentieth centuries unscientific urbanization, agriculturization and industrialization are the various major threats to environment and human-being,the world. Industrial vomit fills our sky and seas. Pesticides and herbicides filter into our foods . Dispersion and transport of toxic pollutants has no boundaries and is a global problem which leads to cause a major threat to the living system on the earth . Issues such as global warming, acid rain, toxic organic and inorganic chemicals, climate change are all man made harmful agents which has direct alarming lethal effects on the health of humans, plants, animals, crops, water and air and also alter the quality of food and biological systems. The widespread use of chemicals in agriculture and industry has spread over through air, water and soil as well as through the food chain and thus pose a potential threat to human beings (11). A wide range of communicable diseases can be spread through polluted air, water and soil . Our culture as well as aesthetic heritage is also being lost to pollution. The Statue of Liberty in New York and Taj Mahal in India and many other monuments of historical importance are in increasing danger of being destroyed by the constituents of a polluted atmosphere (7, 4 ). Environment is a heritage for all . Each of us has a role to play in rehabilitating our environment. It is thus constitutional obligation of the state and of every citizen of the country to preserve and protect the natural environment. One must recognize that the situation has not reached the end point. It is time to think (9). It is an endeavour to avoid the overuse, misuse and abuse of the resources in the environment.

A new scientific approach is essentially needed to change the harmful nature of environment .It is a challenge for the chemistry community to avoid/stop the threat and adverse harmful effects of environmental pollution on living systems.It is important that chemistry develop a new school namely “Green Chemistry” for the benefit of human beings. Green chemistry is a special science especially for Sustainable development . The word Green chemistry was coined by Paul T Anastas, which means the judicious use of chemistry for prevention of pollution .The aim and dream of green chemistry is environmentally “Benign synthesis”. Green chemistry is an important area for science and technology to pursue for the benefit of the human being, environment and industry

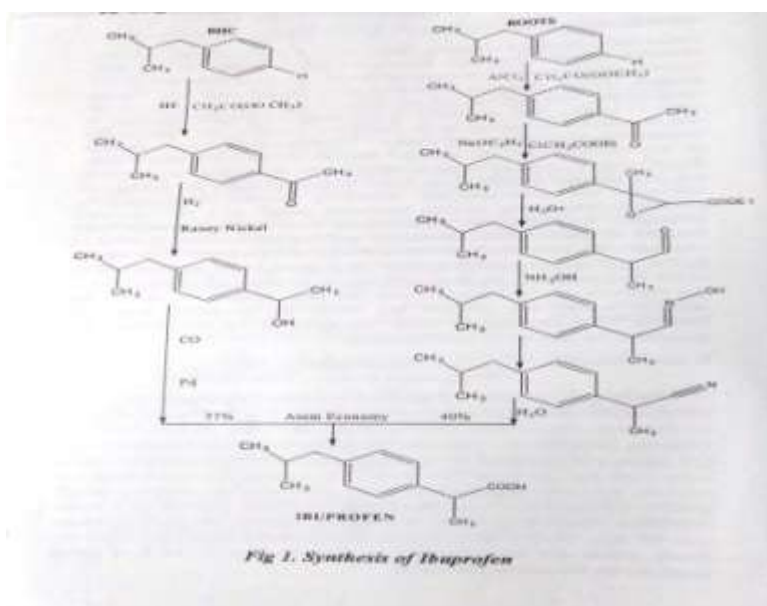
(16). It involves the designing of products and processes using environmentally safe alternatives that reduce the generation of hazardous substances. Green chemistry is unique that which involves modified engineering practices, bioremediation, ecofriendly reaction media and concept of atom economy leading to almost zero waste (2).

Green chemistry is being practiced within at least 4 regimes :

1. Traditional basic academic research,
2. Industry – specific research and development,
3. Government – Industry – Academic collaborations and
4. Technology generation and transfer among government national laboratories [3].

### Green method: BHC – Ibuprofen:

The concept of atom economy was developed by Barrytrost, — How much of the reactants end up in the final product . An ideal synthesis is in which all the atoms in the reactants are incorporated into the final product. This reaction would not produce any waste by products (20). Example : A suitable example is the BHC company synthesis of Ibuprofen, which creates less waste and fewer by products (Fig. 1). The % economy for the 3 step catalytic green synthesis (BHC) vs. the six step brown synthesis (BOOTS) is 77% and 40% respectively. Considering the fact that acetic acid generated in step1 of green synthesis is recovered, the % atom economy climbs to 99% from 77%. Besides the brown synthesis requires auxiliary reagents ( $\text{AlCl}_3$ ). In stoichiometric amounts, which generates large amounts of Aluminium trichloride hydrate as a waste by product, which is generally land filled, in contrast the Green synthesis uses HF as a catalyst that is recovered and reused repeatedly. Even the Raney nickel and the palladium catalyst in steps 2 and 3 of Green synthesis are recovered and reused (5).



### Green chemistry-Supercritical fluids (SCF)

Supercritical fluids (SCF) are produced by heating a gas above its critical temperature or compressing a liquid above its critical pressure . An important incentive for the use of Supercritical Fluids (SCF) in synthetic chemistry comes from this increasing demand for environmentally and toxicologically benign processes for the production of high value chemicals (14). A supercritical fluid (SCF) has both the gaseous property of being able to

penetrate anything, and the liquid property of being able to dissolve materials into their components. These properties make supercritical fluids efficient extraction solvents with high mass transfer characteristics (12 and 13). On this account use of carbon dioxide or water in the form of a supercritical fluid offers a substitute for an organic solvent in the fields of food processing, petrochemicals, Pharmaceutical industry, Biotechnology, environmental protection and a wide range of other industrial and analytical applications. Supercritical carbon dioxide (sc-CO<sub>2</sub>) is a benign alternative because it is inexpensive and possess no threat to the human health and environment (21).

### **Green Method – Biocatalysts:**

In the first issue of New Scientist (1956) Sir Cyril Hinshelwood President of Royal Society, wrote Bacteria are capable of bringing about chemical reactions in short time. Microorganisms are Biocatalysts using in Biocatalytic processes can increase the productivity by decreasing the waste production, cost saving but also result in reduced hazardous products.

#### **Example:**

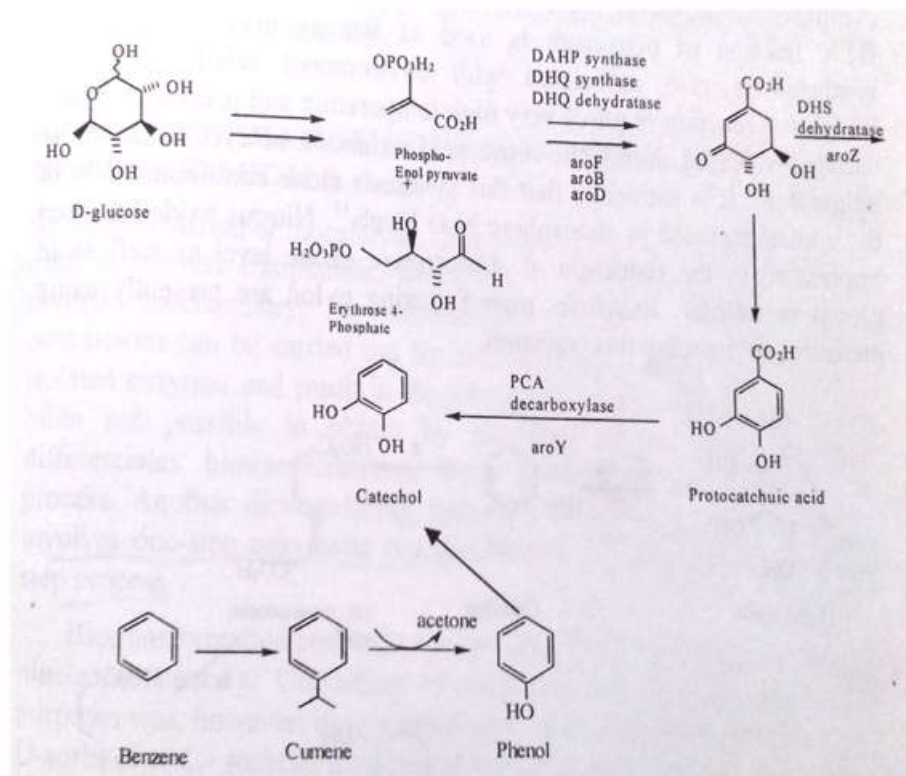
1. Clostridium acetobutylicum (Biocatalyst) was used to convert starchy material such as corn to acetone, butanol and ethanol. Genetically manipulated microbes to yield products of commercial importance like catechol and adipic acid from carbohydrates (6). Pharmaceutical industry is combining innovations from Green chemistry and microbiology to generate benign pathways for drug production.
2. A specific example is the synthesis of an anticonvulsant drug LY300164 from Lilly laboratories, which is developed for epilepsy and Neurodegenerative disorders. Chemical synthesis generated a large volume of organic solvent and chromium. Significant environmental improvement was achieved by using a Green method which started with the Biocatalytic reduction of a Ketone to an optically pure alcohol using Zygosaccharomyces rouxii (Biocatalyst). Using this modification 34000L of solvent and 300 kg of chromium waste were eliminated for every 100 kg of LY300164 produced (22).

### **Green Method- Catechol and Adipic acid:**

Implementation of Green chemistry by using —Microbes as Biocatalysts to Commercial synthesis of catechol and adipic acid by Green method-benign pathway.

#### **Green Method - Catechol:**

Catechol is the starting material for the synthesis of many pharmaceuticals, agrochemicals, antioxidants and flavours etc. It is synthesized from benzene. Chemical synthesis of catechol from benzene involves initial alkylation to cumene, which is then oxidized to phenol. Phenol is further hydroxylated to yield a mixture of catechol and hydroquinone which are then separated by distillation. Benzene and phenol are toxic. The former is Human carcinogen. To eliminate these problems Draths and Frost discovered a Green method Biocatalytic pathway (Fig.2) for catechol synthesis (6). Catechol production requires the expression of genes for two enzymes namely 3-dihydroshikimic acid dehydratase (DHS) and Protocatechuic acid decarboxylase (PCA decarboxylase) which are absent in E.coli. The genes for these enzymes had to be isolated from different bacteria, and expressed in a single host. Extensive work was available with E.coli for heterologous expression of many enzymes. Hence required enzymes for this pathway were expressed in the host organism and Biocatalyst namely E.coli. According to Draths and Frost the Biocatalyst can convert Glucose to catechol in a Biocatalytic Green method. Using molecular biology techniques, a novel biosynthetic pathway whose ultimate product is catechol was created (6). Biocatalyst creation and its evaluation has been described in detailed by Draths and Frost (6) who have discovered this process.



**Figure 2: Chemical and Biocatalytic pathway for Catechol synthesis (6)**

### Green Method – Adipic acid:

As in catechol synthesis benzene is used as a starting material in the chemical synthesis of Adipic acid.. Hence this synthesis is also associated with environment related problems. Benzene is a known Human carcinogen. Hence, to eliminate these problems Draths and Frost discovered a Green method Biocatalytic pathway (Fig.3) for the synthesis of Adipic acid (6). Glucose is converted to cis-cis muconic acid using genetically engineered E. coli construct expressing the biosynthetic pathway which does not exist in nature. The pathway was assembled by introducing the required genes for catechol 1,2 dioxygenase from *Acinetobacter calcoaceticus* to E.coli strain construct developed for the conversion of glucose to catechol mentioned earlier. Biocatalysts synthesized cis-cis muconic acid from glucose. After separating the bacterial cells, cis-cis muconic acid was directly reduced to Adipic acid using platinum as catalyst (6).

Microorganisms have been a novel source of bioactive compounds since last century. *C. quercina* has excellent antifungal activity against important Human fungal pathogens – candida albicans and *Trychophyton* spp. Under invitro conditions it produces a unique peptide antimycotic, termed cryptocandin (17). Cryptocandin is currently being considered to treat fungi diseases of skin and nails. Biological matrix i.e. plant microbe or a marine to be screened for bioactive compounds is the primary focus in a natural product drug discovery program . The basis of selection of the biological matrix is dependent on ethnomedicinal use, chemotaxonomic distribution. Information managed approach is adopted which is usually a combination of ethno medical, biological and chemical information (8). The discovery of vinblastine is an anticancer agent came as a surprise during screening the hypoglycemic activity of *Catharanthus roseus* (19). Microbes provide a higher degree manipulation of genes encoding for a particular product can be transferred from the parent microorganism to more convenient microorganism whose growth conditions can be optimized in a stringent manner for commercial production. This approach has been successfully

used for the production of an anti-cancer polyketide “Epothilone” from a slow growing myxobacterium. The genes responsible for the production of “Epothilones” were transferred from the myxobacterium to *Streptomyces coelicolor*, which eventually provided more biomass and availability of the target compound (18).

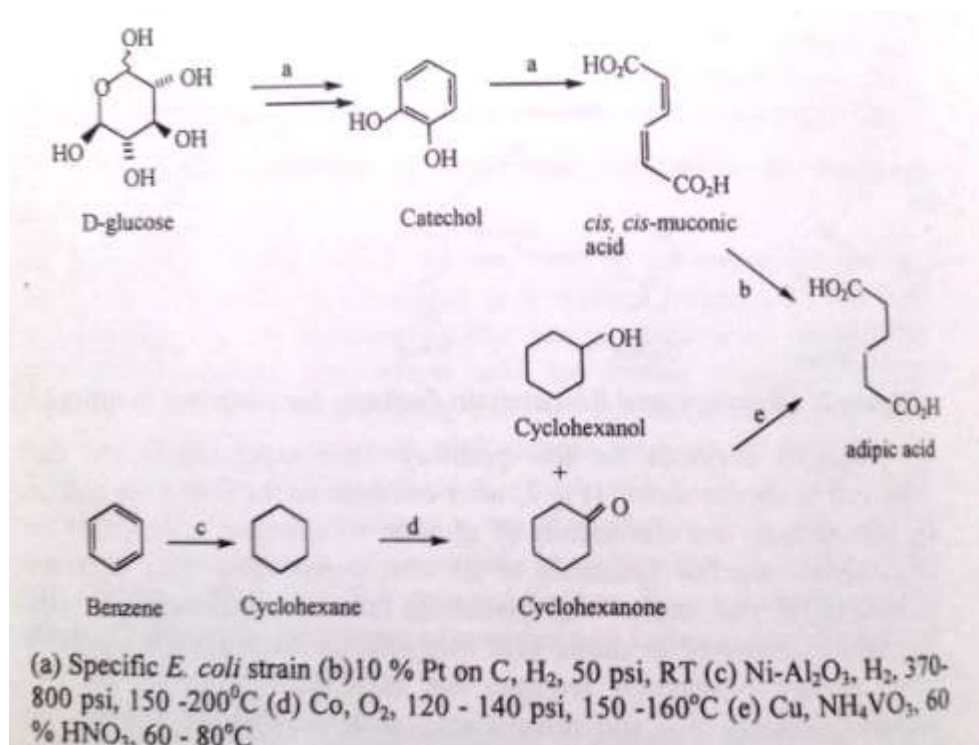


Figure 3: Chemical and Biocatalytic Pathway for Production of Adipic acid (6)

#### Green Method: Conversion of D-Sorbitol to L-Sorboside:

Biotransformation is a process where a biological agent is used to convert compounds. It is an important green method to save environment & human beings.

Ex: 1. The conversion of D-Sorbitol to L-Sorboside is a biotransformation step, where biocatalyst *Gluconobacter oxydans* is used. It is a part in the production of Ascorbic Acid by **green method** which is a benign route known as ecofriendly method.

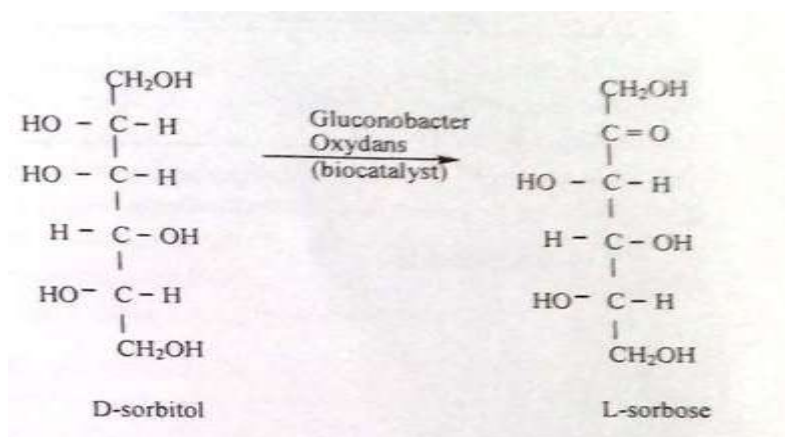


Figure 4: Conversion of D-sorbitol to L-sorboside

**Bioinsecticides:**

Pests (insects plant pathogens and weeds) cause a significant threat to cropping systems and account for huge losses economically. The use of hazardous pesticides causing suffering to millions of people as well as deterioration of the environment. Hence, need of new pest control methods to suppress these pests is a major aspect for crop protection and enhancing yield in agriculture. One of the most widely used bioinsecticides is produced by a soil bacterium *Bacillus thuringiensis* (Bt) that produces a protein poisonous to insects. The organism after 15 minutes being eaten, the poison begins to create ulcers in the insect's stomach lining. Eventually the insect stops eating and dies. These toxins produced by Bt are known as Alpha and Beta endotoxins.

Examples:

- (1) Certan and Dipel are some registered Bt products by united states environmental protection agency (USEPA), these products are used to control leaf feeding caterpillars .
- (2) *Lagenidium giganteum* is developed and marketed as anti mosquito product under the name LAGINEX by Agra Quest U.S.A .

**Green reaction and zero waste management:**

Promoting a reaction photochemically rather than thermally is greener, since light is the green reagent par excellence. Photochemistry (1) offers an inexhaustible source of new chemistry via chemical reactions of the excited state, which are much faster and little dependent on conditions, affording a large freedom of choice. Similarly, reactions by a microwave have an advantage of less or no solvent, very little time, no side products and better yields with better selectives compared to those carried out by a conventional means . Green chemistry attempts to reduce and eliminate the hazardous substances. If you do not use or produce hazardous substances then the risk is zero. Zero waste is the ultimate goal of Green chemistry cleaner production, pushes the industry from pollution prevention and control, into the new paradigm which is to become the industry standard enter into the benign industrial output and products (10) . Waste management is an area where we can help ourselves. The waste of biological and chemical process will become the feed stock of the next process. So that energy, carbon content and water are fully conserved, this is the most important green method. When less waste is generated, environmental compliance costs go down. Treatment and disposal become unnecessary when waste is eliminated.

**Conclusion:**

Herbals have been associated with Humans since the advent of the civilization for the development of novel herbal formulas are bioactive compounds for designing new therapeutic treatments. The trend continues today as scientists are in search for alternative therapeutic treatments as well as in discovery of new chemical entities to combat a variety of diseases in their quest to provide “ Quality health to all” (15).

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# GROUNDWATER QUALITY AND ITS SUITABILITY FOR WATER SUPPLY AND IRRIGATION IN VILLAGES AROUND GORAMBE, MAHARASHTRA

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## Abstract:

The present study has been undertaken in and around Gorambe village. About, 19 surface and Groundwater samples were collected from entire study area depicting different environment and landuse. The water chemistry in study area is dominantly controlled by lithology as Ca, Na, Mg and HCO<sub>3</sub> are major ionic phases. The water shift towards Ca+Mg-SO<sub>4</sub> (Alkaline earth, strong acid), Na+K-HCO<sub>3</sub> (Alkali metals, weak acid), Na + K- Cl + SO<sub>4</sub> (alkali metals and strong acids)\_categories. The majority of water alkaline earth exceed the alkalis (Ca+Mg>Na+K) except for a few samples from study area. The study area water chemistry is governed by rock water interaction. High correlation within HCO<sub>3</sub> and Na, K, Mg suggests its natural source of weathering of basaltic rocks. The different indices like SAR, PI, SSP, SP, KR and TDS to Shows their values which are within permissible limit which suggests the water quality is suitable for drinking as well as irrigation purpose.

**Keywords:** Gorambe, Water quality, Irrigation, Nitrate etc.

## Introduction:

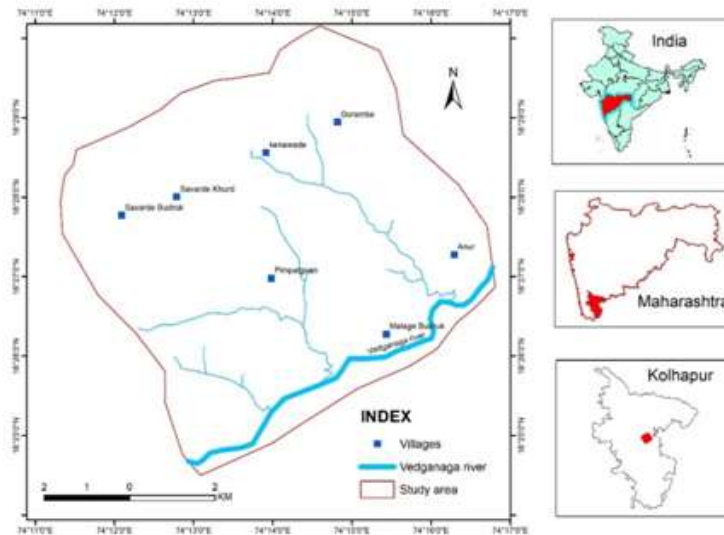
Most of the population is mainly depending on groundwater as prime sources of water for drinking, irrigation, industrial and for livestock [1]. The problem of water scarcity is increasing as population explosion in developing country such as India. This water scarceness leads to increase in the use of groundwater for urban as well as rural sector [2]. The agriculture runoff changes in land use pattern urbanisation are the basic cause of groundwater contamination. Though there is number of studies has been taking places for groundwater contamination [3] by trace elements and major ions, the study also have been carried out in arid and semi-arid regions in the world.

The perusal of literature shows that no data is available on the ground water chemistry and groundwater contamination in villages around Gorambe, with general water level and major ion content from GSDA. Therefore, the present study was undertaken in this area to delineate the quality of groundwater and its suitability for drinking and irrigation purpose.

Since, major ion determine the 'suitability of water for various purposes like drinking, agricultural and industrial use. It was necessary to understand the geochemistry of groundwaters from Gorambe and surrounding villages to search for evidence the processes that affect the quality of Groundwater in some villages. Relatively less variation in lithology, least climatic variability and large-scale urbanization in the area would provide an opportunity to identifying noticeably, the role of lithogenic as well as anthropogenic factors. The ground waters are in prolonged contact with local rocks enabling it to react with mineral phases, which otherwise are apathic to respond. There, are wide numbers of activities that are associated with man's introduction for foreign chemical materials in the subsurface environment. In the long run the most potential hazardous of these may be the use of chemical pesticides in agriculture. Large scale of Agriculture and domestic activity affected on Groundwater pollution in a Kolhapur sub-urban region. the types of pesticides used in agriculture practice infiltrate in groundwater and result of groundwater pollution.

### Study area:

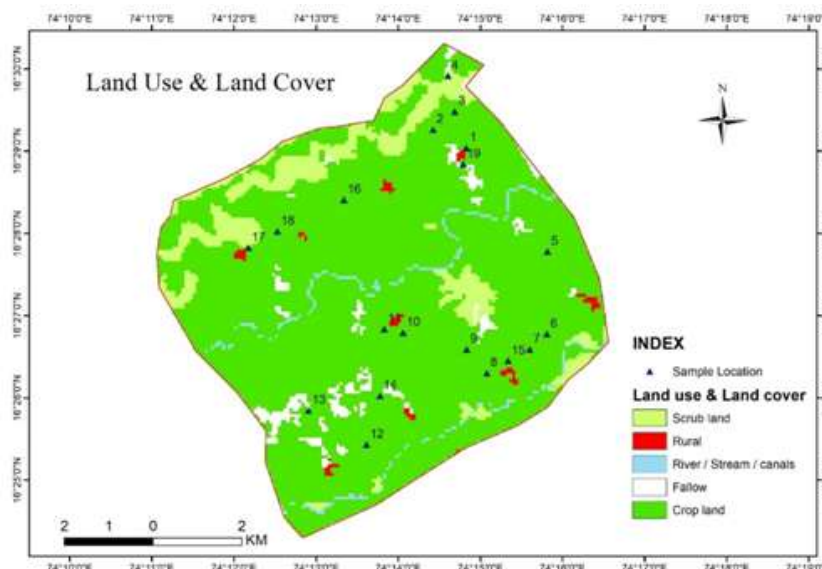
The study area is located in Kagal taluka, Kolhapur district of Maharashtra state, India. The annual rainfall of the village as collected from the taluka place at Kagal in 785 mm, for the year 1978-79. The temperature variation as collected from the nearby station at Bidri as maximum – april-39- 38.4<sup>0</sup>c. The area under study is a part of Vedganga river microwatershed in Kagal taluka, Kolhapur district, Maharashtra, India. The study area is located on 74.24 to 74.21 and latitude 16.46 to 16.44. Gorambe village and around area is about 59 Km<sup>2</sup>. Physiographically, the area is flat in middle and southern part of study area and the hilly in the northern part of study area. Geomorphologically, The Study area is situated in undulating terrain. Then the boundary of the study area is marked by steeply slopping hill rock undulating terrain. The southern part of the study area is made up of highly to moderately undulating terrain. The general slope of the village is in SSE- direction and is moderate. Hydrologically, the study area is covered by number of Nallas emerging from the southern hill rocks and flowing towards SSE. The S-W boundary of the village is marked by a major nalla emerging outside the village boundary and flowing from 7-15 mts, and bed rock is exposed in some Nallas and Road cuttings. The drainage exhibits parallel pattern to Vedganga river basin.



**Figure1: Location Map of the study area**

### Geology:

Geology of the area is characterized by unclassified basalt lava flows [4] belonging to the deccan trap of upper cretaceous to lower Eocene period about 68 m.a. In study area, Northern part presence of brownish black highly weathered prominently vertical jointed massive traps at 620 -598 MSL. Red bole encountered at a grey vesicular zeolite trap at 598-587 MSL and its moderately weathered yellowish grey, prominently vertical and poorly horizontal jointed, massive Basaltic trap at bellow 587 MSL [5]. Generally, study area covered by brownish to black soil spread over, highly weather vesicular basalt and major part of study are is covered by deccan basalt rest over alluvium of quaternary deposits [6].



**Figure 2: Water sampling stations in a study area**

**Methodology:**

The water samples were collected in pre-monsoon (2017) the random sampling was used in order to represent different land-use patterns. Nineteen representative water samples from wells were collected for major ions analysis. Water samples were collected in plastic containers of one-liter capacity for detail chemical analysis from the selected dug wells, borewell and irrigation tank. These containers were washed thoroughly with distilled water and dried before being filled with water samples. The containers were numbered serially along with a proper record of well/sample location, date, static water level, of well etc. prior to the sampling. The samples were collected and analyzed using Standard techniques[7, 8]. All the elemental concentrations measured were in mg/l or ppm.

**Table 1: chemical methods used for major element analysis in groundwater**

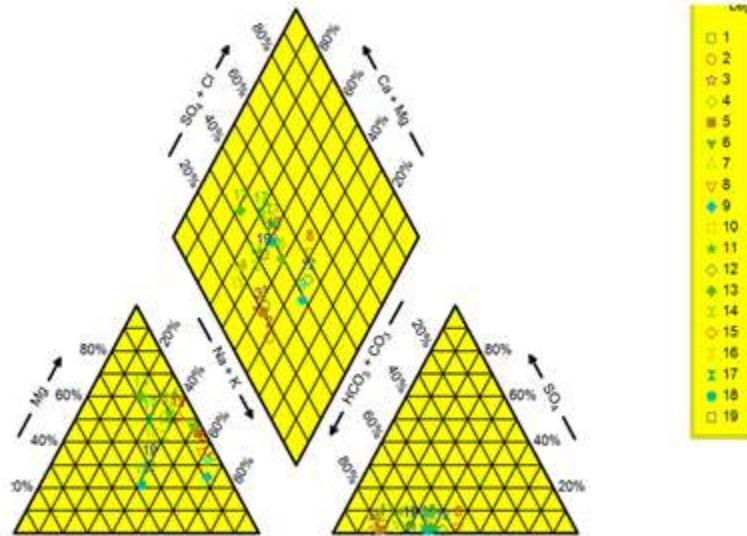
Element	Method of chemical analysis
Na, K	Flame photometer
Ca and Mg	Titration using 0.05 N EDTA
Cl	Titration using 0.05 N AgNO <sub>3</sub>
HCO <sub>3</sub> and CO <sub>3</sub>	Titration using 0.01 N H <sub>2</sub> SO <sub>4</sub>
SO <sub>4</sub> and NO <sub>3</sub>	UV- Visible spectrophotometer methods
pH and EC	pH digital meter and EC digital meter

**Results and Discussions:**

**Groundwater Hydro-geochemistry:**

To categorize and differentiate the groundwater on the basis of its chemical composition the Piper’s Trilinear diagram was used (Fig.3). In order to visualize the variation with space and time in terms of hydro-chemical facies of groundwater from the area, the data were plotted on the trilinear diagram [9] using Aqua software. The most of the water In study area shows Ca, Mg and HCO<sub>3</sub> dominant type of water which suggests the groundwater chemistry is controlled by rock water interaction as high content of HCO<sub>3</sub> is the product of weathering

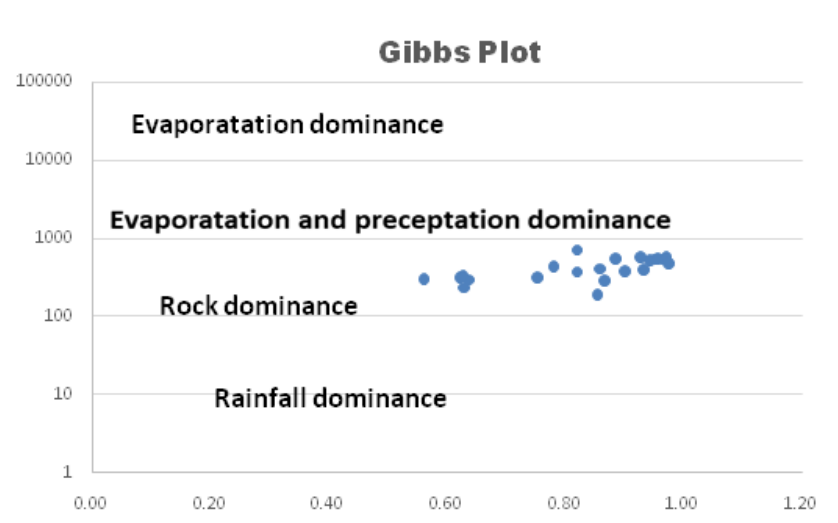
of rocks. 7 samples show  $(Na + K > Ca + Mg)$  facies, followed by  $(Ca + Mg > Na + K)$  by 13 samples (fig.3). The surface water sample and effluent sample show  $(Na + K > Ca + Mg)$  facies. In case of anions majority of samples fall in the category of weak acids  $(HCO_3 + CO_3 > Cl + SO_4 + NO_3)$ , 18 samples and 1 sample in the category of strong acids  $(Cl + SO_4 + NO_3 > HCO_3 + CO_3)$  indicating its external source other than natural.



**Figure 3: Classification of groundwater from study area**

**Gibbs plot:**

Gibbs [10] identified three different mechanisms that control composition of water. The plot of  $(Na+K)/(Na+K+Ca)$  Vs. TDS illustrates these mechanisms. Gibbs plot gives idea about the reactions bringing about changes in water chemistry. Almost all the groundwater samples from the study area represent the water rock interaction which is primarily controlling the major ion chemistry of ground water in this region. (Fig. 4)



**Figure 4: Gibbs Plot**

Water chemistry reflects more uniform chemical composition controlled by lithological and some extend may be anthropogenic factor as variation in chemical characteristics of water attributable predominantly to lithological factors. The variation reflects input from multiple sources possibly related to human activity like agriculture an also urbanization spreading in agriculture area.

#### **Water geochemistry:**

The pH values vary from (7.5 - 6.53) with average of 6.81, EC values varies from (1683-221 $\mu$ m), Ca average conc. 10.57 ppm and are within the permissible limits given by ISI, similarly Mg varying from 10.1 to 59.4 ppm, Na 14ppm to 112 ppm, K 0.1 to >200 ppm, NO<sub>3</sub> 9.27 to 58.94 ppm ,Cl 25.56 to 76.68 ppm and SO<sub>4</sub> 0.35ppm to 9.75 ppm. The Nitrate and Chloride values are seen higher in some wells No. 5 and 12. In general, in the pH value of study area is neutral. The average pH value is 6.81. And the lowest pH value 6.53 recorded in village of Pimpalgaon Budruk.

Comparison of anion data suggest that bicarbonates is the principle anion followed by Sulphate> Nitrate> Chloride suggesting HCO<sub>3</sub> from weathering of silicates and SO<sub>4</sub>, NO<sub>3</sub>, Cl, from Household and agricultural activity. The bicarbonates account for more than 70% of the total anions present in Ground water with minimum value 120 ppm and maximum value 350 ppm. increases in bicarbonates involve 1). Loss of CO<sub>2</sub> and precipitation of mineral salt. 2) continuous infiltration of urban wastewater into the aquifer. Chloride in ground water from study area is not significant under conditions of weathering processes as the basaltic lithology is devoid of Cl-bearing minerals. Cl in Banage village is higher 96 ppm. contribution is from human activities. It is considered as indicator of pollution in present case. Excluding bicarbonates, Cl, SO<sub>4</sub>, NO<sub>3</sub> likely to contributes from anthropogenic sources in village of Anur and Malage Budruk. In this two Villages Nitrate value is > 45 ppm.

On a spatial scale, High concentration NO<sub>3</sub> anomalies corresponding with rural and intensive agricultural areas confirm urban effluents and Nitrogen fertilizer (eg. Uria) as a additional source. The nitrate swing over from minimum value 9.27 ppm to maximum 58.94 ppm respectively. Which suggests their possible sources agricultural runoff. Cl values are higher in well No 7 and 8 which suggests their point sources like domestic sewage, washing of cloths etc.

The TDS concentration varies from 64ppm to 325 ppm for 19 samples in study area. which belong to the agricultural and urban areas, hence majority of the wells are suitable for drinking purpose.

#### **Inter-ionic alliances:**

Inter-ionic alliance and piper-trilinear variations of major and minor constituents in subsurface aquatic system of the study area. And identifying point and non-point sources of pollution of groundwater for better understanding and interpretation concerning transport of "pollutants". The HCO<sub>3</sub> portrays positive affiliation with Na, K and Mg in order to preference (0.59, 0.69 and 0.79). the above inferences that all these constituents are derived chiefly from common source i.e. Lithogenic. Further slightly higher value of correlation between Mg and HCO<sub>3</sub> (0.79) suggest, the weathering of olivine followed by pyroxene (augite) with K vs HCO<sub>3</sub> (0.69) further followed by orthoclase feldspar with Na vs HCO<sub>3</sub> (0.59). the Cl vs SO<sub>4</sub> (0.5) suggest, the source is derived from human activity. In addition to the above it is interesting to note that HCO<sub>3</sub> display negative affiliation with other anionic constituent like Cl to derived from non-lithogenic sources. Further followed by HCO<sub>3</sub> vs NO<sub>3</sub> is neutral indicates the diverse source.

**Table 2: Inter-ionic alliance**

	Cl	Ca	Mg	TH	Na	K	HCO <sub>3</sub>	NO <sub>3</sub>	SO <sub>4</sub>	PO <sub>4</sub>
Cl	1									
Ca	-0.34	1								
Mg	0.24	-0.60	1							
TH	0.17	-0.53	0.78	1						
pH	0.24	-0.10	-0.10	0.08						
EC	0.00	0.00	0.00	0.00						
Na	0.27	-0.70	0.32	0.49	1					
K	-0.09	-0.41	0.53	0.25	0.28	1				
HCO <sub>3</sub>	-0.12	-0.56	0.79	0.78	0.59	0.67	1			
NO <sub>3</sub>	0.00	-0.23	0.06	-0.16	0.16	0.09	0.02	1		
SO <sub>4</sub>	0.52	-0.38	0.36	0.42	0.29	-0.16	0.20	-0.10	1	
PO <sub>4</sub>	0.09	0.04	0.17	0.30	0.17	-0.20	0.24	-0.16	0.51	1

**Groundwater quality for irrigation purposes:**

Assessment of suitability of water for agricultural purpose requires consideration of the following chemical constituents:

- Total dissolved solids
- Relative proportion of Na to Ca and Mg.
- Relative proportion of HCO<sub>3</sub> to Ca and Mg, and
- Presence of toxic substances.

The quality of groundwater for irrigation also depends on the factors such as nature and composition of soil, depth of water table, topography, climate and type of crop.

In addition to this there are various other parameters that help in determining the quality of water for irrigation. These are as follows:

**Sodium Absorption Ration (SAR):**

The ability of water expel calcium and magnesium by sodium can be estimated with the aid of sodium absorption ration (SAR). High SAR value indicates the risk of displacement of the alkaline earths. It also adversely affects the soil structure.

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}}$$

The water having SAR values less than 10 are considered excellent, 10 to 18 as good, 18-26 as a fair, and above 26 are unsuitable for irrigation use (USDA, 1954). In the present study the SAR values are less than 10 to 18 are observed in all the well in the study area. The water from the study area can thus, be graded as excellent for irrigation use.

**Kelly ratio:** Kelly's ratio was calculated by using the following expression

$$\text{KR} = \frac{\text{Na}^+}{\text{Ca}^{2+} + \text{Mg}^{2+}}$$

**Table 4: Quality of Groundwater used for irrigation in the study area**

Sample No.	SAR	SP	SSP	PI	RSC	KR	TDS
1	18.06	0.6631	66.82	66.82	306.8	2.0138	325
2	24.15	0.3190	74.17	74.17	301	2.8717	244
3	13.35	0.4879	59.55	59.59	304.5	1.4725	170
4	7.026	0.3071	42.01	42.01	284.79	0.7245	192
5	15.137	0.5419	63.96	63.96	261.92	1.8644	150
6	14.457	0.5590	61.64	61.64	235.2	1.6071	316
7	10.09	0.4347	47.99	47.99	234.99	0.9229	247
8	16.30	0.6229	69.98	69.98	130.84	2.3319	120
9	17.41	0.6634	74.85	74.85	166.49	2.9774	64
10	7.07	0.3983	44.73	44.73	230.58	0.8093	268
11	7.46	0.4114	46.39	46.39	153.78	0.8654	224
12	22.60	0.6907	75.44	75.44	170.7	3.0716	112
13	2.54	0.1993	236.36	23.63	114.77	0.3095	72
14	6.127	0.3930	466.41	46.64	150.68	0.8741	91
15	8.829	0.5563	556.30	55.63	120.49	1.2538	101
16	5.889	0.4793	479.33	47.93	88.5	0.9206	62
17	5.46	0.4092	409.27	40.92	116.7	0.6928	112
18	6.340	0.4862	486.20	48.62	107.9	0.9462	52
19	6.13	0.4263	466.04	46.60	220.1	0.8728	66
<b>Max</b>	<b>24.16</b>	<b>0.6907</b>	<b>556.30</b>	<b>55.63</b>	<b>306.8</b>	<b>3.0716</b>	<b>325</b>
<b>Min</b>	<b>2.546</b>	<b>0.1993</b>	<b>42.012</b>	<b>42.01</b>	<b>88.5</b>	<b>0.3095</b>	<b>52</b>
<b>Average</b>	<b>11.28</b>	<b>0.47630</b>	<b>201.44</b>	<b>20.14</b>	<b>194.7753</b>	<b>1.4422</b>	<b>160</b>

[Note: Where all values are in ppm.]

This ratio reflects the alkali hazard of the water. If the Kelly's ratio is less than one or equal to one, water is good for irrigation. As against this, the KR values above one are considered indicative of causing alkali hazard to soils. It is observed from that most the wells are showing values above unity. Most of the wells showing the higher values lie in upper and middle stretch. This suggests that continuous use of water from these wells for irrigation may lead to alkali / sodium hazard.

#### Variations in the Kelly's ratio

<b>-KR &lt; 1</b> (No. of wells)	<b>KR &gt; 1</b> (No. of wells)
10	09

**Soluble Sodium Percentage (SSP):**

The soluble sodium percentage was calculated by using following formula:

$$SSP = \frac{Na \times 100}{Ca + Mg + Na}$$

SSP less than 50 indicates good quality of water and higher values show that the water is of unsafe quality for irrigation (USDA, 1954). It is observed from the data that in general, SSP values are higher than 50 in more than 60% samples throughout the sampling period. On the whole the quality of groundwater is inappropriate for irrigation purpose.

**Classification of groundwater's on basis of SSP.**

SSP < 50 (No. of wells)	SSP > 50 (No. of wells)
10	9

**Residual Sodium Carbonate (RSC):**

If the water contains carbonate and bicarbonate, in excess of calcium and magnesium, then it is likely to precipitate calcium displaced by exchange reaction. The result is an increase in sodium hazard of water (USDA, 1954). This excess quantity of carbonate and bicarbonate is denoted by residual sodium carbonate (RSC) and is determined by the formula:

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$$

Where, all the concentrations are expressed in epm. If RSC is less than 1.25 epm, then the water is safe for irrigation. The values between 1.25 to 2.50 epm denote that the water is of marginal quality, while those above 2.50 epm indicate that the water is unsuitable for irrigation.

**RSC values of groundwaters**

RSC < 1.25	RSC = 1.25 to 2.5	RSC > 2.5
4	10	5

Values of RSC calculated for the groundwater to shows most of the wells fall in the category of high RSC values to moderate which implies its poor quality for irrigation purpose.

**Permeability Index (PI):** Certain water constituents reduce the soil permeability. The resultant poor permeability makes it more difficult to supply crops with water for better growth. It may also add to waterlogging, soil and water salinity, growth of weed and nutritional problems. The permeability problem is evaluated by comparing the quality of sodium present in water relative to calcium and magnesium. Carbonates and bicarbonates can also affect soil permeability under certain conditions. PI is used for evaluating the quality of water for irrigation use. This is based on the solubility of salts and the reaction occurring in the soil solution from cation exchange. The PI is calculated as:

$$PI = \frac{Na + \sqrt{HCO_3} \times 100}{(Ca + Mg + Na)}$$

### Classification of groundwater for irrigation on basis of PI

Class	PI	No. of sample
Excellent	>75	Nil
Good	25-75	16
Unsuitable	<25	3

It is seen from above, that most of the wells in the category of good for agriculture use. However, these 3 wells drop in unsuitable class. It indicates that water is on the perimeter to be unsuitable for irrigation.

#### Conclusions:

The water chemistry in study area is dominantly controlled by lithology as Ca, Na, Mg and  $\text{HCO}_3$  are major ionic phases this results of piper are complimented by Gibbs plot. The water shift towards Ca+Mg- $\text{SO}_4$  (Alkaline earth, strong acid), Na+K- $\text{HCO}_3$  (Alkali metals, weak acid), Na + K- Cl +  $\text{SO}_4$  (alkali metals and strong acids) categories. The majority of water alkaline earth exceed the alkalis (Ca+Mg>Na+K) except for a few samples from study area. The study area water chemistry is governed by rock water interaction. High correlation within  $\text{HCO}_3$  and Na, K, Mg suggests its natural source of weathering of basaltic rocks. At places high levels of  $\text{NO}_3$  is observed which is the influence of agricultural activities and is supported with good correlation of  $\text{SO}_4$  and  $\text{PO}_4$  which have point source of sulphate and phosphate fertilizers. Also Cl concentration is higher in some wells which suggests its point source of domestic sewage and washing of clothes. The different indices like SAR, SP, SSP, PI, RSC, KR, and TDS were worked out for water quality for irrigation purpose this all parameters shows values within the permissible limit which suggests that water from study area is suitable for irrigation purpose also for drinking purpose except some wells.

#### Aknowlegement:

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# INFLUENCE OF VERMIWASH ON GERMINATION AND GROWTH OF RICE (*ORYZA SATIVA*) VARIETY BHOGAVATI

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## Abstract:

Vermiwash is becoming popular as alternative to conventional agricultural practices in favor of nutrient supply and pesticide properties. Vermiwash is a rich source of vitamins, hormones, enzymes, macronutrients and micronutrients when applied to plants helps in efficient growth. Vermiwash is the wash of earthworms celomic fluid and the watery extract of the bedding materials. The present study deals with the influence of vermiwash on germination and growth of rice var. bhogavati for a period of 140-160 days. Three different concentrations of vermiwash such as 1%,5%, and 10% were prepared for experiment. The parameters like germination percentage, average height, length of inflorescence and no. of seeds per inflorescence. Growth parameters were higher in 5%, and 10% of vermiwash sprayed.

**Key words:** Vermiwash, Germination, Growth, Rice

## Introduction :

Vermiwash , the extracted body fluid of earthworms is also nutrient rich with components promoting good plant growth [1]. Vermitech methods are becoming popular in modern farms as alternative to conventional agricultural practices in favor of nutrient supply and pesticide properties. Vermi technology is a technology , which uses surface and sub surface local earthworm species in composting and soil management. Vermiwash is a widely used application of vermin technology where the wash of the earthworms celomic fluid and the watery extract of the bedding materials are collected. Vermiwash is a liquid collected after the passage of water through a column of vermibed. This vermiwash is very useful as a foliar spray to enhance the plant growth yield and to check development of disease. It contains significant amount of soluble macro and micronutrients, natural growth hormones, beneficial microbes, vitamins, amino acids [2] and nematicidal properties [5]. Vermiwash is very good liquid manure and affect significantly on the growth and productivity of crop during foliar spray[6].

Vermiwash stimulates the growth and yields of crops and even develops resistance in crops. Vermiwash consist of nitrogen in the form of mucus, nitrogenous excretory substances growth stimulating hormones and enzyme [7]. It significantly influences the soil microbial biomass and has proved to be a better alternative source to Albert's solution for lettuce growth under hydroponic culture [8]. Vermiwash spray has significantly enhanced the growth and yield parameter and also flowering and fruiting ratio was increased. It has reported that vermiwash as foliar spray was effective in increasing the growth and yield response of *Anthurium* [3]. It has observed the application of vermiwash enhanced plant height, no. of leaves, spike length and no. of florets in *Gladiolus* [4].

## Materials and Methods:

**Chemicals :-** Vermiwash , 0.1% HgCl<sub>2</sub> solution.

**Plant materials :-** Rice (*Oryza sativa* L.) variety- Bhogavati.

### 1) Preparation of Vermiwash concentration:

Fresh vermiwash was taken and prepare the different concentration like control, 1%, 5% and 10%. The concentration was prepared with the help of distilled water. The prepared concentration of vermiwash were stored and used for treating the seeds of rice.

2) Pot culture experiment was followed for germination studies. Seed were purchased from farmer and were used to determine the growth of in relation to different concentrations of vermiwash. Growth parameters like germination (%), average height, length of inflorescence and no. of seeds per inflorescence of *Oryza sativa* (Rice) L. Seeds were sterilized with 0.1% HgCl<sub>2</sub> and washed with distilled water for several times and then 50 seeds are kept for germination in pots. A control was maintained with distilled water. Seedlings performance was observed day by day up to harvesting stage.

### Results and Discussion:

**Table 1: Effect of different concentrations of a vermiwash spray on germination, average height, length of inflorescence , number of seeds per inflorescence of *Oryza sativa* (Rice) L. variety Bhogavati .**

Parameters	Control	1%	5%	10%
Germination (%)	90	90	70	100
Average height of Plant (cm)	58	60	56	52
Average length of Inflorescence (cm)	8	12	15	10
Average no. of seeds per Inflorescence	12	14	16	21

The effect of different concentrations of vermiwash spray on germination, average height, length of inflorescence, number of seeds per inflorescence of *Oryza sativa* (Rice) L. variety Bhogavati were presented in table no. 1. In the present study the germination percentage was more in control, 1% and 10% respectively. The average height of plant was more in 1% and control. The average length of inflorescence was 10, 12 and 15 for 10%, 1% and 5% of vermiwash respectively. The no. of seeds per inflorescence increased than the control.

### Acknowledgment:

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# PROCESSING AND HEALTH BENEFITS OF FISH

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## Introduction:

Fish are the oldest vertebrates of the world. The first fish is supposed to be found about 500 million years ago. There are over 28,000 known species of fish found throughout the world. Fish can be kept in an aquarium as the pets or used to prepare wonderful recipes.

Fish processing in India is done almost entirely for export. Open sun dried fish and fish meal are the only major exceptions. At present India has freezing units, cold stores, ice plants, canning units and fish meal plants. Capacity of most of these, processing and storage units are small when compared to the facilities in fish processing industry in technologically advanced countries.

India ranks second in the global fresh water aquaculture production and third in total global farmed fish production. Fisheries sector contributes 2.5% of the total GDP. Fish and fish products are the traditional exquisite delicacies of all the north eastern states of India. Fish oils are named as functional foods due to the fact that they are excellent dietary sources of the important fatty acids especially polysaturated fatty acid (PUFA), EPA (Eicosapentaenoic acid) and DHA (Docosahexaenoic acid). And supplemental fish oil may be beneficial for the healthy function of the heart, brain and nervous system [1].

## Consumption rate:

The per capita consumption of fish is 14.3 kgs per year, globally. The European Union consumes 23.6 kg per capita annually and Southeast Asia 23 kg. It is expected that the per capita consumption of fish will rise to 35.9 kg in China alone and 25.8 kg per year in South East Asia. But India consumes 20.6 kg per capita annually.

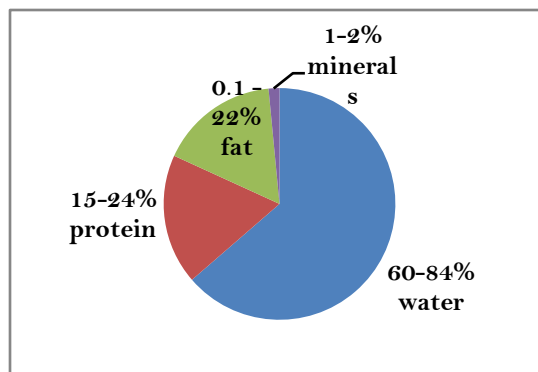
## Export rate:

In the Global Market there is a definite inclination towards India fish which is now considered as the brain food. This is a major boon for developing countries like India, which along with other Southeast Asian countries is earning more than \$33 billion annually from the export of fish. In 1990 India fish exports increased from 3.7 million tons to 5.3 million tons in 1999.

## Nutrient composition of fish:

### Classification of fish:

- Small pelagic species
- Large pelagic species
- Small demersal species
- Large demersal species



**Habitat and characteristics**

- Tropical fish
- Cold water fish
- Marine fish
- Fresh water fish

**Tropical fish:**

Are fish that live in either salt or freshwater but needs a warm (tropical) medium or temperature to live. Ex: Angelfish, catfish, rasbora, puffer fish, etc..

**Coldwater fish:**

These fish can be salt or fresh water fish which needs colder water temperatures. EX: japanesekoi, carps, etc

**Marine fish:**

These are fish that live in salty seawater. Most commonly, marine fishes need tropical climate. Ex: Star fish, lion fish, jelly fish, cuttle fish, dolphins, etc

**Freshwater fish:**

These fish live in freshwater and are usually the fish that you would find in inland rivers and streams of most continents. They can be as colorful as marine fish and yet need less care. Most freshwater fish in the ornamental hobby are tropical fish, which require a heater. Ex.: Oscar fish, betta fish, bala shark, etc.

**Small pelagic species:**

These species are very delicate spoil quickly and contain high proportion of oil with large seasonal variation. They are sold as fresh, salted, dried, fermented, smoked, and canned. A large of this group are utilized for fish meal and oil and hence they are termed as industrial fish, they occasionally form glut. e.g herring, sardines, anchovies mackerels

**Large pelagic species:**

The most important fish of this group is tuna. They reach a weight of 100kg each, the flesh is firm, with moderate amount of oil, and posses a considerable proportion of dark flesh. They are highly priced and are best suited for canning. Certain specialized cured products such as maldive fish (massmin) and katsubushi are prepared from tuna.

**Small demersal fish:**

The group include a variety of species, viz. crockers, jew fish, silver bellies, cat fish etc. they are usually bottom living species with a firm flesh, fairly low oil with little variation in quantity.

**Large demersal fish:**

They include two groups of fishes, the cartilaginous fishes like shark, skates and rays and bony fishes like jew fishes, mullet, snappers, thread fin etc. the first group is entirely utilized in salted and dried form, the bony fishes find demand in fresh form. Recently increasing quantities of demersal fish species are exported as surimi which is nothing but mechanically separated, minced, washed fish meat with cryoprotectants added.

**Fish processing:****Byproduct manufacture:****Surimi:**

Is a Japanese loan word referring to a fish-based food product intended to mimic the texture and color of the meat of lobster, crab and other shellfish. It is typically made from white-fleshed fish (such as pollock or hake)

that has been pulverized to a paste and attains a rubbery texture when cooked. The term is also commonly applied to food products made from lean meat prepared in a similar process. Surimi is a much-enjoyed food product in many Asian cultures and is available in many shapes, forms, and textures. The most common surimi product in the Western market is imitation or artificial crab legs. Such a product often is sold as *sea legs* and *krabin* America, and as seafood sticks, crab sticks, fish sticks or seafood extender in Commonwealth nations.

#### **Fish glue:**

Animal glue is an adhesive that is created by prolonged boiling of animal connective tissue. These protein colloid glues are formed through hydrolysis of the collagen from skins, bones, tendons, and other tissues, similar to gelatin. The word "collagen" itself derives from Greek *kolla*, glue. These proteins form a molecular bond with the glued object.

#### **Fish emulsion:**

Fish emulsion is a fertilizer emulsion that is produced from the fluid remains of fish processed for fish oil and fish meal industrially. Since fish emulsion is naturally derived, it is considered appropriate for use in organic horticulture. In addition to having a typical N-P-K analysis of 5-2-2, fish emulsion adds micronutrients.

#### **Fish hydrolysate:**

Fish hydrolysate, in its simplest form, is ground up fish carcasses. After the usable portions are removed for human consumption, the remaining fish body, which means the guts, bones, cartilage, scales, meat, etc., is put into water and ground up. Some fish hydrolysate is ground more finely than others so more bone material is able to remain suspended. Enzymes may also be used to solubilize bones, scale and meat. If the larger chunks of bone and scales are screened out, calcium or protein, or mineral content may be lacking in the finished product form. If purchasing fish hydrolysate for agricultural applications, one should look at the label carefully for the concentration of mineral elements in the liquid. Some fish hydrolysates have been made into a dried product, but most of the oil is left behind in this process, which means a great deal of the fungal-food component would be lacking.

#### **Fish sauce:**

Fish sauce is a condiment that is derived from fish that have been allowed to ferment. It is an essential ingredient in many curries and sauces. Fish sauce is a staple ingredient in Filipino, Vietnamese, Thai, Lao, and Cambodian cuisine and is used in other Southeast Asian countries. In addition to being added to dishes during the cooking process, fish sauce can also be used in mixed form as a dipping condiment, and it is done in many different ways by each country mentioned for fish, shrimp, pork, and chicken. In parts of southern China, it is used as an ingredient for soups and casseroles. Fish sauce, and its derivatives, imparts an umami flavor to food due to their glutamate content.

#### **Isinglass:**

Is a substance obtained from the dried swim bladders of fish. It is a form of collagen used mainly for the clarification of wine and beer. It can also be cooked into a paste for specialized gluing purposes.

Isinglass was originally made exclusively from sturgeon, especially Beluga sturgeon, until the 1795 invention by William Murdoch of a cheap substitute using cod. This was extensively used in Britain in place of Russian isinglass. The bladders, once removed from the fish, processed and dried, are formed into various shapes for use. Eggs to be preserved whole in the shell should be clean and dry.

Storing in isinglass: The eggs are layered point down in an earthenware crock or glass jar. The cooled liquid is poured over the eggs, ensuring the top layer of eggs is completely submerged, and then covered for cleanliness and prevent evaporation. Eggs stored thus will keep from six months to a year, but they should be used for baking or made dishes as they have a slight taste if boiled or poached and the shells will crack if boiled. After six months the whites become thin, so they are not suitable for whipping.

**Tatami Iwashi :**

Is a Japanese processed food product made from baby sardines or *shirasu* laid out and dried while entwined in a single layer to form a large mat-like sheet. Typically, this is done by drying them in the sun on a bamboo frame, a process that is evocative of the manufacture of traditional Japanese paper.

Tatami Iwashi can then be cut to various sizes and used in different ways. Common serving styles include use as an ingredient in soup or cut into small pieces for use as a snack or accompaniment to sake or beer drinking, known as sakana. This food item is named for its resemblance to a straw tatami mat common in traditional Japanese-style rooms or houses.

**Fish meal:**

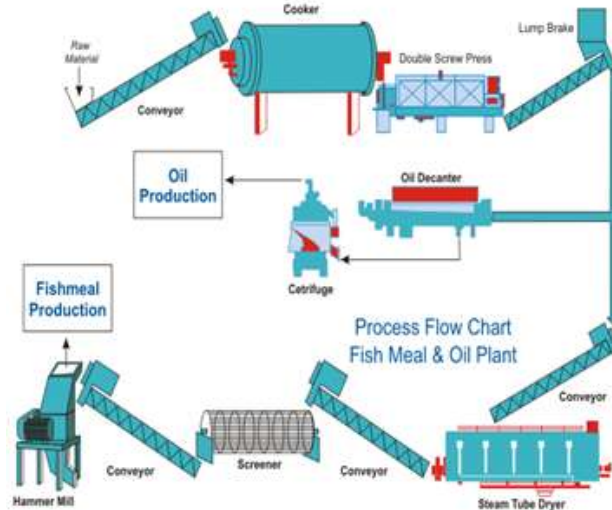
Fishmeal is a commercial product made from both whole fish and the bones and offal from processed fish. It is a brown powder or cake obtained by rendering pressing the cooked whole fish or fish trimmings to remove most of the fish oil and water, and then ground. What remains is the "fishmeal". The major use of fish meal is as a high-protein supplement in aquaculture feed. The main producing countries in 2004 were Peru, Chile, China, Thailand, USA, Japan and Denmark. Worldwide production is about 6.3 million tons annually. Fish meal differs from fish hydrolysate in that the hydrolysate form has the oil and the protein included in the product.

**Fish oil:**

Is oil derived from the tissues of oily fish. It is recommended [1] for a healthy diet because it contains the omega-3 fatty acids, eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA), precursors to eicosanoids that reduce inflammation throughout the body. Fish do not actually produce omega-3 fatty acids, but instead accumulate them from either consuming microalgae that produce these fatty acids, as is the case with fish like herring and sardines, or, as is the case with fatty predatory fish, by eating prey fish that have accumulated omega-3 fatty acids from microalgae. Such fatty predatory fish like mackerel, lake trout, flounder, albacore tuna and salmon may be high in omega-3 fatty acids, but due to their position at the top of the food chain, these species can accumulate toxic substances (see biomagnification). For this reason, the FDA recommends limiting consumption of certain (predatory) fish species (e.g. albacore tuna, shark, and swordfish) due to high levels of toxic contaminants such as mercury, dioxin, PCBs and chlordane.<sup>[2]</sup> More than 50 percent of the world fish oil production is fed to farmed salmon [3].

**Fish Meal and Fish Oil Processing:**

The fish is first cleaned with fresh water in a tank and are put into a hopper of the first conveyor, which carries the fish to a continuous cooker. The fish is steam cooked in the cooker. The cooker then empties the cooked fish into a Double Screw Press, which squeezes the steamed fish. The discharged sticky fluid and its solids come out through two different outlets. The sticky liquid is pumped to a tank for settling. The water content settles down due to its higher specific gravity and oil that floats above is pumped out. The settled oil is thereafter pumped into barrels. The fish cake is then carried to the Steam Tube Dryer through the second conveyor to the Lump brake then carries to the Dryer with third Conveyor and it is dried through Steam Tube Drier. The dried fish meal is then carried through the fourth conveyor to the Screener. After Screening dried fish meal is carried to the Hammer Mill through the Fifth conveyor. The cake is hammered to the required size and then it is packed in polythene lined jute bags. Since the manufacturing process is automatic it's very simple to operate. The entire plant can be managed by seven labour force and one office staff per shift.



### Fish canning:

1. Pre cooking method
2. Raw packing method

Fish processing includes both the canning of fish for human consumption and the production of fish byproducts such as meal and oil. Either a precooking method or a raw pack method can be used in canning. In the precooking method, the raw fish are cleaned and cooked before the canning step. In the raw pack method, the raw fish are cleaned and placed in cans before cooking. The precooking method is used typically for larger fish such as tuna, while the raw pack method is used for smaller fish such as sardines. The byproduct manufacture segment of the fish industry uses canning or filleting wastes and fish that are not suitable for human consumption to produce fish meal and fish oil.

### Pre cooking method:

The precooking method of canning begins with thawing the fish, if necessary. The fish are eviscerated and washed, then cooked. Cooking is accomplished using steam, oil, hot air, or smoke for 1.5 to 10 hours, depending on fish size. Precooking removes the fish oils and coagulates the protein in the fish to loosen the meat. The fish are then cooled, which may take several hours. Refrigeration may be used to reduce the cooling time. After cooling, the head, fins, bones, and undesirable meat are removed, and the remainder is cut or chopped to be put in cans. Oil, brine, and/or water are added to the cans, which are sealed and pressure cooked before shipment.

### Raw packing method:

The raw pack method of canning also begins with thawing and weighing the fish. They are then washed and possibly brined, or "nobbled", which is removing the heads, viscera, and tails. The fish are placed in cans and then cooked, drained, and dried. After drying, liquid, which may be oil, brine, water, sauce, or other liquids, is added to the cans. Finally, the cans are sealed, washed, and sterilized with steam or hot water.

### Traditional methods:

The traditional seafood processing methods include salting, drying, smoking, pickling, marinating and fermentation. These are confined to particular reason and are evolved out of necessity making use of local seasonal surplus, all these methods are time tested and perfected over generations. Many processes are unchanged for sanctuaries. They are important in saving sea foods from losses and are low cost simple processes, labour intensive and suitable for small scale operations. The problems with traditional technologies are low productivity

involving more effort and time and sometimes have limited storage life. The sanitation and hygiene standards are poor and lack R and D efforts.

#### **Salting:**

Involve mixing fish and salt and resting for period of time. Both salt crystals and salt solution may be used. During the process some water is removed from the fish, reducing the water activity, (a measure of the water available to biological reactions) as the salt concentration increases, the action of spoilage bacteria are reduced, salting of sea foods is used mainly in combination with drying. Quality of salt, salt to fish ratio, freshness and fat content and thickness of fish decides the salting duration and quality of final product.

#### **Drying:**

Involve removing water from seafood's. Process is simple, common in tropical countries. They are particularly suited to low income group. Simple improvements such as use of drying racks raised above the ground level can increase drying rates and reduce contamination and make products of good quality. Mechanical dryers are relatively expensive to operate, considerable interest has been shown in solar drying of fish. The principle is simple; air gets heated as it flows over black surface. During certain times, when sun drying is not possible agro waste dryers have been tested to dry fish by burning agricultural by-products e.g. rice coconut husks

In tropical climates salted and dried fish are suitable to various types of spoilage of which pink discoloration due to growth of halophilic bacteria. Insect infestation and mould growth are common problems. Use of chemical additives are not viable commercially, upgrading hygiene and sanitation at every stage reduce quality problems in cured sea foods.

#### **Smoking:**

A combination of salting, drying and smoking preserves smoked fish, the application of smoke imparts color and distinctive flavor, based on the temperature during the process they are conventionally classified into hot and cold smoking, the types of smoked products is specific to region. The presence of 3, 4 benzopyrene, a polynuclear hydrocarbon in smoked products are of much concern, hence liquid smoke after condensing the smoke components are relatively safe.

#### **Pickling:**

Pickling, also known as brining or corning is the process of preserving food by anaerobic fermentation in brine (a solution of salt in water) to produce lactic acid, or marinating and storing it in an acid solution, usually vinegar (acetic acid). The resulting food is called a *pickle*. Seafood may be selected from the group consisting of the crustacea, the mollusks and fish.

#### **Marinades:**

The preservation of small fishes in a mixture of acetic acid and salt. This imparts characteristic flavor. The three varieties of marinades are cooked, fried and spiced.

#### **Freezing:**

This method of preservation enable sea food to be kept in condition closed to that of fresh sea food for any longer periods enabling sea foods to be distributed and sold in distant markets. The freshness of fish, rapid freezing, use of right packaging and good frozen storage practice provide a superior quality frozen product. However certain changes due to interaction of protein, water, lipid, salts and formaldehyde results in changes in texture referred as denaturation. Fatty fishes are less stable than lean fishes and fresh water fish keep longer than marine species under similar conditions. The use of certain chemical preservatives such as sulphites and phosphates keep the deteriorative changes in check.

**Health aspects of fish:****Heart Disease:**

According to the American Heart Association (AHA), clinical trials have proved that omega 3 is effective in reducing the incidence of cardiovascular diseases (CVD). Fish oil, which is abundant in omega 3, therefore, reduces the risk of heart diseases and heart arrhythmias. It lowers the levels of LDL cholesterol, which is bad cholesterol, and increases the HDL levels, which is good cholesterol. Fish oil prevents accumulation of triglycerides and further reduces the levels of excess triglycerides. Preliminary research has also shown that fish oil can be used for preventing atherosclerosis in coronary patients. Thus fish oil is effective in treating heart strokes and regular usage of fish oil can help avoid numerous sudden cardiac deaths. According to the American Heart Association, these preliminary findings should be confirmed by detailed research.

**Weight Loss:**

Fish oil also aids in weight loss process. Research conducted by Professor Peter Howe at the University of South Australia has shown that fish oil improves the efficacy of exercise in reducing weight. Volunteers who were given fish oil diet showed greater weight loss as compared to those who did not consume fish oil diet. Exercise combined with fish oil had a positive effect on the body shape and body composition of the patients.

**Blood Circulation:**

It is believed that fish oil has the ability to improve blood circulation along with reducing triglyceride and serum cholesterol levels.

**Immunity:**

It is believed that regular consumption of fish oil aids in increasing your immunity thereby enabling you to resist incidence of common diseases such as cold, cough and flu. Omega-3 fatty acids present in fish oil benefit the immune system by effecting cytokines and eicosanoids present in our body. Researchers have also studied the effect of fish meal and fish oil on the immune system of pigs and found that fish oil aided in the growth of the animals. Similar research conducted on mice at Taichung Veterans General Hospital, Taiwan, also gave positive results. Thus fish oil has the potential to enhance the immune system of humans. Fish oil is also beneficial to patients suffering from lupus, which is a disease characterized by the attacks of immune system of the body on various organs and tissues. Fish oil helps in reducing the pain and inflammation that may occur in joints, eyes, kidney, heart, blood vessels, lungs, nerves, etc. It also helps in reducing associated fever, skin rashes and fatigue.

**Inflammation:**

Fish oil has anti inflammatory properties; therefore, it is effective in reducing inflammation in blood and tissues. Regular consumption of fish oil supplements, tablets, pills and capsules is helpful to those suffering from chronic inflammatory diseases. Fish oil is effective in treating gastrointestinal disorders, sprue, short bowel syndrome and inflammatory bowel disease (IBD) including Crohn's Disease and ulcerative colitis, which are typical disorders of the intestine. Patients suffering from Crohn's disease find it difficult to absorb vitamins, fats and essential supplements. Fish oil supplements are an effective diet for such patients. In ulcerative colitis, fish oil prevents the accumulation of leukotriene on the colon. It should be noted that the anti inflammatory properties of fish oil are limited to reducing inflammation. Fish oil provides little effect in preventing inflammation. Research is also being conducted to enhance the anti-inflammatory action of fish oil by addition of other dietary supplements and drugs.

**Eye Disorders:**

It is well known that fish oil is good for its ability to improve vision. It also helps in avoiding age related macular degeneration. The National Eye Institute at the National Institute of Health, US, plans to conduct a nationwide study to evaluate the effect of fish oil in treating macular degeneration. This study will provide strong scientific

evidence to the benefits of fish oil for eye care, thereby enabling government agencies and physicians to strongly recommend fish oil for macular degeneration.

#### **Skin Care:**

Fish oil helps in improving the condition of poor and dry skin by making it shiny and glowing. It is useful in treating various skin problems such as eczema, psoriasis, itching, redness of skin, skin lesions, and rashes. In case of psoriasis, the EPA present in fish oil restricts the growth of pro-inflammatory agents by producing arachidonic acid. Fish oil can also be applied topically to obtain relief from psoriasis. Regular intake of fish oil capsules helps in reducing loss of moisture from the skin. It is also claimed by some people that fish oil helps in preventing sunburns.

#### **Acne:**

Fish oil is effective for acne as well. EPA is known to inhibit androgen formation. Androgen can affect the formation of sebum in hair follicle.

#### **Hair Care:**

Fish oil helps maintain a good luster of the hair. Omega-3 has hair growing properties as it provides nourishment to the follicles. It therefore aids in faster development of hair and preventing hair loss. A good supply of proteins is also necessary for hair growth. Since most fish varieties are rich in protein, eating fish helps in keeping healthy hair.

#### **Pregnancy:**

Fish oil is very useful for pregnant women as DHA present in it helps in the development of the eyes and brain of the baby. It helps in avoiding premature births, low weight at birth, and miscarriage.

#### **Depression and Anxiety:**

Due to the presence of Omega 3 fatty acids, fish oil is good for relieving depression, sadness, anxiety, restlessness, mental fatigue, stress, decreased sexual desire, suicidal tendencies and other nervous disorders. Researchers at the Case Western Reserve University School of Medicine, Cleveland, Ohio in their research publication titled “Fish Oils and Bipolar Disorder: A Promising but Untested Treatment” state that fish oil can be useful in mood stabilizing and treating bipolar disorders. No wonder, it has been found that countries where fish is eaten often have low incidence of depression. Similarly research conducted on prisoners has shown that when prisoners were fed with sea food containing higher amount of Omega-3 fatty acids, there was a significant drop in the homicide rate.

#### **Alzheimer’s disease:**

Research conducted at the Louisiana State University has shown that fatty acids are effective in treating Alzheimer’s disease. Since fish oil is one of the best sources of essential fatty acids including EPA and DHA, it helps in Alzheimer disease. Research conducted at the University of California at Los Angeles (UCLA) validates the usefulness of fish oil as a possible remedy for the disease. The Alzheimer’s Association recommends fish containing higher content of omega-3 fatty acids to patients as it acts as a protective diet during Alzheimer disease and dementia.

#### **Arthritis:**

Fish oil is useful in treating arthritis, rheumatism, Raynaud’s symptoms and similar conditions. Usage of fish oil can help reducing the dosage of NSAIDs (non-steroidal anti-inflammatory drugs). The Royal Adelaide Hospital, Australia, and University of Newcastle, Australia have reported that large quantities of fish oil have shown positive effect on the treatment of arthritis. In case of osteoarthritis, fish oil can be helpful in reducing the impact of enzymes that destroy cartilages. However, since the dosage of fish oil required for desirable effect in the improvement of a patient is unknown, the Arthritis Center, Department of Rheumatology, John Hopkins University, considers including omega 3 fatty acids and fish oil in the treatment of arthritis as controversial. The University also

cautions that there may appear certain side effect due to the use of fish oil in arthritis patients. Read more about arthritis on the webpage of Arthritis Foundation and Arthritis Center.

### Dosage of Fish Oil Supplements

Essential fatty acids comprise a family of long chain of polyunsaturated fatty acids — Eicosapentaenoic acid (EPA), Docosahexaenoic acid (DHA), and Alpha lenolenic acid (ALA). Of the three ALA is the parent. These essential fatty acids can be provided only through diet as your body cannot make them.

The amount of EPA and DHA present in a supplement decide the dosages for that supplement. It is also a point of major difference between a good quality and a lower quality supplement.

**A high-end supplement** provides a higher concentration of these acids while lower-end, cheap supplement provide you with lesser concentration of these acids. Optimum dosages of the acids are 2 to 4 grams of EPA/ DHA.

**A lower-end supplement** of 1 gram of fish oil will provide you with just 180 mg of EPA and 120 mg of DHA and the rest of it is a complex of other marine minerals and vitamins.

Therefore, to get the required dosage of omega 3, you will have to pop up around 10 such pills, which can cause burping, diarrhea and other side effects. On the other hand, a good quality fish oil supplement, such as **Omega Daily™** will provide 600 to 850 grams of EPA/ DHA per capsule.

### Side Effects of Fish Oil Supplements:

The following are some of the most common fish oil side effects that may occur under specific conditions:

- **Allergy** – It is a common side effect in people with the history of hypersensitivity to fish and fish products.
- **Bleeding** – It is associated with a reduced clotting response in blood, when very high dosages of fish oil supplements are taken.
- **Warfarin and Heparin associated risks** – Fish oil supplements should not be taken along with these drugs as these are blood thinning drugs used to retard clotting in blood vessels.
- **Gastrointestinal upset** – It is associated with self-limiting diarrhea, occasional burping, and indigestion in some people, but with improved processing techniques this has significantly reduced.
- **Low blood pressure** – It is associated with acute low blood pressure when taken along with other low blood pressure medications and should be avoided.

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# CAUSES, EFFECTS AND CONTROL MEASURES OF EUTROPHICATION

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## **Introduction:**

Water is the life of every living organism. It is transparent, tasteless, odorless, colourless chemical substance, which is main constituent on earth's stream, lake, ocean and main constituent of living organism. The gaseous state of water is steam or water vapor. Fishing, Agriculture, food processing, chemical industry, power plants, etc., are totally dependent on water hence plays an important role in world economy. From biological standpoint, water has many distinct properties which are very important for all metabolic activities and proliferation of life. The earliest life form appeared in water, nearly all fish life live exclusively in water and there are many types of marine mammals. Plant in the form of algae grows in the water and is the basis for some under water ecosystem. Water can become polluted by a number of sources, ranging from sewage treatment plants and factories to mining activities, paved roads and agricultural runoff, according to the U.S. Environmental Protection Agency. Water pollution has a wide variety of effects on plant life and on the environment in general. Pollution in water not only harms plant growth but also allows plants to absorb dangerous chemicals from the water and pass them on to animals that rely on them for survival. Water pollution can have dire consequences for plants, animals and even ecosystems as a whole. The specific effects vary depending on what pollutants enter the environment. Sometimes, water pollution causes an explosion of new plant growth by providing necessary nutrients and food. Other times, it can harm or kill plants by changing growing conditions, such as by raising or lowering the environment's acidity.

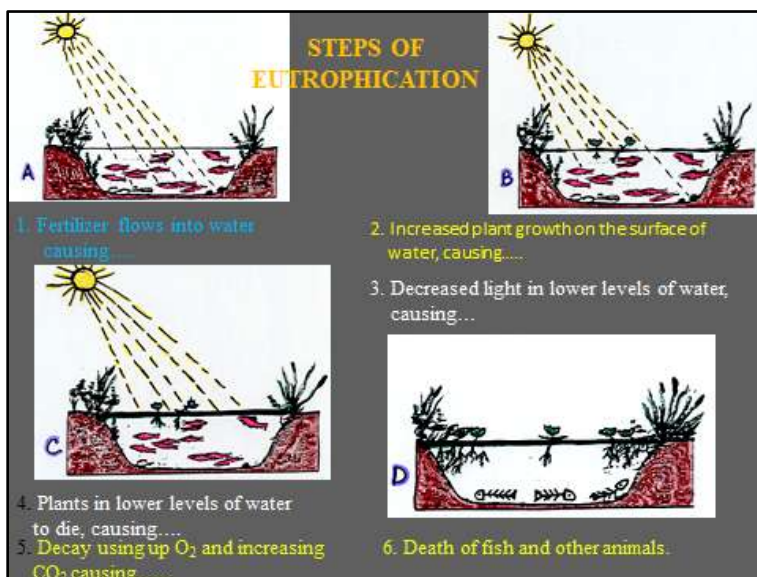
## **Eutrophication:**

Harmful changes in water caused by too much fertilizer or nutrients getting into aquatic ecosystems. An increase in nitrogen concentration in coastal water obtains leads to low oxygen (hypoxia) or no oxygen (anoxia) in bottom waters are due to the decomposition of algal blooms. Eutrophication is also a cause of the loss of diversity in the sea floor community (including corals, sea weeds, sea grasses), and among planktonic organism. Planktonic algae are the basis of marine food webs and a change in the dominant species can have a domino effect throughout the food web. In cases where nuisance algae come to dominate the algal community, toxic or nuisance algal blooms result. Over-enrichment of nutrients appear to be at least partly to blame for the more frequent occurrences of nuisance algal blooms and the resulting extensive die-offs of fish and shellfish in estuaries and coastal waters.

## **Steps of Eutrophication:**

1. Oligotrophic lake with a low level of nutrients.
2. Artificial input of nutrients from run-off and discharge of effluent.
3. Eutrophic lake with a high level of nutrients. Nitrogen and phosphorus are usually the bio-limiting element in freshwater lakes.
4. Rapid growth of algae and other biomass resulting in a decrease in the concentration of dissolved oxygen.

5. Turbidity (cloudiness) of water increases as does rate of sedimentation.
6. Increased growth of rooted plants such as reeds.
7. Algal blooms during the summer months. Note that dissolved oxygen levels are at their lowest at night when plants respire rather than undergo photosynthesis.
8. Development of anoxic conditions and release of noxious gases such as hydrogen sulphide and ammonia.



**Figure 1: Process of eutrophication**

### **Eutrophication is a natural process!**

However, humans in their everyday activities can exacerbate the process: point sources (can locate the cause) are sewage treatment plant discharges, storm sewer discharges and industrial discharges as well as non-point sources (can't locate the cause, it's everywhere) are fertilizers and atmospheric deposition.

### **Fertilizers:**

Fertilizers are used by farmers and homeowners to maintain and improve the quality of crops and garden plants; increased use of fertilizer has caused concern about pollution of lakes and groundwater. Excessive use of fertilizer may not only harm the environment – specially ground and surface water but may in fact result in injury to crop plants. The chemicals are runoff in lakes by rainwater. Water with over 10 parts per million nitrate-nitrogen can cause methemoglobinemia and inability to use oxygen in infants. The nutrient phosphorus harms clear- free water by creating algal blooms turns the water green, clouds the water cause odour problems and depletes the oxygen for fish and other species, effectively suffocating them.

### **Atmospheric deposition:**

Addition of excess nutrients from a variety of sources results in the rapid aging of aquatic ecosystems. During this process the species composition of the aquatic community changes. Atmospheric deposition occurs when unwanted materials like, discharge of domestic and industrial effluent wastes, leakage from water tanks, marine dumping, radioactive waste, domestic waste enter into water. Heavy metals that dispose of and industrial waste can accumulate in lakes and river, providing harmful to humans and animals. Toxins in industrial waste are

the major cause of immune suppression, reproductive failure and acute poisoning; infective disease, like cholera, typhoid fever, gastroenteritis, diarrhoea, vomiting, skin and kidney problems are spreading through polluted water. Deposited pollutants are killing sea weeds, mollusks, marine birds, fishes, other sea organisms that serve as food for human.

#### **Effects of Eutrophication:**

- i. an excessive nutrients in water bodies promote plant growth and decay (mainly in algae and plankton) which leads to a drop in water quality, disruption of the natural ecosystem, e.g. lack of oxygen for shellfish and marine life (causing a drop in their population). This happens because of algal shading, which is an effect of eutrophication that prevents marine plants from receiving enough sunlight to photosynthesize. The amount of dissolved oxygen thus decreases and many marine animals cannot survive (which is what is happening in the Barnegat Bay Watershed in the USA and the Baltic Sea).
- ii. Decrease in the recreational and aesthetic value of water bodies.
- iii. Health problems when it occurs in drinking water reserves.
- iv. Coral reef declines; coral reefs are important as they provide habitats for marine life (which much of the ecosystem depends on) and protect the shore from erosion by storm waves however, they are the most nutrient-sensitive of all habitats, requiring the lowest external inputs to trigger eutrophication. This can lead to the death of coral reefs and thus endanger marine reef life.

#### **What are algae blooms?**

Chlorophyll (an indicator of algae presence) concentrations of more than 40 micrograms per liter are called an “algal blooms”. Under certain conditions, several species of true algae as well as the cyanobacteria are capable of causing various nuisance effects in fresh water, such as excessive accumulations of foams, scums, and discoloration of the water. When the numbers of algae in a lake or a river increase explosively, an algal "bloom" is the result. Lakes, ponds, and slow-moving rivers are most susceptible to blooms.

Algal blooms are natural occurrences, and may occur with regularity (e.g., every summer), depending on weather and water conditions. The likelihood of a bloom depends on local conditions and characteristics of the particular body of water. Blooms generally occur where there are high levels of nutrients present, together with the occurrence of warm, sunny, calm conditions. However, human activity often can trigger or accelerate algal blooms. Natural sources of nutrients such as phosphorus or nitrogen compounds can be supplemented by a variety of human activities.

#### **Harmful algal blooms:**

Harmful algal blooms commonly occur as surface scums and “blooms.” Harmful algal blooms can appear quickly and form ugly floating mats of various colors, or they can discolor the water. They can also have a pungent, foul odor while it is estimated most blooms are toxic, it is difficult to predict exactly when or even if a bloom is producing toxins. Most occur in warm, still or slow moving, green-water lakes during summer and early fall months. They are often found in farm dams or ponds where very little mixing occurs, allowing warm water layers to form near the surface. It takes a few days to sample blooms and test them for toxicity, and by that time the toxicity may have changed. Furthermore, the harmful effects of blooms may even occur when a surface scum is not visible.

Though many types of algae can form blooms, harmful algal blooms in lakes and other freshwaters have the ability to produce toxins that are dangerous to other organisms, including humans and aquatic life such as fish.

Harmful algal blooms are formed by certain types of photosynthetic organisms called cyanobacteria or blue-green algae.



**Figure2: Algal blooms in river Pus**

Blooms that occur in drinking water sources can produce compounds that lead to toxicity as well as taste and odor problems. Toxicity can even occur in drinking water without taste and odor compounds. Depending on the region, harmful blooms can be a significant concern if drinking water comes from reservoirs or natural lakes.

#### **Identification of harmful algal blooms:**

The need for rapid identification of the blooming algal species would be most beneficial. Mass spectrometry methods are able to identify and characterize microorganisms with accuracy and speed. The spectral fingerprinting allowed rapid identification of the species. The protein profiles can be used as a reference for quickly identifying an algal bloom species in the future. One benefit of using this method is the quick identification between toxic and nontoxic algal blooms.

#### **Health Concerns:**

The toxins produced by harmful algal blooms are a concern for human health. Toxins are produced within the cells and remain there until the cells break open, which may lead to the unpredictable toxicity of blooms. Water treatment processes can sometimes remove cyanobacteria and the toxins they produce although sometimes further steps are necessary because certain toxins are more difficult to remove than others. Toxins can also break down naturally in lakes. The World Health Organization (WHO) says that 100,000 cells/mL is a moderate human health risk, but there are currently no standards for cell or toxin concentrations in the United States. The most common toxin is called microcystins. There are at least 60 different types of microcystins, and their toxicity can vary significantly. The WHO standard for microcystin-LR in drinking water is 1.0 $\mu$ g/L, but there are no similar standards for waters in the United States. Other toxins found in harmful algal blooms include nodularin, anatoxins, lyngbya, and cylindrospermopsis. Nodularin are similar to microcystins and have the same effects. Anatoxins are usually more toxic than microcystins, and saxitoxins, the cause of paralytic shellfish poisons, are highly poisonous. Lyngbya toxin and aplysiatoxins are both carcinogenic, and lyngbya toxin causes seaweed dermatitis. Cylindrospermopsis is most harmful to the liver, but other organs may also be damaged by it.

#### **Controlling of Algal Blooms:**

Repeated episodes of algal blooms can be an indication that a river or lake is being contaminated, or that other aspects of a lake's ecology are out of balance. While cyanobacterial blooms receive the most public and

scientific attention, the excessive growth of other algae and other aquatic plants also can cause significant degradation of a lake or pond, particularly in waters receiving sewage or agricultural runoff. Aquatic biologists and other water-quality specialists often are called to identify the causes and recommend management steps to reduce or control the problem.

However, prevention of a problem is always better than trying to fix the problem after it happens. Controlling agricultural, urban, and stormwater runoff; properly maintaining septic systems; and properly managing residential applications of fertilizers are probably the most effective measures that can be taken to help prevent human-induced fresh-water algal blooms. Some of the techniques used to control or remove blooms can increase the water's toxicity, such as the use of algaecides. They may also be detrimental to organisms other than cyanobacteria and are generally not recommended. The most effective method to reduce blooms is through broad community effort to reduce nutrient loading into lakes. This is most often achieved through reducing the input of phosphorus, as well as nitrogen in a more limited extent. Though cyanobacteria are found in some of the oldest fossils and are natural to aquatic habitats, harmful algal blooms are increasing in frequency in the United States and across the world and are becoming more of a problem as eutrophication increases.

### **Solutions to Eutrophication:**

The eutrophication problem can be solved by reducing the external load of nutrients or directly manipulating the water body ecosystem. Different solutions for the problem of eutrophication are being analysed or are already applied. A list of common ways to decrease the problem of eutrophication is: (i) Nutrients limitation, (ii) algae filtration, (iii) ultrasonic irradiation.

An alternative, generally more expensive technique is to remove the sediment entirely, thus both taking away the internal source of phosphorous and deepening the lake. Other technique experimented in the past to prevent the recycling of nutrients or to accelerate the outflow of nutrients have included sealing lake bottoms with polyethylene sheeting, selectively discharging hypolimnetic water in water supply reservoirs, or diluting with water from an oligotrophic sources.

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# MANGO PEELS - A POTENTIAL SOURCE OF NUTRIENTS IN THE FOOD

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## Abstract:

India is the largest producer of mango which is a seasonal fruits. The fruit finds its way to the food processing industry where several products are made out of it but the peels only form a part of waste despite the fact that it is a good source of nutrients and antioxidants and can be used as natural preservative in ready to eat products. Use of ready to eat food products has increase drastically in the recent few years and to increase the shelf life of these products the use of synthetic antioxidants has gone up. Several studies have thrown light on the ill effects of synthetic antioxidant demonstrating the need for natural antioxidants. There is a need to find a natural source of antioxidant which would be cheap and would also enhance the nutritional value for the food product. Mango peels is probably a good answer to the question.

**Keywords :** Mango peel, cookies, ready to eat foods, antioxidant

## Introduction:

Mango (*Mangifera indica*) belonging to the family of *Anacardiaceae*, is one of the most important tropical fruit and India ranks first among the world's mango producing countries accounting to about 52 % of world's mango production. In India, about 1500 varieties are grown with 1000 commercial varieties. Table 1 shows the list of various varieties (state wise) grown in India. It is rich source of antioxidants, including ascorbic acid, beta carotenoid and phenolic compound. Flavonol and xanthone glycosides as well as gallotannins and benzophenone derivatives have been demonstrated to be present mainly in the peels, though pronounced inter- varietal differences have been observed in terms of quantitative composition of these compounds [1].

As mango is a seasonal fruit, about 20 % of fruits are processed for products such as puree, nectar, leather, pickles and canned slices, among others, which have worldwide popularity. During processing of ripe mango, peel is a major by-product and several tons of mango wastes are produced annually from factories. Peels contribute to 15 – 20 % of the fruit [2]. Mango peel is not currently utilized for any commercial purposes and is discarded as a waste, becoming a source of pollution [3]. Researchers feel that this waste should be treated as a specialized residue due to high levels of phenolics, flavonoid and beta carotene content. Ajila *et al.* [4] reported that mango peel contains a number of valuable compounds such as polyphenols, carotenoids, enzymes and dietary fibre. U.S. Patent application US 2002/0187239 A1 have proposed the use of mango by-products as a source of nutritional constituents [5] observed that the higher antioxidant activity of the peel was related to the higher content of antioxidant compounds in comparison to other parts of the fruit. Bound polyphenolic and flavonoid contents were in the range of 8.1–29.5 and 0.101–0.392 mg/g, respectively, and were found to be more in ripe peel than in raw peel. Gallic, protocatechuic and syringic acids were the bound phenolic acids, and kaempferol and quercetin were the major flavonoids of the peels of Raspuri and Badami varieties. Kalpna [6] also reported that mango peel showed best antioxidant capacity may be because of its higher phenolic content which normally is the major determinant of antioxidant potential of food plants. Therefore, mango peel may become important as a cheap and noticeable natural source of compounds with health protective potential, which can be used in pharmaceutical, nutraceutical and food preparation. Kim *et al.*

[7] noted that the mango peels exhibited good antioxidant activity by effectively scavenging various free radicals, such as DPPH radicals, hydroxyl radicals and alkyl radicals.

**Table 1: Varieties of mango grown in India (state wise)**

State	Varieties grown
Andhra Pradesh	Allumpur Baneshan, Banganapalli, Bangalora, Cherukurasam, Himayuddin, Suvernakha, Neelum, Totapuri
Bihar	Bathua, Bombai, Himsagar, Kishen Bhog, Sukul, Gulab Khas, Zardalu, Langra, Chausa, Dashehari, Fazli, <i>desi</i>
Goa	Fernandin, Mankurad
Gujarat	Alphonso, Kesar, Rajapuri, Vanraj, Jamadar, Totapuri, Neelum, Dashehari, Langra
Haryana	Dashehari, Langra, Sarauli, Chausa, Fazli, <i>desi</i>
Himachal Pradesh	Chausa, Dashehari, Langra
Jharkhand	Jardalu, Amrapalli, Mallika, Bombai, Langra, Himsagar, Chausa, Gulabkhas, <i>desi</i>
Karnataka	Alphonso, Bangalora, Mulgoa, Neelum, Pairi, Baganapalli, Totapuri
Kerala	Mundappa, Olour, Pairi, <i>desi</i>
Madhya Pradesh	Alphonso, Bombay Green, Langra, Sunderja, Dashehari, Fazli, Neelum, Amrapalli, Mallika, <i>desi</i>
Maharashtra	Alphonso, Mankurad, Mulgoa, Pairi, Rajapuri, Kesar, Gulabi, Vanraj
Orissa	Baneshan, Langra, Neelum, Suvarnakha, Amrapalli, Mallika, <i>desi</i>
Punjab	Dashehari, Langra, Chausa, Malda, <i>desi</i>
Rajasthan	Bombay Green, Chausa, Dashehari, Langra, <i>desi</i>
Tamil Nadu	Banganapalli, Bangalora, Neelum, Rumani, Mulgoa, Alphonso, Totapuri
Uttar Pradesh	Bombay Green, Dashehari, Langra, Safeda Lucknow, Chausa, Fazli, <i>desi</i>
West Bengal	Bombai, Himsagar, Kishen Bhog, Langra, Fazli, Gulabkhas, Amrapalli, Mallika, <i>desi</i>

Source: Bouayed and Bohn [24]

In another study the peel of mango showed the highest values of bioactive compounds and antioxidant capacity [8]. The peel presented values of 5.997 mg of gallic acid/g of fresh weight, 4.455 mg of quercetin/g and 47.97% DPPH radical scavenging activity at the concentration of 322 mg/ml corresponding to the content of total phenolics, total flavonoids and antioxidant capacity, respectively. Phenolic compounds appear to be responsible for the high free radical inhibition activity. Ajila *et al.* [9] found that mango peel contained 51.2% of total dietary fiber, 96 mg GAE/g of polyphenols and 3092 mg/g of carotenoids. The author also investigated the effect of mango peel powder on the physical, biochemical, and sensory characteristics of soft dough biscuits and found that the mango

peel powder moisture content was 10.5%, fat content 2.2%, the total protein content was 3.6% and the carbohydrate content was 80.7%.

Ribeiro *et al.* [1] found that the peel and seed of “Uba” mango had a total phenolic content of 0.0572 mg/g and 0.08254 mg/g of dry matter, these values were 4.6 and 7.3 times higher than those in the pulp, respectively. It was also found that the phenolic content in the peel of this mango cultivar was 3.3 times higher than that found in apple peel. DPPH radical scavenging activity of mango peel showed a higher inhibition value (53.3%) followed by the seed (24.2%) and finally the pulp. Polyphenol, anthocyanin and carotenoid contents in acetone extract of peels were determined. Ajila *et al.* [4] reported that ripe peels contained higher amount of anthocyanins and carotenoids compared to raw peels while raw mango peel had high polyphenol content. The author analysed the mango peels for the scavenging effect on DPPH radical and it was found that Raspuri extracts showed low IC<sub>50</sub> values (1.83–1.98 lg of GAE) compared to that of Badami peel extracts (3.67–4.54 lg of GAE). The free radical scavenging activity of mango peel extracts was compared with BHA. It was found that the acetone extracts of Raspuri raw and ripe mango peels showed higher scavenging activity than that of BHA. The carotenoid content was found to be 4–8 times higher in ripe mango peels compared to raw fruit peels [4]. According to Mahattanatawee *et al.* [10] mango peel exhibit important antioxidant capacity and significant polyphenol contents among other fruits. In the last few decades transition has been seen in the eating habits of people in India.

The production and usage of RTE food products have increased over the years and is still increasing at a very fast pace. This may be owing to the change in life style which has made every individual very busy. According to NSW [11], RTE foods maybe defined as foods that are ordinarily consumed in the same state, in which it is sold and does not include nuts in the shell and whole, raw fruits and vegetables that are intended for hulling, peeling or washing by the consumer. Several RTE food products are being prepared, marketed and consumed all over the country. Ready to eat foods may also be defined as food products that are in the form that is edible without additional preparation. The consumption of ready to eat food products has been noted to increase in the past few decades. Change in food habits is due to the increased purchasing power, urbanization, changing life style, imitating the western culture, increased production and easy availability of such food items etc. Generally ready to eat food items like chips, cookies etc. are baked and fried products which contain lots of fats and oil.

Owing to which they have short shelf life, as they gets oxidized easily, resulting in reversion of taste and finally the product becomes rancid. In order to overcome the problem of rancidity manufactures and producers use synthetic antioxidant like BHA, BHT, propyl gallate etc. which does extend the shelf life of the food products but in turn affect the human health. Several long term studies have demonstrated the ill effects of synthetic antioxidants [12]. Hence, the focus has been shifted towards the natural antioxidants that are cheap, can extend the shelf life of RTE foods and are safe for human consumption. Peels of several fruits and vegetables have been reported to be potent source of antioxidants [6]. India is the leading producer of the king of the fruits i.e., mangoes (*Mangifera indica*). Mangoes are extensively consumed by the processing units to prepare several products where the peels just form a part of the waste material. Studies have shown that mango peel possesses highest values of bioactive compounds and anti-oxidative properties. To elucidate the same local variety of ripe mangoes were purchased from the local market of Udaipur in a single lot. Mango peels were cleaned, washed and then dried simultaneously in hot air oven 40<sup>0</sup>C and used for further study. Proximate composition was analyzed by AOAC methods, carbohydrate by difference method and energy by calorific value method.

Any potential item could prove it’s worth in food industry or as a source of nutrition to mankind only if it could be consumed. The researcher suggested that cookies are one of the most favorite experimental RTE food products for enhancement of nutrient composition, either by partial or whole substitution. Bakery products are popular both in urban and rural India. Among bakery products cookies and biscuits are the most popular and well

accepted snack food. Cookies are RTE convenience food product which derives its name from *kokje* meaning small cake which is baked between hot plate from a fluid batter. According to Ballolli [13] cookies are chemically leavened products in which refined wheat flour is used as the base ingredient.

### Results:

The moisture content of fresh mango peel (Udaipur local variety) was found to be  $70.91 \pm 0.57 \text{ g } 100\text{g}^{-1}$  while on drying the moisture content was observed as  $3.94 \pm 0.50 \text{ g } 100\text{g}^{-1}$  (Table 2). The results were in accordance with the findings of Ajila *et al.* (2007), but higher than the findings of Arumugam and Manikandan [14], who observed moisture content of 59.98 % in fresh mango peel, however relatively low moisture content for the MPP ( $2.90 \pm 0.96 \%$ ) was found, though the findings were in close comparison with the values reported by other scientists [2, 15]. Whereas, the results reported by Ojokoh [16], Vergara-Valencia [17] and Ajila *et al.* [9] were quite higher *i.e.*,  $6.56 \pm 0.10$ ,  $8.10 \pm 0.02$  and  $10.50 \pm 0.50 \%$  respectively.

The crude protein content of MPP was observed to be  $4.87 \pm 0.96 \text{ g per } 100 \text{ g}$ . The results are in agreement with Vergara-Valencia *et al.* [17] and Arumugam and Manikandan [14], who found the protein content to be 4.28 % and 4.27 % respectively. Hassan *et al.* (2011), also evaluated the mango peel of *bambangan* variety and reported a protein content of 4.60 % on dry weight basis. Whereas, Ojokoh [16] reported a relatively higher protein content of 6.16 % on dry weight basis. Ashoush and Gadallah [2] reported a protein content of 3.60 %. Even lower values for protein in the mango peel of *raspuri* and *badami* varieties have been reported by Ajila *et al.* [4].

The fat % in the MPP was found to be  $0.41 \pm 0.27 \%$  which was quite lower than the literature reported by other researchers. Vergara-Valencia *et al.* [17], Ajila *et al.* [9], Hassan *et al.* [15], and Arumugam and Manikandan [14], have documented a slightly higher values of  $2.35 \pm 0.02$ , 2.22, 2.66,  $2.90 \pm 0.30$  and 3.20 % respectively. [2] reported a fat content of 1.23 % in the *zebda* variety of mango peel.

The crude fibre content of the MPP was observed to be  $9.56 \pm 1.15 \text{ g per } 100\text{g}$  which was in line with the findings of [2] who reported a content of  $9.33 \pm 0.61 \%$ . While [4] indicated a slightly lower values of dietary fibre in the peels of *raspuri* and *badami* variety of mango as  $5.80 \pm 0.01$  and  $7.40 \pm 0.20$  respectively. Whereas, [16] found high fibre content (16.40 %) in the peel of mango.

**Table 2: Nutrient composition of MPP**

Nutrient constituents	(Mean $\pm$ SD)
Moisture (g per 100 g)	$3.94 \pm 0.50$
Protein (g per 100 g)	$4.87 \pm 0.34$
Fat (g per 100 g)	$0.41 \pm 0.27$
Fibre (g per 100 g)	$9.56 \pm 1.15$
Ash (g per 100 g)	$3.37 \pm 0.28$
Carbohydrate (g per 100 g)	$78.93 \pm 1.98$
Energy (Kcal/100g)	$338.76 \pm 9.16$
Vitamin C (mg/100g)	$45.31 \pm 2.26$
Beta carotene ( $\mu\text{g/g}$ )	$171.38 \pm 6.18$

Values are expressed on dry weight basis

The ash content in the present study for MPP was found to be  $3.37 \pm 0.28 \%$  which is in accordance with the results of [17], who found the ash content of *Tommy Aktins* to be  $2.83 \pm 0.01 \%$ . [9] also found ash content of mango peel as  $3.00 \pm 0.18 \%$  and Ashoush and Gadallah (2011) who studied on the *zebda* variety of mango peel

found ash content to be  $3.88 \pm 0.59$  %. Whereas, [14] and [4] have reported a still lower ash content in the peels of mango *i.e.*, in a range of 1.16 to 1.87 %.

The carbohydrate content of MPP was found to be  $78.93 \pm 1.98$  %. The results were consistent with the findings of [9] and [2], who reported a content of 80.70 and 77.04 % respectively. The energy content of MPP was observed to be 338.76 kcal per 100 g.

The vitamin C content of fresh mango peel was found to be  $168.15 \pm 3.36$  mg per 100 g which was observed to be lower than the vitamin C content of *raspuri* and *badami* variety of mango, in which [4] reported a content of  $349 \pm 11$  and  $392 \pm 21$  mg per 100 g. While, on drying the peels the vitamin C content was observed to decrease drastically to  $45.31 \pm 2.26$  mg per 100 g.

The beta carotene content of fresh mango peel was found to be  $38.12 \pm 2.34$   $\mu\text{g}$  per g. The beta carotene content in dried samples was  $171.38 \pm 6.18$   $\mu\text{g}$  per g. The findings are quite low when compared to the findings of [4]. The major reason for this difference can be accorded to the fact that the researcher estimated total carotenoid while in the present study only beta carotene content was estimated.

The variation in nutrient content of the various studies varied, which might have due to difference in the method of quantification and more importantly due to varietal difference [4,6]. Though the peels of ripe mango are potential source of nutrients, flavonoids, antioxidants, beta carotene *etc.* it cannot be consumed as such. So, cookies were formulated and standardized by incorporating mango peel powder (MPP) at different levels viz. 5, 10, 15 and 20 % and was organoleptically evaluated by a panel of ten judges, for different quality parameters on a nine point hedonic scale. Cookies prepared with incorporation at a rate of 15 % of MPP was found as acceptable as those of control. The most preferred treatments (*i.e.*, level of addition) prepared by adding MPP along with their control was analysed for their nutritional content to find out its potential as food component.

#### Organoleptic acceptability of MPP incorporated cookies:

The mean sensory scores have been presented in the Table 3. It is clear from the data in the table that control obtained highest scores for all the sensory attributes *i.e.*,  $8.74 \pm 0.06$  (appearance),  $8.80 \pm 0.11$  (colour),  $8.84 \pm 0.06$  (flavour),  $8.84 \pm 0.06$  (taste),  $8.84 \pm 0.06$  (texture) and  $8.81 \pm 0.07$  (overall acceptability) as compared to the treatments. Among the treatments of diamond cookies, sensory scores of TM3 *i.e.*, with 15 % level of incorporation was found to be ranked the highest in all sensory attributes viz.,  $8.17 \pm 0.16$  (appearance),  $8.27 \pm 0.12$  (colour),  $8.84 \pm 0.06$  (flavour),  $8.77 \pm 0.12$  (taste),  $8.67 \pm 0.06$  (texture) and  $8.38 \pm 0.10$  (overall acceptability) than the diamond cookies prepared with 5, 10 and 20 % level of MPP. The overall acceptability scores ranged between  $7.77 \pm 0.14$  to  $8.81 \pm 0.07$  indicating that the recipes fell under the category of —liked moderatelyl to —liked very much.

**Table 3: Mean acceptability scores of MPP added diamond cookies**

Quality attributes	Control	TM1(5%)	TM2 (10%)	TM3 (15%)	TM4 (20%)
Appearance	$8.74 \pm 0.06$	$8.00 \pm 0.10$	$8.04 \pm 0.16$	$8.17 \pm 0.16$	$6.97 \pm 0.16$
Colour	$8.80 \pm 0.11$	$8.20 \pm 0.16$	$8.24 \pm 0.12$	$8.27 \pm 0.12$	$7.80 \pm 0.30$
Flavour	$8.84 \pm 0.06$	$8.72 \pm 0.11$	$8.77 \pm 0.12$	$8.84 \pm 0.06$	$8.64 \pm 0.06$
Taste	$8.84 \pm 0.06$	$8.24 \pm 0.06$	$8.40 \pm 0.06$	$8.77 \pm 0.12$	$7.47 \pm 0.12$
Texture	$8.84 \pm 0.06$	$8.24 \pm 0.12$	$8.34 \pm 0.21$	$8.67 \pm 0.06$	$7.97 \pm 0.06$
Overall acceptability	$8.81 \pm 0.07$	$8.32 \pm 0.11$	$8.28 \pm 0.10$	$8.38 \pm 0.10$	$7.77 \pm 0.14$

Further it can be discerned that there was an increase in the scores of the sensory attributes with the increase in the incorporation level of MPP up to 15 %, the sensory scores decreased with a further increase of incorporation

level of MPP to 20 %. It is clear from the data that the panellist liked the diamond cookies with 15 % incorporation of MPP very much on an overall basis. At 20 % level of incorporation of MPP caused relatively dark colour, the increase in the darkness was reflected in the scores of colour and appearance of the products which may be due to enzymatic browning. Aziah and Komathi [18] reported that MPP at higher level i.e., at 20 % imparted a dark brown colour to crackers; this might have given the panelists an impression of over-baked product, thus affecting their likings. But the products were well accepted up to 15 % incorporation level.

#### Nutrient content of MPP incorporated cookies:

Nutrient analysis of foods provides vital information regarding its quality and is an important part of quality assurance. Moisture ( $0.36 \pm 0.01$  %), protein ( $5.75 \pm 0.17$  %), fat ( $20.80 \pm 0.17$  %), fibre ( $0.82 \pm 0.08$  %), ash ( $1.25 \pm 0.02$  %), carbohydrate ( $71.02 \pm 0.29$  %) and energy content ( $494.28 \pm 3.74$  kcal per 100 g) for control sample of cookies (Table 4). MPP added cookies were discerned to contain  $0.33 \pm 0.07$

**Table 4: Nutrient composition of MPP added diamond cookies**

Nutrient constituents	Control	Treatment	t-value
Moisture (g/100g)	$0.36 \pm 0.01$	$0.33 \pm 0.07$	NS
Protein (g/100g)	$5.75 \pm 0.17$	$6.72 \pm 0.03$	2.37*
Fat (g/100g)	$20.80 \pm 0.17$	$20.96 \pm 1.57$	3.13*
Fibre (g/100g)	$0.82 \pm 0.08$	$3.77 \pm 0.13$	6.76*
Ash (g/100g)	$1.25 \pm 0.02$	$1.69 \pm 0.20$	2.83*
Carbohydrate (g/100g)	$71.02 \pm 0.29$	$66.53 \pm 1.78$	9.12*
Energy (Kcal/100g)	$494.28 \pm 3.74$	$481.64 \pm 6.99$	11.69*
Beta carotene ( $\mu\text{g/g}$ )	$0.56 \pm 0.07$	$1.76 \pm 0.08$	10.42*

NS – Non Significant at 5 % significance level, \* - Significant at 5 % significance level

Values are expressed on dry weight basis.

Level of MPP incorporation -15 % of moisture,  $6.72 \pm 0.03$  % protein,  $20.96 \pm 1.57$  % fat,  $3.77 \pm 0.13$  % fibre,  $1.69 \pm 0.20$  % ash,  $66.53 \pm 1.78$  % carbohydrate and  $481.64 \pm 6.99$  kcal of energy. Beta carotene content was indicated to be  $1.76 \pm 0.08$   $\mu\text{g}$  per g for MPP added cookies, whereas it was observed to be  $0.56 \pm 0.07$   $\mu\text{g}$  per g for its control counterpart. Statistically significant difference was noted between control and MPP added cookies with regards to all the nutrients except moisture content ( $P \leq 0.05$ ).

The increase in the nutrient content of treatment when compared to its control (except for moisture, carbohydrate and energy content) was clearly due to the incorporation of the MPP powders in the product which enhanced the nutrient composition of cookies. As dry powders were added to the treatment, it did not affect the moisture content of the cookies. Carbohydrate content of control was found to be higher when compared to the treatment owing to the fact that difference method was used for its calculation and fibre was observed to be a major factor contributing towards it.

The protein, fat, fibre, carbohydrate and energy contents of the control are in accordance with the findings of Vaidehi [19]. Similar protein and carbohydrate content in cookies but slightly lower fat and carbohydrate values when compared to the control was reported by Pasricha [20]. While, Gafoorunissa and Krishnaswamy [21] indicated higher values for protein, fat and energy for control. The ash content of control was consistent with the observations of Mahmood *et.al.* [22] for retinylacetate fortified cookies. Whereas the ash content documented by Sharif *et.al.* [23] in cookies was in a range of 2.72 – 2.75 which was higher than the results of the present investigation.

Exploration of MPP as an ingredient in foods for enhancement of its nutrients or as an antioxidant has been very limited.

### Conclusion:

Thus it can be concluded that mango peel, which is considered as a waste has great nutrient potential and can be easily used within organoleptically acceptable limits for the enhancing the nutritional content of food products.

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# PLANT TISSUE, ORGAN AND CELL CULTURE FOR ALKALOID PRODUCTION: A MINI REVIEW

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## Abstract:

Plants are engrossed in the production of primary metabolites (as their prime need) accompanied by secondary metabolites (as a defensive measure to counter exogenous influences). Under in vitro biotechnological approaches, numerous plant cell suspension, tissue and organ culture methods have been pursued so far. Furthermore, improvements in the tissue culture approaches and standardization of cultural conditions have been affected quite competently. The emphasis of this review is to explain the advancement, outlooks and restraints of diverse in vitro regeneration methods that have been proven to increase the production of alkaloids meeting the demands of pharmaceutical industries and sustaining the natural plant population as well.

**Key words:** Alkaloids; Cell suspension; In vitro culture; Secondary metabolites

## Introduction:

Medicinal plants possess various secondary metabolites such as terpenes, alkaloids, phenols, and flavonoids. Alkaloids are the large group of nitrogen containing secondary metabolites. It also includes some neutral and acidic properties containing compounds [1]. Moreover, some synthetic compounds with related structure are also considered as alkaloids [2]. Few alkaloids possess the elements such as oxygen, sulfur and infrequently, other elements for example bromine, chlorine and phosphorous along with nitrogen, carbon, and hydrogen (Chemical Encyclopedia: alkaloids).

Basically, alkaloids have shown a broad spectrum of remedial and pharmaceutical benefits, which includes anticancer (homoharringtonine), antiasthma (ephedrine), antimalarial (quinine), cholinomimetic (glutamine), vasodilatory (vincamine), antiarrhythmic (quinidine), analgesic (morphine) and antibacterial (Chelerythrine) [3,4,5,6]. The alkaloid word comes from a German word 'Alkaloide' and first presented by German Chemist Carl Friedrich in 1819 and derived from Latin word 'alkali' and Arabic word 'al-qalawi' meaning plant ashes. Human civilizations have exploited these plant-derived alkaloids thousands year ago for therapeutic and recreational uses. A series of discovery of alkaloids led the breakthrough for its large-scale usage such as xanthine (year 1817), strychnine (1819), atropine (1819), quinine (1820), caffeine (1820), nicotine (1828), Colchicine (1833) and later sparteine (1851) and cocaine (1886) [7].

## Groups of Alkaloids:

There are five groups of alkaloids:

- 1) True alkaloids with nitrogen in the heterocycle and amino acid precursors derived alkaloids e.g. nicotine, atropine, and morphine [8]. Besides, some non-amino acid precursor derived alkaloids including piperidine alkaloids coniceine and coniine [9].
- 2) Protoalkaloids- contains both nitrogen-containing and amino acids derived [8] e.g. ephedrine, mescaline, and adrenaline.
- 3) Polyamine alkaloids- originated from spermine, spermidine, and putrescine
- 4) Alkaloids with peptide and cyclopeptide
- 5) Pseudoalkaloids- not the true to the type as they are not derived from amino acids. e.g. steroid like and terpene-like alkaloids [10].

#### **Alkaloids, Chemical and Physical Aspects:**

Depending on the presence of oxygen in alkaloids, makes it colorless crystals at ambient temperature whilst, the oxygen less alkaloid structure usually colorless, volatile and oily liquids such as nicotine and coniine. The rest alkaloids are yellow as in berberine while sanguinarine is orange in color [11]. Majority of the alkaloids dissolve freely in organic solvents such as chloroform or 1, 2-dichloroethane and diethyl ether but weakly miscible in water. When alkaloids mix with acids to make salts of different strengths and these salts are easily miscible both in water and alcohol whilst weakly dissolve in many organic solvents. In the adverse conditions of injury or to avoid grazing animals, alkaloids seem to have diverted their metabolic pathway. Still few cattle can able to detoxify alkaloids [12].

#### **Biotechnology Approaches for Alkaloid Production:**

In the last two to three decades, the large-scale production of secondary metabolites can be possible by the inclusion of biotechnology approaches. These approaches mainly target the selection of plants, improve the strains and characterize medicinal plants. The entrant of bioreactor makes it possible for the production of secondary metabolites from plants and microorganisms in an extensive way [13]. There are specific secondary metabolites, which are the renewable source and can be produced only by plant cell culture techniques and cannot be produced by an alternate source such as microorganisms or chemically synthesized [14]. Among the secondary metabolites, alkaloids have the major role in many pharmaceutical measures towards the economical point of view.

#### **Plant Cell and Tissue Culture:**

The plant tissue culture technique involves the contribution of different explants both for the whole regeneration of plants and also for the production of therapeutic pharmaceutical compounds.

#### **Influence of Media Compositions:**

The growth and the secondary metabolite production depends on the media composition along with the physical parameters such as the influence of light, temperature, pH etc. These two aspects are inversely related, both, in the case of cell and plant cultures. Generally, secondary metabolites are produced in the late stationary phase when the medium gets exhausted from some of its important ingredients. The growth inhibition is recurrently amalgamated with cytodifferentiation leads the involvement of certain enzymes for the production of secondary metabolites. Hence, it needs a dual culture system. The one “growth medium” is meant for the cell proliferation and later transfer of these cells to the second medium i.e. “production medium” which supports the desired product yield but does not support the cellular growth. These dual systems were first introduced by Zenk *et al.* (1977) [15] for the production of *Catharanthus roseus* cells. The same approach was followed by Fujita *et al.* (1981, 1982) [16, 17] to

construct a protocol for commercial production of shikonin by cell cultures of *Lithospermum erythrorhizon* (Table 1).

Earlier in the 1980s, different media have been tried. But, the last decade experiments were conducted with the involvement of Murashige and Skoog (MS) media [18]. Initially MS media was used for the proliferation of stem, internodes, leaves and meristematic tissues of *Taxus globosa* [19] (Table 1). But, for the production of baccatin III, a modified Gamborg's B5 medium [20] was used and successfully produced though not paclitaxel. Panigrahi *et al.* (2017) [21] obtained both the regeneration of the shooting, rooting, callusing along with the production of vasicinone from *Adhatoda vasica* Nees. with only the use of MS media (Table 1 and Fig 2). But the production of vasicinone might be the obtained in the later part of the growth phase or early part of stationary phase and the depletion of nutrients made the regenerated parts of *A. vasica* to divert towards the secondary metabolism.

#### **Influence of Light:**

It is a mandatory to have the role of light in plant tissue culture either in the early growth phase of the explant or in the inhibitory phase for the production of secondary metabolites. Once the plant cells achieved a stage, the photoperiod may be reversed and even darkness favors the paclitaxel productions as in *Taxus globosa* (Table 1). Likewise, in *Taxus x media* var. Hicksii, for the production of baccatin-III, the hairy root culture was put under darkness. In case of *Withania coagulans*, the culture was maintained throughout in white light for the production of withaferin. 16/8 h light regime was provided to plants such as in *A. vasica*, *Solanum tuberosum*, *Chonemorpha grandifolia*, *Lycopodiella inundata*, *Papaver bracteatum*, *Rauwolfia serpentine*, *Solanum nigrum* and *Taxus globosa* (Table 1) for their respective alkaloid production.

#### **Influence of Temperature and pH:**

The temperature and pH does have regulatory role in the production of alkaloids in plant tissue culture. There is diverse array of temperature used for this purpose started from +23°C to -35°C (Table 1). This temperature also being supplied to the culture for a certain period; it may last for 2 to 4 weeks (Table 1). This may be due to the alkaloid metabolism which needs the presence of certain enzymes and specific temperature for its activation. The pH of the medium is influencing the permeability of the cell and thus, helps in releasing the intracellular alkaloids [22, 23, 24].

#### **Influence of Aeration:**

The aeration particularly oxygen and carbon dioxide may influence the production of alkaloids during cell culture. At times, increase in oxygen mass transfer coefficient may reduce the time period without affecting the final yield as in serpentine production of *C. roseus* [25]. Possibly, presence of increase dissolved oxygen influenced the production of serpentine from ajamlicine via the oxidative metabolism. It has also been found that increase in dissolved oxygen supports the higher production of ajmalicine as compared to less availability of dissolved oxygen concentration [26]. This assures that aeration may proliferate the conversion rate towards the secondary metabolites production.

#### **Influence of Plant Growth Regulators:**

The influence of plant growth regulators definitely involves in the growth and differentiation of cells which directly affect the alkaloid production. Individual auxin or cytokinin may work for the production of alkaloids. Though, the cellular growth needs the growth regulators and once it is being removed the production of alkaloids gets enhanced. As 2, 4-D seems stimulates the proliferation and differentiation of cells but once it is excluding or

available in less amount it works for the vasicinone production (Table 1). However, the alkaloid yield was also increased by the combinatorial effects of auxin and cytokinin. For the production of alkaloids, the best combination was 1, 5 ppm BA and 1-1.5ppm NAA while 0.5 ppm BA and 2 ppm IAA works better for glycoalkaloids (Table 1). But, 2mg/l NAA + 2mg/l IAA + 0.1 mg/l Kinetin combination of plant growth regulators was remarkably increased in the production of catharanthine and ajmalicine in *C roseus*. Moreover, the combination of PABA (1ppm) and NAA (4 ppm) gave significant boost to the reserpine production. Thus, the exogenous supply of plant growth regulators not only involves in enhance the biomass but also influences the alkaloid production. However, gibberellic acid (GA<sub>3</sub>) do not support the secondary metabolite production [27]. In catharanthine production from *C. roseus*, no effect of GA<sub>3</sub> was observed. However, berberine production enhanced by the exogenous supply of GA<sub>3</sub> (10<sup>-8</sup> to 10<sup>-5</sup> M) is a rare event. This enhancement is due to the degradation of starch into sucrose and diverted towards the alkaloid metabolism and decrease in nitrogen uptake [28].

### **Influence of Additives:**

Depending on the endogenous content of the explant, the in vitro grown plants require exogenous supply of plant growth regulators, nutrients in form of media and also some additives both for growth and the secondary metabolism. The additives such as sucrose as carbon source, tyrosine and phenylalanine as amino acids or nitrogen source, myoinositol as vitamin source etc. are being used. For the production of ajmalicine and catharanthine, two different concentrations of sucrose have been used. 30 g/l sucrose was used for the *C roseus* cell culture while 50 g/l sucrose concentration was meant for the alkaloid production medium. This suggests that for the production of these alkaloids sucrose quantity was more as carbon source. But, for the Lycopodiales, 'tropane' and 'withaferin A' alkaloids, the fixed concentrations of sucrose (20 g/l, 30 g/l and 30 g/l) were fortified in the media respectively both for growth and production (Table 1). In a specific study of alkaloid production from *Cereus peruvianus* 125 g/l of tyrosine influenced positively. Without tyrosine, it does reduce the alkaloid production. The tyrosine does directly involve as precursor of several secondary metabolites along with tyramine synthesis [29]. The use of L-phenylalanine did show significant effects in dry biomass as well as the 10-deacetylbaicatin III accumulation in *Taxus x media* var. *Hicksii* plant culture as compared to the untreated one (Table 1).

### **Conclusion:**

Medicinal plants owing to its capacity of holding the secondary metabolites could be the major exploitation reason both in vitro and in vivo conditions. Due to increasing demand of phytomedicines, in vitro plant regeneration are the modern techniques used both for its own multiplication along with certain strategies have been implicated to produce the secondary metabolites specifically alkaloids. The various strategies utilized till date are variation in media composition, light, temperature, pH, aeration, growth regulators and some additives. Despite the yield in of respective alkaloids from the various medicinal plants and its purification, still there is need of more production within the same in vitro plant parts by the application of certain modification of the biosynthetic pathway or else constraints or restrict the pathway that leads to the particular alkaloids. Recent pharmaceutical companies are in this track and developed new strategies to fulfill the huge demand of these alkaloids. For this some biochemical engineering methods, the use of high performance thin layer chromatography, mass spectroscopy must be devised to improve the yield but keeping it in mind that the production cost should not be high enough.

### **Author Contribution:**

All the authors have equally contributed. All the authors read, compiled and approved this manuscript.

### **Conflict of interest:**

The authors declare that there is no conflict of interest.

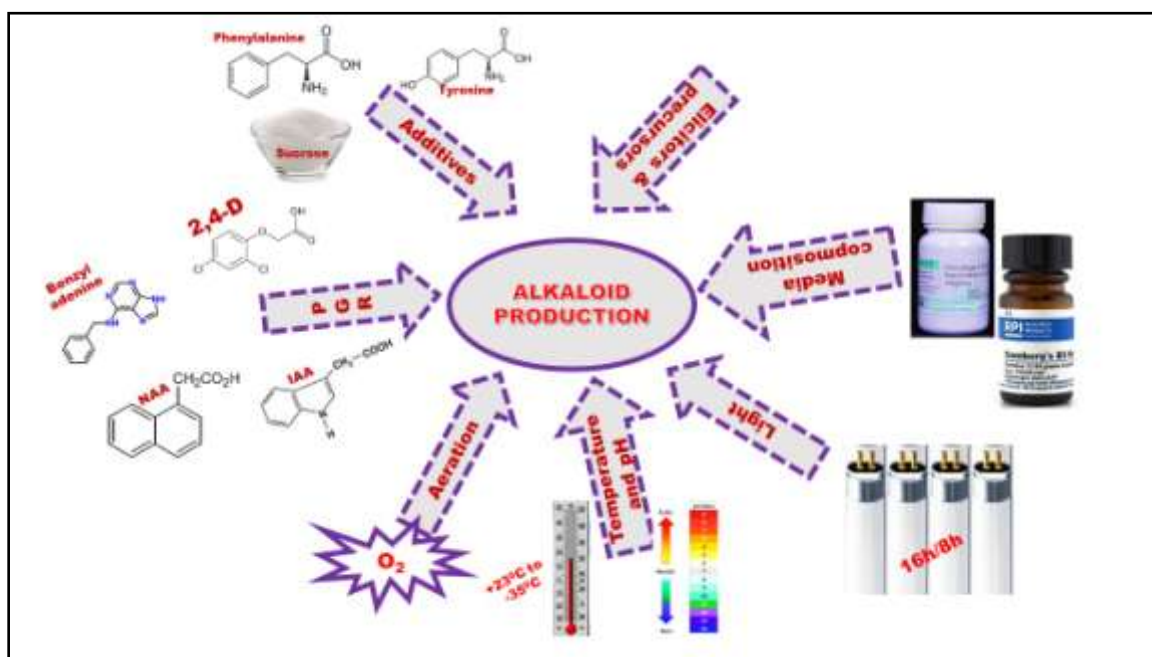
**Ethical approval:**

The article does not contain any animal studies used by the authors.

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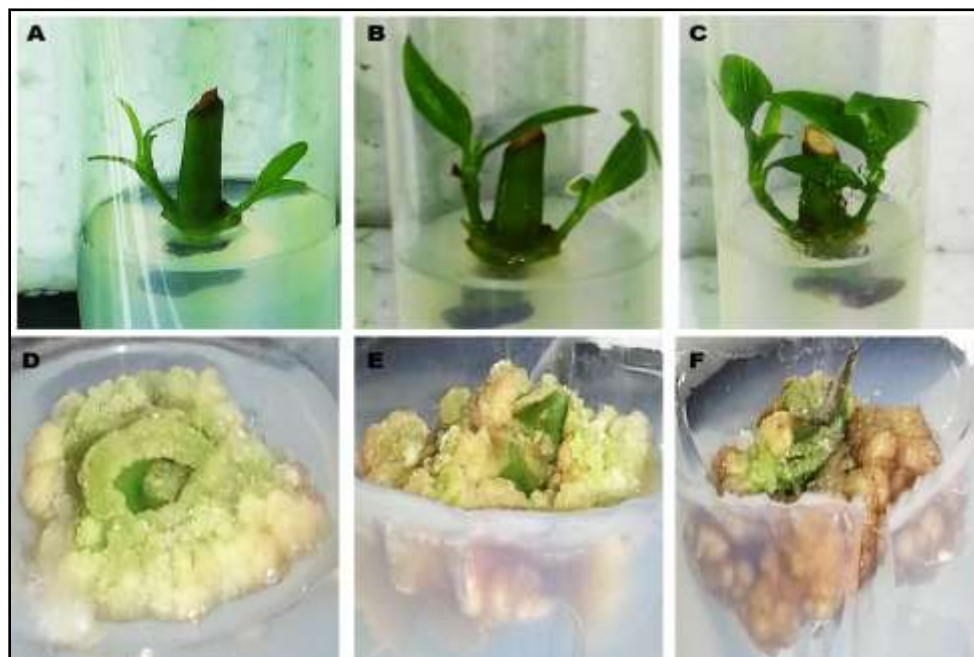
**Figure 1: An illustration of the different biotechnological approaches and factors affecting the production of alkaloids**

**Table 1: Explants, culture medium composition, culture conditions that influenced alkaloids production in different medicinal plants**

Plant name	Explant	Culture medium composition	Culture condition	Alkaloids produced	Reference
<i>Adhatoda vasica</i> Nees.	Nodal segment	MS+1.1 mg/l N <sup>6</sup> -benzyl adenine; MS+ 1mg/l of 2,4-D	Illuminated under 16/8 h photoperiod	Vasicinone	[21]
<i>Anisodus luridus</i>	Leaf discs	MS+ 300 mg/l cefotaxime	Infected with <i>A. tumefaciens</i> and grown in the dark for 2 days	Tropane	[30]
<i>Catharanthus roseus</i>	Leaf, stem	MS+NAA (2 mg/l), IAA (2 mg/l), kinetin (0.1 mg/l), sucrose (3%)/	incubated on rotaryshaker at 23±2°C in darkness	Ajamalicine, catharanthine	[31]
<i>Catharanthus roseus</i>	Petiole segments of seedlings	MS+NAA (0.1, 5, 10, 20 ppm), Kin (0.1,5,10,20 ppm);	maintained in dark for first 2 weeks followed by 24 hlight period (fluorescent, cool white light, 7 W/m <sup>2</sup> ) fornext 2 weeks at temp -35°C	Dimeric indole alkaloids: Vindoline, vincristine, vinblastine	[32]
<i>Cereus peruvianus</i>	Shoots	MS+tyrosine	incubated at temp -25±1°C under dark conditions	Alkaloids	[29]
<i>Chonemorpha grandiflora</i>	Inter-nodal segments of stem	MS+2,4-D (4.52 µM)	16/8 h (light/dark) photoperiod, temp -25°C	Camptothecin	[33]
<i>Leucojum aestivum</i>	Bulb, shoot	MS+BAP(2mg/l), NAA(0.15 mg/l)	cultured underillumination provided by fluorescent tubes or underdark at 25°C	Galanthamine	[34]
<i>Leucojum aestivum</i>	Somatic embryos	MS+ Meta-topolin, Benzyladenine	Bioreactor system and solid media	Galanthamine, lycorine	[35]
<i>Lycopodiella inundata</i>	Vegetative apices	MS+ sucrose 20 g/l, myoinositol 0.05 M IBA and 1.4 M kinetin	pH was adjusted at 5.4, placed on an orbital shaker at 75 rpm and maintained at 230C under a 16 h photoperiod with fluorescent light	Lycopodiales alkaloids	[36]
<i>Papaver bracteatum</i>	Seeds	MS	Germinated in growth chamber at 24°C under 35 µmols <sup>-1</sup> m <sup>-2</sup> flux rate and 16 h photoperiod	benzylisoquinoline	[37]
<i>Przewalskia tangutica</i>	Seeds, germinated seedlings, leaves	liquid MS; genetic transformation-MS+AS (100 µmol/l)+30% sucrose+3.0 g/l phytoigel/250 mg/l;	germination of seeds at 25±0.5°C Bacterial preparation carried out in orbital shaker at180 rpm at 28°C for 30 min, culturing of hairy rootsat 110 rpm at 25±1°C	Tropane alkaloids	[38]

<i>Rauwolfia serpentine</i>	Leaves	MS+PABA (1 ppm)+NAA (4 ppm);	temp -25±2°C, photoperiod of 16/8 light and dark cycle; some leaf explants incubated under total dark conditions to observe root growth	Reserpine	[39]
<i>Schizanthus hookeri</i>	Roots, callus for generating shoots	MS+ + NAA (2.69 µM), BA (2.22 µM)/ BA (4.44 µM)+NAA (0.54 µM)	temp -22±1°C, light regimen of 14 h at 48 µmol/m <sup>2</sup> /s	Pyrrrolidine derivatives to tropane esters derived from angelic acid, tiglic acid, seneciocic acid and methyl mesaconic acid, tropane alkaloids-3α-methylmescaonyloxytropane	[40]
<i>Solanum nigrum</i>	Seeds, germinated plantlets	MS+2,4-D (0.5 ppm), Kin (0.5 ppm)	temp -25°C light/20°C dark, photoperiod of 16 h by photon flux density of 100 µmol/m <sup>2</sup> /s	Solasodine	[41]
<i>Solanum tuberosum</i>	Tubers	MS+BA (0.5 ppm), IAA (2 ppm) Kinetin	temp -26°C+16/8 light/dark cycle	Glycoalkaloids	[42]
<i>Taxus x media</i> var. Hicksii	Roots	MS+1-phenylalanine (1 µM);	temp -25°C in dark conditions on a gyrorotary shaker at 122 rpm	Taxane, paclitaxel, baccatin III, 10-deacetyl-baccatin	[43]
<i>Taxus globosa</i>	Stem, internodes, leaves, meristematic tissues	modified Gamborg B5+methyl jasmonate (0.1, 1.0, 10, 100 µM)	incubated at 25±1°C under dark conditions or 16 h photoperiod, light is provided by fluorescent lighting of 1500 W	Baccatin III, paclitaxel	[19]
<i>Vernonia cinerea</i>	Young leaves	MS+NAA (1, 1.5 ppm), BA (1, 5 ppm)	Cultures incubated at 25±2°C with 16/8 h (light/dark) photoperiod under cool white fluorescent tubes	Alkaloids	[44]
<i>Withania coagulans</i>	Seeds	MS+IBA (0.2 ppm), sucrose (3%)	provided with continuous white light illumination at 25°C on rotary shaker at 80 rpm	Withaferin A	[45]

<i>Withania somnifera</i>	Single shoot tips	MS+BA (1 mg/l), sucrose (3%)	incubated at 16 h/8 h (light/dark) photoperiod withrel. humidity of 55-60% maintained at temp -25±2°C		[46]
<i>Withania somnifera</i>	Seeds	½ strength MS+150 μM acetosyringone	MES buffer (20mM)+ 3% sucrose+ 0.2% phytagel and co-cultivated in dark at 25 ± 2 °C for 5 days	Withanolide Withanone Withaferin A	A, and [47]



**Figure 2:** The formation of shoots and callus from nodal explant of *Adhatoda vasica* under in vitro condition. A) BA 1.1 mg/l (shoot initiation from nodal explant after 1 week); B) BA 1.1 mg/l (shoot elongation from nodal explant after 10 days); C) BA 1.1 mg/l (shoot multiplication from nodal explant after 14 days); D) 2,4-D 1 mg/l (Whitish green callus initiation from nodal explant after 10days); E) 2,4-D 1 mg/l (Light yellow callus after 17days); F) 2,4-D 1 mg/l (Friable callus after 20 days) [Source: Original and unpublished photographs depicted from the experiments carried out by the authors].

# STUDENTS AWARENESS PROGRAMME FOR SUSTAINABLE DEVELOPMENT OF ENVIRONMENT

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## **Abstract:**

To live a happy and prosperous life, man needs appropriate natural and social health. Technological progress, has led to degradation of almost all natural resources. Consumption of natural resources by few groups of people is completely against the principle of sustainable development which includes equality to all and purity of resources. Development means not only economic growth, but it should be sustainable. To meet the aim of sustainable development, the development should be such a that it meets the needs of the present generation without compromising the ability of future generations to meet their own needs. By using the principles of optimum use, recycle and reuse, use of resources within their carrying capacity is the only solution for this. Environmental sensitivity in our country can only grow through a major public awareness. The purpose of this paper is to study students awareness programme for sustainable development of environment. Researcher has tried to suggest students awareness programme for sustainable development of environment through this paper.

**Keywords:** Environment, Awareness Programme, Sustainable Development.

## **Introduction:**

The education for environmental awareness is essential for the younger and older generations. Environmental education helps students and general public towards

- 1) **Awareness:** Acquire sensitivity to the total environment and its allied problems,
- 2) **Skill :** Acquire skills for identifying environmental problems.
- 3) **Knowledge:** To know conservation of natural resources.
- 4) **Evaluation ability:** To evaluate environmental measures and education programmes in terms of social, economic, ecological and aesthetic factors.
- 5) **Attitude and participation**

## **Principles of Environmental Education:**

- 1) To consider environment in its totality (natural, artificial, technological, moral, aesthetic)
- 2) To consider a continuous life process.
- 3) To be interdisciplinary in approach.
- 4) To focus on current, potential environmental situations.
- 5) To emphasize active participation in prevention and control of pollution.
- 6) To examine root cause of environmental degradation.
- 7) To provide an opportunity for making decisions and accepting their consequences.

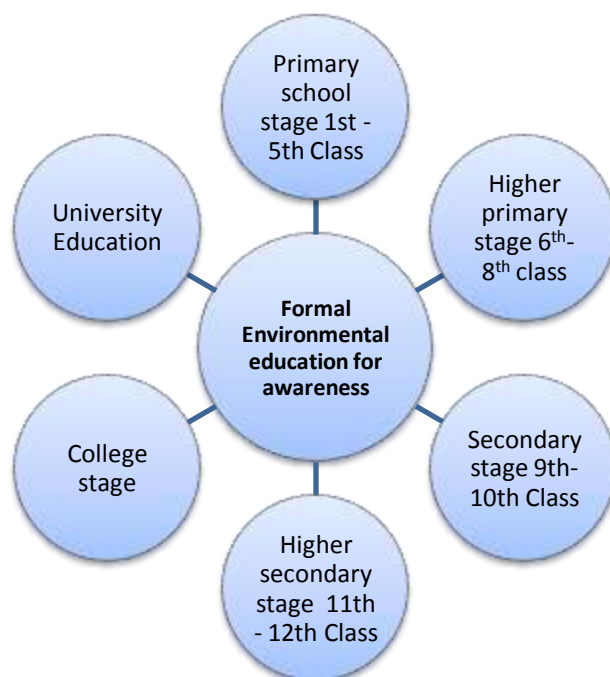
## **Environmental Educational programmes:**

It involves a three-fold classification of environmental education based on different disciplines:

- 1) **Environmental Studies:** It is concerned with environmental disturbances and minimization of their impacts through changes in social sciences.
- 2) **Environmental Science:** It deals with the study of the processes in water, air, soil and organisms which lead to environmental damage.
- 3) **Environmental Engineering:** It involves the study of technical process used to minimize pollution.

#### **Environmental Education among students:**

The environment scenario of India is very wide indeed. At the first level, special attention must be paid to children. They are to be made aware of health, nutrition, sanitation, hygiene, development, water and food contamination, fodder and fuel wood etc. school & colleges have to play a significant role in environmental education and awareness.



#### **A) Formal Environmental Education:**

The spectrum of environmental education has four major interrelated components i.e. Awareness, real life situation, conservation and sustainable development.

##### **1. Primary School Stage:**

The attempt is made to sensitize the child environs. Emphasis should be mostly (75 %) on building up awareness, followed by real life situation (20 %) and conservation (5 %). Teaching strategy includes audiovisual and field visits.

##### **2. Lower secondary stage:**

At this level objective must be real life experience, awareness and problem identification. The contents are supplemented with general science. Teaching, practical's and field visits are to be done.

##### **3. Higher secondary school stage:**

The emphasis must be on conservation, assimilation of knowledge problem identification and action skills. contents problem identification and action skills. Contents may be science based and action oriented work.

4. **College stage:**

Maximum emphasis should be on knowledge regarding sustainable development and conservation. The content must be college based on science and technology. Teaching Practical's and action: oriented field work is to be done. In the school education, NCERT has been playing vital role in designing syllabi, text books, guide books, charts and Kits etc.

5. **University Education:**

Environmental Education at this level is being looked after the UGC. The University education has three major components Teaching, Research & Extension. At post graduate level, four major areas are recognized environmental engineering, conservation and management, environmental health, social ecology.

B) **Non: Formal Environmental Education:**

This education is designed for any age group, participating in cultural, social, economic development of the country. They forms clubs and arrange exhibition, public lectures, meetings, environmental campaigns. Following are the main constituents of this education.

- 1) **Adult Education:** Adults may influence the society to protect the precious environs by generating posters, slides, audio: visual and information pictures.
- 2) **Rural youth and Non: student youth:** They may act as volunteers.
- 3) **Tribal's & Forest Dwellers:** They are an important media to protect the forest wealth.
- 4) **Children Activities:** The National Museum of Natural History (NMNH) conducts spot painting modeling and poster design about environment for children.
- 5) **Non Government Organisations:** There are many (more than 200) NGOs engaged in environmental protection.
- 6) **Public Representatives:** India has environmental forums for MPs and MLAs to discuss environmental problems facing the country. They simulate public interest for saving the environs.
- 7) **Training Executives:** Regular courses should be arranged for environ activities among administrators.
- 8) **Foundation Courses:** The courses for the probationers selected for the IAS, IFS, IPS and cadets of three wings of Armed forces need to be supplemented with foundation courses on environment relevant to their area of specialization.
- 9) **Development of Educational material and Teaching Aids.:** Materials for media (T.V. radio, news: papers etc.) audio, mobile exhibitions, audio: visual materials must be operated by competent manpower. One such centre in India is centre for environmental Education, Ahmedabad
- 10) **Development of Trained Manpower:** Department of Environment (DOE) must organize training programmes for the professors, technical personnel, lectures, and legal experts.
- 11) **National Environment Awareness campaign or national Environment Month:** Commencing from 1986, DOEn conducts NEAC and NEM. From November 19<sup>th</sup> to December 18<sup>th</sup> every year is observed as NEM.
- 12) **World Environment Day:** All Govts. in the states UTs universities, schools, colleges, academic institution and voluntary organizations organize suitable activities on world Environmental Day i.e. 5<sup>th</sup> June of each year. DOE supports the function financially.

**By environmental education we can learn:**

1. How to handle environmental issues.
2. How to lead a better life with less pollution.

3. How to prevent the ecological crisis.
4. How to ensure socio: economic development and make this earth a better place to live in for the present and further generations.

**So in present study researcher has tried to aware secondary stage students about the environment for sustainable development of environment through environmental activities.**

There are several days of special environmental significant which can be celebrated in the community and can be used for creating environmental awareness.

**February 2: Worlds Wetland Day** is celebrated to create awareness about wetlands and their value to mankind. On February 2<sup>nd</sup> 1971, the Ramsar Convention on Wetlands of International importance was signed at Ramsar in Iran. You can initiate a campaign for proper use and maintenance of wetlands in the vicinity of the city or village.

**March 21: Worlds Forestry Day** can be used to initiate a public awareness campaign about the extremely rapid disappearance of our forests. The program must be action oriented and become an ongoing process with activities such as tree plantation.

**April 7: World Health Day:** The World Health Organisation (WHO) came into existence on this day in 1948. A campaign for personal sanitation and hygiene to understanding issues of public health, occupational health, etc. can be carried out. Topics that deal with environment related diseases and their spread can be discussed and preventive measures suggested.

**April 18: World Heritage Day** can be used to arrange a visit to a local fort or museum. Environment also includes our cultural monuments. Students could use this opportunity to create awareness among the local people about their very valuable heritage sites.

**April 22: Earth Day** was first celebrate in 1970 by a group of people in the USA to draw attention to increasing environmental problems caused by humans on earth. This day is now celebrated all over the world with rallies, festivals, clean: ups, special shows and lectures.

**June 5: World Environment Day** marks the anniversary of the Stockholm Conference on Human Environment in Sweden in 1972, where nations of the world gathered to share their concern over human progress at the expense of the environment. This day can be used to project the various environmental activities that the college has undertaken during the year. New pledges must be made to strengthen an environmental at the college level.

**June 11: World Population Day** is a day when the vital link between population and environment could be discussed in seminars held at college and other NGOs.

**August 6: Hiroshima Day** could be used to discuss our own Bhopal Gas Tragedy and the Chernobyl disaster.

**September 16: World Ozone Day** was proclaimed by the United Nations as the International Day for the preservation of the ozone layer. This is good occasion for students to find out more about the threats to this layer and initiate discussion on what they can do to help mitigate this global threat. The day marks the Montreal Protocol signed in 1987 to control production and consumption of ozone depleting substances.

**October 1: 7: Wildlife Week** can consist of seminars on conserving our species and threatened ecosystems. The State forest Departments organize various activities in which every student should take part. A poster display, a street play to highlight India's rich biodiversity can be planned. Wildlife does not only mean animals, but includes plants as well.

**What can we do ?**

Most of us are always complaining about the deteriorating environmental situation in our country. We also blame the government for in action. However how many of us actually do anything about our own environment?

We can think about the things we can do that support the environment in our daily life, in our profession and in our community. We can take others follow our environment friendly actions. A famous dictum is to ‘think globally and act locally’ to improve our own environment . We can make a difference to our world.

### **Biodiversity Conservation:**

A great proportion of the residual wilderness of India is now under great threat. Its unique landscapes are shrinking as the intensive forms of agriculture and industrial growth spreads through a process called ‘development’. Modern science has serious doubts about the possibility of the long term survival of the human race if man continues to degrade natural habitats, extinguishes millions of years of evolution through an extinction spasm, and looks only at short: term gains. The extinction of species cannot be reversed. Once a species is lost, it is gone forever. Future generations will hold us responsible for this great loss.

We frequently forget that we are a part of a great complex web of life and our existence depends on the integrity of 1.8 million species of plants and animals on earth that live in a large number of ecosystems.

The following are some of the things we can do to contribute towards our ecological security and biodiversity conservation.

### **Dos:**

1. Plant more trees of local or indigenous species around your home and our workplace. Encourage our friends to do so. Plants are vital to our survival in many ways.
2. If our urban garden is too small for trees, plant local shrubs and creepers instead. These support bird and insect life that form a vital component of the food chains in nature. Urban biodiversity conservation is feasible and can support a limited but valuable diversity of life.
3. If we live in apartment, grow a terrace or balcony garden using potted plants. Window boxes can be used to grow small flowering plants, which also add to the beauty of our house.
4. Whenever and wherever possible prevent trees from being cut, or if it is not possible for you to prevent this, report it immediately to the concerned authorities. Old trees are especially important.
5. Insist on keeping our hills free of settlements or similar encroachments. Degradation of hill slopes leads to severe environmental problems.
6. When shopping, choose products in limited packaging. It will not only help cut down on the amount of waste in landfills, but also helps reduce our need to cut trees for paper and packaging.
7. Look for ways to reduce the use of paper. Use both sides of every sheet of paper. Send your waste paper for recycling.
8. Buy recycled paper products for our home. For example sheets of paper, envelopes, etc.
9. Reuse cartons and gift wrapping paper, Recycle newspaper and waste paper instead of throwing it away as garbage.
10. Donate used books and magazines to school, hospitals, or libraries. The donations will not only help these organizations, but also will reduce the exploitation of natural resources used to produce paper.
11. Participate in the events that highlight the need for creating Sanctuaries and National Parks, nature trails, open space, and saving forests.
12. Support Project Tiger, Project Elephant, etc. and join NGOs that deal with environmental protection and nature conservation.
13. Involve yourself and friends in activities carried out during Wildlife Week and other public functions such as free plantation drives and protests against destruction of the environment.

**Don'ts:**

1. Do not present flower bouquets instead give a potted plant and encourage your friends to do so.
2. Do not collect unnecessary pamphlets and leaflets just because they are free.
3. Do not use paper plates and tissues or paper decorations when you hold a party.

**Habitat preservation:**

The rapid destruction of forests, and the growth of human habitations and activities have reduced the natural habitats of animals and birds. Loss of habitat is one of the major pressures on several species and has led to the extinction of several rare and endemic species. Many others are seriously threatened. We therefore have the responsibility to preserve remaining habitats and their inhabitants.

The Following are some 'dos and don'ts that can help preserve threatened ecosystems.

**Dos:**

1. Visit forests responsibly. Remember to bring out everything you take in, and clean up litter left by others. Stay on marked trails, and respect the fact that wildlife need peace and quiet. Study the ecosystem; it gives one a greater sense of responsibility to conserve it.
2. Be kind to animals. Stop friends from disturbing or being cruel to wild creatures such as birds, frogs, snakes lizards and insects.
3. Learn about birds, Identify birds that are common in your area. Understand their food requirements and feeding habits. Construct artificial nesting boxes for birds. This will encourage birds to stay in your neighborhood, even if their nesting habit is scare. You can learn more about birds by making a birdbath. Birds need water to drink and to keep their feathers clean. You can make a birdbath out of a big ceramic or plastic saucer. Having birds arounds your home, school college can even help increase species diversity in the area.
4. Attract wildlife such as small mammals, such as squirrels, to our garden by providing running or dripping water. Make a hole in the bottom of a bucket and poke a string though to serve as a wick. Hang a bucket on a tree branch above your birdbath to fill it gradually with water though out the day.
5. Protect wildlife, especially birds and insects that are insectivorous and live in our neighborhood by eliminating the use of chemicals in our garden. Instead, use organic measures from vermicomposting and by introducing natural pest predators. Do our gardening and landscaping using local plants, to contol pests in our garden.
6. If we have pets, feed them well and give them a proper home and in an emergency proper medical care.
7. When we visit a zoo learn about the animals that are found there but do not tease or hurt them through the bars of their cage. They have a right to a peaceful existence. The zoo is in any case not an ideal home for them.

**Don'ts:**

1. Do not disturb, tease, hurt or throw stone at animals in protected area and stop others from doing so. if you see an injured animal contact the Forest Officials.
2. Do not disturb or destroy the natural habitats or bird animals.
3. Do not use articles like leather handbags and lipsticks, which are made from animal product. No wildlife product should be used.
4. Do no catch or kill butterflies or other insects, Butterflies or other insect, Butterflies, moths, bees, beetles and ants are important pollinators.

5. Do not kill small animals and insects like dragonflies and spiders as they act as biological pest control mechanisms.
6. Do not bring home animals or plants collected in the wild. we could be seriously harming wild populations and natural ecosystems where they were collected.
7. Do not buy products like purses, wallters, boots and that are made form reptile skins, if you are not certain that a product is made from a wild species, its better to avoid using it.
8. Do not buy products made from ivory Elephants are killed for their tusks. which are used to make a variety of ivory products.

Researcher arranged activities for secondary students like that: vruksha Bandhan, plantation, Gram swachata, poster presentation, speech competition and Essay Competition on environmental days, Health, Quiz competition, Morning Assembly on environment etc. Such a way researcher tries to aware secondary stage students for sustainable development of environment.

#### **Definition of sustainable Development:**

The sustainable development is defined as:

- 1) The development that meets the needs of the present generations without compromising the ability of future generations to meet their own needs.
- 2) Sustainable development improves the quality of human life while living within, the carrying capacity of nature's life support systems.

#### **Principles of sustainable Development:**

The Rio Declaration on Environment and development fleshes out the definition by listing following principles of sustainability.

- 1) People are entitled to a healthy and productive life in harmony with nature.
- 2) Development today must not undermine the development and environment needs of present and future generations
- 3) Nations have the sovereign right to exploit their own resources but without causing environmental damages beyond their borders.
- 4) Nations shall develop international laws to provide compensation for damage that activities under their control cause to areas beyond their borders.
- 5) Nations shall use the precautionary approach to protect the environment. Where are threats of seious or irreversible damage, scientific uncertainty shall not be used to postpone cost: effective measures to prevent environment degradation.
- 6) In order to achieve sustainable development environmental protection shall constitute an integral part of the development process and cannot be considered in isolation from it.
- 7) Eradicating poverty and reducing disparities in living standards in different parts of the world are essential to achieve sustainable development and to meet the needs of the majority of people.
- 8) Nations shall cooperate to conseve, protect and restore the health and integrity of the Earth's ecosystem. The developed countries acknowledge the responsibility of sustainable development.
- 9) Nations should reduce and eliminate unsustainable patterns of production and consumption and promote appropriate demographic policies.

- 10) Environmental issues are best handled with the participation of all concerned citizens. Nations shall facilitate and encourage public awareness and participation by making environmental information widely available.
- 11) Nations shall enact effective environmental laws and develop national law regarding liability for the victims of pollution and other environment damages. |Where they have authority, nations shall assess the environmental impact of proposed activities that are likely to have a significant adverse impact.
- 12) Nations should cooperate to promote an open international economic system that will lead to economic growth and sustainable development in all countries. Environmental policies should not be used as an unjustifiable means of restricting international trade.
- 13) The polluter should, in principle, bear the cost of pollution.
- 14) Nations shall warn one another of natural disasters or activities that may have harmful transboundary impacts.
- 15) Sustainable development requires better scientific understanding of the problems. Nations should share knowledge and innovative technologies to achieve the goal of sustainability.
- 16) The full participation of women is essential to achieve sustainable development. The creativity, ideal and course of youth and the knowledge of indigenous people are needed too. Nations should recognize and support the identity, culture and interests of indigenous people.
- 17) Warfare is inherently destructive of sustainable development. Nations shall respect international laws protecting the environment in times of armed conflict and shall cooperate in their further establishment.
- 18) Peace, development and environmental protection are interdependent and indivisible.

In present research purpose of researcher is to aware secondary stage student for sustainable development of environment through this paper

**Problem statement:**

Students awareness Programme for sustainable development of environment.

**Research objectives:**

- 1) To find out secondary stage students awareness about environment.
- 2) To prepare awareness programme for sustainable development of environment for secondary stage students.
- 3) To implement awareness programme for secondary stage students.

**Assumptions of the Research:**

- 1) Secondary stage students are having less number for environmental awareness.
- 2) Teacher has possible to aware secondary stage student about environment through environment awareness programme.

**Research Hypothesis:**

Environment awareness programme create environment awareness among secondary stage student.

**Scope and Delimitation of Research:**

- 1) The present research is limited to Kumar Bhavan, Shengaon Marathi medium school, Tal: Bhudargad, Dist: Kolhapur
- 2) The present research is limited to secondary stage students in academic year 2018: 19.

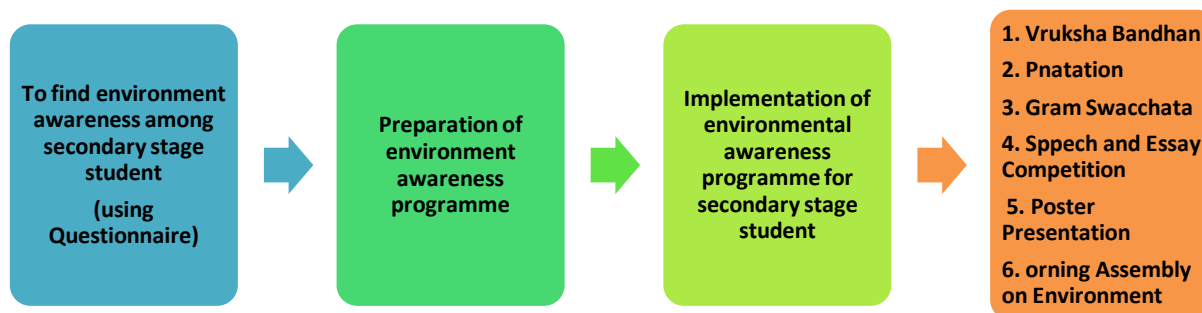
**Importance of Research:**

- 1) Present research is important to students and teachers of primary stage, higher secondary stage, college and university education.
- 2) Present research is important to society.

**Research Methodology:**

The researcher has used survey method:

Flow chart of Research work:

**Research sample:**

Purposive sampling method has been used in the present research.

**School:** Kumar Bhavan, Shengaon high school

**Class:** Secondary stage Student 100% (IX<sup>th</sup> & X<sup>th</sup> std.)

**Total Samples:** 60 Students

**Research Tools:**

The researcher has used following research tools for data collection.

- 1) Questionnaire: Researcher prepared.
- 2) Percentage.

**Analysis of the data:**

It was observed by overall assessment of students answer sheets that the students had very less awareness about environment.

**Table 1: Percentage of environmental Awareness among secondary stage students**

Sr. No.	Standar	No. of student	% of students had environmental awareness.
1	IX	30	22
2	X	30	25

From the above table it is clear that the secondary students had very less amount of environmental awareness.

**Conclusions:**

Main conclusions according to objectives

**Objective 1) To find out secondary stage students awareness about environment.**

- 1) IX<sup>th</sup> Std. students have (22%) less amount of environment awareness.
- 2) X<sup>th</sup> std. students have (25%) less amount of environmental awareness

**Objective 2) To prepare awareness programme for sustainable development of environment for secondary stage students.**

- 1) It is possible to teacher to prepare environmental awareness programme for sustainable development of environment.

**Objective 3) To implement awareness programme for secondary stage students.**

- 1) Teacher can implement environmental awareness programme for secondary stage students.

**Recommendations:**

- 1) Primary, higher secondary, college, university stage students should be made aware about environment for sustainable development of environment.
- 2) Primary, secondary, higher secondary, college, University stage teacher should develop multimedia software on environmental awareness and also visit to historical places to discuss how these places can be secured.
- 3) Visit to rich environmental places, to know natures richness and its importance to human being and aware about sustainable development of environment.
- 4) Teacher must give opportunity to student for implementation of various activity of environmental awareness for sustainable development of environment.

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## SOME MATHEMATICAL TECHNIQUES USEFUL IN GRADING WATER QUALITY

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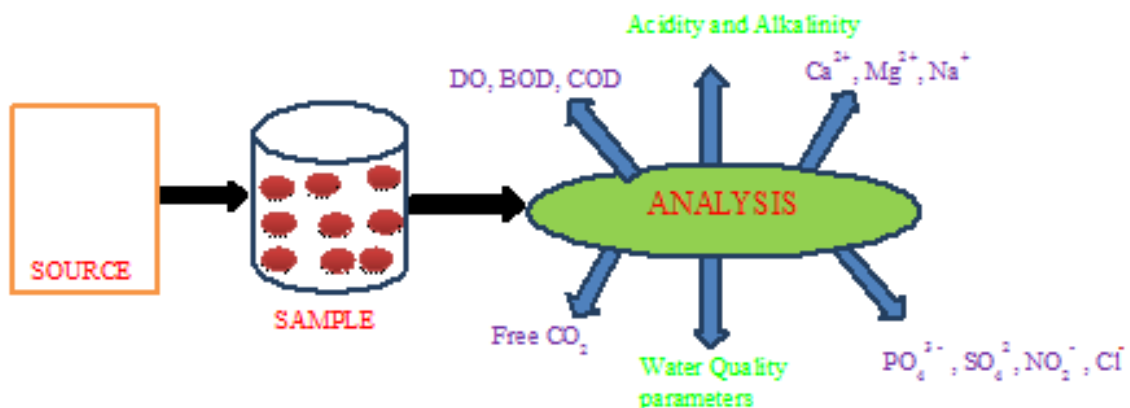
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### Abstract:

Water is the most important in shaping the land and regulating the climate. It is one of the most important compounds that profoundly influence life. The quality of water is usually described according to its physical, chemical and biological characteristics. Rapid industrialization and indiscriminate use of chemical fertilizers and pesticides in agriculture are causing heavy and varied pollution in aquatic environment leading to deterioration of water quality. Water quality monitoring has been high priority to determine the current conditions of the water system. Water quality indices provide the first hand assessment in a simplified manner on the quality and possible uses for irrigation. Many indices are required for specifying the quality of water for irrigation purposes as a single parameter can be restrictive at times. pH, conductivity, total hardness, nitrite, alkalinity, sodium, magnesium, DO, TDS etc were analyzed. Permeability Index (PI), Kelly's ratio, Sodium Adsorption Ratio (SAR), Magnesium Hazard (MH) was calculated based on the analytical results. Water Quality Index Computation is also useful data interpretation technique. It was observed that water quality profile was good and normal for irrigation purposes.

**Keywords:** Water Quality, Kelly Ratio, SAR, PI

### Introduction:



Water is an essential component for the survival of life on earth, which contains minerals, important for humans as well as for earth and aquatic life [1]. Water, a prime natural resource and precious national asset, forms the chief constituent of the ecosystem [2]. In agricultural practices, water is an important input for the growth of plants. This input

is the basis of planning an intensive system of agricultural exploitation with sustainable characteristics [3]. The kind of water for irrigation has effects on the quality, production and the type of soil. Moreover, irrespective of its source water contains soluble salts and impurities which might render it ideal for domestic purposes but not for agricultural practices, therefore water quality should be verified before putting it to use for agricultural purposes [4].

As a matter of fact, it is worthwhile to mention that water quality is an important criterion as water used in irrigation influences the nature and permeability of soil besides the fertility. In fact, the suitability of water for irrigation depends on the water quality characteristics that ensure maximum yield under good soil and water management practices. But the quality characteristics of irrigation water depends upon the water soluble constituents like calcium, apart from the catchment water balance, soil types, climate, crop tolerance and drainage characteristics [5, 6]. Thus irrigation water influences the crop yield by affecting the soil characteristics like soil permeability, toxicity, texture etc. So quality of irrigation water needs to be evaluated for its suitability in agriculture. The use of the indices is very important to evaluate the quality water, because they relate at least two variables and give a more extended and wide point of view. The indices which relate the salinity risks and hazards were proposed to assess irrigation water quality [7, 8]. These utilize the water quality data and help in the modification of policies, which are formulated by various environmental monitoring agencies. It has been realized that the use of individual water quality variable in order to describe the water quality for common public is not easily understandable [9]. That is why; these techniques have the capability to reduce the bulk of the information into a single value to express the data in a simplified and logical form [10].

#### Analytical procedure for the physicochemical parameters:

Physico-chemical parameters of water, their units and method of analysis are summarized in Table 1.

**Table 1: Water quality parameters associated with their abbreviations, units and analytical methods used**

Parameters	Abbreviations	Units	Analytical methods
pH	pH	pH unit	pH meter
Air temperature	A –Temp	<sup>0</sup> C	Thermometric
Water temperature	W –Temp	<sup>0</sup> C	Thermometric
Colour	Colour	Hazen units	Visually
Electrical conductivity	EC	$\mu\text{Scm}^{-1}$	Electrometric
Salinity	Salinity	ppm	Electrometric
Total Dissolved Solids	TDS	ppm	Evap. Method
Total Hardness	T-Hard	ppm	Titrimetric
Turbidity	Turbidity	NTU	Turb metric
Dissolved Oxygen	DO	ppm	Prob. Method
Chemical Oxygen Demand	COD	ppm	Spectroquant photometric
Biochemical Oxygen Demand	BOD	ppm	Prob. method (5 days later)
Total Alkalinity	T-Alk	ppm	Titrimetric
Phosphate	PO <sub>4</sub>	ppm	Photometric
Sulphate	SO <sub>4</sub>	ppm	Gravimetric
Nitrite	NO <sub>2</sub>	ppm	Spectroquant NOVA 60
Free carbon dioxide	Free CO <sub>2</sub>	ppm	Titrimetric
Acidity	Acidity	ppm	Titrimetric
Total Chloride	T-Cl	ppm	Titrimetric

Calcium	Ca	ppm	AAS
Magnesium	Mg	ppm	AAS
Sodium	Na	ppm	AAS

### Data treatment by Mathematical Methods:

#### I) Water Quality Index Computation:

Weighed arithmetic water quality index method classified the water quality according to the degree of purity by using the most commonly measured water quality variables. The method has been widely used by various scientists and the calculation of WQI was made by using the following equation:

$$WQI = \frac{\sum QiWi}{\sum Wi}$$

The quality rating scale (Qi) for each parameter is calculated by using this expression

$$Qi = 100[(Vi - Vo / Si - Vo)]$$

Where,

Vi is estimated concentration of ith parameter in the analyzed water

Vo is the ideal value of this parameter in pure water

Vo = 0 (except pH = 7.0)

Si is the recommended standard value of ith parameter

The unit weight (Wi) for each water quality parameter is calculated is calculated by using the following formula:

$$Wi = K/Si$$

Where,

K = proportionality constant and can also be calculated by using the following equation:

$$K = 1 / \sum \left( \frac{1}{Si} \right)$$

The rating of water quality according to this WQI is given below in table 2.

**Table 2: Water Quality Rating as per Weight Arithmetic Water Quality Index Method**

WQI Value	Rating of Water Quality	Grading
0-25	Excellent water quality	A
26-50	Good water quality	B
51-75	Poor water quality	C
76-100	Very poor water quality	D

By employing important physico-chemical parameters like COD, EC, TDS, BOD, nitrite, total alkalinity, sulfate, chloride, Ca and Mg ions for which the recommended standard values were available in arithmetic water quality index equation and doing the required simulations.

**II) The Permeability Index (PI):**

The PI is also a useful tool which indicates whether water samples are suitable for irrigation. The classification of water is done as Class I (>75%), Class II (25-75%) and Class III (<25%) to find out suitability of water for irrigation purpose. Irrigated water influenced by Na, Ca, Mg and HCO<sub>3</sub> ion contents affects the permeability of the soil after a long term use. Class I and II are categorized as good water quality for irrigation and Class III as unsuitable for irrigation having a maximum permeability of 25%. The PI was calculated employing the following equation, where all the ions are expressed in meq/L.

$$\text{PI} = \frac{\text{Na}^+ + \sqrt{\text{HCO}_3} \times 100}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+}$$

**III) Kelly's Ratio (KR):**

KR was calculated employing the following equation:

$$\text{KR} = \frac{\text{Na}^+}{\text{Ca}^{2+} + \text{Mg}^{2+}}$$

Kelly's ratio less than one is generally considered suitable for irrigation.

**IV) Sodium Adsorption Ratio (SAR):**

The SAR parameter evaluates the sodium hazard in relation to calcium and magnesium concentrations. This parameter is commonly used as an index to evaluate water suitability for irrigation purposes. The SAR was calculated by the following equation:

$$\text{SAR} = \frac{\text{Na}^+}{\sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2}}$$

If SAR value is < 10, the water is safe for irrigation with no structural deterioration. On the other hand, the SAR value is > 6-9, the irrigation water will cause permeability problems on shrinking and swelling types of clayey soils. Continued use of water having high SAR leads to breakdown in the physical structure of the soil particles.

**IV) Magnesium Hazard (MH):**

Magnesium concentration of water plays an important role in determining the quality of water for irrigation purposes and hence, agricultural use. Magnesium hazard was determined by employing the following equation:

$$\text{MH} = \frac{\text{Mg}^{2+}}{\text{Ca}^{2+} + \text{Mg}^{2+}} \times 100$$

Generally, magnesium hazard more than 50 is considered harmful and unsuitable for irrigation use.

**Conclusion:**

From the above mathematical treatments we can determine the quality of water of any water body for many useful purposes including irrigation. An irrigation water quality factor alone is not enough to evaluate potential salinity and hazards which may be confronted under irrigated agriculture. The concept of quality is multiplicative in nature. They can be so different that at times they can be incompatible among themselves. It would be more relevant to discuss the quality profile. This means that instead of a unique value, we can bring many values to reach a better understanding

about the kind of water. From the analysis of the different parameters measured and the application of indices and quality norms.

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## A STUDY OF FECUNDITY

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### Introduction:

Fecundity may be defined as the reproductive capacity of a female fish to lay total number of eggs in a single spawning season [1]. It can be used to assess the population of fish. The knowledge of fecundity is essential for evaluating the commercial potentialities of its stocks, life history, practical culture and actual management of the fishery [2]. Study of fecundity is very significant to determine the number of ova in the ovaries released in a season. It varies in species to species and even in the within species. It is also found varied with status of ovary, length, age and weight of the fish.

Studies on fecundity and its relationships with various body parameters viz. total length (TL), total weight (TW), ovary length (OL) and ovary weight (OW) are useful in increasing the yield of fish species, stock management and assessment of any water body.

### Fixatives and preservatives of ova:

The ovaries of the fish collected for the estimation of fecundity. The collected ovaries commonly preserved in formalin and Glisson's fluid.

### Preparation of Gilsons fluid:

- |                        |   |                   |
|------------------------|---|-------------------|
| 1. Nitric acid 80%     | - | 15ml.             |
| 2. Glacial acetic acid | - | 09 ml.            |
| 3. Alcohol 60%         | - | 100ml.            |
| 4. Distilled water     | - | 880ml .           |
| 5. Mercuric chloride   | - | 20gm. (Sublimate) |

### Methods of Estimation:

The volumetric and gravimetric methods are used to estimate the fecundity of fishes [3]

- a) **Volumetric method:** In this method the total volume of the ovary is measured. The small pieces of the ovary are taken as random from the anterior, middle and posterior part of the ovary and the number of ova in each sample is counted along with the volume of the sample. The total number of ova in the total volume of the ovary is then calculated. Fecundity is estimated by the following formula.

$$F = n V / v$$

Where, F = fecundity, n= number of ova in the subsample V = volume to which the total number

- b) **Gravimetric method:** Formalin preserved ovary can be used to estimate the fecundity. In the gravimetric method Three sample of 1gm each are taken from the anterior, posterior and middle region of each ovary then number of eggs in each of the sub-sample are multiplied by the weight of ovary and fecundity is estimated by the following formula.

$$F = n G / g$$

Where “F” is the fecundity, n = the average number of eggs, G = weight of gonads and g = weight sub sample. (Gilsons fluid used to separate eggs from ovary).

**Fecundity - length relationship:** The fecundity - length relationship can be determined by the equation:

$$F = aL^b$$

Where, F= fecundity, L = length of fish, and a and b constant

The above analysis usually performed after a logarithmic transformation by fitting the straight line regression of fecundity of log length i.e

$$\text{Log } F = \text{log } a + b \text{ log } L$$

### **A study of fecundity of *Cyprinus carpio*:**

The present study is useful to understanding the relationship of fecundity with various body parameters viz. total length (TL), total weight (TW), ovary length (OL) and ovary weight (OW). During the present study, the total length of the specimens ranged from 15 cm to 45 cm and total weight ranged from 370 gm to 1112 gm and the results are given below along with the relationship separately.

#### **I. Relationship between fecundity (F) and total length (TL):**

The relationship between fecundity and total length of fish is shown in the table 1 and 2. According to it the number of eggs varied from 49,829 for a fish of length 15 cm to 3,89,384 for a fish of length 45 cm. The relationship between fecundity and the total length can be expressed as:

$$F = 2.42 + 1.910 \text{ TL} \quad (r = 0.983)$$

Where, F = fecundity, TL = Total length in cm.

The number of eggs contained was more or less directly proportional to the total length of the fish body. The regression equation is found to be linear (Figure 1). The correlation coefficient  $r = 0.983$  which corresponds to a very strong positive correlation. It is highly significant. It is clear from the equations that, the growth frequency of *Cyprinus carpio* increase at the rate being nearly directly proportional to the increase in length and the graph plotted between fecundity and body length showing straight line relationship (fig. 1).

#### **II. Relationship between fecundity (F) and total body weight (TW):**

The relationship between fecundity and total body weight of fish is shown in table 1&3. The number of ova varied from 49,829 for a fish of weight 370 g to 3,89,384 in the fish weighing 1112 gm. The relationship between fecundity and the total body weight can be expressed as:

$$F = 4.96 + 1.908 \text{ TW} \quad (r = 0.983)$$

Where, F = fecundity, TW = Total weight of fish in grams.

Fecundity increased as the body weight increased. The relationship between fecundity and the total body weight is found to be linear and highly significant with the correlation coefficient  $r = 0.985$  and ( $r = 0.984$ ) It is clear from the equations that, the growth frequency of *Cyprinus carpio* increase at the rate being nearly directly proportional to the increase in body weight and the graph plotted between fecundity and body weight showing straight line relationship (Figure 2). The regression equation  $Y = 4.96 + 1.908 X$

#### **III. Relationship between fecundity (F) and total ovary length (OL):**

The relationship between fecundity and ovary length of fish is shown in table 1and 4. Number of ova varied from 31500 in an ovary of length 12.5cm to 345384 numbers of ova in the ovary of length 26.8 cm. The relationship between fecundity and the ovary length can be expressed as:

$$F = 0.129 + 1.787 \text{ OL} \quad (r = 0.945)$$

Where, F = fecundity, OL = Length of ovary in cm.

Fecundity increased with ovary length. A significant linear relationship was observed between fecundity and ovary length (Figure 3). The correlation coefficient  $r = 0.945$

#### IV. Relationship between fecundity (F) and total ovary weight (OW):

The relationship between fecundity and ovary weight of fish is shown in Table 1 and 5. Number of ova varied from 31500 for a fish of ovary weight 35 g to 345384 for a fish of ovary weight 332.1 gm. and number of ova varied from 36750 for a fish of ovary weight 37.5 gm to 355630 for a fish of ovary weight 2943 gm. The relationship between fecundity and total body weight can be expressed as:

$$F = 0.490 + 1.946 \text{ OW} \quad (r = 0.972)$$

Where, F = fecundity, OW = Weight of ovary in grams.

Analysis of regression showed that there is a significant relationship between numbers of eggs in the ovary (fecundity) and the weight of ovary (Figure 4). Number of eggs per female increased with increasing ovary weight. The correlation Coefficient was found to be  $r = 0.972$  which high degree of positive correlation and the regression equation  $Y = 0.490 + 1.946 X$

The present study has been assessing fecundity in female *Cypricus carpio* was carried out to estimate the average and range in the number of ova laid by individual female during the breeding season, and to study the fecundity (f) with total length (TL), total body weight (TW), ovary length (OL) and ovary weight (OW).

Different relations have been found to exist between fecundity and the above body parameters by various workers. [4&5] have observed linear relationship between fecundity and total length. [6] found the relationship to be curvilinear in *P. sarana* from Loni reservoir.

A linear relationship between the fecundity and the fish weight, ovary weight, has been reported by various worker [7-10].

The values of correlation coefficient 'r' in the present study indicate that among the above four parameters studied, closest correlation of fecundity was observed with the ovary weight i.e., OW ( $r = 0.97$ ) followed by total body length i.e., TL ( $r = 0.98$ ), ovary length i.e., OL ( $r = 0.94$ ) and body weight i.e., TW ( $r = 0.94$ ). Hence, it is concluded that the ovary weight is a better index of fecundity than the total length, total weight and ovary length.

**Table 1: Total Length and fecundity in fish *Cyprinus carpio***

Sr. no.	Length of fish cm. (L)	Weight of fish gm.(W)	Weight of ovary gm. (Wo)	Length of ovary cm. (Lo)	Fecundity (F)
1	35	865	305	17	239730
2	40	988	340	18.4	302910
3	36	889	308.5	16.5	202918
4	37	914	330.5	19.2	275885
5	25	617	221.5	11.14	103486
6	22	543	200.4	11.2	90576
7	35	865	355.2	16.3	271728
8	32	790	304.1	13.5	205522
9	45	1112	412.1	19.8	389384
10	43	1062	395.7	19.2	383796

11	20	494	174.6	8.9	61822
12	18	444	150.7	9.2	58788
13	27	667	244.3	14.5	145052
14	22	543	201.5	8.5	104987
15	15	370	148.4	5.9	49829
16	17	420	168.4	8.2	57236
17	19	469	170.4	10.5	82227
18	20	494	186.9	10.8	87525
19	25	617	228.6	13.8	128816
20	22	543	225.4	12.3	103997
21	42	1038	380.7	21.5	341716
22	35	865	292.4	15.8	219300
23	36	889	326.9	18	219724
24	37	914	320.3	18.6	229465
25	25	617	326.4	13.1	150634

**Table 2: Correlation and Regression between Log total length and Log fecundity**

Sr. No.	Log L (X)	Log F(Y)	XY	X <sup>2</sup>	Y <sup>2</sup>
1	1.54406804	5.379722385	8.306657423	2.384146126	28.94141
2	1.60205999	5.481313611	8.781393236	2.566596216	30.0448
3	1.5563025	5.307320573	8.25979628	2.422077474	28.16765

**Table 3: Correlation and Regression between Log total weight and Log fecundity**

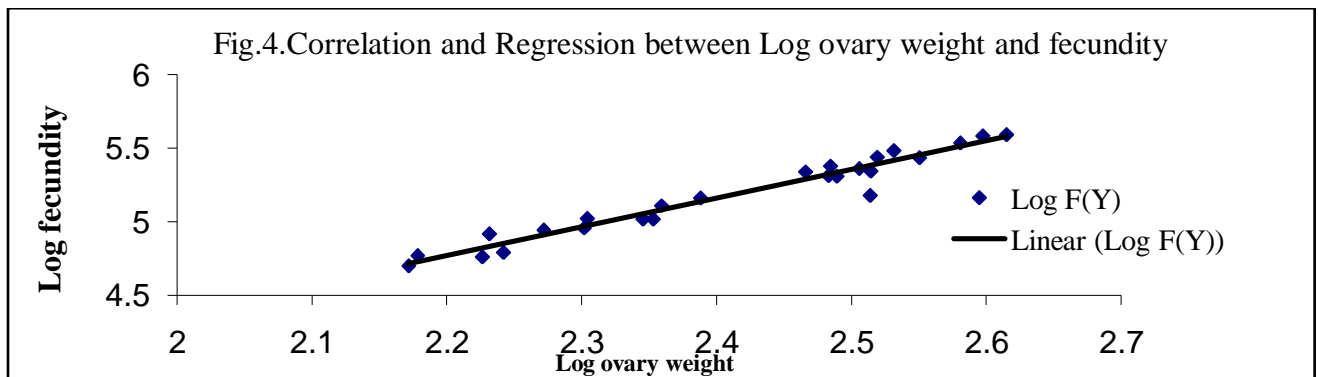
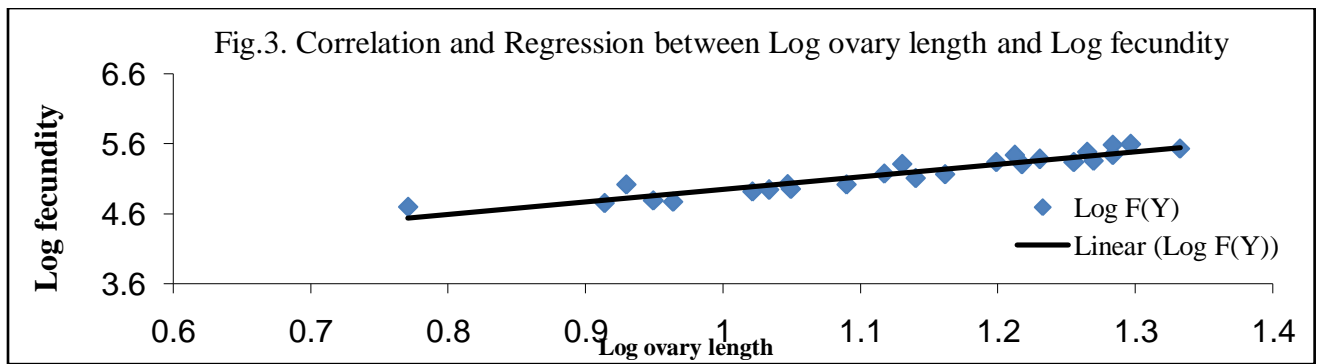
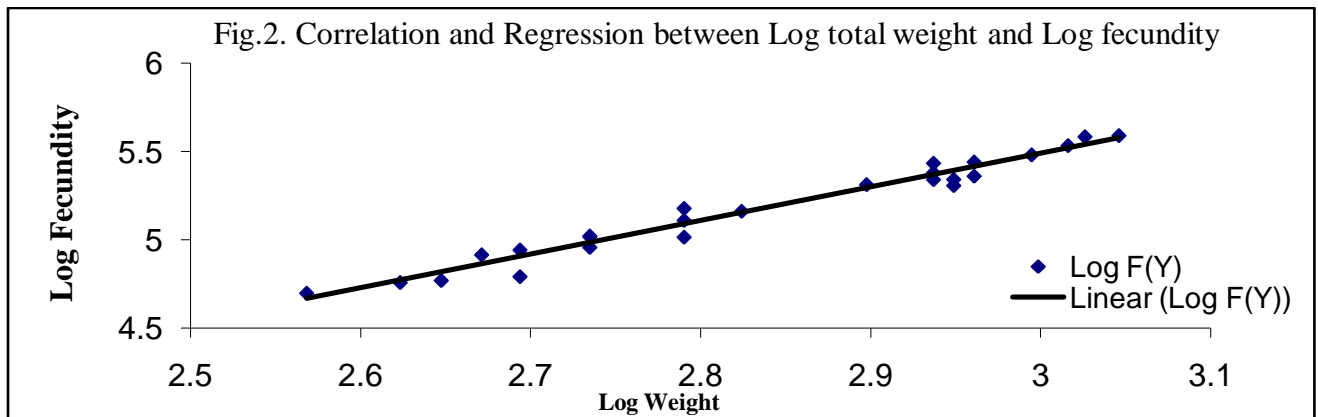
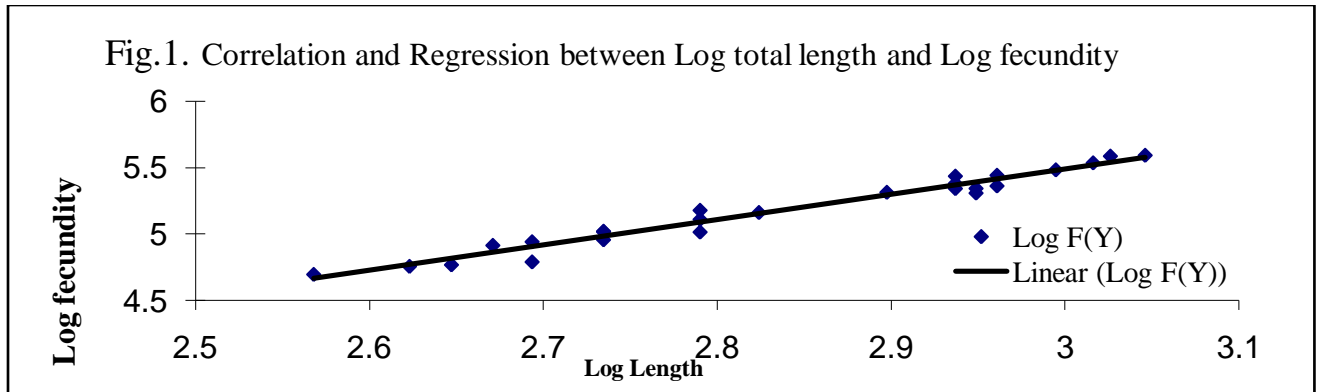
Sr. No.	Log W (X)	Log F(Y)	XY	X <sup>2</sup>	Y <sup>2</sup>
1	2.93701611	5.379722385	15.8003313	8.626063616	28.94141
2	2.99475694	5.481313611	16.415202	8.968569157	30.0448
3	2.94890176	5.307320573	15.65076698	8.696021596	28.16765

**Table 4: Correlation and Regression between Log ovary length and Log fecundity**

Sr. No.	Log OL (X)	Log F(Y)	XY	X <sup>2</sup>	Y <sup>2</sup>
1	1.230448921	5.379722385	6.619473606	1.514005	28.94141
2	1.264817823	5.481313611	6.932863149	1.599764	30.0448
3	1.217483944	5.307320573	6.461577585	1.482267	28.16765

**Table 5: Correlation and Regression between Log ovary weight and Log fecundity**

Sr. No.	Log OW (X)	Log F(Y)	XY	X <sup>2</sup>	Y <sup>2</sup>
1	2.484299839	5.379722385	13.36484346	6.171746	28.94141
2	2.531478917	5.481313611	13.87582984	6.408386	30.0448
3	2.489255168	5.307320573	13.21127517	6.196391	28.16765



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