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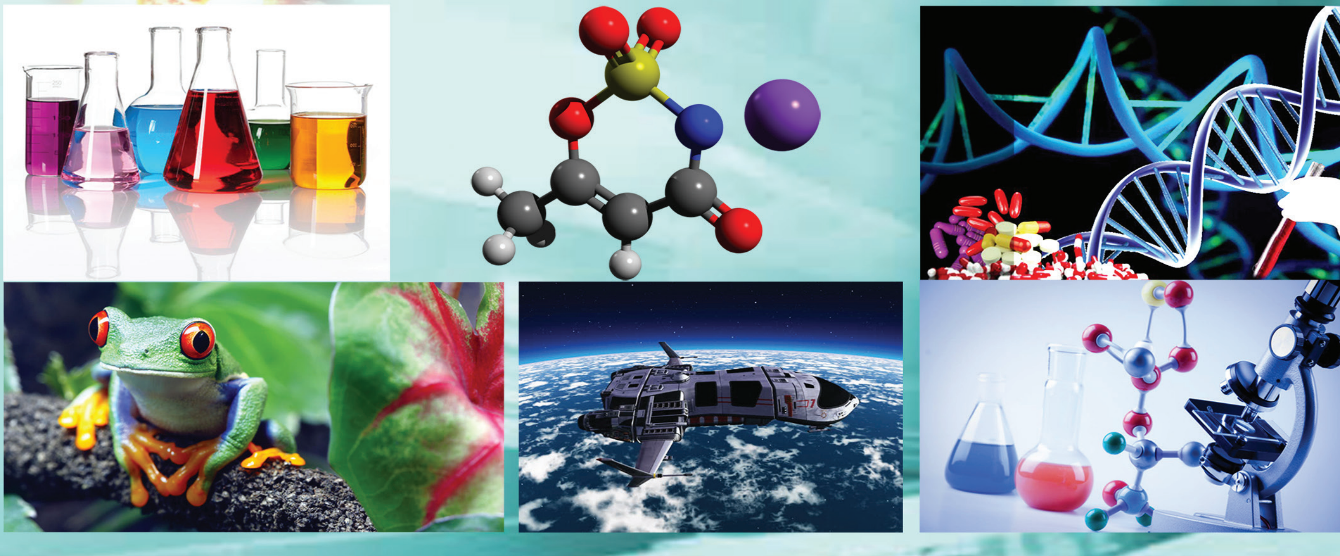

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STRATEGY PAPER

Hybrid Materials - Ushering a Promising Future

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Hybrid materials also referred to as 'composites' consists of two constituents (inorganic – organic) at the nanometer or molecular level. Hybrid materials differ from the traditional composites in which the constituents are at the macroscopic level (micrometer to millimeter). Composites accessed at the microscopic scale are more homogeneous material revealing characteristics of both the original phases or even new properties. Usually, the inorganic component provides mechanical strength and the organic part connects the inorganic building blocks and/or the soft tissue. Bones or nacre is typical examples of such materials. The field of functional nanoscale hybrid materials is one of the most promising and rapidly emerging areas in materials chemistry.

Nanoscale hybrid materials can be broadly defined as synthetic materials with organic and inorganic components linked together by noncovalent bonds (**Class I**, linked by hydrogen bond, electrostatic force, or van der Waals force) or covalent bonds (**Class II**) at nanometer scale. The wide range of possiblities of combinations of the distinct properties of inorganic, organic, or even bioactive components in a single material have been a fascinating aspect of such materials. Vast number of novel advanced materials possessing structures that are well defined with variety of functions furnishes immense opportunities for practical innovations. The field of applications include optoelectronic materials, biomaterials, catalysis, sensing, coating, and energy storage. The preparative methods, evaluation procedures, the stability mechanisms, and their potential applications in heat transfer intensification, mass transfer enhancement, energy fields, mechanical fields, and biomedical fields are of widespread interests.

The obvious advantages of hybrid materials over traditional composites are -

- Inorganic clusters or nanoparticles with specific optical, electronic or magnetic properties can be incorporated in organic polymer matrices.

- While pure inorganic materials often require a high temperature treatment for their synthesis, processing, hybrid materials due to their higher organic content or cross linked inorganic networks from small molecular precursors are much softer and readily processed at a relatively lower temperature.

- Hybrid materials and nanocomposites are optically more transparent. [1]

Development of state-of-the-art low cost electrocatalysts using commercially available precursors is important criterion in the advancement of next-generation electrochemical energy storage/ conversion systems. Noble metal-free and graphene-supported nanocomposites are of are considered excellent candidate as energy-device and sensor-related electrode materials for their high electrical conductivity, large specific surface area, high-speed electron/ heat mobility, and reasonably good mechanical strength. In the wide domain of graphene based hybrid materials, graphene-metal oxide nanohybrids hold great promise toward engineering efficient electrocatalysts drawing attention of scientific communities and industrial partners internationally [1-4]. There are several advantages - firstly, the large surface area and 2D flexibility of graphene nanosheets can offer sufficient space to accommodate different nanomaterials and prevent their agglomeration; secondly, due to the good superficial characteristics of graphene, solid-air contact efficiency increases enhancing oxygen adsorption; third, the electrical conductivity of graphene promotes the electron transfer rate on the surface. The structural defects of graphene also provide more active sites for newer modification by different functional groups promoting selective electrocatalysis [5]. Most metal oxides nanomaterials TiO_2, Fe_2O_3, Co_3O_4, MnO_2, CuO, NiO, ZnO have been incorporated in graphene forming nanohybrids.

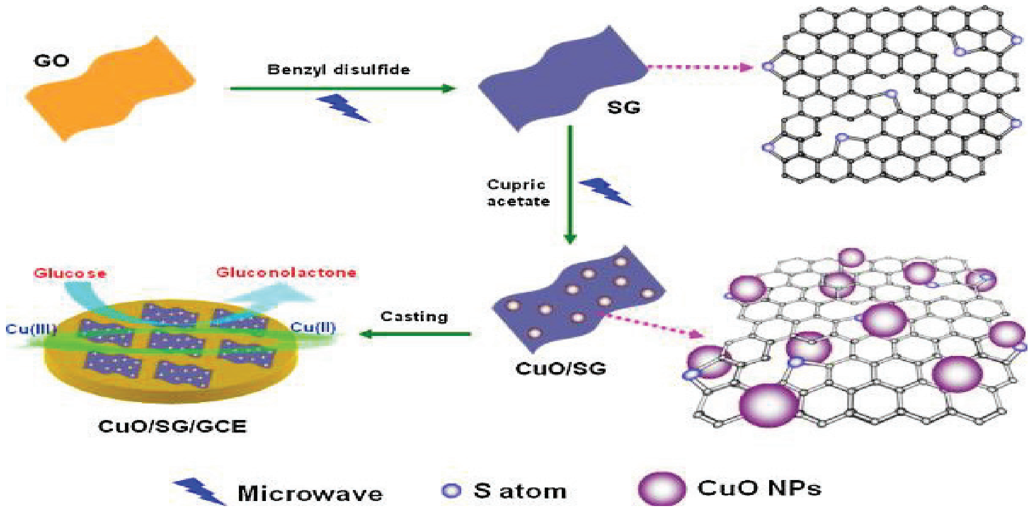

Figure 1. Illustration of the MW-assisted synthesis of CuO nanoparticle supported on S-doped graphene/SG and CuO/SG on glassy carbon electrode for glucose sensing. (Y. Tian, Y. Liu, W. Wang, X. Zhang, and W. Peng, Electrochim. Acta, 2015,156, 244.)

Various chalcogenide quantum dots (QDs) such as CdS, ZnS, Cu_2S, MoS_2, Sn_3S_4, and CdTe have been successfully immobilized on graphene by hydrothermal methods. These semiconductor hybrid nanostructures have drawn enormous interests due to their tremendous potential in optoelectronic, magnetic, and catalytic applications. Specifically, for biological applications, QDs provide a high quantum yield (0.1- 0.8 [visible], 0.2-0.7 [NIR] vs 0.5–1.0 [visible], 0.05–0.25 [NIR] for organic dyes), high molecular extinction coefficients (~10–100× that of organic dyes), broad absorption with narrow symmetric photoluminescence spectra (full-width at half-maximum ~25–40 nm) spanning from ultraviolet (UV) to NIR, high resistance to photobleaching, and exceptional resistance to photo- and chemical degradation. Size-tunable fluorescence emission and the broad excitation spectra of QDs offer significant advantage over molecular dyes [6]. Some transition metal nitrides exhibit noble-metal-like behaviors toward the reduction of tri-iodide ions because of their similar electronic structures and hence can be utilized as low-cost and platinum-free counter electrode in dye-sensitized solar cells (DSSCs). Highly ordered titanium nitrides (TiN), with high electrical and thermal conductivity, high catalytic activity as well as low-temperature superconductivity, are excellent alternatives as counter electrodes for DSSCs. But TiN electrode is not as efficient due to low electrical conductivity because of electron transport barrier across the boundaries of TiN nanocrystallites. Titanium nitride/graphene hybrid has been prepared and demonstrated comparable catalytic ability for triiodide ions reduction with Pt counter electrode in DSSCs [7]. Development of a facile approach for the synthesis of Au-reduced graphene oxide (RGO) nanohybrids with uniform distribution of Au NPs over RGO. High surface area and negative surface charge renders Au-RGO nanohybrids highly efficient for dye removal through electrostatic and π–π interactions [8].

Another interesting facet is the incorporation of nanomaterials into the self-assembly of discotic liquid crystals exploring new functional materials and realize their technological applications. The liquid crystal field has witnessed a paradigm shift with the advent of nanoscience and nanotechnology. Liquid crystal- nano composites is an emerging area of research dealing with the symbiotic association between liquid crystals and nanoscience. Thermotropic(temperature dependent) as well as lyotropic (concentration dependent) liquid crystals have been employed in recent times to access nano-LC hybrids. Dispersion of nanoparticles into liquid crystals is a captivating area of research [9]. The Liquid crystal (LC)-nano hybrid material allows for investigation of a mutually beneficial combination of the unique properties of the individual entities of liquid crystals and nanomaterials. Modulation of nanoparticle properties using LCs as well as tuning the LC properties through nanomaterial has been an attractive option for researchers as such hybrid materials are anticipated to be very useful in many high performance device applications viz. photoconductors, light emitting diodes, photo-voltaic solar cells, thin film transistors, etc. [10].

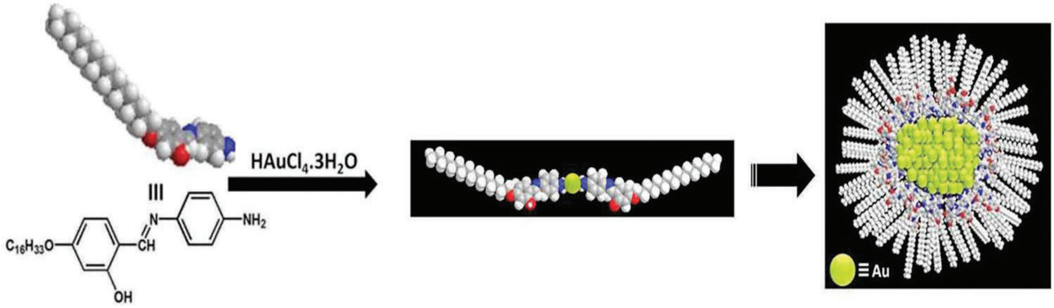

Figure 2: Synthesis scheme for Au-LC nanohybrid material

An asymmetrical nanoparticle pair containing both metal and semiconductors would be particularly interesting, as band structures and interfacial charge transfer processes can be deliberately influenced mutually. This can also lead to significant improvements in the catalytic, luminescent, sensing and magnetic properties. Some wet-chemical techniques are documented on free standing metal-semiconductor nanoparticle pairs [11]. In the optical domain, metal-based hybrid nano-objects are particularly interesting as plasmonic effects can be combined with the optical response of the other component materials. Thus, metal-semiconductor nanohybrids offer the possibilities of combining plasmonics and quantum confinement effects leading to enhanced or quenched optical responses [12].

Very recently, carbon dot (CD) metal based nanohybrids have been exploited for several photochemical and electrochemical applications due to their unique and interesting up-conversion photoluminescence and photo-induced electron charge transfer properties. The CD-metal based nanohybrids are envisaged to dominate the fields of photochemical and electrochemical devices due to their interesting up- and down-conversion photoluminescence characteristics as well as electron or charge transport properties with potential applications in the photo-catalysis, solar cell or photovoltaic, sensor, energy storage, etc [13].

Porous metal–organic frameworks (MOFs) and dense hybrid frameworks are emergent multifunctional materials that have garnered major developments in the last decade. Indeed the incredibly rich structural diversity of this new class of materials in combination with their “designable” physical and chemical properties has caught the imagination of scientists, engineers and technologists from multiple cognate disciplines. By virtue of their immense versatility and functionalities, a number of promising applications have already been proposed many of which aimed at challenging industrial sectors, *e.g.* energy harvesting and storage, biomedicine, sensing and microelectronics, carbon capture and environmental sustainability.

Search for advanced hybrid materials has generated cutting-edge research at the interface where crystalline engineering meets materials science, chemistry, solid-state physics and biology [14].

Currently, the most intricate technological challenges are - the need to reduce fossil fuel consumption and to capture CO_2 - producing hydrogen fuel from water, to efficiently sequester and store CO_2, and improve energy storage and rechargeable batteries have engaged the attention of present researchers. Microelectronics and smart technologies based on advances in optoelectronics, actuation and sensing are the key current issues having bearing on the development of public health and medicine, inexpensive, benign and efficient water desalination methods, drug encapsulation and targeted delivery technologies. An exciting class of materials called metal organic frameworks (MOFs) first developed in the 1990s is crystalline hybrid materials accessed from both organic and inorganic molecules via molecular self-assembly. Their fabrication involves linkers - long chains, typically of carbon and hydrogen oxides decorated with nitrogen atoms - and positively charged metal ions, which form nodes that bind the arms of the linkers together. Strategically the linker and metal are heated in a solvent for anything from hours to days until they settle into an orderly MOF structure. These MOFs have been processed into porous fabrics, glass, flexible thin films and biocompatible membranes. Given the large variations in metals and solvents that can be employed, MOFs have emerged as highly diverse chemical and structural make ups that suit specific functionalities. The enormous surface areas within their 3D open-framework structures are the highest of any known materials. MOFs are also extremely light - a pea-sized gram of MOF material can host the equivalent surface area of 40 tennis courts as most of their bulk is empty space. These material offers perfectly repeating networks of functionalized, molecular-scale cages, which can be tuned in size and shape to serve a specific function by adapting their chemistry[15]. The MOFs are crystalline hybrid materials constructed from inorganic and organic building blocks and accessed via the fundamental process of self-assembly at the molecular level. The resulting nanoporous materials encompass a myriad of 3D open-framework structures which vast chemical and structural diversity. The current research activities on MOF - materials are quite vibrant with cross-cutting disciplines capturing the attention and imagination of scientists, researchers and technologists alike. The option and handle to precisely control and functionalize the nanosized pore volume to afford unique multifunctional properties, unconventional physicochemical and thermomechanical characteristics have opened up new vistas for exploring multiple branches of chemistry, cognate fields of materials science, nanotechnology, physics, biology, medicine, and environmental engineering. Multitude of applications related to gas adsorption characteristics, selective separations and gas storage capacities; luminescence and chemical sensing response; ferroelectric, magnetic, and catalytic properties of MOFs are anticipated to evolve [16-21].

Conclusion

In conclusion, research related to hybrid materials have made tremendous progress in establishing a very promising field, which is now at a crossroad destined to make a significant impact in the future technology sector in turn bringing dramatic development in our modern living style in tandem with keeping a balance with the environment and energy. It is indeed exhilarating to anticipate smart applications and new innovations that are yet to be achieved next, and to realise the applications on a sustainable and commercial scale. Intense research in forthcoming years, discovery of newer materials and related fundamental studies will certainly hold key to such prospects.

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Discotic Liquid Crystals: Semiconductors of the Near Future.

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These days everybody is using a large variety of electronic devices such as notebook and tablet computers, smart phones, digital cameras, MP3 players, flat panel TVs, as well as embedded systems in household appliances, automobiles, and large industrial facilities. However, there is still an urgent need for downsizing such electronic equipment in order to save costs, space, weight, raw materials and more importantly energy and the carbon footprint. While calamitic (rod-like) liquid crystals have already contributed a lot to this development such as in large area flat panel displays, their corresponding discotic (disk-like) counterparts, besides some selected applications as optical compensator films for LCD and gas sensors, are still in the proof-of concept device state. Nevertheless, a lot of progress has been in this field and extensive research efforts world wide have been devoted to the development of such novel materials. There is a focussed effort in understanding of structure–property relationships in order to tailor compounds with desirable mesomorphic and other physical properties for the use of discotic liquid crystals asanisotropic organic semiconductors in organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), and organic photovoltaic devices (OPVs). The discussion of discotic liquid crystals started in 1923, when Vorländer suggested the possibility of liquid crystalline phases with a packing behaviour similar to “Voltas columns”while studying flat molecules such as triphenylene and perylene. Unfortunately, he was not able to observe any mesomorphism (liquid crystalline behaviour) for these compounds, which were later recognized as the archetypal core units of many discotics. The experimental breakthrough came in 1977, when Chandrasekhar published his findings on the mesomorphic properties of benzene-hexa-n-alkanoates, which were studied by differential scanning calorimetry (DSC), polarizing optical microscopy(POM), and X-ray diffraction (XRD). This is today considered as the birth of discotic liquid crystals. Besides this first observation of thermotropic mesomorphism of a disk-shaped molecule, Chandrasekhar made a comment in the introduction of his seminal paper, which must be considered from retrospective as a statement of great foresight. He wrote that "Mesophases composed of large plate-like molecules are known to occur at high temperatures during the carbonization of graphitizable substances, such as petroleum and coal tar pitches, but these are rather complex materials and certainly cannot be regarded as single-component liquid crystalline systems." Thus, Brooks and Taylor, who already in 1965 described mesophases consisting of planar aromatic compounds of high molecular weight as well as Zimmer and White, who reported on disclinations in the carbonaceous mesophase and proposeda model with lamellar organization can be considered as the grandfathers of graphene and polycyclicaromatic hydrocarbon derived columnar liquid crystals, which have received enormous interest over the last two decades due to their high electronic charge carrier mobility up to1.1 $cm^2 V^{-1} s^{-1}$, which is comparable to amorphous silicon. However, not only potential applications of discotic liquid crystals have driven the research but also basic questions regarding the origin of self-assembly in such systems. According to the classical view, liquid crystalline phases appear due to strong interactions between π-conjugated cores that are counter-balanced by the thermal motion of the alkyl chains thus inhibiting crystallization into a 3D structure with true 3D long-range translational and orientational order. Thus, it was generally thought that shape-anisotropic rod-like molecules prefer the formation of nematic or smectic mesophases, whereas disk-shaped molecules favour the self-assembly into1D columns eventually leading to 2D columnar mesophases with 1D long-range orientational order and 2D translational order or alternatively into 3D cubic mesophases. However, with the occurrence of non conventional mesogens, which are neither rod-nor disk-shaped, such as polyphilic mesogens, the significance of nano segregation between aromatic cores and alkyl chains as driving force for mesophases formation became commonly accepted. Therefore, incompatible side chains (alkyl, oligoethylene glycol, perfluoroalkyl, etc.) can induce liquid crystalline phases.

Structures of Discotic Liquid Crystals

The basic structures of discotic liquid crystals are:

Columnar Stacking: The stacking of the disk-like mesogens of discotic liquid crystals into 1D columns is fundamental for their most common phases. The columns are in the ideal case of infinite length and the molecules in a column exhibit only short-range positional order. The mesogens with their rigid, relatively flat cores self-organize into columns. This is caused by steric packing and π–π interactions between the cores. As a result of the high entropy and disorder of the flexible aliphatic chains on the periphery, the formation of a 3D crystal is hindered. The columnar stacking also leads to nano segregation between the cores and the tails. Different types of stacking can be found in the columns: There are "disordered columns" with irregular stacking of the disks, "ordered columns" where the cores are equidistant while the flexible alkyl-tails are still disordered as well as "tilted columns" with the cores of the disks being tilted with respect to the column axis. All these columns do not exhibit true 1D-translational order and can therefore be considered as 1D-fluids.

Nematic Phases: Nematic phases (also called the ND) are the simplest liquid crystalline phases formed since they only have long-range orientational order (of molecules, columns, etc.) and no degree of long-range translational order. For discotic molecules different kinds of nematic phases are known. In a discotic nematic mesophase ND the nematic phase is built of single flat molecules which possess full translational and orientational freedom around their principal short axes. Their long axes however are on average oriented parallel to a general plane in contrast to the rather waxy columnar phases the nematic phases are fluid. There is also a chiral variant of the discotic nematic phase known as the cholesteric phase ND* which is formed by chiral discotic mesogens or after the addition of a chiral dopant to an achiral discoticnematic phase. It exhibits a twisted nematic structure where the director field is continuously twisted in the direction normal to the local directions (r) with the pitch p of the helical structure. The columnar nematic mesophase Nc is formed out of columns as building blocks. The columns arrange parallel to each other in a columnar nematicmesophase and therefore exhibit positional short-range and orientational long-range order. Besides these two nematic phases also the lateral nematic phase NL has been reported. The lateral nematic phase is built of aggregates formed by multiple discoticmesogens. These supra-molecular aggregates then organize into a nematic phase one direction but also in two additional mutually perpendicular directions. These biaxial nematic phases are known for quite some time in lyotropic, polymeric, and more recently in mineral liquid crystals. In the case of discotic liquid crystals the formation of a biaxial nematic phase is expected in mixtures of rod- and disc-like mesogens. This mixing of rod- and disc like molecules was investigated by many groups using computer simulation. In these simulations the occurrence of a biaxial nematic phase was shown.

Columnar Phases: Discoticmesogens tend to form columns that are the building blocks of the columnar phases. In these phases, the columns order in a 2D-lattice with the column axes being parallel to each other. Due to the arrangement of the columns in a 2D-lattice, columnar phases can be considered as 1D fluid (along the columns) and 2Dcrystalline (along the 2D lattice vectors). Depending on the crystal system hexagonal (Colh), rectalgular (Colr) or oblique (Colob) phases are distinguished.

Lamellar Mesophase: In a lamellar mesophase DL the mesogens are ordered in layers like in calamitic smectic phases. The structure of the lamellar mesophase is still not completely understood. Recently lamellar discotic phases were observed for triphenylenesilanes by Mansueto et al. and in dimeric discotic mesogens by Prasad et al. and Ong et al.

Intra-columnar Helical: *Order* Unique macroscopic chirality effects in liquid crystals such as helicity and ferro electricity have been widely investigated in the case of rod-like calamitic mesogens since many years. In chiral nematic (cholesteric) or chiral smectic C (SmC*) phases of rod-like molecules the helical structures (as well as the spontaneous electric polarization of the SmC* layers) originate from the molecular chirality of the mesogens. In the more recently discovered case of bent-core ("banana-shaped") mesogens, however, spontaneous a chiral symmetry breaking results from steric interactions and close chiral packing of inherently non chiral but bent-shaped mesogens. This particular case of supra-molecular chirality gives rise to a plethora of chirality related phenomena such as the spontaneous formation of chiral domains, polar electro-optics witching, electric-field-driven deracemization, and helicalnano-filament phases. In comparison to their calamitic counterparts, the understanding of chirality effects and helical structures in discotic liquid crystals is not so far developed, even though indications of an intra-columnar helical structure in nonchiral hexa-alkoxytriphenylenes were found by Levelut et al. as early as in 1979, only two years after the discovery of discotic liquid crystals by Chandrasekhar et al.

Ferroelectric Columnar Liquid Crystals: Pyroelectric crystals have nonzero electric polarization even in the absence of an electric field. This polarization is thus denoted as spontaneous electric polarization Ps. If the direction of Ps can be switched by an external electric field between two stable states of equivalent energy, the material is called ferroelectric. Pyro- and ferro-electricity are by symmetry allowed only in media belonging to the ten polar point groups, namely Cs, Cn (n = 1, 2, 3, 4, and 6), and Cnv (n = 2, 3, 4, and 6). As ferro-electricity requires long-range dipole correlations it was believed that it is unique to the crystalline state of matter. In 1974 however, Meyer realized that a smectic C phase of chiral (rod-shaped) molecules has indeed polar C2 symmetry and thereby enables a spontaneous electric polarization in a fluid, liquid-crystalline state of matter. The pioneering work of Meyer et al. set-off a whole new field of liquid crystal research, namely that on ferro-electric, and lateral so anti-ferroelectric liquid crystals. Following the symmetry argument from Meyer, columnar phases of tilted, disc-shaped and chiral molecules also have polar C2-symmetry and should thus allow the appearance of a spontaneous electric polarization along the polar C2 axis, transverse to the column axis

Charge Transport Properties

Discotic Liquid Crystals are destined to become the Organic Semiconductors in near future. Organic semiconductors differ in many aspects from in organic semiconductors In inorganic semi-conducting materials, like e.g. silicon, all atoms are arranged on the fixed sites of a crystal lattice. Because of the dense packing and the resulting significant orbital overlaps of the single atoms, broad energy bands are formed (several eV wide).The delocalization of the energy states of the electrons leads to a large energy gain. The valence orbitals are responsible for the formation of the valence band and the conduction band. The valence band has binding character and is occupied with electrons down to zero absolute temperature. The conduction band in contrast is of non-binding character. At room temperature, electrons can also be found in the conduction band depending on the size of the band gap, so the Fermi level can be localized between the valence and conduction band. By the transfer of an electron from the valence band into the conduction band via optical or thermic stimulation a weakly bonded electron–hole pair (Mott exciton) is formed. If the binding energy is overcome, the charge carriers (electron and hole) can move separately in the delocalizedstates of the conduction and valence band. This is possible in inorganic semiconductors because of the hindered recombination of the charge carriers by the large width of the bands. Due to the easy creation of free charge carriers silicon fulfills the requirements for its application in microelectronic systems. The charge carrier mobility is one of the crucial parameters for the application of semiconductors in electronic devices, because fast switching times, especially in transistors, can only be achieved with high mobilities. Charge transport in in organic semiconductors, which can be described with the band theory, is very dependent on the temperature. With increasing temperature lattice vibrations increase, which increase the scattering of charge carriers and thus decrease their mobility. The mobility also depends on the degree of crystallinity. In a single crystal of silicon a very high electron mobility up to 1400 cm^2 V^{-1} s^{-1}at room temperature can be observed. In amorphous silicon charge carriers have to overcome grain boundaries. Here, the mobility is in the range of 0.5–1 cm^2 V^{-1} s^{-1} measured with thin film transistors (TFT). Although the mobility is much lower than in single crystal silicon, amorphous silicon is used in electronic devices, because the processing is very cost- and energy-efficient. In crystalline organic semiconductors the transport of charge carriers normally depends strongly on the packing of the molecules. Delocalized π-states are generated by overlapping of p-orbitals of the carbon atoms in the plane of the flat aromatic system. The molecules indeed are usually very small (except graphene) and the electrons are free to move within the π-system. Because of the limited dimensions of the conjugated systems the energy gap between the highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO) of the molecules is comparatively large (several eV). In organic molecular crystals the dimensions of the π-orbitals (HOMOs or LUMOs) are large enough to overlap with neighbouring molecules in the crystal. Therefore, a transfer of charge carriers is enabled. The transport of electrons takes place in the overlapping LUMOs and holes are transported through the HOMOs (comparable to conduction and valence band). In the past few years research in the field of organic electronic was intensified. Molecular crystals of conjugated organic semiconductors with mobilities of 40–60 cm^2 V^{-1} s^{-1} are suitable for the prospective application in electronic devices. In disordered organic semiconductors the charge carrier transport is basically treated differently. By investigations of the transport in various organic semi-conducting materials one could show that the mean free path length of a charge carrier is often shorter than the lattice constant. The overlap of the orbitals is thus not sufficient to form broad energy bands. Additionally, the charge transport in disordered semiconductors is nearly independent from temperature. The band model is therefore not suitable to explain charge carrier transport in disordered organic semiconductors (as the columnar phases of discotic liquid crystals). For mesogens of appropriate molecular shape columnar liquid crystal phases can be observed with a mean intra-columnar stacking distance less than 3.5 Å .With an aromatic π-system in the center of the mesogens, an overlap between theπ-orbitals (HOMOs or LUMOs) of adjacent molecules can be observed. Due to the large HOMO–LUMO energy gap of the single molecule no intrinsic charge carriers exist in the material. Charge carriers can, however, be generated in the columnar system by chemical doping (oxidation or reduction), optical stimulation or injection at metallic surfaces and can then be transported through the material. The electric contact between a metal and the disordered columnar semiconductor can be of Ohmic or Schottky character, due to the different Fermi levels of the metal and the semiconductor. In the case of electrical contact, electrons will flow from the metal into the semiconductor or reverse until the Fermi levels match each other. This leads to the formation of a space-charge region at the contact surface and to a band bending in the semiconductor. If the Fermi level of the semiconductor is higher, electrons will be rejected from the negative charged

The overall objectives of the research conducted on discotic semiconductors are to achieve the control of: (i) function through molecular structure and supra-molecular order; (ii) order from nm to mm scales; (iii) alignment to reach performance in devices and finally (iv) to link charge transport to dynamics and supra-molecular order. Although the field of discotics as semiconductors is still in its infancy, impressive achievements have been obtained. Original disc-like molecules of unprecedented size and structure have been synthesized. Their thermotropic behavior, solid state packing, alignment and processing have been tailored with the structural modifications of their side chains. The availability of pure discotic mesogens in sufficient amounts and with tailored mesophases has prompted their studies as semiconductors. It has become evident that the electronic delocalization in the x, y plane of the molecules and in the z direction of the column axes presents unusual aspects: (i) low band gap and low reorganization energies associated with the chemical stability in ambient conditions, (ii) high charge carrier mobility for electrons even in the presence of water and oxygen, (iii) high sensitivity of charge transport to structural defects and dynamics due to its quasi one-dimensional character, (iv) bandwidth comparable to that of graphite, (v) high quantum yield of fluorescence, and (vi) large exciton diffusion length, to mention only the most prominent features. It is stressed that the two-dimensional delocalization of electrons which is characteristic for disc-like molecules leads to molecular electronic features that are not observed in linear oligomers and polymers. In addition, molecular electronic properties are amplified at the supra-molecular level due to the extended interactions between p-systems. Therefore, discotics are a truly new generation of organic semiconductors, even if they have seldom been exploited in devices until now. Considerable work on device fabrication and optimization is obviously needed to uncover the full potential of discotic semiconductors. Numerous perspectives of new and exciting research exist, notably the control of supra molecular order, the miscibility and the morphology of discotic blends, the understanding of solution self-assembly and its translation into solid state packing, the use of helical columnar structures for generation of large non-linear optical responses, the combination of charge transport with magnetic properties, and the incorporation of columnar structures in membranes.

RESEARCH PAPER

Production Of Anti Microbial Soap And Assessment of its Quality Parameters from Non-Edible *Jatropa curcus*. L Seed (Jatropa Oil)

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Abstract

In this paper, Jatropha seeds were collected from Garo hills, a district in the state of Meghalaya, India. Oil was extracted using Soxlet apparatus to prepare sample soap with Jatropha oil adding caustic soda solution in appropriate temperature range. Different quality parameters of the soap were tested including antimicrobial activity against two species of bacteria i.e *E. coli* and *Bacillus thurengensis*. It was recorded that pH value, total alkali content, conductivity were within the permissible limit prescribed by Bureau of Indian Standards. Moreover, total fatty matter value of the prepared sample soap was 80% which can be considered as a Grade I soap according to the standards given by BIS. Antibacterial activity against two species of bacteria has revealed significant bactericidal effect as compared to the commercial antiseptic soap purchased from market which designate that Jatropha soap prepared from Jatropha oil can be utilized for production of high quality soap having medicinal value.

Keywords: **Jatropha, Medicinal soap, Jatropha oil, Garo hills**

Introduction

Jatropha is known for its use as purgative/laxative, and other medicinal uses. All parts of the plant, including seeds, leaves and bark, fresh or as a decoction, are used in traditional and folk medicine and veterinary purposes (Duke,1988). The oil is a strong purgative and is used in skin ailments and in rheumatism (Warra,2012). Antifungal and antibacterial properties of Jatropa oil could be found in many studies worldwide (Warra and Singh,2012). Oleic acid (44%), Linoleic acid (34%),Palmitic acid (14%) and Stearic acid (6%) are the main fatty acid components of *Jatropha curcas* seed oil. The oil is classified as unsaturated due to the presence of sufficient amounts of Oleic and Linoleic acids (Joshi *et al.,* 2011).Local soap industries use *Jatropha* oil which is one of the most economically attractive alternative uses of the oil. The glycerin by-product of the trans-esertification process of *Jatropha* oil can be used to make a high quality soap, or it can be refined and sold at a range of prices, depending on its purity, to be used in an immense range of products, including cosmetics, toothpaste, embalming fluids, pipe joint cement, cough medicine, and tobacco (as a moistening agent). The soap has positive effects on the skin and is therefore marketed for medicinal purposes. Oil for soap making is the most profitable use; the fruit of *Jatropha* contain viscous oil that can be used for soap making (Openshaw, 2000). It is rich in palmitic acid, with high levels of hydrophobicity, and makes a soft, durable soap under even the simplest of manufacturing processes. Soap from Jatropha Oil contains ingredients which have antifungal and bactericidal effect and it also prevents skin rashes (Gupta *et al.,* 2009).

Jatropha plants are abundantly growing in Garo hills, a district located in Meghalaya, the North eastern part of India. As there are many small scale industries for preparation of different products by utilizing native plants of the region, Jatropha oil can be used for such industries in preparation of soap.

Materials and Methods

Oil extraction from *Jatropha curcas* seeds by Soxhlet Extractor

From 3-6 years old plant, mature/ripe seeds of *Jatropha curcas.*Linn were collected from West Garo Hills , Meghalaya.

150 grams of *Jatropha curcas.* Linn seeds were used for extraction of oil in the Soxhlet apparatus. A soxhlet extractor is a piece of laboratory apparatus designed for the extraction od a lipid from a solid material. Typically, a soxhlet extraction is used when the desired compound has a limited solubility in a solvent, and the impurity is insoluble in that solvent. It allows for unmonitored and unmanaged operation while efficiently recycling a small amount of solvent to dissolve a large amount of material.

Soap preparation in the laboratory

Jatropha curcas seed oil has been used as one of the essential oil in making a antimicrobial/ antibacterial soap. The soap is prepared by using the traditional soap making method, first a lye solution is prepared by making a solution of Sodium hydroxide with distilled water, 100 grams of the Sodium hydroxide pellets was dissolved in 200 ml of distilled water. Then the solution is stirred with a wooden spoon , it is a exothermic reaction (care is taken not to put the water into the pellet) then the different oils i.e refined vegetable oil (100ml) Avacado oil (30ml) and *Jatropha* oil (3ml) is measured and mixed well. The lye solution is poured into the oil and then it is mixed properly using a hand mixer. When the reaction mass turned viscous like honey it was poured in moulds for solidification. After complete drying, crude soap was unloaded from mould and spray washed with water so as to remove unreacted caustic soda.

Antimicrobial activity in seed oil of *Jatropha curcas* L plant

Pure bacterial cultures namely *Bacillus thuringiensis* and *Escherichia coli* are obtained from Department of Biotechnology, University of Science and Technology Meghalaya, Ribhoi, Meghalaya.

In vitro antimicrobial studies were carried out on different bacterial cultures against test extract (seed oil) by agar disc diffusion assay method. 100µl aliquots of bacterial (about 10^6 cells/ml) were evenly spread on the agar plates using a sterile glass rod spreader, respectively. The plates were left at room temperature for 15 minutes to allow the agar surface to dry. The sterile disc containing the standard compounds and test compounds were placed on the inoculated plates. Then the plates are incubated at 37^0C and 30^oC for 24 hours to 48 hours, respectively. Experiment was performed under strict aseptic conditions. Cleared zones were scored as antimicrobial activity of standard compound against different tested microorganisms. The antimicrobial activity was evaluated by measuring the diameter of the inhibition zone. The experiment were performed in triplicate and the data were calculated as mean ± SD.

Calculation of % yield of Jatropha Soap

% Yield = (out/input) x 100

Determination of pH

pH of aquous *Jatropha* soap solution was recorded by using pH meter .

Determination of conductivity

0.1 M solution of Pure *Jatropha* soap was prepared. Conductivity of this soap solution was determined by using well calibrated conductivity meter. By using the above stock solution various dilutions were prepared viz. 0.05 M, 0.01 M , 0.005 M, 0.001M, 0.0001M .Conductivity of all above solutions were recorded with the help of conductivity meter and a graph was plotted between conductivity v/s concentration.

Determination of Total Alkali Content in the Soap Samples

5gm of soap sample is dissolved in 100ml hot water. About 40ml of 0.5N HNO_3 is added to make it acidic. The mixture is heated until fatty acids are floating as a layer above the solution. It is cooled in ice water to solidify the fatty acids. The fatty acids were separated and the aqueous solution was treated with 50ml chloroform to remove the remaining fatty acids. The aqueous solution was measured and 10ml of it was titrated against 0.5N NaOH using methyl orange as indicator and from the titer value the total alkali content was calculated using the following method.

Calculation:

Total volume of the aqueous solution: V ml
10 ml of aqueous solution required t ml of NaOH

V ml of aqueous solution requires: V x t /10 = A ml.

Amount of NaOH required by acid in aqueous solution: A ml

Volume of HNO3 required, B ml : A x Normality of NaOH / Normality of HNO3

Volume of HNO3 required for neutralizing NaOH : C=40 – B

Amount of NaOH in 1000 cc of soap solution (E): (C x 40 x Normality of HNO3 g) /1000

250 cc of soap solution contains (F): (E x 250) / 1000 g

2 NaOH ------- Na2O + H2O
80 gram of NaOH 62 g of Na2O

F g of NaOH requires (Y) = (62 x F) / (80) g of Na2O

Weight of soap taken: 5 g

% of alkalinity: (Y x 100) / w

Determination of the Total Fatty Matter in Soaps

5gm of soap sample is dissolved in 100ml hot water. About 40ml of 0.5N HNO3 is added to make it acidic. The mixture is heated until fatty acids are floating as a layer above the solution. It is cooled in ice water to solidify the fatty acids. The fatty acids were separated and the aqueous solution was treated with 50ml chloroform to remove the remaining fatty acids. The separated fatty matter was mixed together, solvent was evaporated and the yield is noted. The total fatty matter can be calculated using the following method.

Calculation

Weight of the china dish (x)

Weight of china dish + Soap after drying (y)

Weight of soap sample = 5 g

% of fatty mater = (y – x) x 100

Figure 1: Preparation of soap from Jatropa curcus oil

Result and Discussion

150gms of seeds of Jatropa curcus. L produced 27ml of oil which was used for the preparation of soap.

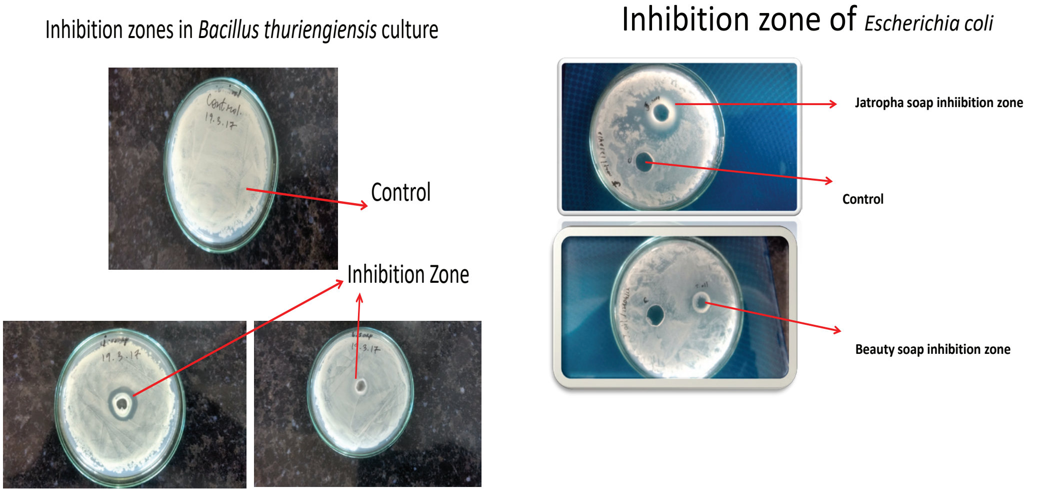
In order to investigate the antibacterial activity of Jatropa soap, disc diffusion assay was performed. The presence of zones of clearance of the soap solution present in the disc has antibacterial activity. The Jatropa soap has shown 44% of inhibition against *Bacillus thuringiensis* compared to the beauty soap which has 16% of inhibition. 60% inhibition could be observed in case of *Escherichia coli* compared to the beauty soap which has shown 50% of inhibition. Antimicrobial activity of Jatropha has earlier been reported by several workers (Ali and Geetha, 2014) Therefore, the present observations suggest that *Jatropha curcas* L. is a potential source of bioactive antimicrobial agents.

Inhibition agent used	**a (in mm) diameter of sample**	**b (mm) diameter of control**	**a-b (in mm)**	**% inhibition** **(a-b)/a *100**
Jatropha soap	18	10	8	44 %
Beauty soap	12	10	2	16 %

Table 1: Inhibition percentage of Jatropha soap against Bacillus thuringiensis

Inhibition agent used.	a (in mm)	b (mm)	a-b (in mm)	% inhibition (a-b)/a * 100
Jatropha soap	25	10	15	60 %
Beauty soap	15	10	5	33.33 %
Jatropha oil	14	10	4	28 %

Table 2: Inhibition percentage of Jatropha soap against Escherichia coli


Inhibition zones in *Bacillus thuriengiensis* culture

Inhibition zone of *Escherichia coli*

Figure 2: Inhibiton activity of Jatropha soap

It was observed that % yield of pure Jatropha oil soap was found to be 80.5%. (360gm of soap from 447 ml of oil).The alkali content of the soap was found to be 2. According to Bureau of Indian Standards (BIS), good quality soaps must have less than 5% of alkali content whereas according to ISO specification, soaps should have only below 2% of alkali content (Bureau of Indian standards,2011 and The International standard specification for soaps,1975).

TFM value of the soap was 80%.pH was recorded to be 8.1. According to BIS norms, this soap can be categorized as grade I soap and can be commercialized as a general bathing soap. According to International standards (ISO) good quality soap must have TFM above 76% (Lewkowltsch, 1922).The low total fatty matter is associated with hardness and lower quality of soap and it is the most important characteristics describing the quality of soap. The microbicidal activity of Jatropha extracts is probably due to their ability to form complex with extra cellular and soluble proteins and bacterial cell walls by nonspecific forces such as hydrogen bonding and hydrophobic effects, as well as by covalent bond formation. Thus, their mode of antimicrobial actions may be related to their ability to inactive microbial adhesins, enzymes, cell envelope transport proteins, etc. There is also evidence for direct inactivation of microorganisms (Scalbert,1991 and The International standard specification for soaps, 1975).

Therefore, the present observations suggest that *Jatropha curcas* is a potential source of bioactive antimicrobial agents.

It has been observed that research work on Jatropha oil is confined to the production of biodiesel. There is significant scope in soap production from non edible Jatropha oil due to low price, high availability and inexpensive technique of production. In Garo hills, where Jatropha plant is available in abundance, there is entirely no report of soap production from Jotropha oil. From experiments carried out during this research work it is clear that Soaps produced from non edible oil such as Jatropha has several quality parameters such as TFM, Total alkali content, pH etc. which makes it suitable for production of high quality soap.

Conclusion

Jatropha soap was prepared by using Jatropha Oil. Quality parameters such as TFM Value, Total Alkali Content, Free Caustic Alkali content, pH value etc. were found suitable for production of Toilet/Bathing Soap. Antimicrobial activity of Jatropha oil could be utilized for production of medicinal soap and also there is possibility of production of cheap surfactants for purpose of micellar catalysis.

Acknowledgement

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Mushroom Cultivation: A Source of Additional Income to Rural Households-A Case Study

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Abstract

West Garo Hills district of Meghalaya enjoys climatic condition congenial for growing oyster mushroom. Farmers are mostly small, marginal and landless labourers. Mushrooms are considered to be a good cash crop as it gives quick return and requires minimum land. Hence under the NICRA Project, KVK, West Garo Hills for the first time introduced Oyster mushroom cultivation among women SHGs in three villages viz. Marapara, Sanangre and Rongbokgre under Dalu Block of West Garo Hills district. Results obtained were encouraging as the SHGs on an average earned a net profit of Rs 5375/- per cycle of 50 days and have got heavy demand and market too. Thus, it is concluded that Oyster mushroom can be grown successfully to supplement additional income for the family.

Keywords: **Oyster mushroom, Women SHG, income generating activity, West Garo Hills**

Introduction

Agriculture is the back bone of Indian economy. After achieving food security by growing various kinds of agricultural crops, quest for achieving nutritional security is on. As the demand for quality food is increasing with the changes in lifestyle and income, these challenges can be meted out by diversifying the agricultural activity. Mushroom is one such component that imparts diversification and also provide quality food along with health and environmental security. Mushroom production in India is about 1.2 lakh metric tonnes, which is 3 % of world production (Prakasam,V., 2012). Per capita consumption of oyster mushroom in India is dismal 30-40 g as compared to 2-3 kg in USA and Europe (Singh, *et. al.*, 2012). Meghalaya produces 2 tonnes of oyster mushroom annually (Singh *et al.*,2011).West Garo Hills district of Meghalaya enjoys environmental conditions congenial for growing oyster mushroom. The local farmers grow Sali paddy with intermittent vegetable output during rainy season. Paddy straw after harvest are either fed to the cattle or are burnt to ashes which otherwise could have been profitably used for growing mushroom. Since the local tribal people are engaged in collection and consumption of wild edible mushroom and have readily available market too, cultivation of oyster mushroom could be a profitable venture. Keeping this in mind mushroom cultivation was introduced by KVK West Garo Hills under NICRA Project in three villages namely, Marapara, Sanangre and Rongbokgre. These villages are located between 90° 14′12.1″ to 90° 15′34.9″E longitude and 25° 20′48″ to 25° 20′54.1″N latitude in Dalu Block of West Garo Hills district of Meghalaya. Some important features of the villages are given below (Fig a & b; Table A)

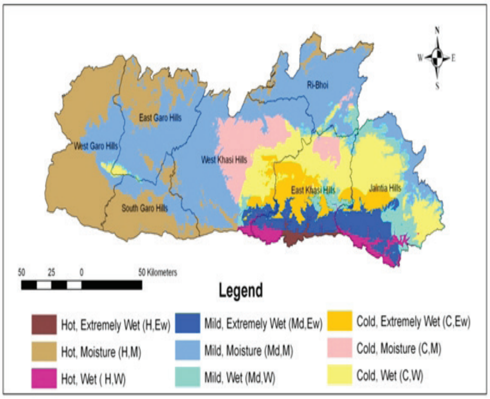

Figure: a

Figure: b

Villages/Item	Marapara	Sanangre	Rongbokgre
Number of Households	63	16	14
Total population (number)	390	92	89
Percentage of ST	98.97	97.83	97.75
Total Number of SHGs	06	02	01
Literacy %	63.47	62.82	83.58

Table: A (Source: *www.censusindia.co.in/subdistrict/dalu-block-west-garo-hills-meghalaya-1969 accessed on 25 Oct 2017 at 10:20 am*)

Out of these three villages (Marapara, Sanangre and Rongbokgre) one SHG was selected from each village based on their willingness to participate in the NICRA Project. As October to February is generally considered a lean period under rain fed agriculture situations, therefore the rural women were encouraged to grow oyster mushroom through Self Help Groups to earn additional income for the family. Since most of the materials needed for growing mushroom are obtained locally therefore cultivation process is bound to be economically viable.

Materials and methods

Members of the SHGs were given rigorous trainings and method demonstrations on oyster mushroom cultivation before taking up the activity. Cultivation of these mushrooms was done following the method of Vijay and Sohi (1987) with certain modifications. Cultivation method involved cutting the paddy straw in small pieces (3-4 inches) and soaking in clean water overnight. The soaked straw is then boiled in clean water in a drum for 45 minutes to disinfect the substrate and subsequently cooled and dried till moisture is 60-65 percent. Mushroom cultivation was done in HDPE bag (60cm x 45 cm) each of which was filled with 1 kg of the substrate and one bag (200g) of spawn placing in layers. The bags were kept at room temperature in the dark for 15 days for spawn running. On the 16th day after spawn running was complete the polythene bags were cut open to allow the mycelia running substrate for fruit body formation. Bags were hung on the bamboo in the cropping house and watered regularly to keep the substrate moist. Fully matured fruit bodies were harvested by twisting in upward direction and were weighed for recording data.

In this study each of the self help groups viz. Niji SHG, Sanangre SHG and Tangkame SHG from Marapara, Sanangre and Rongbokgre respectively were supported with low cost mushroom house and other basic requisites like spawn, HDPE bags, plastic rope, dettol, cotton, Knapsack sprayer, weighing balance, drum, bucket, black polythene required to grow mushroom. Paddy straw and fire wood were obtained locally. Monitoring was done timely and frequently by KVK officials to help the Self help groups to overcome the problems faced by them during growing mushrooms. Technical literature of mushroom cultivation was also provided to the SHG members after the training programme.

Results

Results have been presented in Figure: a, b and Table: A. It was observed that each of the SHG produced oyster mushroom successfully and on an average yielded 750g to 1 kg of mushroom from 1kg of dry straw. Among the three self help groups Niji SHG reported higher yield followed by Sanangre SHG and Tangkame SHG. Among the three varieties of Oyster mushroom *Pleurotus cornucopiae* performed better with an average yield of 1.23 kg per bag followed by *Pleurotus sajor-caju* (0.92 kg/bag) and *Pleurotus sapidus* (0.79 kg/bag).

	Average yield of *Pleurotus sapidus* per bag of wet paddy straw of 5 kg weight(g)			Mean Yield(kg/ bag)
SHG	1st flush	2nd flush	3rd flush	
Niji	484.40	297.00	168.20	0.95
Tankame	367.50	205.00	104.70	0.68
Sanangre	418.70	212.60	117.00	0.75
Mean	423.53	238.20	129.97	0.79

Table 1. Performance of Oyster mushroom *Pleurotus sapidus*

	Average yield of *Pleurotus cornucopiae* per bag of wet paddy straw of 5 kg weight (g)			Mean Yield(kg/ bag)
SHG	1st flush	2nd flush	3rd flush	
Niji	631.20	425.40	217.40	1.27

Tankame	596.70	388.20	194.20	1.18
Sanangre	622.50	415.20	206.70	1.24
Mean	616.80	409.60	206.10	1.23

Table 2. Performance of Oyster mushroom *Pleurotus cornucopiae*

Average yield of *Pleurotus sajorcaju* per bag of wet paddy straw of 5 kg weight (g)				
SHG	1st flush(g)	2nd flush(g)	3rd flush(g)	Mean Yield(kg/ bag)
Niji	570.40	283.40	140.40	0.99
Tankame	450.00	211.00	139.30	0.80
Sanangre	545.20	274.50	143.00	0.96
Mean	521.87	256.30	140.90	0.92

Table 3. Performance of Oyster mushroom *Pleurotus sajorcaju*

Mushroom was cultivated from September 2011 to March 2012, as it is generally considered to be congenial period for growing Oyster mushroom under Garo Hills condition, where the temperature ranges from 20-30°C and RH 80-85 %. Each of the SHGs on an average produced 50.5 kg from 60 bags prepared in a cycle lasting for about 50 days till the harvesting of the third flush. Total Cost involvement for preparing one bag (1 packet spawn (200g) for Rs 20/-,1 HDPE bag for Rs 3/- and dettol, cotton, plastic rope, drum etc for Rs 7/-) is Rs 30/-. For preparing 60 bags Rs 1800/- was required. The nominal selling price of oyster mushroom in West Garo Hills is Rs150/- per kg. Transportation and other miscellaneous cost like plastic bags for packaging mushroom included Rs 400/-.Thus, selling price of 50.5 kg @ of Rs 150/- per kg of fresh mushroom was Rs 7575/-with a net profit of Rs (7575-1800-400)= Rs 5375/- in one cycle of production. A farmer can have a minimum of four cycles during September to March season. Thus by selling oyster mushroom each of the self help groups contributed immensely to their common fund. Similar findings were reported by (Dass *et al*., 2008)

Some glimpse of the Case study under the NICRA Project

Fig1. Training the beneficiaries in mushroom cultivation

Fig 2. Low cost mushroom shed

Fig 3. Mushroom grown by the SHGs

Fig 4. Mushroom ready hor harvest

Fig 5. Harvesting of Oyster mushroom

Fig 6. 1st flush of Oyster mushroom

Fig 7. Recording data

Fig 8. Selling matured mushroom

Fig 9. Fully matured Oyster mushroom

Conclusion

Thus it is seen that under the NICRA project through KVK's intervention each of the Self Help group on an average earned an additional net profit of Rs 5375/ per cycle by growing oyster mushroom. All the SHGs selected had only women members. Hence each of the beneficiaries contributed additional income for their family along with easy source of nutrition in their diet. Since Oyster mushrooms are rich in protein, vitamins and minerals can provide an affordable alternative which in turn can reduce malnutrition.

The net profit obtained in mushroom cultivation attracted and encouraged other SHGs to take up the venture on small scale. People from the nearby villages also showed interest for mushroom cultivation and approached KVK for imparting technical support. As current market value and demand for mushrooms are high, the SHGs are interested to take up mushroom cultivation throughout the year to generate additional income and employment.

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Comparison of a Few Simple Prescriptions for the Selection of Number of Bins in a Univariate Histogram for Normally Distributed Samples Using Simulations

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Abstract

The mean squared error estimate is used to characterise the performance of 7 methods for determining the number of bins in a histogram, which serves to determine the underlying normal probability density function that generated the samples. The simpler and direct method of simulation is used to achieve the objectives of the present study. Random samples from normal distributions with 10 different values of standard deviation and 20 different sample sizes are used with 1000 runs for each combination. A fitting procedure is performed on the estimated mean squared error, which is then used to identify the prescription that gives the least error– determined to be the rule prescribed by Scott in the present study.

***Keywords* – histogram, simulation, least-square fit, mean squared error**

Introduction

One of the simplest methods of estimating the underlying probability distribution of a given set of samples is the histogram[1, 2]. Although, the term histogram is usually associated with the visual representation similar to a bar-graph with touching adjacent sides, but, in the current context it was deemed useful to expand the definition to include the entire process of generating the processed data for the graph from the raw dataset. For the construction of a histogram for a given dataset (assumed univariate in the present case), the total range of the data values is divided into non-overlapping intervals or 'bins' of equal size[1] and then for each interval the number of data points that lie in that interval is counted; with this data we can generate a frequency table with boundary values of the bins in one column and the corresponding frequencies (number of data points in that particular bin) in another column. The bar-graph plotted with each bar-width enclosing a bin and the bar-height equal to the corresponding frequency of data points is a histogram. Sometimes a few values are either too high or too low in comparison to the bulk of the dataset; such values are called outliers and may be either valid data points or the result of some gross errors in the measurements/calculations; in either case, the outliers are generally removed before the construction of the histogram and analysed separately. In the present case, it is assumed that the dataset has no outliers or that it has been removed. To obtain the probability density values, the frequency in each data bin is divided by the total number of data points, further divided by the bin-width.

The basic purpose of the histogram is to show the shape of the generating frequency distribution over the given range of values; in its construction, the primary concern is the number of bins to be taken – too few bins could over-smooth the shape leaving out important details and too many bins could under-smooth the shape and generate spurious details. Over the years, there have been a handful of suggestions for determination of the optimal bin-width or alternatively number of bins – some *ad hoc* methods (see table 1) and some based on statistical optimisation procedures. In the present paper, we will analyse the performance of 7 methods of determining the number of bins for a given univariate dataset taken from normal distribution. The comparative effectiveness and the simplicity of the *ad hoc* methods for the estimation of the bin-widths or the number of bins is exemplified in their usage in popular software packages for statistical calculations like Microsoft Excel 2017[2], which uses the Scott's rule.

Methodology

The 7 methods for determining the number of bins or the bin-number for the construction of the histogram used in the present paper are listed in table 1.

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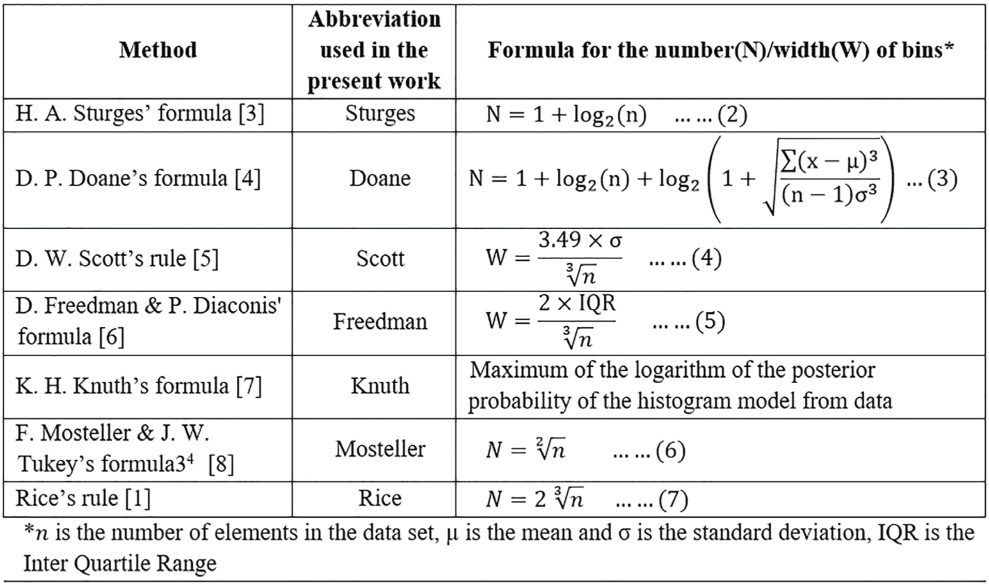
[1] The conditions of non-overlapping and equal size for the bins is not a strict requirement but is generally used to simplify the construction of the histogram.

[2] from online Microsoft Excel 2017 help at https://support.office.com/

The details about the individual methods may be obtained from the relevant references. A few of the tabulated methods calculate the bin-width (W) instead of the bin-number (N) – the relationship between the two is given by,

$$N = \frac{(range\ of\ data)}{W} \qquad \ldots\ldots(1)$$

Table 1: List of the methods used for estimating the bin-number/ number for drawing histogram from data.



Method	Abbreviation used in the present work	Formula for the number(N)/width(W) of bins*
H. A. Sturges' formula [3]	Sturges	$N = 1 + \log_2(n) \quad \ldots\ldots(2)$
D. P. Doane's formula [4]	Doane	$N = 1 + \log_2(n) + \log_2\left(1 + \sqrt{\frac{\sum(x-\mu)^3}{(n-1)\sigma^3}}\right) \ldots(3)$
D. W. Scott's rule [5]	Scott	$W = \frac{3.49 \times \sigma}{\sqrt[3]{n}} \quad \ldots\ldots(4)$
D. Freedman & P. Diaconis' formula [6]	Freedman	$W = \frac{2 \times IQR}{\sqrt[3]{n}} \quad \ldots\ldots(5)$
K. H. Knuth's formula [7]	Knuth	Maximum of the logarithm of the posterior probability of the histogram model from data
F. Mosteller & J. W. Tukey's formula3[4] [8]	Mosteller	$N = \sqrt[2]{n} \quad \ldots\ldots(6)$
Rice's rule [1]	Rice	$N = 2\sqrt[3]{n} \quad \ldots\ldots(7)$

*n is the number of elements in the data set, μ is the mean and σ is the standard deviation, IQR is the Inter Quartile Range

Since, the bin-number has to be an integer, therefore the computed values are rounded off to the nearest integer. The current work tries to rank the performances based on the results of simulation. All calculations and simulations have been done in the MATLAB computing environment.

Since, most of the above methods have been formulated with the normal distribution in mind, we have therefore carried out the simulations only for normal distribution with different values of the standard deviation (σ); since, the mean (μ) plays no role in the shape of the distribution, the same value of mean was used throughout.

The simulations were performed

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[4] also known as the square root choice

as follows 10 different normal distributions were considered with values ranging from 0.5 to 50 with almost exponential spacing viz. 0.5, 1, 2, 3, 5, 8, 13, 20, 32 and 50. For each of the normal distribution constructed, 20 different values of sample sizes ranging from 30 to 10000 were studied, again with almost exponential spacing between them. A certain number –the sample size – of pseudo-random numbers are then generated from the given normal distribution using MATLAB. 1000 simulations were done for each type. Using the various prescriptions, the histogram is constructed for each simulated sample and, from the data of the histogram, the probability distribution is computed. To estimate the difference of the computed probability distribution with the actual probability distribution function, we have used the mean squared error (MSE) as a measure of the difference. The MSE [2] is the mean value of the squared difference between the values of the constructed and actual probability densities at each evaluated point for each sample considered. The lower the MSE value the better is the agreement between the computed and actual values.

Results and Discussion

The mean value (of the 1000 simulation runs) of the probability density for each of the bin-number prescriptions along with standard deviation (shown as error-bars) is plotted in figure 1.It may be mentioned here that the prescriptions as given by Sturges, Mosteller and by Rice are purely functions of the sample size and hence the simulations do not affect their output i.e. bin-numbers prescribed, therefore, there are no error-bars in the corresponding plots in figure 1. Plots corresponding to different standard deviation (σ) values (of normal distribution for the same method are plotted in similar colour immediately adjacent to each other. It can be observed that the prescriptions of Mosteller and that of Freedman have relatively larger bin-numbers for higher sample sizes.

The mean values of the MSE score as a function of the sample size for different σ values are plotted in figure 2 as separate graphs for each prescription. We observe the expected pattern of higher MSE values at lower sample sizes and lower MSE values at higher sample sizes i.e. the MSE values decreases almost steadily with increasing sample size (*n*). This decrease in the MSE values with increasing *n* is found to nearly follow an inverse law i.e. the MSE values decreases as the reciprocal of *n*, therefore we decided to fit the MSE values from the various prescriptions to a function of the form:

$$\mathrm{MSE} = \frac{1}{n}\, a \qquad \ldots\ldots (8)$$

where, '*a*' is a parameter to be determined from least square fitting.

The values of the fitting parameter '*a*' obtained after performing a least square fit (at 95% confidence bounds) between the MSE values and *n* are plotted in figure 3; the error-bar represents the lower and upper confidence bounds. The parameter '*a*' also shows a non-linear decrease with increasing values, similar to (1/σ) trend; this can be understood as the result of the difficulty in capturing sharper peaks of a normal distribution curve (characteristic of small σ values) with relatively few equally spaced histogram bins.

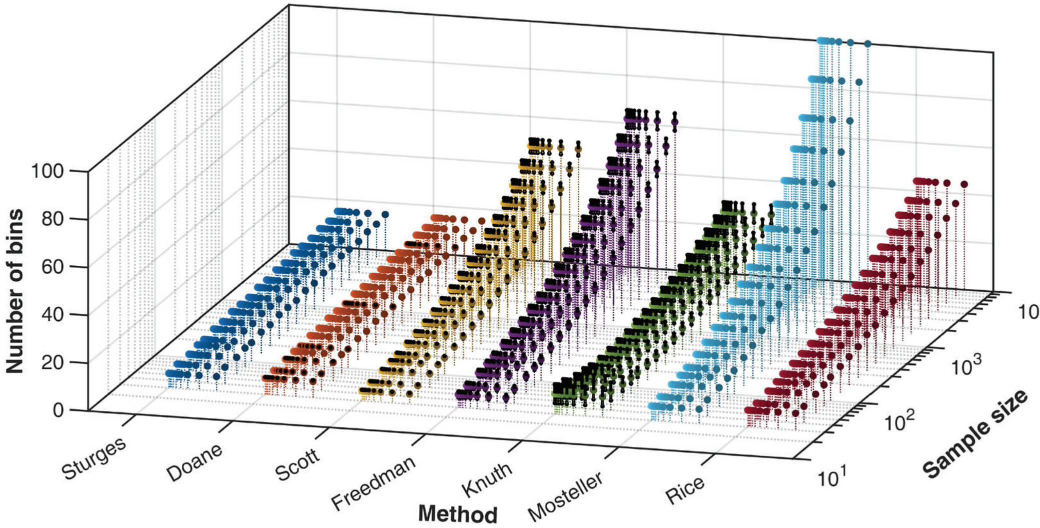

Figure 1: Plot of the number of bins of histogram for different sample sizes and methods of determining them. The name of the method employed is plotted in the x-axis and is self-evident. The 10 different values of σ are plotted in the same colour adjacently with their separation proportional to the value of σ .

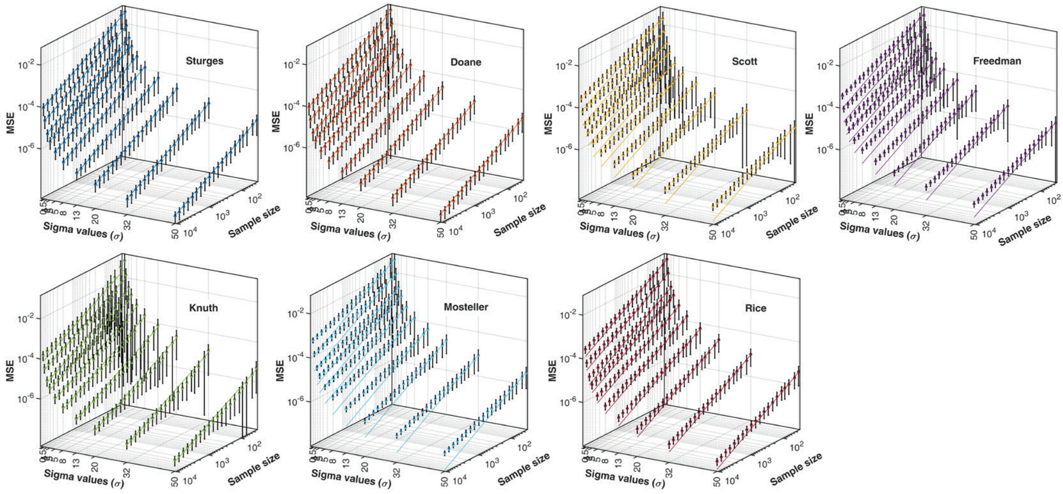

Figure 2: Plot of the MSE for different sample sizes and methods of determining them shown as coloured dots with error-bars (in black) representing standard deviation. The coloured solid lines are the best-fit lines according to equation (8).

The best-fit curve as obtained from the above fit is shown in figure 2 as a solid curve across the sample size. While noting the discrepancy between the actual data points and the best-fit curve in figure 2, we must remember that the graph has been logarithmically scaled.

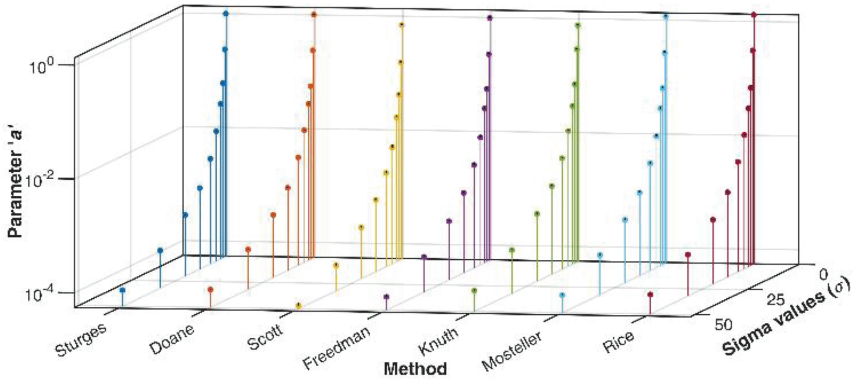

Figure 3: The least square fitting parameter 'a' for different methods at different values σ

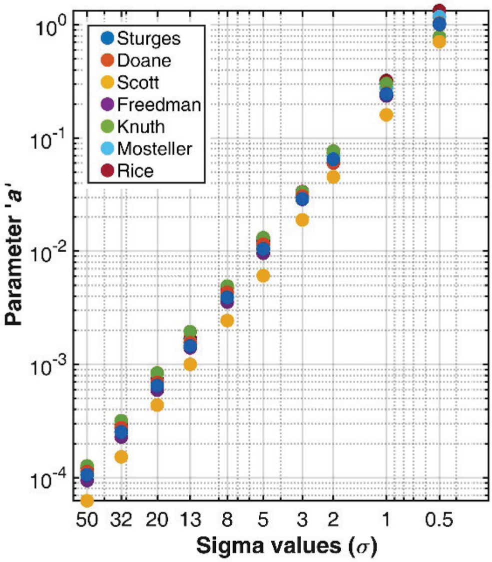

Figure 4: The values of the parameter 'a' for the different values of σ with colour coding for different methods employed in the estimation of the bin-number.

The figure 3 viewed as a 2D plot (as seen from the side) is given in figure 4. In this figure, the y-axis representing σ has been changed to logarithmic scale and since the 95% confidence bounds fall within the marker size of the scatter plot (as seen in figure 3), we have removed the error-bars in this plot. The figure 4 is plotted to show the variation of the MSE values between the different prescriptions. It is easily seen that the prescription given by Scott has the lowest '*a*' value for every σ value used in the present simulation.

From equation (8), it is easily seen that the value of '*a*' controls the rate of decrease of MSE with increase in *n* – lower the value '*a*' the faster is the decrease and vice-versa. Thus, we can take the value of '*a*' as the overall performance index of a given prescription in terms of the MSE measure. From figure 3, the Scott's prescription is found to have the lowest value of '*a*' and thus can be considered the optimal method as per the MSE measure.

Conclusion

The decrease in discrepancy in the estimation of the probability density function of a normal distribution using the method of histograms in terms of the

MSE measure is seen to have a non-linear rate of decrease viz. a decrease proportional to the reciprocal of the sample size with reasonable accuracy. This relation can be used to infer the number of samples that would be required to estimate the underlying normal probability density function for a given experiment to a specified level of accuracy. Further, from among the different methods for the estimation of the bin-number of histogram, the Scott's prescription is found to perform the best in our simulations in terms of the MSE score.

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REVIEW PAPER

Economics of Turmeric (*Curcura longa*) Cultivation in Goalpara District of Assam

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Abstract

The present paper is an attempt to study the participation of people in the form of Cluster approach in turmeric (*Curcura longa*) cultivation in Goalpara district of Assam. The present study is based on Primary data collected from Balijana block of Goalpara district, where 140 sample farmers were randomly selected from seven villages of the block. The Economics of Turmeric cultivation was examined by using various cost concepts. The study revealed that the return from management in the average farm situation of individual turmeric growers was estimated to be Rs 6188.89. Amongst the various size groups, return from management was found to be exhibited a decreasing trend with the increase in farm size. While the return from management in the average farm situation of cluster turmeric growers was estimated to be Rs 4649.33. Amongst the various size groups, return from management was found to be exhibited an increasing trend with the increase in farm size.

Keywords: **Economics, Cost Concept, Turmeric Cultivation, Cluster Based Approach.**

Introduction

Turmeric (*Curcura longa*) is known as the king of spices, and it is said that this spice belongs to India and also called 'Indian Saffron'. India is the largest producer, consumer and exporter of turmeric which constitutes 82% of world production followed by China, Myanmar and Bangladesh. As per Spice board of India- Annual report 2012-13, turmeric occupies about 6% of the total area under spices and condiment products in India. In the year 2008-09 the production was 94.59 thousand tons under 195.07 thousand ha of land which increased up to 973.09 tons under 192.91 thousand ha of land (Spice board of India- Annual report 2012-13).

Similarly the production of turmeric in Assam was 15583 tons with an area of 16309 ha in 2012-13 which has increased to 15906 tons with an area of 16244 ha in 2014-15 (Government of Assam, Directorate of economics and statistic, 2015). Turmeric is a valuable cash crop for cultivators as it is a ready cash crop and contributes to national economy as one of the major export commodities. The increase in production is possible mainly through improvement in productivity of the crop that could be achieved by efficient utilization of available resources.

As per 2010-11 turmeric production in North Eastern region is 6400.2 tons under 22,848 ha of land. Assam is endowed with diverse agro-climatic conditions, which permit growing of wide range of horticultural crops including spices and condiments. Horticulture crops cover an area of 5.75 lakh hectares which account for 14.04 per cent of the total cultivable area of 40.99 lakh hectares in the state in the year 2011-12 (NEDFI).

Concerned over low agricultural growth rate and low levels of farm income, the Union agricultural ministry is working towards a plan to introduce cluster-based farming in the country. The cluster-based approach is aimed at forming a consolidated cultivable holding dedicated to specific food grains, vegetables, spices and condiments, fruits and other horticulture crops (*Leisa India*, Jun 2013). Cluster approach has the potential to contribute immensely as it involves organized effort for collective production and sharing of knowledge and available resources.

The cluster concept has gained prominence as an economic policy tool aimed to foster innovation and the growth of a competitive private sector in developing countries. A cluster consists of firms and related economic actors and institutions that draw productive advantage from their mutual proximity and connections. Over the last 2-3 decades, clusters approach has drawn substantial interest from policy makers, legislatures, business leaders, academics, economic development practitioners and development agencies (Irshad, 2009).

Methods and Materials

The present study was conducted in Goalpara district of Assam covering a total 140 sample turmeric growers. Out of 140 sample turmeric growers, 70 each belong to individual and cluster turmeric growers. The samples were selected by using random sampling procedure. The selected turmeric cultivator then stratified into three groups based on the area under turmeric cultivation viz., Group I (0-1.0 ha), Group II (1.01 to 2.00 ha) and Group III (2.01ha and above). The study mainly based on primary data which was collected by using survey schedule through the personal interview method of sampling.

Economics of turmeric cultivation was estimated based on various cost concepts like Cost-A, Cost-B and Cost-C along with per quintal net return, per hectare gross and net income following tabular analysis (Sharma *et al.,*1989). The cost and income concepts used in the present study are discussed below:

Cost Cost C_2: It includes 10% of the total Cost (C_1) on account of managerial function performed by the turmeric farmers.

Concept: Cost A_1: Cost A_1 includes hired human labour, value of seed of turmeric, marketing transportation cost and depreciation on equipments and interest on working capital.

Cost B_1: Cost A_1 + interest value on fixed capital asset.

Cost C_1: Cost B_1 + imputed value of family labour

Variable Cost: Variable cost used in the present study includes the cost of labour, seed value and implements.

Fixed cost: Fixed cost includes the depreciation cost of land, implements and interest on fixed capital.

The family labour income was calculated by deducting cost B_1 from gross income.

Net income: Net income was calculated by deducting Cost C_1 from gross income.

Return from management: It was calculated by deducting Cost C_2 from gross income.

Benefit cost ratio: Benefit cost ratio based on variable cost

BCR = Gross income / Variable cost

Benefit cost ratio on total cost (BCR) = Gross income / Total cost

Result and Discussion

Economics of turmeric production of individual turmeric growers across size groups:

In order to estimate the economics of turmeric production of individual turmeric growers, the concept of cost A1, Cost B1, Cost C1 and Cost C2 were estimated and discussed below.

Cost A1: The average cost A1 per hectare was estimated 61815.20 which was found to be highest in group-III farm (Rs 68386.73) and lowest group-II farm (Rs 57834.71). It was observed from the table that amongst the various items of Cost A1 in turmeric production of individual turmeric growers, value of rhizomes was highest at Rs 31588.95 per hectare in average situation followed by cost of fencing Rs 10280.02 per hectare.

Cost B1: Cost B1 was computed by adding the interest on value of own capital asset to Cost A1. The average Cost B1 per hectare was found to be Rs 61858.62 which were found to be highest in the group-III and lowest in group-II farm.

Cost C1: In the present study Cost C1 was worked by adding the imputed value of family labour to Cost B1. The average Cost C1 per hectare was Rs 66393.86, which was found to be highest in group-III and lowest in group-II farm.

Cost C2: Cost C2 was computed by taking 10% of the total cost on account of managerial function performed by individual turmeric growers. The average Cost C2 was found to be Rs 72575.38 per hectare. Like the Cost C1, the Cost C2 per hectare was highest in group-III and lowest in group-II farm.

BCR based on variable cost: the variable cost used in the present study were cost of labour, rhizome, fencing, land preparation, fertilizer, mulching and cost of harvesting etc. The BCR based on variable cost was estimated to be 1.28 in the average farm situation. This was found to be exhibited a decreasing trend with the increase in farm size being varied from 1.39 in group-I to 1.11 in group-III.

BCR based on total cost: The BCR based on total cost was also estimated and it was 1.10 in the average farm situation. Like the BCR based on variable cost, this was also The BCR based on variable cost was estimated to be 1.28 in the average farm situation. This was found to be exhibited a decreasing trend with the increase in farm size being varied from 1.22 in group-I to 0.92 in group-III.

Return from management: The return from management was calculated by deducting cost C2 from gross income. The return from management in the average farm situation was estimated to be Rs 6188.89. Amongst the various size groups, return from management was found to be exhibited a decreasing trend with the increase in farm size being varied from Rs 14599.29 in group-I to Rs 6887.96 in group-III. However, the return from management in the group-III farm was found to be negative which was due to higher cost of C2.

Sl no	Particulars	Group I	Group II	Group III	Average
1	Cost A1 (Interest on working capital (13%)	59224.16	57834.71	68386.73	61815.20
2	Cost B1	59273.43	57904.01	68398.43	61858.62
3	Cost C1	61647.86	61442.97	76090.74	66393.86
4	Cost C2	67570.28	67226.44	82929.41	72575.38
5	Gross Return	82169.57	78081.17	76041.45	78764.06
6	Family Labour Income	22896.14	20177.16	7643.02	16905.44
7	BCR based on variable cost	1.39	1.35	1.11	1.28
8	BCR based on total cost	1.22	1.16	0.92	1.10
9	Return from management	14599.29	10854.73	-6887.96	6188.69

Table: 1. Economics of turmeric production of individual turmeric growers across size groups (in Rs)

Economics of turmeric production of cluster turmeric growers across size groups:

In order to estimate the economics of turmeric production of individual turmeric growers, the concept of cost A1, Cost B1, Cost C1 and Cost C2 were estimated and discussed below.

Cost A1: The average cost A1 per hectare was estimated 61253.18 which was found to be highest in group-III farm (Rs 66168.05) and lowest group-I farm (Rs 52363.48). It was observed from the table that amongst the various items of Cost A1 in turmeric production of individual turmeric growers, value of human labour was highest at Rs 19663.64 per hectare in average situation followed by cost of fencing Rs 10280.02 per hectare.

Cost B1: Cost B1 was computed by adding the interest on value of own capital asset to Cost A1. The average Cost B1 per hectare was found to be Rs 61260.00 which were found to be highest in the group-III and lowest in group-I farm.

Cost C1: In the present study Cost C1 was worked by adding the imputed value of family labour to Cost B1. The average Cost C1 per hectare was Rs 80923.64, which was found to be highest in group-II and lowest in group-I farm.

Cost C2: Cost C2 was computed by taking 10% of the total cost on account of managerial function performed by individual turmeric growers. The average Cost C2 was found to be Rs 87048.96 per hectare. Like the Cost C1, the Cost C2 per hectare was highest in group-II and lowest in group-I farm.

BCR based on variable cost: The variable cost used in the present study were cost of labour, rhizome, fencing, land preparation, fertilizer, mulching and cost of harvesting etc. The BCR based on variable cost was estimated to be 1.50 in the average farm situation. This was found to be exhibited a decreasing trend with the increase in farm size being varied from 1.55 in group-I to 1.67 in group-III.

BCR based on total cost: The BCR based on total cost was also estimated and it was 1.06 in the average farm situation. Like the BCR based on variable cost, this was also The BCR based on variable cost was estimated to be 1.50 in the average farm situation. This was found to be highest in group-III (1.17) and lowest in group-II (0.88).

Return from management: The return from management was calculated by deducting cost C2 from gross income. The return from management in the average farm situation was estimated to be Rs 4649.33. Amongst the various size groups, return from management was found to be exhibited an increasing trend with the increase in farm size being varied from Rs 8445.45in group-I to Rs 16410.36 in group-III. However, the return from management in the group-II farm was found to be negative which was due to higher cost of family labour included in cost C2.

Sl no	Particulars	Group I	Group II	Group III	Average
1	Cost A1 (Interest on working capital (13%)	52363.48	65228.00	66168.05	61253.18
2	Cost B1	52381.03	65230.34	66168.64	61260.00
3	Cost C1	67701.54	87750.39	87318.99	80923.64
4	Cost C2	72937.89	94273.19	93935.80	87048.96
5	Gross Return	81383.34	83365.38	110346.15	91698.29
6	Family Labour Income	29002.31	18135.04	44177.51	30438.29
7	BCR based on variable cost	1.55	1.28	1.67	1.50
8	BCR based on total cost	1.12	0.88	1.17	1.06
9	Return from management	8445.45	-10907.81	16410.36	4649.33

Table: 2. Economics of turmeric production of cluster turmeric growers across size groups (in Rs)

Conclusion

The above results showed that the return from management in the average farm situation of individual turmeric growers was estimated to be Rs 6188.89. Amongst the various size groups, return from management was found to be exhibited a decreasing trend with the increase in farm size. However, the return from management in the group-III farm was found to be negative which was due to higher cost of C2. On the other hand, the return from management in the average farm situation of cluster turmeric growers was estimated to be Rs 4649.33. Amongst the various size groups, return from management was found to be exhibited an increasing trend with the increase in farm size. However, the return from management in the group-II farm was found to be negative which was due to higher cost of family labour included in cost C2. Thus it can be concluded that the cluster turmeric growers found to be more profitable than individual turmeric growers.

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Yield Variation of Rice and its Per Capita Requirement over Past Five Decades in North Eastern States of India

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Abstract

This paper investigates the temporal variations in rice yield along with per capita requirement in the states of north eastern India. The study period was from 1966-67 to 2014-15 and it had been divided into five periods: 1966-67 to 1974-75, 1975-76 to 1984-85, 1985-86 to 1994-95, 1995-96 to 2004-05 and 2005-06 to 2014-15 to have an understanding of decadal performance among the states. Variance analysis has depicted that yield varies slowly over each study period with a large variability among the states suggesting the identifiable state specific factors. During the last decade i.e. 2005-06 to 2014-15 the average yield of an individual state over the years was between 287.5 (Mizoram in 2008) to 2903.3 (Tripura in 2015) and varied by 1316.3 across the states, but varied by 350 for each individual state over time. Similar pattern was observed in rest of the periods as well as in the entire period. Despite the north eastern regionhas shown a steady upward trend in area, production and productivity of rice in every period of the study, the region still has a deficit of 613 thousand tons of rice against the requirement of the last census year during which only Arunachal Pradesh, Manipur Nagaland and Tripura are well sufficient while other states are all deficit in rice requirement. Though the projected figure of deficit in 2021 (5.9%) is lower than that of 2011(8.6%), the region will fail to feed its population

of 53.25 million in 2021. Considering that rice is an irreplaceable staple of the region and states like Mizoram and Sikkim showing decreasing growth in area under rice during the last decade, the scope of meeting the rice requirement of the region depend highly on productivity improvement.

Keywords: **Rice yield, between variance and within variance, surplus, deficit.**

Introduction

Household food and nutritional security of North-eastern region (NER) of India predominantly depends on rice. Rice is the principal food grain crop of the North Eastern hilly ecosystem followed by maize, occupying 3.51 million hectares which accounts for more than 80% of thetotal cultivated area of the region and 7.8 per cent of the total rice area in India while its share in national rice production is only 5.9 per cent (RKMP, DRR). The total rice production of the region is estimated to be around 7.1 million tones with average productivity of 2.1 t/ha, which is much below the national average of 2.4 t/ha as per triennium ending 2015 (GOI, 2016). During the post-green revolution period due to introduction of improved varieties, the rice yield in the region has been enhanced up to 40% that plays a pivotal role in increasing the productivity (RKMP, DRR). Rice cultivation in the region is exposed to different biotic and abiotic stresses that include extreme temperatures at the time of flowering and grain filling stages thus resulting a very dismal figure in rice productivity and production of the region which in turn reflects a lower per capita consumption as well. The NE region is considered to be one of the hot pockets of rice genetic resources in the world and a potential rice-growing region with extremely diverse rice growing conditions as compared to other parts of the country. With the above background and with broad objective of analyzing the variability of domestic rice yield, the present study was taken up with the specific objective to analyze the temporal dynamics of between and within vitiation whereby estimating the per capita requirement of rice in the region.

Materials and methods

Secondary data on area, production and productivity of rice from department of economics and statistics, Ministry of agriculture were compiled. According to the availability of data the study was made for the entire period 1966-67 to 2014-15 and in turn the entire period was decomposed into five periods viz Period 1: 1966-67 to 1974-

75, Period 2:1975-76 to 1984-85, Period 3:1985-86 to 1994-95, Period 4:1995-96 to 2004-05 and Period 5:2005-06 to 2014-15 to have an understanding of decadal performance.

Variation types

Variance analysis was carried out to measure the average degree to which each point differs from the average of area, production and yield across the individual states over the sequence of five consecutive decades. By inspection through the time series cross sectional data used in the study it is obvious and vivid that, there is a large variation in area and production among the states while yield being the ratio of the two is more stationery and proportionate; and hence, variation analysis on yield, rather than area and production, is more meaningful. Here, three variation types viz overall, between and within variations are discussed. Overall variation refers to variation over time and individuals. Between variations examines the variation that exists between individuals that may be caused by specific identifiable factors. Within variation is a measure of how much an individual in the sample tends to change (or vary) over time. In other words, within variation is the mean of the change for the average individual case in the sample. These variations are inspected to have an idea of variation across the individuals over time. [Gelman, Andrew (2005), *Anscombe, F. J. (1948), Bailey, R. A. (2008).]*

Overall variance $s_O^2 = \frac{1}{NT-1}\sum_i\sum_t(x_{it} - \bar{x})^2$

Between variance $s_B^2 = \frac{1}{N-1}\sum_i(\bar{x}_i - \bar{x})^2$

Within variance $s_W^2 = \frac{1}{NT-N}\sum_i\sum_t(x_{it} - \bar{x}_i)^2 = \frac{1}{NT-1}\sum_i\sum_t(x_{it} - \bar{x}_i + \bar{x})^2$

Per capita requirement analysis

To work out whether the rice production in the states of the region is sufficient in feeding the increasing population, triennium ending (TE) productions of 1970-71, 1980-81, 1990-91, 2000-01 and 2010-11 have been worked out and corresponding surplus or deficits were generated using population data of 1971, 1981, 1991, 2001 and 2011. ICMR recommendation of 157Kg per person per year was used as standard to estimate the surplus and deficit. Besides, rice production of 2020-21 for each state have been estimated using growth rate of last decade ie. 2005-06 to 2014-15 so also the population 2021 has been estimated based on the population growth of respective states during 2001 to 2011 to have an estimated requirement of rice.

Result and discussion

Before proceeding to the analytical part lets have an overview of area, production and yield of rice in terms of Triennium Ending (TE) in five periods viz. TE 1974-75, TE 1984-85, TE 1994-95, TE 2004-05 and TE 2014-15 (Table 1). Considering the triennium figures, on an average, no doubt Assam registered the highest area and production under rice followed by Tripura, Manipur, Nagaland, Meghalaya, Arunachal Pradesh and Mizoram while Sikkim has shown the least area and production under rice. When yield is considered, on an average Manipur ranked first followed by Tripura, Meghalaya, Assam, Sikkim, Nagaland and Mizoram while lowest yield was observed in Assam as per the studied triennium figures. Though fluctuations were shown by few states in the studied triennium endings, gradual increment in area, production and yield were observed in NER(Table 1 and Figure 1).

State	Arunachal Pradesh	Assam	Manipur	Meghalaya	Mizoram	Nagaland	Sikkim	Tripura	NER	India
Area in 000' ha										
TE 1974-75	63	2068	164	100	68	63	NA	293	2819	37621
TE 1984-85	102	2313	162	110	52	116	15	282	3153	40222
TE 1994-95	116	2500	157	104	64	135	16	252	3342	42377
TE 2004-05	122	2482	160	110	57	153	15	245	3343	41892
TE 2014-15	128	2478	190	110	30	189	11	255	3392	43667

Production in 000' tons										
TE 1974-75	55	2076	222	110	56	37		290	2845	40958
TE 1984-85	109	2512	269	126	37	101	14	390	3558	55183
TE 1994-95	122	3323	365	114	94	177	21	448	4665	78327
TE 2004-05	147	3696	383	195	109	244	21	555	5352	81159
TE 2014-15	275	5093	330	268	50	430	21	724	7190	105790
Yield in kg/ha										
TE 1974-75	874	1004	1350	1102	811	581		991	1009	1089
TE 1984-85	1065	1086	1658	1147	719	871	895	1384	1129	1372
TE 1994-95	1058	1330	2330	1101	1474	1309	1286	1782	1396	1848
TE 2004-05	1210	1489	2402	1780	1913	1597	1448	2262	1601	1937
TE 2014-15	2139	2056	1737	2442	1663	2269	1807	2835	2120	2423

NA: data not available

Table1: Triennium ending area, production and yield of rice in the states of NER for TE 1974-75, TE 1984-85, TE 1994-95, TE 2004-05 and TE 2014-15

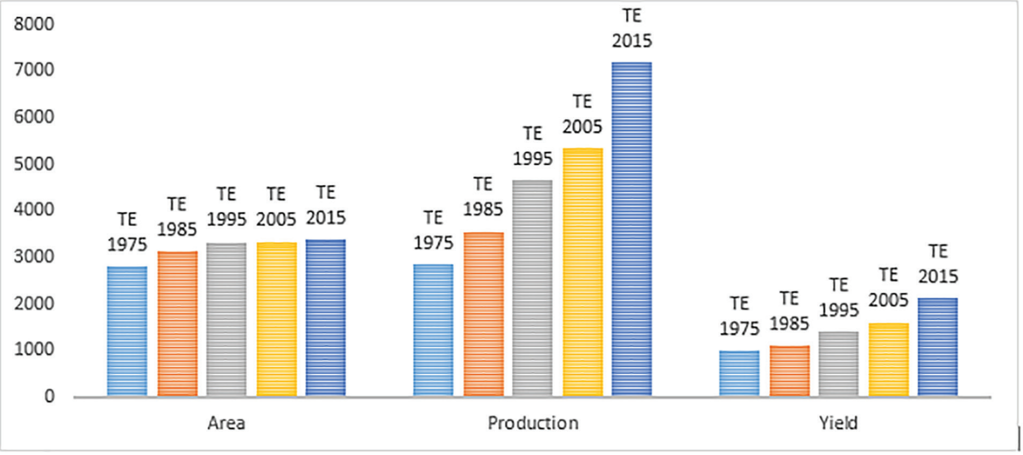

Figure 1: Area, production and yield of rice in NER for TE 1974-75, TE 1984-85, TE 1994-95, TE 2004-05 and TE 2014-15

Variation of yield across the individual states over the years

TE ending average of area, production and yield as discussed above is simply the average of the data point used. Here the interest is on variation to measure the average degree to which each point differs from the average. In all the five periods as well as the entire period yield was found more between variations than within variation. Overall variation of yield across the individual states over each period of years was quite less than that of the between variation as the within variation is comparatively lower. This indicates the existence of specific identifiable state specific factors that causes the variation in a large scale. The probable state specific factors may be government policies, agriculture input technologies, topography, soil fertility, natural resources, agriculture functionaries, etc. As an example for discussion let's take period 5, being the most recent decade (2005-06 to 2014-15) in which the average yield of Mizoram, by inspection the studied dataset is 1227 kg/ha being the lowest while that of Manipur is 2180.6 kg/ha being the highest. The year 2007 has the lowest average (1481.1 kg/ ha) and the year 2013 has the highest average (2034.2 kg/ha) yield when we look time wise during the period.However, in this period the average yield of an individual state over the years is between 287.5 kg/ha (Mizoram in 2008) to 2903.3 kg/ha (Tripura in 2015) and varies by 1316.3 across the states (between variation), but varies by 350 for each individual state over time (within variation). Smaller within variation of yield indicates that for every state, on an average the yield does not vary much as compared to overall and between variations of yield during this period. Similar pattern was observed in rest of the periods as well as in the entire period i. e. yield has shown more between variation than within variation as shown in table 2. This means the yield varies slowly over each study period with a large variability among the states.

Variable	**Variation**	**Mean**	**Standard deviation**	**Minimum**	**Maximum**
Period 1: 1966-67 to 1974-75					
Yield	Overall	985.8	269.9	531.2	1796.4
	Between		656.4	809.3	1216.0
	Within		167.6	685.8	1426.9
Period 2: 1975-76 to 1984-85					
Yield	Overall	1087.1	294.4	308.5	1989.3
	Between		842.1	876.6	1284.2
	Within		143.8	659.2	1575.3
Period 3: 1985-86 to 1994-95					
Yield	Overall	1316.6	368.2	692.8	3010.1
	Between		978.4	1027.7	1683.0
	Within		236.0	968.3	1956.9
Period 4: 1995-96 to 2004-05					
Yield	Overall	1634.4	417.6	891.6	2472.5
	Between		1247.0	1286.3	1835.3
	Within		200.4	1091.1	2326.2
Period 5: 2005-06 to 2014-15					
Yield	Overall	1893.2	515.0	287.5	2903.3
	Between		1316.3	1366.3	2358.2
	Within		350.0	1123.7	2647.8
Entire Period: 1966-67 to 2014-15					

Yield	Overall	1415.2	512.6	287.5	3010.1
	Between		1830.2	734.0	2404.2
	Within		450.5	910.1	1998.0

Table 2: Overall, between and within variation of yield

Referring figure. 2, it was clearly observed that overall, between and within variation of rice yield exhibit gradual increase over the period 1 to period 5 where the quantity and rate of increment is highest for between variation and least for within variation during this five consecutive periods. This means that state specific factors are becoming more specific resulting into the variability larger among the states in the course of time. If the between variance is smaller than the within variance, then the means are really close to each other and we will fail to reject the claim that they are all equal.

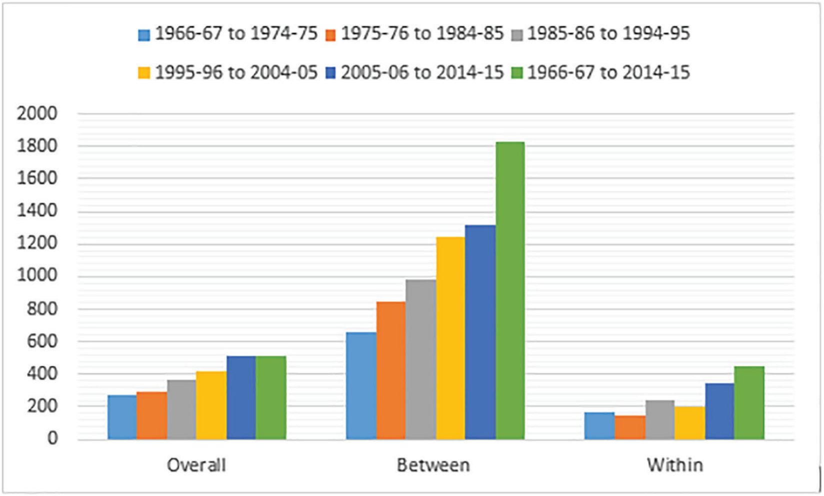

Figure. 2: Overall, between and within variation of rice yield during the decades 1966-67 to 1974-75, 1975-76 to 1984-85, 185-86 to 1994-95, 1995-96 to 2004-05 and 2005-06 to 2014-15 and entire period 1966-67 to 2014-15

Requirement Analysis (Surplus and Deficit)

Table 3 clearly shows that in all the five periods all the states are deficit in rice except few states like Manipur and Tripura. From 1971 till 2001 same pattern was observed where only Manipur and Tripura have been surplus states and rest of the states shown deficit including total NER and India. When it reaches the census year 2011, Arunachal Pradesh and Nagaland became surplus besides Manipur and Tripura. As per 1971 population, highest deficit was observed in Mizoram followed by Meghalaya. Sikkim, right from the beginning i.e. from 1981 till 2011 had been the highest deficit (more than 60%) followed by Mizoram and Meghalaya in all the cases. As per 2011 population and TE production 2010-11, Tripura (19%) topped with highest surplus followed by Manipur (10%), Arunachal Pradesh (7.6%) and Nagaland (7.1%); and highest deficit was observed in Sikkim (76.9%) followed by Mizoram (71.6%), Meghalaya (54.9%) and Assam (7.4%). On an average all the states have been reducing the deficit over decades except Meghalaya, Mizoram and Sikkim in which the rice deficit is consistent in all the periods. For NER, the deficits are decreasing over the five periods though the rate is slow. However the rate of increment in deficit of the nation is at a faster rate (table 3). Assuming growth rate of rice production of each states during the last decade to be continued and population growth rate of each state during 2001 to 2011 keeps on, the requirement of rice in the states in the year 2021 have been worked out. In 2021 total requirement of rice in NER will be 8383 thousand tones to feed its increasing population of 53.25 million. Against this requirement, the estimated production in the region in 2021 will be 7866 thousand tons resulting a deficit of 494 thousand tones which is 5.9%. Though the percentage figure of deficit in 2021 (5.9%) is lower than that of 2011 which was 8.6%, it is to remembered that the region will not be able to feed its population in 2021 if the current scenario is continuing. Assam, Meghalaya, Mizoram and Sikkim had been deficit in rice requirement as per population of 2011. If the current scenario is continuing, in 2021 except Arunachal Pradesh, Nagaland and Tripura, all other remaining states will be deficit in rice requirements (table 3).

State	Arunachal Pradesh	Assam	Manipur	Meghalaya	Mizoram	Nagaland	Sikkim	Tripura	NER	India
1971										
TE Production	47	1982	183	74	18	46	NA	254	2604	41908
Requirement	74	2296	169	159	52	81	33	244	3108	86061
Surplus/ Deficit	-26	-314	15	-85	-34	-35	NA	10	-503	-44153
% Surplus/ Deficit	-36.0	-13.7	8.1	-53.4	-65.0	-43.6	NA	3.8	-16.2	-51.3
1981										
TE Production	87	2213	251	126	25	81	12	347	3134	49737
Requirement	99	2832	223	210	78	122	50	322	3936	107283
Surplus/ Deficit	-13	-619	28	-83	-52	-41	-38	25	-802	-57546
% Surplus/ Deficit	-12.6	-21.9	11.2	-39.7	-67.3	-33.9	-75.9	7.1	-20.4	-53.6
1991										
TE Production	141	3087	287	119	65	152	24	478	4353	74181
Requirement	136	3519	289	279	108	190	64	433	5017	132888
Surplus/ Deficit	6	-432	-2	-159	-44	-38	-40	45	-664	-58708
% Surplus/ Deficit	3.9	-12.3	-0.7	-57.2	-40.4	-20.0	-63.1	9.5	-13.2	-44.2
2001										
TE Production	134	3905	378	180	99	200	22	536	5453	89333

Requirement	172	4182	360	362	140	312	85	501	6115	161512
Surplus/ Deficit	-38	-278	18	-183	-40	-113	-63	34	-662	-72179
% Surplus/ Deficit	-22.3	-6.6	4.7	-50.4	-28.9	-36.0	-73.7	6.4	-10.8	-44.7
2011										
TE Production	235	4530	478	210	49	335	22	687	6544	96795
Requirement	217	4894	427	465	171	311	95	576	7157	190000
Surplus/ Deficit	18	-364	50	-255	-123	24	-73	111	-613	-93206
% Surplus/ Deficit	7.6	-7.4	10.5	-54.9	-71.6	7.1	-76.9	19.2	-8.6	-49.1
2021										
Estimated Production	315	5581	330	317	62	489	20	772	7866	107519
Estimated Requirement	274	5736	479	596	213	309	108	662	8360	223681
Estimated Surplus/ Deficit	41	-154	-148	-279	-150	180	-88	109	-494	-116161
% Surplus/ Deficit	13.0	-2.7	-31.0	-46.7	-70.6	36.8	-81.7	14.2	-5.9	-51.9

–ve: deficit otherwise surplus
All figures being in '000 tones ICMR recommendation: 157Kg per person per year
NA: data not available

Table 3: Requirement of rice as per the population of 1971, 1981, 1991, 2001 and 2011 with corresponding productions of TE 1970-71, TE 1980-81, TE 1990-91, TE 2000-01 and TE 2010-11 along with corresponding surplus or deficit in the states of NER.

Summary and Conclusion

Temporal analysis of variation in five decades reveals that in all the five periods as well as the entire period yield has more between variations than within variation. Overall variation of yield across the individual states over each period of years is quite less than that of the between variation as the within variation is comparatively lower. This indicates the existence of identifiable state specific factors that causes the variation in a large scale. The probable state specific factors may be government policies, agriculture input technologies, topography, soil fertility, natural resources, agriculture functionaries, etc. Among the various state specific factors, location specific high yielding varieties (HYVs) and their adoption are most important. Because of wide variation in agroclimatic conditions varietal requirements are highly specific and a good number of HYVs are needed to fulfill requirement. Though area, production and productivity of rice in NER have shown a steady upward trend in every period of the study, the result of surplus and deficit analysis shows that only Arunachal Pradesh, Manipur Nagaland and Tripura are well sufficient while other states are all deficit in rice requirement as per the population of census year 2011. In spite of the projected figure of deficit in 2021 (5.9%) is lower than that of 2011(8.6%), it is to remember that the region will not be able to feed its 53. 25 million population in 2021 where only Arunachal Pradesh, Nagaland and Tripura will be rice sufficient states if the current scenario is continuing. Considering that rice is an irreplaceable staple of the region and states like Mizoram and Sikkim showing decreasing growth in area under rice during the last decade as seen from the dataset used in the study, the scope of meeting the rice requirement of the region depend highly on productivity improvement.

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Prospects of Quality Protein Maize (QPM) Production for Food and Nutritional Security – An Overview

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Abstract

The article represents the nutritional benefits of Quality Protein Maize (QPM) over conventional maize varieties and presents a brief overview of its historical development, nutritional quality, production technology and value addition, etc. It also provides information on QPM varieties available for commercial production in different agro-ecologies of North Eastern Hill Region and the agronomic management practices required for seed and grain production. It further depicts a general guide on how to establish field demonstration plots and conduct field days on QPM varieties. This paper is prepared to serve as a reference for extension experts, farmers and other stakeholders who are involved in the production, demonstration, and extension of QPM in North East India in general and Meghalaya in particular. To some extent, it would be a useful source of information to health professionals who are involved in health extension, and to students and teachers in agricultural and animal husbandry for food, feed and nutritional properties of QPM.

Keywords: **Quality Protein Maize (QPM), North Eastern States**

Introduction

Maize (*Zea mays* L.) is one of the most versatile and multi utility crops, having wider adaptability in diverse ecologies. Globally, maize is known as 'Queen of Cereals' because it has the highest genetic yield potential among the cereals. It is cultivated on nearly 150 m ha in about 160 countries having wider diversity of soil, climate, biodiversity and management practices that contributes 36 % (782 mt) in the global grain production. The United States of America (USA) is the largest producer of maize contributes nearly 35 % of the total production in the world and maize is the driver of the US economy. The USA has the highest productivity (> 9.6 t ha^{-1}) which is double than the global average (4.92 t ha^{-1}). Whereas, the average productivity in India is only 2.43 t ha^{-1}. In India, maize is the third most important food crops after rice and wheat. According to advance estimate it is cultivated in about 8.7 m ha (2010) mainly during *Kharif* season which covers 80% area. Maize in India, contributes nearly 9 % in the national food basket and more than Rs. 100 billion to the agricultural GDP at current prices apart from the generating employment to over 100 million mandays at the farm and downstream agricultural and industrial sectors. In addition to staple food for human being and quality feed for animals, maize serves as a basic raw material as an ingredient to thousands of industrial products that includes starch, oil, protein, alcoholic beverages, food sweeteners, pharmaceutical, cosmetic, film, textile, gum, package and paper industries, etc is the major source of staple food (17%), feed (61%), fodder and industrial raw material (22%) and provides enormous opportunity for crop diversification, value addition and employment generation (Jat *et al.,* 2011). Presently, maize production is 21.8million tons and projected demand of maize to be 45 million tonnes by 2030 (Kumar *et al.,* 2013). This demand of maize will be met either by technological intervention or by bringing more area under maize cultivation. The technological interventions for meeting this demand will be adoption of high yielding single cross hybrids seeds, biotechnological intervention and improved package of practices in different agro- ecological regions of the country. Maize is also grown for many other special purposes *viz* . quality protein maize, sweet corn, baby corn, pop corn, waxy corn, high oil and high amylase corn. It is also a solution for various stresses like weed and lowering water table and abiotic stresses like drought, terminal heat, cold, *etc.* besides providing opportunity for farm mechanization and conservation agriculture and consequently increasing the resource-use efficiency and farm profitability. It is now well established that the adoption of appropriate management practices may prove favourable for sustaining crop productivity and reducing ecological hazards. There is a scope of manipulating production technologies in respect of crop diversification, resource conservation, insect-pest control for improving crop yields on sustainable basis. To make farming sustainable and economically viable, there is a need for rethinking, planning and management in order to face the emerging challenges. Research on maize production systems has therefore provided exciting opportunities for improving input use efficiency, productivity and sustainability. Innovative practices are being attempted to improve productivity, resource-use efficiency and livelihood security. Presently, in India, maize is mainly used for preparation of poultry feed (51%) and extraction of starch (12%) and also provides food (23%), cattle feed (12%), brewery (1%), seeds (1%) fodder and basic raw material for the various industries *viz*. bio-fuel, food sweeteners, cosmetics and alcoholic beverages etc (Jat *et al.*, 2011). These diversified uses of maize also prompted higher production across the country.

Maize is the second largest cereal crop cultivated in the North Eastern Region except Sikkim where it is the principal crop. It is grown in a wide range of climatic conditions and altitude ranging from low (upto 800m), medium (800-1300 m) to high (1300 and above) as a rainfed crop in *Jhum* land both as monocrop or mixed crop. It has very high potential and is a promising crop for the purpose of human consumption as well as animal feed. The average productivity of maize in North Eastern Hill (NEH) region is even lower than that of national average and far behind global average, showing a greater need to enhance the yield potential of this crop. The yield can be increased through adoption of high yielding varieties and improved management technologies. Maize is a good source of carbohydrates, fats, proteins and some of the important vitamins and minerals. However, in spite of several important uses, maize has been found to be deficient in two essential amino acids i.e. lysine and tryptophan. This leads to poor net protein utilization and low biological value of traditional maize. In order to overcome this problem, quality protein maize has been developed by maize breeders by incorporating *opaque-2* mutant gene which is responsible for enhancing lysine and tryptophan content of maize endosperm protein. QPM looks and taste like ordinary maize with same or higher yield potential, but it contains nearly twice the quantity of essential amino acids, lysine and tryptophan which makes it rich in quality proteins. The maize varieties presently grown by farmers, hereafter referred to as conventional maize (CM) varieties, are deficient in this two essential amino acids *i.e.,* lysine and tryptophan. Essential amino acids are not synthesized through the metabolic processes of monogastric animals such as human beings and must be present in the food consumed by these animals. Failure to obtain these essential amino acids from the daily diet results in protein deficiency and may be a particular problem among young children and pregnant and/or lactating women whose diet is dominated by maize and who have limited alternative sources of these amino acids. An important factor that determines protein quality is how closely the ratio of essential amino acids present in a particular food item matches the human requirement. Meat, eggs, milk and legumes are known to be good sources of essential amino acids. But animal proteins are not affordable for a large segment of small-scale farmers. To overcome this problem, scientists have used conventional breeding methods to develop maize cultivars that have higher lysine and tryptophan content than CM genotypes and a vitreous endosperm like that of CM to ensure acceptable kernel characteristics. When modified to produce a vitreous endosperm resembling that of CM, maize that contains approximately double the amount of lysine and tryptophan has been named as "quality protein maize" (QPM). QPM is a cheap source of protein, given that farmers can grow, manage, harvest, and consume it in the same way they do CM varieties.

The frontline demonstration on QPM was launched during kharif 2010-2011 in North-Eastern states and the technologies developed through research activities were demonstrated under actual field conditions of the farmers. The results of the frontline demonstration revealed that still nearly 20% realizable yield potential exists, a targeted and focused approach in spreading the awareness about the improved technologies shall increase the rate of adoption and raise productivity of the crop. For this an understanding of the economic potential of each of the selected improved technology is necessary. As vast yield gaps still persist between potential yield recorded at KVK's instructional farm and front line demonstration (FLDs) with the available management technologies and it is possible to further increase the QPM productivity in the districts of North Eastern states in general and Meghalaya in particular.

The data in Table 1 depicted demonstrations of QPM through 78 KVKs in NER and found to be good in terms of yield as compared to farmers' practices (21.5-27.9 q/ha). However, due to high nutrient requirements, it was not upto the mark to obtain the higher yield in the states of less nutrient users in NE India. The only option left for the farmers for getting higher benefit was by selling maize green cob at higher price as compared to traditional varieties due its taste.

Variety	**Maturity (days)**	**Yield (q ha^{-1})**			**Yield Gaps (q ha^{-1})**
		Potential yield	**Instructional Field**	**Farmers Field (FLD)**	
HQPM 1	95-100	60-65	54.6	47.5	17.5
Vivek QPM 9	75-80	40-45	37-45	28.9	16.1

Table 1. QPM varieties demonstrated at farmers field for suitability for NEH Region

State	**Area (000ha)**	**Production (000 tonnes)**	**Productivity (kg/ha)**
Arunachal Pradesh	48.0	75.0	1563
Assam	28.0	93.2	3333
Manipur	26.2	58.8	2243
Meghalaya	18.0	40.8	2259
Mizoram	5.7	8.6	1515
Nagaland	68.8	135.9	1962
Sikkim	39.9	68.9	1682
Tripura	4.5	5.9	1310
NE India	239.1	487.1	2037
All India	9185.4	24172.7	2632

Source: Directorate of Economics & Statistics, Govt. of India (2014-15)

Table 2. Area production and productivity of maize in NE Region

Variety	**Maturity (days)**	**Potential Yield (q/ha)**
Vijay composite	125	50-55
RCM 1 -75	95	50-55
RCM 1-76	95	50-55

Gujarat Makki-1	120	55-60
Lakshmi	125	50-55
Hemant	125	45-50
RCM 1-1	125	55-60
RCM 1-2	110	35-40
RCM 1-3	125	65-70
DA 61 A	120	45-55

Source: Technical Bulletin/Annual Report of ICAR & KVK

Table 3 Improved maize varieties suitable for NEH Region

History of QPM

Lynn Bates (a Ph. D. Student working with Professor Edwin Mertz at Purdue University of USA in1963) discovered high lysine and tryptophan mutant of maize namely *Opaque-2*. *Opaque-2* maizekernels were chalky and had 15-20 % less grain weight but having diseases and insects susceptibility. Dr. S. K.Vasal (a breeder) and Dr. E. Villegeas at CIMMYT overcame above defects of *Opaque-2* and developed QPM in 1990s. For their achievement, they won the 2000 World Food Prize.

Importance of QPM

QPM is useful in fulfilling the protein requirements of different sections of society (infants, lactating mothers' convalescing patients, Kwashiorkor diseased, old persons and infirm, etc.) to prevent malnutrition. Children fed QPM porridge gain body weight 12% and height 9% higher than normal maize porridge & save them from infectious diseases (diarrhoea).

QPM contains high carbohydrates, fats, better quality proteins, some of vitamins and minerals, so it is nutritious feed for poultry, livestock, swine, fish, etc. Use of QPM as poultry feed leads to early development of broilers, save energy and feed, and also the extra cost incurred on lysine and tryptophan fortification.

Digestibility of QPM is similar to that of normal maize and food processing does not affect QPM quality.

QPM is not categorised under GM crops. So, its production and consumption is not detrimental to consumers & environment.

The term QPM refers to maize genotypes whose lysine and tryptophan levels in the endosperm of the kernels are about twice higher than in common maize (CM) varieties. Lysine levels in conventional and QPM maize average 2.0% and 4.0% of total protein in whole grain flour, respectively. These levels can vary across genetic backgrounds with ranges of 1.6-2.6% in CM and 2.7-4.5% in converted QPM counterparts (Table 4). Despite the nutritional differences, QPM varieties look and perform like CM varieties and one cannot visually distinguish between the two by the physical appearance of the plants or their ears and grains alone. Rather, biochemical analysis is required to determine the lysine and tryptophan content of the seed and confirm whether or not it is QPM. In addition to staple food for human being and quality feed for animals, maize serves as a basic raw materials to the industry for production of starch, oil, protein, alcoholic beverages, food sweeteners and more recently bio-fuel and being a potential crop in India, maize occupies and important place as a source of human food (25%), animal feed (12%), poultry feed (49%), industrial products mainly as starch (12%) and 1 % each in brewery and seed (Dass *et al*., 2009). As maize is a good source of carbohydrates, fats, protein and some of the important vitamins and minerals. However, inspite of several important uses, maize has an in-built drawback of being deficient in to essential amino acids viz. lysine and tryptophan. This leads to poor net protein utilization and low biological value of traditional maize genotypes.

Traits	**CM**	**QPM**
Protein (%)	> 8	> 8
Lysine in endosperm protein (%)	1.6-2.6 (mean 2.0)	2.7-4.5 (mean 4.0)
Tryptophan in endosperm protein (%)	0.2-0.6 (mean 0.4)	0.5-1.1 (mean 0.8)

Source: Vivek *et al.* (2008)

Table 4. Lysine and tryptophan levels as percentages of total protein in whole grain flour of conventional and QPM (o2o2) genotypes.

Nutritive Value of Quality Protein Maize

Maize consists of three main parts – the hull of bran coat with high fiber contain, germ rich in oil and starchy endosperm and normal maize grain under Indian conditions on an average contains 14.9 % moisture, 11.1 % protein, 3.6% fat, 2.7% fibre , 66.2% other carbohydrates and 1.5% minerals (National Institute of Nutrition 2002). Maize kernel protein is made up of five different fractions. The percentage of different fractions to total nitrogen in maize kernel is albumin 7%.globulin 5%, non protein nitrogen 6%, prolamine 52% and glutelin 25% and the left over 5% is residual nitrogen. Protein being the primary structural and functional component of every living cell is one of the most important ingredients that determine the quality of food and feed.

The quality of protein in normal maize grain is poor due to the presence of largest concentration of an alcohol soluble protein fraction 'prolamine' also known as '*zein*' in the endosperm and in immature maize the amount of *zein* is low and increase as the grain matures. *Zein* is very low in lysine and tryptophan content which contribute more than 50% of total protein and that's why the protein of normal maize grain is low in lysine and tryptophan content, on the other hand, *zein* fractions contains very high amount of leucine and imbalanced proportion of isoleucine. On the whole, the ill proportion of all these four essential amino acid in maize due to the high content of *zein* results into the poor quality of protein in normal maize. The high quality of protein in other fractions in other parts of maize kernel becomes recessive due to the dominance of *zein* in normal maize. The poor quality of protein in normal maize affects its 'biological value' *i.e.*, the availability of protein in the body. Therefore it was realized to improve the biological value of protein in maize genotypes and for this purpose, a new corn type known as quality protein maize (QPM) was developed by lowering the concentration of *zein* by 30%. As a result, the concentration of two essential amino acids *viz.,* lysine and tryptophan in grain was increased in QPM genotypes as compared to normal maize grain genotypes. The lowest content of leucine in QPM further balances the ratio of leucine to isoleucine content (Table 5).

Amino acid	**Amino acid content (mg per g N)**	
	Normal grain	**QPM grain**
Lysine	177	256
Isoleucine	206	193
Leucine	827	507
Sulfur amino acids	188	188

Aromatic amino acids	505	502
Threonine	213	199
Tryptophan	35	78
Valine	292	298

Table 5. Comparisons on essential amino acid content in normal maize and QPM grain

The balanced proportion of all these essential amino acid in Quality Protein Maize (QPM) enhanced the biological value of protein. The true protein digestibility of normal maize and QPM is almost same, but the biological value of normal maize is just half as compared to that QPM varieties (Table 6).

Quality measures	Normal	QPM
True protein digestibility (%)	82-91	92
Biological value (%)	40-47	80
Amount needed for equilibrium	547	230

Table 6. Protein quality of maize grain

The quality parameters viz. protein content as well as lysine and tryptophan content of QPM hybrids released for cultivation in India are given in Table 7.

Hybrid name	Hybrid type	Protein content in grains (%)	Tryptophan content in protein (%)
HQPM-7	Single cross	9.42	0.72
Vivek QPM-9	Single cross	8.46	0.83
HQPM-5	Single cross	9.80	0.76
HQPM-1	Single cross	9.36	0.94
Shaktiman -4	Single cross	9.98	0.93
Shaktiman -3	Single cross	9.63	0.73
Shaktiman -2	Single cross	9.30	1.04
Shaktiman -1	Three way cross	9.60	1.01

Table 7. Quality characters of QPM hybrids released in India

Impact Dietary Assessment Studies

Most important target group for QPM consumption are children. Out of the 189 nations listed by UNICEF, Malawa, Mozambique, India and Bolivia have highest under five mortalities. The impact of QPM can be highly significant in such target group in these vulnerable nations. An early study on Indian children fed with food supplemented with normal maize, QPM and milk. The results from children taking QPM were encouraging as the growth parameters recorded were comparable to those of milk (Singh, *et al.,* 1980).

A more comprehensive study was carried out in Ghanaian children (0-15 months) given food supplemented with QPM and normal maize (Afriyiet *et al*., 1998). The QPM fed children were healthier, suffered fewer fatalities and had better growth rates. The impact of QPM in human nutrition will however, depend on a number of factors. It needs to be established whether the intake of QPM essentially results in enhanced protein utilization in children and adults. Moreover, the results have to be validated especially in the areas where malnutrition is prevalent and maize is an important component of diet.

Another application of QPM is as animal feed, especially for monogastric animals such as pigs and poultry, which require a more complete protein than cereals alone can provide, as is case with normal maize that is deficient in lysine and tryptophan. A number of studies have proved that the more potential impact of QPM can be its use in commercial feeds for pigs and poultry as it results in improved growth. In Brazil and El-Salvador, use of QPM in animal feed reduced use of soybean meal by about 50% besides reducing use of synthetic lysine substantially (Pereira, 1992). It also resulted in saving of 3-5% in development of feed for pig and poultry. In China, the QPM variety Zhong Dan-9409 has been used in animal feed. It has 8-15 per cent yield advantage and about 80 per cent more lysine and tryptophan.

Zhai (2002) analysed the effect of replacing normal maize with QPM and found that in case of poultry, there was no apparent increase in amino acid digestibility but in case of pigs, there was a significantly higher amino acids and weight gain in case of pigs at various growth stages. Similarly, in Ghana, the QPM variety “Obatampa” has been used in both human nutrition as well as `animal feed. The potential impact of QPM as animal feed is restricted to Mexico, Brazil, China, Bolivia, which have high percapita meat supply.

Contrarily, in African countries, due to the low meat supply market it a less potential marked for QPM as animal feed component.

Babies and adults consuming QPM are healthier and at lower risk for malnutrition disorders such as marasmus and kwashiorkor, and data from Latin America and Africa show the grain's role in reversing the effects of malnutrition in those already affected. About 90% the nutritional value of skim milk, the standard for adequate nutrition value. At a time when UNICEF reports that 1,000,000 infants and small children are starving each month, the inclusion of QPM in daily rations improves health and saves lives. Additionally, pigs fed QPM experience rapid weight gain and are ready for market sooner or can provide an additional quality protein source for small farm families (Mandefro *et al.*, 2001). In India Centre of Excellence on Processing & Value Addition of Maize has been established at Udaipur city of Rajasthan under the Rashtriya Krishi Vikas Yojna to ensure better utilization of quality Protein maize in commercial food products and Industry. This centre has developed several bakery products like Biscuit, cake muffins, extruded products puffcorns and pasta using QPM flour (Patil and Babu 2003). The great impact might be due to QPM's High yield potential (7.2-8.8 t/ha), and its potentiality towards crop diversification and export potential.

Production Technology of Qpm

There are 9 QPM hybrids of different grain colours have been developed and relased in India for their cultivation in different agro-climatic conditions across the country. The production technology of QPM is same as of normal grain maize except isolation as to maintain the purity of QPM, it should be grown in isolation with normal maize.

Soils

Maize can be grown successfully in variety of soils ranging from loamy sand to clay loam. However, soils with good organic matter content having high water holding capacity with neutral pH (5.5 to7.5) are considered good for higher productivity. Being a sensitive crop to moisture stress particularly excess soil moisture and salinity stresses; it is desirable to avoid low lying fields having poor drainage and also the field having higher salinity. Therefore, the fields having provision of proper drainage should be selected for cultivation of maize. The soil of NE is acidic in reaction and need to apply lime in furrows @ 500kg/ha to maintain the required pH.

Land preparation

Two or three deep plowing should be done. The clods should be broken and well pulverized

Time of sowing

Maize can be grown in all seasons viz; *Kharif* (monsoon), post monsoon, *Rabi* (winter) and spring. During *Rabi* and spring seasons to achieve higher yield at farmer's field assured irrigation facilities are required. During *Kharif* season it is desirable to complete the sowing operation 12-15 days before the onset of monsoon. However, in rainfed areas, the sowing time should be coincided with onset of monsoon.

Season	Optimum time of sowing
Kharif	Last week of June to first fortnight July
Rabi	Last week of October for inter cropping and up to 15th of November for sole crop
Spring	First week of February

Table 8. Optimum time of sowing QPM in different seasons

Seed rate and plant geometry

To achieve higher productivity and resource-use efficiencies optimum plant stand is the key factor. The seed rate varies depending on purpose, seed size, plant type, season, sowing methods etc. Seed rate of 16-20 kg/ha or 55-66 thousand plants/ha is required. Row to row spacing 60-75 cm and plant to plant spacing 20-25 cm should be maintained

Seed treatment

To protect the maize crop from seed and major soil borne diseases and insect-pests, seed treatment with fungicides and insecticides before sowing is advisable/ recommended as per the Table 9 given details.

Disease/insect-pest	Fungicide/Pesticide	Rate of application (g kg-1 seed)
Turcicum Leaf Blight,, Banded Leaf and Sheath Blight, Maydis Leaf Blight	Bavistin + Captan in 1:1 ratio	2.0
Pythium Stalk Rot	Captan	2.5
Termite and shoot fly	Imidachlorpit	4.0

Table 9. Seed treatment of QPM for major diseases and pests

Manures and fertilizers

The chemical fertilizer 150:80:80 kg NPK/ha, 10 tones FYM/ha before one month of land preparation are to be applied. Full dose of phosphorous and potash and 20% of nitrogen should be used as basal at the time of final land preparation. The remaining 25% nitrogen at four leaf stage, 30 % at knee height/ eight leaf stage and 20% nitrogen at tasseling time and 5 % at grain filling stage should be applied.

Water management

Irrigation should be given as and when required by the crop depending upon the rains and moisture holding capacity of the soil. Light and frequent irrigations are desirable Young seedlings, knee high stage, flowering and grain filling and 10 days after grain filling are the most sensitive stages for water stress for inbreds and irrigation should ensured at these stages. Water should not overflow on the ridges. The irrigation should be applied in furrows upto 2/3rd height of the ridges. There should be adequate water for growth period upto 40-50 DAS and silking and grain filling period.

Weed management

Weeds are the serious problem in maize seed production plot, particularly in wet (monsoon) season that competes with maize for nutrient and causes yield loss up to 35 %. Atrazine being a selectiveand broad-spectrum herbicide in maize checks the emergence of both broad leaves and most of the grasses. Pre-emergence application of atrazine @ of 1.0-1.5 kg a.i /ha in 600 litre water is effectivefor controlling weeds. While spraying, the person who is doing spray should move backward sothat the atrazine film on the soil surface may not be disturbed. Preferably, three nozzle booms may be used for proper ground coverage and saving time. Two hand weeding (hoeing) are recommendedfor aeration and uprooting of the remaining weeds at 20 and 40 days after sowing.

Eliminating undesirable plants (Roguing)

At early stage i.e. after 12-15 days of sowing, off-type plants and excess plants should be removed and proper. Off types (very tall, very dwarf, or flower much earlier or later) disease and insect infested removed (Rogued out) before pollen shedding starts. If off-type maize plants are detasseled, seeds from such plants should not be used.

Harvesting of seed

The cobs for seed purpose are selected from middle part of fields, away from possible contamination. Ears should be harvested only after black layer is formed on grains attached to cob.

Drying and sorting of seed parent cobs

The drying of the cobs should not be done either on the kuccha or pucca flour, rather it should bedried on tarpoline sheets to avoid seed injury and during night the cobs should be kept covered. Tomaintain the purity, dissimilar, diseased and pest infested cobs should be removed before shelling.The cobs should be dried upto 13-14% moisture content before shelling

Seed processing:

All under size, broken, damaged etc seeds should be removed for maintaining the quality of seed.

Storage and marketing

Seed drying should be done till the moisture content of the seed is reduced to 8% and it should be kept in aerated jute bags. Seed should be stored at cool and dry place preferably in cold storage. Poor storage conditions will lead to loss of vigour and poor germination. Use “super bag” developed by IRRI, Philippines for minimizing insect pest attack. Fumigation with 1 celphos tablet per ton of maize, 10 gm Bojho powder per kg of maize kills insects in storage. Marketing should be done with specifications and standards.

Value Addition

Value addition in maize has a great potential and there are several value added products of maize particularly QPM and baby corn that not only increase the farm income but also provides employment to rural youth and farm women. Value added products developed using normal maize, QPM are:

Baked products: Bread and cake

Extruded products: Vermicelli and pasta

Convenience foods: Instant idli and dhokla mix, porridge mix and sprouted chaat

Popped products: Popcorn and popped laddoo

Traditional products: Laddoo, halwa, Kheer, chapatti, sev, mathi, pakora and cheela

Constraints of Qpm Production In Ner

1. The main constraint in QPM taking off is non-availability of seeds for cultivation and that has to do with the absence of an active seed production

programme, which has been the bane of public sector farm research in recent times.

2. There is no dearth of good publicly-bred hybrid seed material in maize, be it QPM or normal single-crosses. But these cannot reach the farmer unless we have a strong public-private partnership for their large-scale production and multiplication.

3. The Food Corporation of India should be directed to procure QPM for the public distribution system, with the objective of providing a market for farmers as well as meeting broader nutritional security goals.

Conclusion

- QPM is superior to normal maize in its amino acids balance and nutrient composition

- Seed should be obtained from reliable sources and replacement should be done every year to ensure quality seed production

- Quality seed must meet the minimum field, crops and seed standards

- Maintenance of proper isolation distance and rouging of off-type plants are important field operation for seed production

- The proper agronomic practices during different stages of seed multiplication produce greater quantities of high quality seed.

This technology is certainly going to provide solution to the climate change that is rising temperature in northeastern, eastern and some part of central India, lowering water table in rice dominated area and weed menace in wheat belt etc. Therefore it is a potential technology in achieving the nutritional and food security of the nation.

About 86% of the maize produced in the country is directly used as feed (61%) and food (25%). To meet the requirement of food/feed and nutritional security quality protein maize has better say than the normal maize. Therefore in Indian maize programme greater emphasis is given to promote the quality protein maize research. The development of quality protein maize, their cultivation and availability of QPM grain will provide a nutritious feed to poultry/cattle and for poor people particularly those consuming maize as their staple food. QPM can save the poor people - who cannot afford meat and egg from diseases caused due to malnutrition particularly due to non-availability of rich lysine and tryptophan protein in their diet. India has large number of people with protein malnutrition. On the other hand, price of the meat and meat products has also gone up in recent years and has become unaffordable to meet their nutrition requirement. Thus QPM maize is solution to food and nutritional security. QPM is nutritionally superior with high lysine and tryptophan as compared to normal maize. The biological value of QPM is high (80%) as compared to normal maize (45%), which is near to that of the milk (90%). The biological value of QPM is the highest among all cereals. In India seven single cross QPM maize hybrids viz., HQPM 1, HQPM 5, HQPM 7, Vivek QPM 9, Shaktiman 1, Shaktiman 2, Shaktiman 3 and Shaktiman 4 with different maturity groups have been developed, which suits to different agro-climatic conditions under different cropping systems in North Eastern Region in general and Meghalaya in particular.

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Magnetite (Fe_3o_4/Fe_2o_3): An Efficient Catalyst for the Multicomponent Reactions

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Abstract

The introduction of Magnetite (Fe_3O_4/Fe_2O_3) has favored the recovery of catalysts with techniques of magnetic separation. Moreover, the small size of these functionalized particles becomes a well-designed way to bridge the gap between heterogeneous and homogeneous catalysis. This review deals with the main advances in the development of magnetitenano catalytic systems by the immobilization of homogeneous catalysts.

Keywords: **Magnetite, Nanocatalyst, Multicomponent reactions, 1, 3-cyclohexanediones**

Introduction

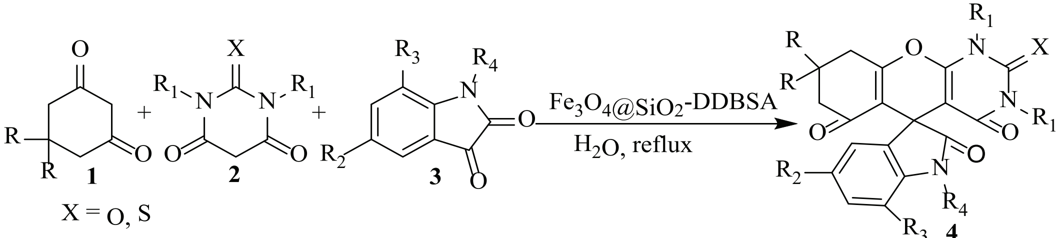
Nanotechnology is of growing importance in many branches of research because of the opportunity for miniaturization and the interesting properties associated with small particle size. In recent decades, nanostructures materials have attracted much attention for their novel electronic, magnetic, optical, chemical, and mechanical properties due to their unique characteristics which are different from bulk materials.[1] Metal nanoparticles have attracted a remarkable academic and industrial research effort due to their potential applications, ranging from fundamental studies in quantum physics to catalysts.[2] Control of the surface properties and reactivates of metal nanoparticles is an important aspect of developing nanomaterial applications. The size, shape, and surface properties of metal nanoparticles are crucially controlled by the nature of protective ligands.[3]The physical and chemical properties of metal nanoparticles can be tuned by variations in both the nature of the ligand shell, and the size of the metal core.[4] Generally, transition metal nanoparticles with small particle size have high catalytic activity and obvious size-dependent properties.[5]

Multicomponent reactions (MCRs)[6] have emerged as a powerful tool to achieve synthetic efficiency, as they have unique advantages such as convergence, operational simplicity, facile automation, flexibility, atom and step economy,[7] besides diminished waste generation. MCRs enable the expedient assembly of structurally complex molecules and also furnish structurally diverse libraries of drug-like molecules,[8,9] thereby playing a pivotal role in lead identification and optimization processes in drug discovery programmes.[10]

Nanoparticles as a heterogeneous catalyst gain much more attention. The reason behind the superiority of nanoparticles is their morphology (high surface/volume ratio), reusability and easily separationtechniques. So, in this new era application of metal nanoparticles as an effective catalyst in one pot multicomponent reaction for the synthesis of heterocycles is an important research area.

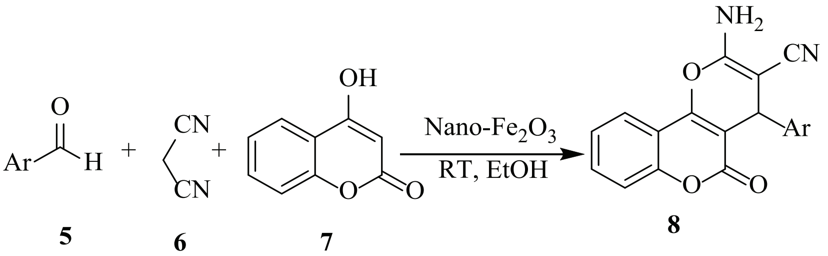
Magnetite (Fe_3O_4/Fe_2O_3) represent an economical, applied and environmentally benign means for catalyst recovery and reusability,[11] providing catalytic properties intermediate between homogeneous[12] and bulk heterogeneous materials.[13,14] Magnetic separation of the magnetic nanoparticles is very simple, economical and promising for industrial applications.[15]Many schemes exist for using magnetically recoverable catalysts: anchoring homogeneous metal complexes,[16]or organocatalysts[17] to a magnetic core, plating a catalytically-active metal,[18]or, more simply, direct use of bare Fe(0) [19] or iron oxide NPs.[20]In recent years, nano Fe_3O_4/Fe_2O_3 (magnetite) has attracted a great attention as heterogeneous catalyst due to its simple handling, ease of recovery with an external magnetic field, oxidative stability, biological compatibility, and high catalytic activities in various organic reactions.[21]Here in this review we have described few selected important multicomponent reaction catalyzed by the Fe_3O_4/Fe_2O_3 (magnetite).

Dodecyl benzenesulfonic acid functionalized silica coated ferrite nanoparticles mediated one pot three component condensation of barbituric acids (**2**), isatins (**3**) and cyclohexane-1,3-diones (**1**) has been described by the Liu and co-workers for the synthesis of library of spirooxindole-pyrimidine deverivates **(4)** in water **(Scheme-1)**.[22] They have screened various catalyst and solvents system but the impressive result was obtained in water. The most prominent advantage of this methodology was; catalyst can be separated by the external magnetic field.



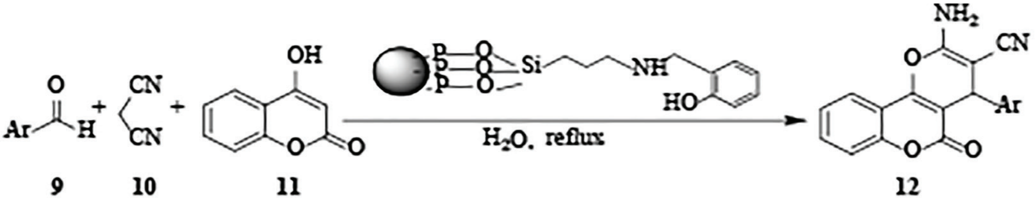
Scheme-1

A series of 3,4-dihydropyran[*c*] chromenes (**8**) was synthesized by Nagabhushana and co-workers[23] *via* a one pot MCR of aldehyde (**5**), malononitrile (**6**) and 4-hydroxy coumarin (**7**) in ethanol in presence of α-Fe_2O_3 nanoparticles (**Scheme-2**). The optimum ceiling of catalyst loading was found to be 10 wt %. This protocol can be applied to aromatic aldehyde bearing electron-withdrawing as well as electron-donating groups and also to heteroaromatic aldehydes. In every case good to excellent result was reported. The product was obtained in high yields within very short period at room temperature.



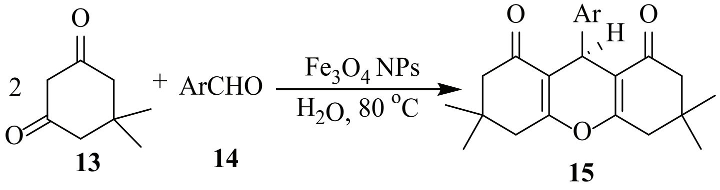
Scheme-2

An efficient inorganic–organic hybrid magnetic nanocatalyst has been prepared for the synthesis of dihydropyrano[*c*]chromenes (**12**) by Shafiee and co-workers.[24] The catalyst was environmental friendly, easy to prepare and highly stable. It is also water-resistant and super paramagnetic in nature. So, it could be easily separated by the external magnetic device and reused conveniently. This protocol can be applied to aromatic and heteroaromatic aldehydes. The nature of the substituent of the aryl aldehydes has no significant impact on the conversion (**Scheme-3**).



Scheme-3

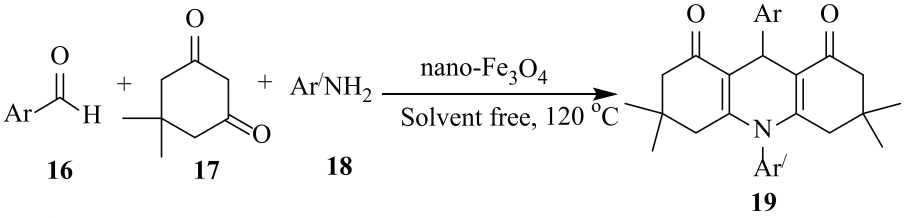
A green approach for the synthesis of xanthene derivatives (**15**) was elaborated by Karami and co-workers[25] by condensation of aryl aldehydes (**14**) and 1,3-cyclohexanediones (**13**) in water using a catalytic amount of Fe_3O_4nanoparticles. The attractive features of this protocol were simple workup, short reaction time, and reusability of the catalyst. Furthermore, products were isolated in excellent yields. Comparison of this method with other synthetic methods have also been investigated but nano Fe_3O_4 was found to best catalyst for this conversion. Under similar reaction conditions several aromatic aldehydes containing electron donating as well as electron withdrawing groups at different positions in aromatic ring gave 9-aryl substituted 1,8-dioxo-octahydroxanthenes in good yields. The products were isolated simply by filtration without any chromatography separation (**Scheme-4**).



Scheme-4

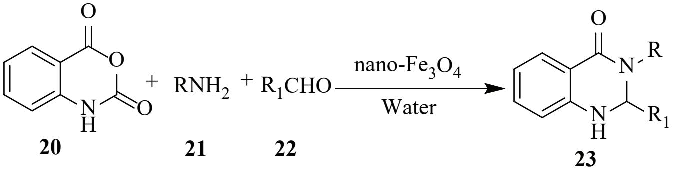
An efficient one pot three-component reaction of aldehydes (**16**), dimedone (**17**) and amines (**18**) has been described by Ghomi*et al.*[25]in presence of nano-Fe_3O_4 NPs under solvent free condition at 120°C, which generated a variety of 1,8-dioxo-decahydroacridine derivatives (**19**) in fairly good yields. The yield was obviously affected by the catalyst loading. It is found that 10 mol % of catalyst was sufficient enough to afford the desired product in good yields. The yield remains unaffected when the catalyst loading was increased up to 20 mol %.

However yield was decreased when the catalyst loading was reduced to 5 mol %. It was also found that the rate of reaction and product yields affected by electronic effect of aryl aldehydes. Electron withdrawing group like NO_2, Cl furnished higher reactivity whereas electron donating groups viz OCH_3, CH_3, reacted slowly. The aliphatic amines/aldehydes under the similar reaction condition did not give the desired product(**Scheme-5**). The advantages of using magnetite Fe_3O_4 was that it can be easily recovered by external magnetic field.



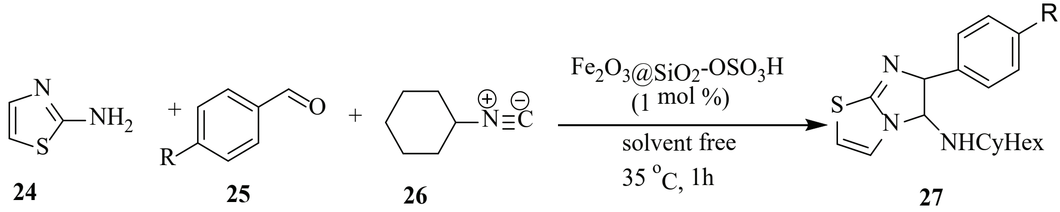
Scheme-5

Zhang*et al.*[26] demonstrated the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones (**23**) in water *via* three-component condensation of isatoic anhydride (**20**), amines (**21**), and aldehydes (**22**) in the presence of Fe_3O_4 NPs (**Scheme-6**). Various catalysts have been evaluated for this reaction, nano-Fe_3O_4 was found to be most effective than the other catalyst and gave the high yield of desire product. The mol % of catalyst was used had significant role in the reaction. 15 mol % of catalyst was sufficient to give the higher yield of the product. Further increase the catalyst loading, yield did not increase. Aromatic amines gave excellent results under this condition but aliphatic amines gave benzamide derivatives. Aliphatic aldehyde furnished quinazolines by using 50 mol % of catalyst. Non-polar solvent afforded lower yield and maximum yield was obtained in water. The catalyst can be readily recovered and reused for several runs.



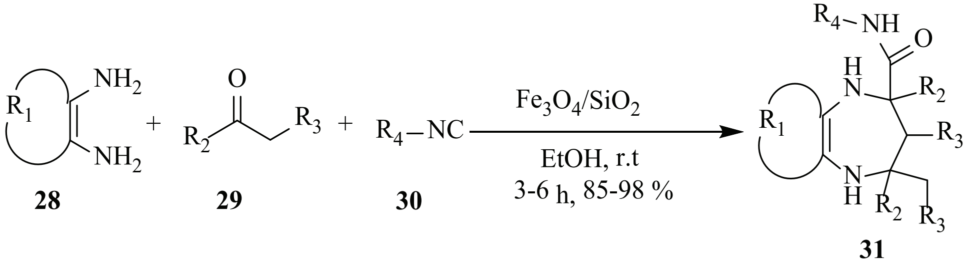
Scheme-6

γ-Fe_2O_3@SiO_2-OSO_3H nanoparticles catalyzed one pot synthesis of amino-imidazopyridine skeletons (**27**) *via* the Ugi-like Groebke-Blackburn-Bienaymé reaction has been described by Rostamnia*et al.*[27] The reaction was carried out under solvent-free condition at 35 °C for 1h and it gave 92 % yield of the product. The yield was increases sharply when the temperature increased from room temperature to 35 °C. The effect of catalyst loading was also studied and it was found 1 mol % of catalyst was enough for this reaction. On increasing the catalyst loading up to 5 mol % did not have any significant effect on the product yield (**Scheme-7**). The γ-Fe_2O_3@SiO_2-OSO_3H catalyst could be recovered and reused up to five reaction cycles.



Scheme-7

Fe_3O_4/SiO_2 nanoparticles were found to be an efficient and magnetically recoverable nanocatalyst for the one pot multicomponent synthesis of diazepines (**31**).[28] In order to check the scope of the reaction substituted diamines (**28**), ketones (**29**), and isocyanides (**30**) had been used for the reaction. In case of asymmetric aromatic diamine, the reaction was highly regioselective and only one isomer was obtained, which was confirmed by NMR spectra. This may be due to the electronic effect of the electron-withdrawing groups, such as NO_2 and COOH, which de- activates the *p*-amino group and the reaction was initiated by the *m*-amino group to give iminium ion as a favored intermediate. The reaction was carried out in various solvents but most convincing results were achieved in ethanol. Various catalysts had been applied to improve the reaction condition and it was found that Fe_3O_4/SiO_2 furnished best result. The reaction proceeds very cleanly under mild conditions at room temperature, and no undesirable side reactions are observed (**Scheme-8**).



Scheme-8

Conclusion

In summary, various biologically relevant heterocycles have been synthesized by magnetite (Fe_3O_4/Fe_2O_3) nanoparticles. The use of this catalyst has various added advantages from the simple heterogeneous catalyst like easy separation, less amount of catalyst loading and good yield.The magnetic properties of the synthesized magnetite provide a facile recovery by external magnet which eliminates the problems arising during catalyst separation by conventional filtration

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Metal Complexes of Dipyrrolylquinoxaline-Based Receptors for Anion Sensing

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Abstract

This is a research note which discusses the solution–state anion recognition chemistry of dipyrrolylquinoxaline system and metal complexes of dipyrrolylquinoxaline–based ligands.

Keywords: **Chromogenic, Fluorogenic, anion-receptor**

Introduction

The development of new chromogenic and fluorogenic molecules for anion detection has gained considerable research attention due to their fundamental roles in biological, environmental, and chemical processes.[1] Chemosensors for anions generally involve the covalent linking of a signaling subunit (chromophore/fluorophore) capable of giving information about the anion binding event with the receptor molecule, which employ hydrogen bond donor functionalities such as, amide, urea, thiourea, pyrrole and indole for anion coordination.[2] Sensors capable of representing anoptical response upon receptor–anion interactions are viable due to the low cost and easy detection of anions in solution. In general, hydrogen bond induced π–electron delocalization, or anion–induced –NH deprotonation, are believed to be responsible for signaling the binding event in sensors that generally employ polarized –NH functions.[3] The ability to establish hydrogen bonds between the anion and receptors with –NH group(s) is usually determined by the degree of electron deficiency on the interacting –NH proton (or proton acidity) and the electro negativity of the anion (or anion basicity). Intense colorations with emergence of new bands in the visible spectral region can also be attributed to the strong anion–π charge transfer interactions involving receptors containing π–acidic groups such as, triazine and naphthaldiimide.[4] Furthermore, sensors based on anion–induced changes in luminescence properties are particularly attractive because of their potential for high selectivity and sensitivity at low substrate-concentrations. The binding of anionic species leads to certain modification of the fluorescence emission behavior such as changes in emission intensity, wavelength or lifetime of the of receptor molecules. Luminescent signaling of anion recognition has been achieved using a variety of luminescent chromophores including naphthalene, naphthalimide, anthracene, pyrene, and quinoxaline derivatives,[2],[5] and also metal complexes of transition metal ions such as, rhenium(I) and ruthenium(II) complexes.[6] This research note aims to provide a brief account of the dipyrrolylquinoxaline-based chromogenic and fluorogenic chemosensors for inorganic anions such as, fluoride, cyanide and hydrogen phosphate.

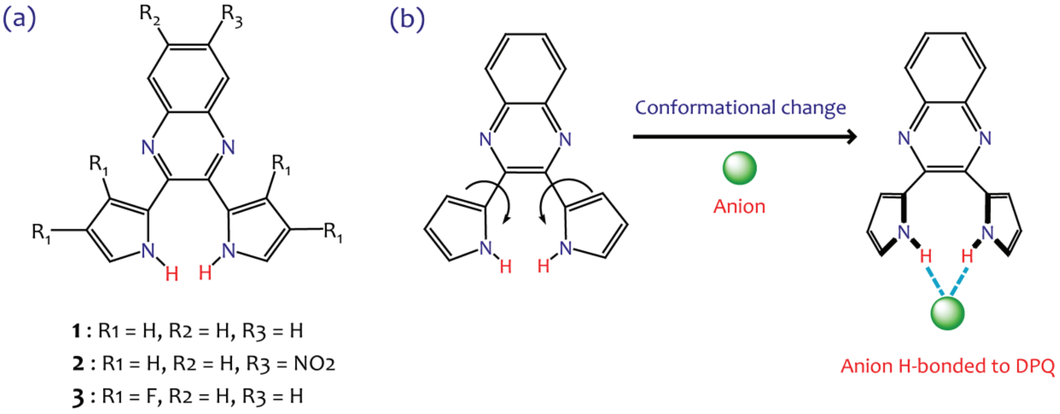

Figure 1(a) Molecular structure of dipyrrolylquinoxaline (DPQ), and (b) proposed mode of anion binding by dipyrrolylquinoxaline (DPQ).

Dipyrrolylquinoxaline anion sensor

Most of the quinoxaline–basedreceptors developed for the purpose of anion sensing have utilized 2,3- dipyrrol-2'-ylquinoxaline (DPQ) derivatives, in which two pyrrole –NH groups could function as anion binding elements and a built-in quinoxaline ring can serve as a chromogenic and fluorogenic reporter of any binding events. The earliest contribution was made by Sessler and coworkers, who first demonstrated the use of DPQ(**1**) and nitro–DPQ(**2**) as efficient chromogenic and fluorogenic chemosensors for fluoride ion (Figure 1a).[7] He proposed that the DPQ system is expected to operate through a combination of electronic and conformational effects (Figure 1b). Both DPQ(**1**) and nitro-DPQ(**2**) display a remarkable fluoride induced color change from yellow to orange (**1** + F^-) and yellow to purple (**2** + F^-), and their fluorescence emission are quenched to all extents in the presence of fluorideanion. Fluoride binding is expected to perturb the orbital overlap between the pyrrole and quinoxaline subunits, thereby changing the optical characteristics of the quinoxaline unit. Due to the greater electron deficiency, nitro–DPQ(**2**) display a binding constant ($K = 1.18 \times 10^5 M^{-1}$ in DCM) that is significantly higher than that of DPQ (**1**) ($K = 1.82 \times 10^4\ M^{-1}$ in DCM) for 1:1 receptor–anion association, and also shows a remarkable selectivity for fluoride over chloride and dihydrogenphosphate (K–F^-/K–Cl^-> 1800, and K–F^-/K–$H_2PO_4^-$> 1400).In contrast, the fluoro–DPQ (**3**) exhibits a sharp yellow to orange color change in the presence of both fluoride and dihydrogen phosphate in DCM solutions and its fluorescence emission are also quenched in the presence of both F^- and $H_2PO_4^-$ ions.[8] These preliminary results from the group of Sessler *et.al*, illustrated how the anion sensing properties of DPQ can effectively be tuned by introducing different electron-withdrawing substituents on the quinoxaline or on the pyrrole subunits of the parent DPQ (Table 1). Following such attractive spectroscopic features of DPQ derivatives have opened up newer opportunities to synthesize variously substituted DPQ and related classes of motifs to develop anion sensors that suit individual application.

Metal Complexes of dipyrrolylquinoxaline-based anion sensors

Synthetic modification of DPQ by strategic incorporation of metal binding group onto the receptor backbone to yield some of their metal complexes, has also resulted in significant enhancement in the anion binding affinity particularly towards fluoride and cyanide. Contribution in this field was first made by Sessler and coworkers, who demonstrated the fluoride recognition properties of ruthenium (II) and cobalt (III) complexes of a phenanthroline fused dipyrrolyl quinoxaline derivative, **4** (Figure 2a). In complexes **4-Ru (II)** and **4-Co(III)**. the electron-withdrawing effects that would render the pyrrole –NH protons more acidic, take place efficiently through the quinoxaline backbone and lead to enhanced anion binding affinities.[9] In

UV-vis spectroscopy, the addition of fluoride to a DMSO solution the **4-Co(III)** resulted in the emergence of a new peak at 652 nm with a concomitant change in color from pink to purple, while the absorbance of the original peaks at 323 and 525 nm decreased.

The proposal of adding cationic charges to a DPQ system can indeed be employed to increase the anion affinities as evidenced by the evaluated binding constants of **4**, **4-Ru(II)** and **4-Co(III)** with F^-, Cl^-, and $H_2PO_4^-$, based on their absorption spectral changes (Table 1). The **4-Co(III)** complex with its incrementally greater charge, displayed a much higher affinity for fluoride anion as compared to **4** and **4-Ru(II)**. The free receptor **4** displayed a rather low affinity for fluoride, presumably as a result of the additional electron density donated to the DPQ functionality from the nitrogen–rich phenanthroline system. In the differential pulse voltammetry (DPV) studies, the addition of fluoride to a DMSO solution of **4-Co(III)** resulted in a complete disappearance of the sharp Co(III)→Co(II) reduction signal, suggestive of the redox inactive nature of the complex formed. Furthermore, the fact that the Co (III)→Co(II) signal can be restored upon the addition of small amount of water indicates that the complexation between **4-Co(III)** and fluoride is reversible.

Based on the above concept, Anzenbacher and coworkers have reported a Ru(II) metal complex of phenanthroline fused dipyrrolylpyrazine, **5-Ru(II)** which acts as a luminescence lifetime-based anion sensor (Figure 2b). Preliminary investigations revealed that the addition of fluoride, cyanide, and phosphate to the DCM/MeCN (98:2 v/v) solutions of **5** and **5-Ru (II)** caused significant changes in their absorption and emission properties.[10] The emission spectrum of **5-Ru(II)** get significantly quenched and red-shifts from 594 to 610 nm (λ_{ex} =493 nm) with increasing cyanide concentration, indicating a lowering in energy of the excited state and enhancement of non–radiative decay. In all cases, the emission-data derived binding constants are substantially higher in **5-Ru (II)** relative to **5**, due to the electron-withdrawing effects caused by the Ru(II) center (Table 1). In absence of anion, **5-Ru (II)** exhibited a single-exponential lifetime of τ= 377 ± 20 ns, and with increasing cyanide concentration the intensity decay exhibited complex kinetics that adequately fit a sum of two exponentials (long τ= 320-370 ns and short τ= 13-17 ns). These emission-lifetime data suggest that there are at least two distinct luminescent species, consisting of anion–bound **5-Ru (II)** (short *τ*) and free **5-Ru (II)** (long *τ*), the sum of which results in the observed lifetime quenching.

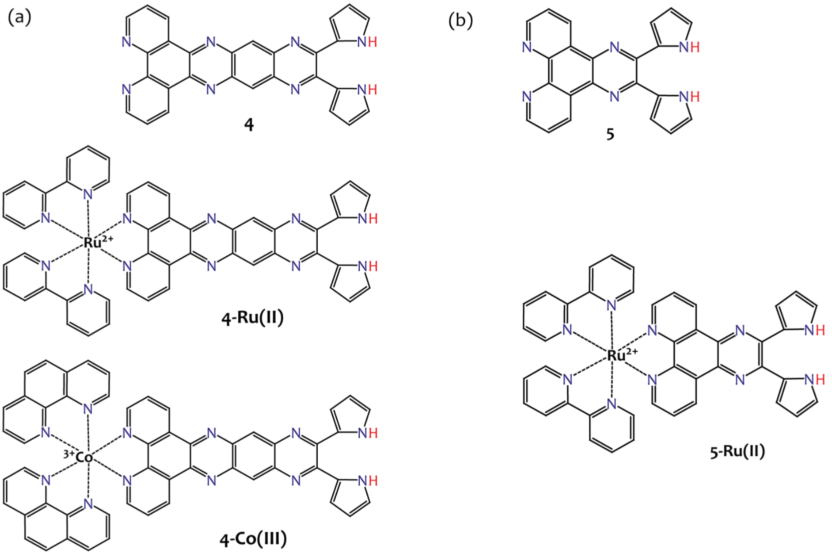

Figure 2 Molecular structures of (a) phenanthroline–fused dipyrrolylquinoxaline (b) phenanthroline–fused dipyrrolylpyrazine and their metal complexes for anion sensing in solution.

Sensors	F^-	Cl^-	$H_2PO_4^-$	CN^-
1	1.82×10^{4}	50	60	×
2	1.18×10^{5}	65	80	×
3	6.16×10^{4}	1.80×١٠^{2}	1.73×10^{4}	×
4	4.40	×	×	×
4-Ru(II)	1.20×10^{4}	10	40	×
4-Co(III)	5.40×10^{4}	20	50	×
5	6.80×10^{4}	5.00×١٠^{2}	1.62×10^{3}	3.45×10^{3}
5-Ru(II)	6.40×١٠^{5}	1.70×10^{3}	1.40×10^{4}	4.28×١٠^{5}

Table 1 Binding constants (K in M^{-1}) of DPQ–based sensors with various anions (TBA salts).

Conclusion

In this research note, a brief account of the anion sensing properties of dipyrrolyl quinoxaline and metal complexes of dipyrrolyl quinoxaline based ligands have been emphasized. Due to the electron deficient nature and π–conjugation in quinoxaline ring, dipyrrolyl quinoxaline and its derivatives can act as both chromogenic and fluorogenic chemosensors for inorganic anions. The examples discussed here illustrate how the integration of metal coordination groups with the dipyrrolyl quinoxaline system could result in highly sensitive anion responsive chemosensors. The concept of anion coordination chemistry coupled with optical signal generation by hydrogen–bond induced changes in the electronic properties is the primary approach employed in the synthesis of these probe molecules/complexes. Innovative design and synthesis of quinoxaline-based molecules and materials by considering their stabilities, geometries for hydrogen bonding interactions, and optoelectronic properties should make it possible to obtain attractive sensory systems and will contribute greatly to the academic foundation of the anion recognition chemistry.

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SHORT COMMUNICATION

Fermented Food and Beverage of the Ethnic Tribes of West Garo Hills, Meghalaya

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Fermentation is an antiquated artistry. Fermented foods and beverages are an essential constituent of the dietary culture of every community worldwide. The process of fermentation is the most frugal method of preserving of food. Wine was believed to be made in the Caucasus and Mesopotamia as early as 6000 BC, and the colonization by Romans spread winemaking all over the Mediterranean. The antiquity of Chinese foods and cuisines has been documented by several historians as far back as 4000 BC based on historical evidence. The ancient monuments of Nepal indicate that Himalayan ethnic foods have been consumed in the region for more than 2500years (Chiang et al. 2006; Deka and Sarma 2010) Fermented foods and beverages are nursed by diverse microorganisms from the environment which include mycelial moulds, yeasts, and bacteria mostly lactic acid bacteria, bacilli, and micrococci. Microorganisms transform the chemical constituents of raw materials during fermentation and enhance the nutritive value of the products, enrich diets with improved flavour and texture preserve, perishable foods, fortify, products with essential amino acids health-promoting bioactive compounds, vitamins, and minerals, degrade undesirable compounds and antinutritive factors, impart antioxidant and antimicrobial properties, improve digestibility and stimulate probiotic functions. Diversity within the species or strains of several functional genera of dominant microorganisms has created ethnic foods with different sensory characteristics (Dung 2004; Kim et al. 2014; Palaniveloo and Vairappan 2013).

The West Garo Hills of Meghalaya is primarily populated by the Garo tribes followed by the *Hajong*, *Bodo* and *Rabha*. The tribal folk possess an interesting food culture where fermented foods and beverage occupy a pivotal position and symbolize their heritage and ethnicity. There are three principal ingredients that are fermented by tribes and consumed on a day to day basis. They are rice, bamboo and fish. Also, millets and fruits like jackfruit and banana are sometimes fermented.

Fermented rice beverage–*'Chubitchi'* (Figure 1)

Chubithi is home brewed rice wine.It is an integral part of the tribal diet, festivals and ceremonies. In the village, the tribes consume on a regular basis daily. *Chubitchi* is prepared in huge quantity during the '*Wangala aka or the Hundred Drums Festival*', a celebration of the annual crop harvest where during the thanks-giving ceremony rice wine is offered to the gods and goddesses. It commands great importance in entertaining guests. Sticky red rice variety called *Menil (Oryzasativa L.*) is mostly used for wine production especially by the Garosas it has higher carbohydrate contents and imparts the desirable sweetness to the wine. The rice is mostly roasted to add an idyllic smoky flavour to the final product.Also, the yellow-black variety of boiled rice called *Mirong* is used by the *Hajons* and *Bodo* of certain regions namely *Tikrikilla* and *Dalu*. The starter rice cake is called *wanti* which is made by pounding together raw rice, chillie, locally available medicinal plants and a little of previously made *wanti* as inoculum. The rice cake starter is inoculated into boiled and cooled rice on bamboo mats which is then transferred into traditional smoked earthen pots. The pots are kept warm near the fire place. During the summers it usually takes a week for the rice to ferment and produce the beveragewhile during the winters it takes about a month.

Fermented fish- '*Nakamsua*' (Figure 2)

Garo tribes who are very fond of fish and dry-fish. Fish is a daily constituent of their diet. They have antiquated an interesting method of preservation of dry-fish through fermentation in hollow stump of bamboo which is unique from the rest of India and the world. The fermented fish preparation is referred to as *Nakamsua*. The procedure involves two stages. The first step is the preparation of a kind of local potash from burnt banana leaves called *kalchi*and the next step involves the preparation of the fish for fermentation. The special kind of potash locally known as *Kalchi*is obtained by burning dry pieces of plantain stems, dowsing the ashes in water and straining in conical shaped bamboo strainer. The dry fish and bamboo stumps are washed with *kalchi* followed by drying the fish again and cramming the semi dry fish into the bamboo stumps. They are then tightly mobbed with dried citrus leaves, capped with plantain leaves and stored away for a month or two during which fermentation of the fish takes place. The fully fermented fish is found to be "aromatic" and relished by the Garos. *Nakamsua* is used as a condiment in their everyday food preparations. It is referred to as a soul-stirring food item and is included in almost every food preparations along with vegetables and/ or meat. It is believed to have medicinal properties and used by many during certain crises periods.

Fermented bamboo(Figure 3)

Bamboo is grown as a cash crop in the north-eastern region of India. In Meghalaya, the fresh succulent bamboo shoots and the fermented preparation of bamboo shoot slices are relished. Fresh succulent shoots of bamboo of B. balcooa and D. strictus are collected during the growing season from May to September and subjected to fermentation by inoculating the thin shoot slices with the exudates obtained from already fermented samples of bamboo shoots in bottles or bamboo planks for 2–3 month. The inner surface of bamboo chamberis lined with banana and citrus leaves. The fermented bamboo is either pickled or cooked with vegetables or meat especially pork.

Conclusion

Scientific research on indigenous fermented food products of Garo Hills is wanting. At present, the products are prepared for local consumption at house-hold level under non-sterile and marginally controlled conditions. Scientific evaluation with respect to the physico-chemical, sensory, microbial association and probiotic efficacy of the products are paramount to systemically and scientifically upgrade, commercialize andto establish their beneficial effects. Improved and optimised production methods and materials will further help to economically and feasibly produce these products with increased shelf life in future at reduced production costs which successively would help to stimulate the rural economy of Garo Hills.

Figure 1: *Nakamsua* (fermented fish)

Figure 2: *Chubitchi* Rice wine

Figure 3: Fermented Bamboo

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ESTEEMED REFEREES OF THE JOURNAL

TRANSIENT

A Journal of Natural Sciences and Allied Subjects

(a peer reviewed journal)

VOLUME VI 2017

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