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Content

PREFACE

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

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

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

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OXIDE-ION CONDUCTING MATERIALS FOR SOLID OXIDE FUEL CELLS: STRUCTURAL AND CONDUCTIVITY APPROACH

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ABSTRACT:

This brief review presents an overview of the various oxide ion conductors for the use as solid electrolytes in solid oxide fuel cells. The structure and conductivity of those oxide ion conductors are discussed. After describing the well known materials, new materials are also discussed even though they have not used as an electrolyte in solid oxide fuel cell. Most of the materials have flexible structures and possess defects. In most of the cases the computational techniques are also discussed with proper references.

INTRODUCTION:

The development of cleaner, sustainable sources of energy is a major worldwide challenge to deal with the global warming. Unfortunately there is no single solution. Energy conversion and storage technologies including fuel cells and lithium ion batteries are developed to cut down the carbon dioxide emissions. The performance of these devices depends on the development of individual components. Thus the development of innovative ideas to materials chemistry is required.

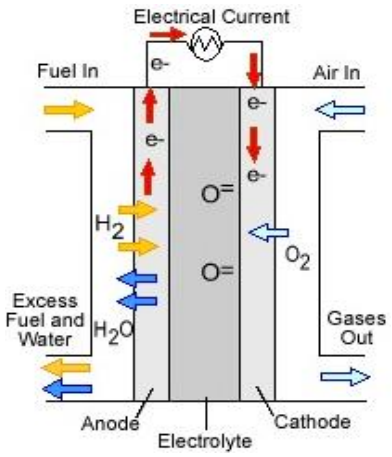

Figure 1. Schematic diagram of a single chamber solid oxide fuel cell (from Wikipedia)

Our leading hero for future power generation is solid oxide fuel cell (SOFC). An SOFC is an electrochemical device which converts chemical energy into electrical energy directly and based on the chemical reaction between hydrogen (at the anode) and oxygen (at the cathode) it produces water. The ceramic electrodes are separated by oxide ion conducting electrolyte which is basically either oxide ions or protons conductors but barrier to gas diffusion. Schematic diagram of SOFC using the ceramic oxide–ion conducting electrolyte is shown in Fig. 1. Both the anode and cathode are porous and electron conducting.

The higher efficiency compared to combustion-based technologies, low emissions and fuel flexibility have made SOFC's popular [1, 2]. SOFC can operate between the temperatures 800^{o}C to 1000^{o}C but depending on the characteristics of anode, cathode and electrolyte materials the operating temperatures can be reduced. Additionally, the target ionic conductivity at moderate operating temperature is 0.1 S cm^{-1}. The important challenge in improving SOFC technology is to reduce the working temperature to 500 – 700^{o}C and then the SOFC is called intermediate temperature solid oxide fuel cell or IT-SOFC. In addition, the lowering of operating temperature is profitable in terms of long-term operation, materials stability, cost and safety. The role of the material scientists is to develop and understanding the high ion conductivities and negligible electronic conductivities at low operating temperatures together with good chemical stability and sustainability for fabrication. A lot of research in this field over the last decade has lead to discovery of several new classes of materials with high oxide ion conductivity. Some materials show different conduction mechanism than that of the vacancy-mediated transport of oxide ion for yttria-stabilized zirconium.

Although numerous examples have been cited previously this review is to give an exhaustive summary on structure and ionic conductivity of electrolytes for SOFC.

CONVENTIONAL OXIDE-ION CONDUCTORS:

a. Fluorite type oxides

Most of the oxide ion conducting materials are fluorite type [2, 3] AO_2, where A is the tetravalent cation and O is oxygen. As per the stoichiometry the cation occupies the face centered position in a cubic unit cell with anions in the eight tetrahedral sites between them. The best known material is acceptor doped ZrO_2. Pure ZrO_2 is not a good ionic conductor and the cubic fluorite symmetry is stabilized above 2300^{o}C [4]. Typical crystal structure of fluorite material is shown in Fig. 2.

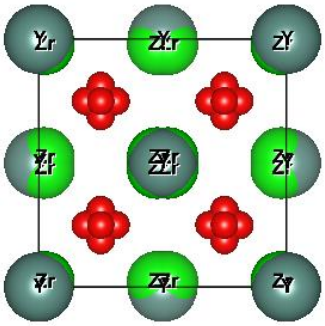

Figure 2. Crystal structure of YSZ at room temperature with viewing direction along (011) plane. The red spheres correspond to O. Y and Z shares almost the same positions

To stabilize the cubic structure at lower temperatures and to increase the oxygen vacancies acceptor dopants are introduced onto the cation sublattice [5, 6]. The incorporation of oxygen vacancy can be described using Kröger-Vink notation

$$MO + Zr_{Zr}^{\times} + O_O^{\times} \rightarrow M_{Zr}^{''} + V_O^{\bullet\bullet} + ZrO_2 \quad (1)$$

$$R_2O_3 + 2Zr_{Zr}^{\times} + O_O^{\times} \rightarrow 2R_{Zr}^{'} + V_O^{\bullet\bullet} + 2ZrO_2 \quad (2)$$

Where M is a divalent cation, R is a trivalent cation, $Zr_{Zr}^{\times}$ is a normal Zr at a Zr site with effective charge zero, $M_{Zr}^{''}$ and $R_{Zr}^{'}$ are dopant substitutionals, $V_O^{\bullet\bullet}$ is oxygen vacancy. It is noteworthy that for conduction, oxygen ion needs hopping through oxygen vacancy. Two well known dopants say Y^{3+} and Ca^{2+} produce calcia-stabilized zirconia (CSZ) and yttria-stabilized

zirconia (YSZ) respectively and among them YSZ exhibits good oxide-ion conductivity above 700°C. The reciprocal temperature dependence of the oxide-ion conductivity of several materials including YSZ is shown in Fig. 3.

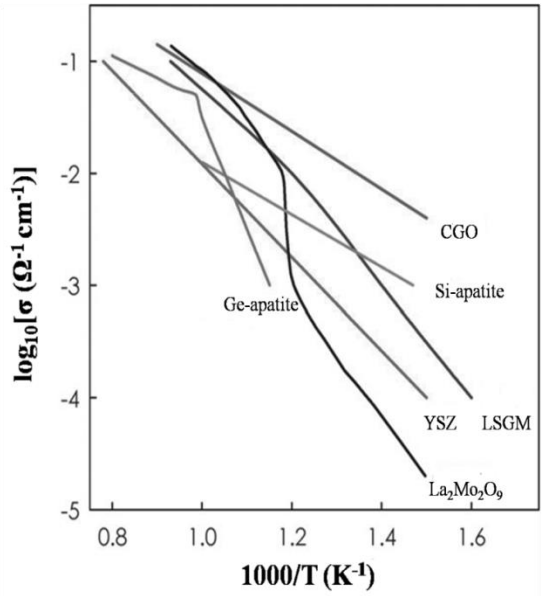

Figure 3. Arrhenius plot of total conductivity for some oxide-ion conductors

Another fluorite type conductor is Gd_2O_3 and Sm_2O_3 doped CeO_2 [7-9]. These compounds have higher oxide-ion conductivity than YSZ even in reduced temperatures say 500 – 700°C. The ionic conductivity for Gd doped CeO_2 is shown in Fig. 3. However, at low oxygen partial pressures and temperatures above 600°C the total conductivity is not found to be purely ionic but with a proportion of electronic conductivity of n type [10]. Despite the difficulties it has been reported that SOFC can be operated with these electrolytes successfully at a working temperature of 500 – 700°C. An alternative strategy is also adopted to enhance the oxide-ion conductivity adding zirconia to ceria or vice versa. As these compounds are mutually soluble a wide range of electrolytes are produced. Additionally, these materials have advantage over YSZ with superior chemical and mechanical properties.

Another fluorite type oxide ion conductor is δ-Bi_2O_3 as shown in Fig. 4 [1, 11]. The δ phase of Bi_2O_3 is stable only above 730°C. Stabilization of this phase to room temperature can be achieved by substituting bismuth with rare earth elements such as Y^{3+}, Dy^{3+} or Er^{3+} [10, 12-14].

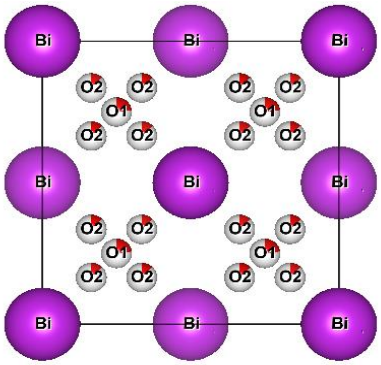

Figure 4. Crystal structure of γ-Bi_2O_3 at 778ºC viewing along (110) direction. The purple spheres for Bi and both O1 and O2 sites are found to be partially occupied as shown by red

This compound has an oxygen sublattice with a high fraction of vacancies. As a result it conducts oxide-ion in a high rate. Neutron diffraction study has shown that there is a similarity between δ and α phase with a distorted square pyramidal arrangement inside the structure. The electron density around the Bi^{3+} ion is crucial for promoting extensive anion disorder as well as oxide-ion conductivity [15].

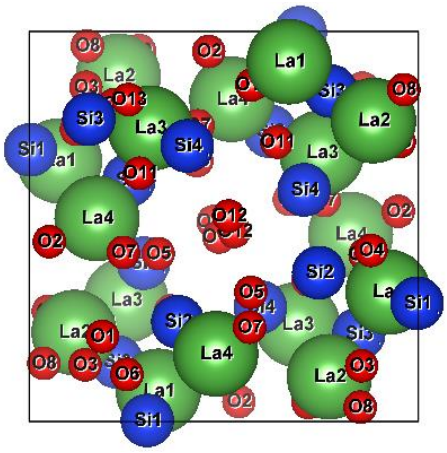

Figure 5. Crystal structure of $La_2Si_2O_7$ with viewing direction (110) plane. The numbers indicate different crystallographic sites

The fluorite type material is extended with the pyrochlore structure with formula $A_2B_2O_7$ as shown in Fig. 5 [16]. This compound has a defective fluorite superstructure, $(A,B)O_{1.75}$ with one oxide-ion vacancy per formula unit yielding very high oxide-ion conductivity. The studied

systems are $Gd_2(Ti_{1-x}Zr_x)_2O_7$ [17] and $Gd_{2-y}Ln_yZr_2O_7$ (where Ln = Sm, Nd, La) [18]. However, these materials are not currently commercialized like YSZ and Gd doped CeO_2.

b. Perovskite type oxides

The cubic perovskite type oxide materials have general formula of ABO_3, where A cation is coordinated to twelve anions and B cation is at six coordinated site forming a corner sharing BO_6 octahedra. The tilting of these octahedral units leads to deviation from ideal cubic symmetry. $LaGaO_3$ possess a higher ionic conductivity than that of stabilized zirconia (YSZ) in the intermediate temperature range 500 - 800^oC [19, 20]. The high ionic conductivity of Sr and Mg co doped $LaGaO_3$ having general formula $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ is also reported over a range of oxygen partial pressure ($10^{-20} < pO_2 < 1$) [21]. More specifically, among all the compositions $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ shows higher ionic conductivity than YSZ as shown in Fig. 3. For practical interest of SOFC, Co or Ni doped LSGM is found to be promising [22]. Difficulty in formation of single phase for LSGM is reported by Matraszek et al. [23] due to the volatility of gallium at high temperatures. The creation of oxygen vacancies can be written using the Kröger-Vink notation

$$2SrO + 2La_{La}^{\times} + O_O^{\times} \rightarrow 2Sr'_{Zr} + V_O^{\bullet\bullet} + La_2O_3 \quad (3)$$

where $La_{La}^{\times}$a normal La at a La site with effective charge zero is similarly $O_O^{\times}$ is a normal O at an O site with effective charge zero, Sr'_{Zr} is dopant substitutional, $V_O^{\bullet\bullet}$ is oxygen vacancy. The X-ray Rietveld refinement has shown that LSGM has a cubic crystal structure as shown in Fig. 6 [21] whereas neutron diffraction identifies a monoclinic structure [24]. The in situ neutron diffraction studies have shown that simultaneously Sr and Mg doping leads to a reduction of the tilt of the GaO_6 octahedra with respect to the parent compound ($LaGaO_3$). This increment in symmetry promotes greater oxide-ion conductivity. The defect chemistry and mobile oxygen ion migration pathway by vacancy hopping between oxygen sites along a GaO_6 octahedron edge are confirmed by computational techniques [25, 26]. The theoretical expedition is also later confirmed by experimentally using maximum entropy method of the neutron diffraction [27].

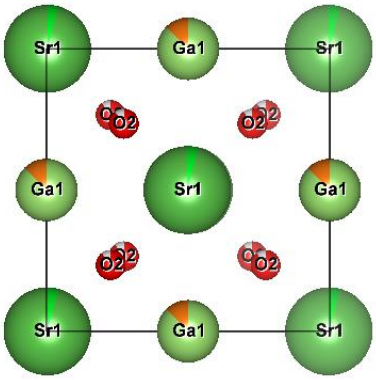

Figure 6. Crystal structure of $La_{0.95}$ $Sr_{0.05}Ga_{0.87}Mg_{0.13}O_{2.74}$ with viewing direction along (011) plane. Rietveld analysis of XRD has shown that Ga and Mg shares the same coordinates

Another perovskites like $NdGa_{0.9}Mg_{0.1}O_{2.95}$ and $Gd_{0.85}Ca_{0.15}AlO_{2.925}$ have shown similar oxide ion conductivity to that of YSZ [28, 29].

NEW OXIDE-ION CONDUCTORS:

Researchers from the solid state community have developed new materials with low electronic conductivity, better thermal and chemical stability and low operating temperatures in a device. In this following section most recent and novel oxide-ion conducting materials will be described.

c. BIMEVOX

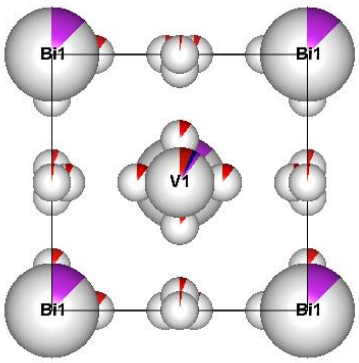

Figure 7. Crystal structure of $Bi_4V_{1.7}Co_{0.3}O_{11}$ oriented along (110) plane

In previous section it is described that δ-Bi_2O_3 has shown oxide-ion conductivity but suffers from phase transition problem. A new type of oxide ion conductor is reported with parent

oxide $Bi_4V_2O_{11}$ [30, 31]. Two main polymorphic transitions say α → β (at 447ºC) β → γ (at 567ºC) are observed [30]. Substitution of V by a host of iso and aliovalent cations leads to stabilization of the highly conducting γ polymorph at room temperature with conductivities on the order of 0.1 - 1.0 S cm^{-1} at 600ºC. The crystal structure is based on the Aurivillius type structure and consists of alternating $Bi_2O_2^{2+}$ and perovskite-like $VO_{3.5}^{2-}$ layers. Crystal structure of Co doped BIMEVOX is shown in Fig. 7. High resolution ^{17}O and ^{51}V magic angle spinning (MAS) and nuclear magnetic resonance (NMR) spectroscopy studies of $Bi_4V_2O_{11}$ have shown that oxide-ion conduction involves anions in the V–O layers with the most mobile ions associated with the more distorted $VO_{3.5}$ groups [32]. Also the ^{17}O two-dimensional NMR studies of the related Nb-doped Bi_2WO_6 have revealed the oxide-ion conduction pathways [33].

Apart from its potential to serve as an electrolyte for SOFC's BIMEVOX has been successfully used as an electrochemical catalyst [34].

d. Si and Ge apatites

Apatite-oxides can be written as $M_{10}(XO_4)_6O_{2+y}$, where M is a rare-earth or alkaline-earth cation, X is a p-block element such as P, Si or Ge and y is the amount of oxygen non-stoichiometry. These materials are isostructure with the well-known hydroxyapatite biomaterials found in bones and teeth. The best apatite oxide-ion conductor is the Si and Ge based lanthanum apatites. These crystals show hexagonal symmetry with space group $P6_3/m$ with lattice parameter *a* of 9.7 - 9.9 Å and *c* of 7 Å [35]. Research has shown that the high ionic conductivity in apatite silicates and germanates are due to interstitial oxide-ions leading to interstitial type transport mechanism.

The structure of cation doping say Mg, Ba, Ga, Co on the germanate has also been extensively examined [36, 37]. $La_{9.33+x}(GeO_4)_6O_{2+3x/2}$ has triclinic symmetry unlikely hexagonal stoichiometry compositions [38]. In order to stabilize the hexagonal lattice and high oxygen contents doping with Y ($La_8Y_2Ge_6O_{27}$) has proven effective, leading to enhancement in low temperature conductivities [39]. Computer modeling of $La_{9.33}Si_6O_{26}$ has shown that oxygen interstitials follow a complex sinusoidal trajectory along the periphery of the La2 channels coupled with SiO_4 tetradedra [40]. Synchrotron studies of $La_{9.71}(Si_{5.81}Mg_{0.18})O_{26.37}$ based on the maximum-entropy method have confirmed the position of the interstitial oxygen near the edge of the La channels and the covalent nature of the Si-O bonds. Electron density maps are also consistent with migration of oxide ions predominantly in the c direction [41]. The enhanced ionic

conductivity of $La_{10-x}(GeO_4)_6O_{3-1.5x}$ materials in wet atmospheres has been attributed to proton conduction below 873°C [42].

e. **$La_2Mo_2O_9$ (LAMOX)**

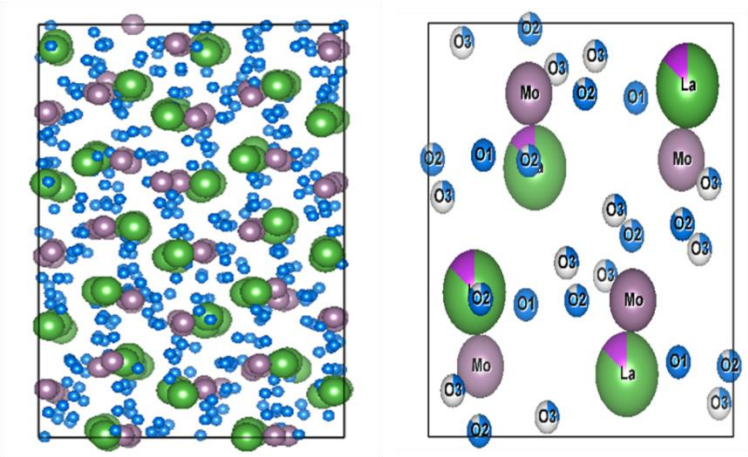

Figure 8. Crystal structures of α-$La_2Mo_2O_9$ and β-$La_2Mo_2O_9$

A new family of fast oxide ion conductors based on the parent compound $La_2Mo_2O_9$ is reported by Lacorre et al. [43]. The compound exhibits first order phase transition from room temperature monoclinic α to high temperature cubic β after 580ºC [43]. The α structure is one of the most complex crystal structures reported so far with 312 crystallographic distinct sites of which 48 La, 48 Mo and 216 O as shown in the left panel of Fig. 8 [44]. Based on the neutron and single crystal X-ray diffraction studies the β structure has three oxygen sites of which O1 is fully occupied, O2 and O3 are partially occupied and characterized by huge thermal displacement parameters B (B_{eq} ~ 20 $Å^2$ for O3 site) [45]. The structure of β-$La_2Mo_2O_9$ emphasizes the coordination environments of the anions as presented in the right panel of Fig. 8. Different approaches have been taken to explain the high ionic conductivity of the compound. A rigid antitetrahedral unit of [O1La3Mo] is surrounded by partly delocalized oxide ions on O2 and O3 sites. The [O1La3Mo] framework contains a tunnel like structure connecting O2 and O3 sites. The tilting and rotation of the unit are helpful in explaining the ion conduction after 580°C [46]. Overall the partial occupancies of the O2 and O3 sites and the very short distances between these pairs of atoms are believed to facilitate the oxygen ion migration. Mechanical and dielectric relaxation studies suggest a possible path for long-range diffusion of oxygen ions in β-$La_2Mo_2O_9$ [47]. According to Ref [48] the oxygen ions or vacancies jump from the O1 site to O2 site and then to O3 site and again to O1 site making a three dimensional conduction pathway

which is also verified by the molecular dynamics simulations [49]. In Fig. 3 it is shown that the conductivity jumps from low temperature Arrhenius to high temperature Arrhenius with the structural phase transition $\alpha \rightarrow \beta$. The β-$La_2Mo_2O_9$ has ionic conductivity of 6×10^{-2} S cm^{-1} at 800ºC similar to that of YSZ [50]. Various alkali, alkaline and rare earth materials have been doped both on La and Mo sites of $La_2Mo_2O_9$ to stabilize the more conducting cubic β phase to room temperature [43, 45, 51-55]. On the other hand, it has been shown that $La_2Mo_2O_9$ reduces in dilute hydrogen leading to the formation of a mixed valent Mo^{5+}/Mo^{6+} phase with composition $La_7Mo_7O_{30}$. Research has shown that $La_2Mo_{2-y}W_yO_9$ compounds could be either electrolytes in single chamber SOFC and duel chamber micro SOFC or anode materials in dual chamber SOFC [56].

f. $Sr_{1-x}(Na/K)_xSiO_{3-0.5x}$ oxide ion conductor

Another type of oxide ion conductor is reported by Singh et al [57]. Compositions of the $Sr_{1-x}Na_xSiO_{3-0.5x}$ offer competitive oxide ion conductivities in the intermediate temperature range 500 - 800ºC, which make them promising electrolytes for an IT-SOFC or for other applications of oxide ion conductors [57]. These electrolytes are stable at 800ºC with a nickel composite anode in a 5% H_2/argon atmosphere [57]. On the other hand $Sr_{1-x}K_xSiO_{3-0.5x}$ are also reported as promising candidates for low temperature SOFC. The acceptor doping of K in $SrSiO_3$ introduces the oxygen vacancies in the Si_3O_9 tetrahedral rings as revealed by the existence of Q^1-linked Si signal [58]. Though $Sr_{1-x}Na_xSiO_{3-0.5x}$ has been tested for SOFC but $Sr_{1-x}K_xSiO_{3-0.5x}$ has no such report.

In general $SrSiO_3$ has monoclinic phase [59]. Rietveld refinements of the XRD patterns of $Sr_{1-x}Na_xSiO_{3-0.5x}$ ($0 \leq x \leq 0.4$) confirm the monoclinic phase [59]. Both XRD and neutron data confirm that for x = 0.4 there is amorphous phase of Na. This result is further verified by ^{29}Si solid state NMR. Recent study has shown that $Sr_{1-x}K_xSiO_{3-0.5x}$ has monoclinic structure with amorphous state [60]. The crystal structure of $Sr_{1-x}K_xSiO_{3-0.5x}$ is shown in Fig. 9. However studies on crystal structure and electron density distribution are missing. Studies have shown that the presence of $K_2Si_2O_5$ glass is responsible for high ionic conductivity in $Sr_{1-x}K_xSiO_{3-0.5x}$ [60].

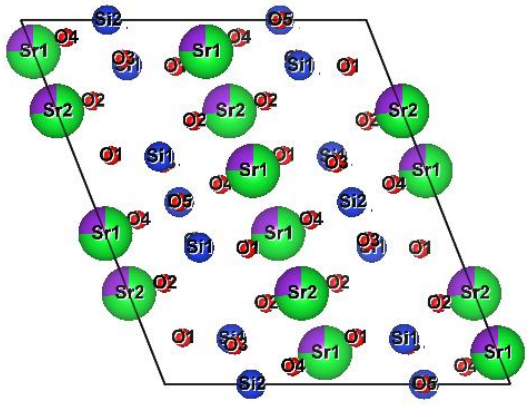

Figure 9. Crystal structure of $Sr_{0.7}K_{0.3}SiO_{2.85}$ along (101) direction

CONCLUSIONS AND FUTURE OUTLOOK:

This brief review has highlighted the diverse classes of oxide ion conductors which has application as an electrolyte in solid oxide fuel cell. The discussion has been made for both conventional and new candidate materials with alternate structures. The structures of these new ionic conductors mainly consist of tetrahedral frameworks. Determination of the flexibility using structural refinement and density functional theory are the key to the ion conduction mechanism in these ionic conductors. The performance over ionic conductivity is also discussed.

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FACILE SYNTHESIS OF NEARLY MONODISPERSE AND UNAGGLOMERATED $CoFe_2O_4$ NANOPARTICLES BY A HYDROTHERMAL TECHNIQUE

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ABSTRACT:

$CoFe_2O_4$ (CFO) has manifold applications in catalysis, ferrofluids, hyperthermia, cancer therapy, and molecular imaging agents in magnetic resonance imaging (MRI). $CoFe_2O_4$ nanoparticles are required to have a narrow size distribution, high magnetization values, a uniform spherical shape and superparamagnetic behaviour at room temperature for biomedical applications. For magnetic particles in general and $CoFe_2O_4$ in particular to be used in the human body physicians need particles free from aggregation and highly stable. There are various synthesis routes for preparation of $CoFe_2O_4$. But they lead to the formation of agglomerated CFO with poor control in size and shape. We have synthesized nearly monodisperse, completely unagglomerated Cobalt Ferrite nanoparticles by the hydrothermal technique. The nanoparticles were obtained by the reaction of $FeCl_3.6H_2O$ and $CoCl_2.6H_2O$ in ethanol/water solution using the capping agents olyl amine, sodium oleate. The X Ray Diffraction and Transmission Electron Microscope results proved that well-defined spherical nanoparticles with an average size of 5.5 nm were successfully synthesized. Magnetic measurement by Superconducting Quantum Interference Device (SQUID) and Vibrating Sample Magnetometer (VSM) indicates that the particles exhibit a very high coercivity of ~ 1Tesla at 4 K and perform superparamagnetism at

room temperature which is further illuminated by ZFC/FC curves. The blocking temperature from the ZFC FC curves came out to be 225 K. The Fourier Transform Infra-Red Spectra (FTIR) of the as prepared Cobalt Ferrite nanoparticles proved that Sodium Oleate and Olyl amine combined with the surface of cobalt ferrite. These superparamagnetic cobalt ferrite nanomaterials are considered to have potential application in the fields of biomedicine. The synthesis method is possible to be a general approach for the preparation of other pure binary and ternary compounds.

KEYWORDS:

Magnetic nanoparticles;Cobalt Ferrite; Superparamagnetic;Monodisperse;Ferrofluids

INTRODUCTION:

$CoFe_2O_4$, is a spinel ferrite, which has wide applications in various fields of electronics [1], photomagnetism [2], catalysis [3], ferrofluids [4], hyperthermia [5], cancer therapy [6] and molecular imaging agents in magnetic resonance imaging (MRI) [7]. The magnetic properties of $CoFe_2O_4$ determine its applications. For biomedical applications, $CoFe_2O_4$ nanoparticles are required to have a narrow size distribution, high magnetization values, a uniform spherical shape, and superparamagnetic behavior at room temperature. Magnetic nanoparticles in general and $CoFe_2O_4$ nanoparticles in particular, have the unique property of getting agglomerated with each other due to the high dipole-dipole attraction. Hence this leads to poor control of size and shape, which greatly restrict their applications [8]. We have synthesized nearly monodisperse, completely unagglomerated Cobalt Ferrite nanoparticles by the hydrothermal technique using Sodium Oleate and Olyl Amine as strong capping agents. These superparamagnetic cobalt ferrite nanoparticles can have potential application in the fields of biomedicine.

EXPERIMENTAL

$FeCl_3.6H_2O$ and $CoCl_2.6H_2O$ taken in stoichiometric ratio were dissolved in a solvent composed of 40 ml of distilled water and 20 ml of ethanol. Now 4 gm of Sodium Oleate and 4 ml of Olyl Amine were added into the above solution with stirring for 2 hours. The precursor solution was then added into a Teflon Lined steel autoclave of capacity 80 ml. The Teflon chamber was kept at 180^0C for 12 hours to crystallize the particles. After that the autoclave was cooled to room temperature naturally [9]. The products were separated from the final reaction

solution by the addition of hexane. The as prepared cobalt ferrite could be deposited by adding ethanol and obtained by centrifugating at a high speed without any size-selecting process. We have prepared three sets of samples and named them as follows. Sample A was prepared using 4 gm of Sodium Oleate, 4ml of Olyl Amine. Sample B was prepared using 2 gm of Sodium Oleate, 2 ml of Olyl Amine. Sample C was prepared using 1 gm of Sodium Oleate and 1 ml of Olyl Amine.

The as-synthesized sample was characterised through several techniques. The phase contents and crystal structures of the samples were analyzed by X-ray diffraction (XRD) with Cu K_α radiation on a Philips X'pert diffractometer. High-resolution Transmission Electron Microscope (HRTEM) analysis was carried out on a FEI-2010 transmission electron microscope with an accelerating voltage of 200 kV. One droplet of hexane dispersion of $CoFe_2O_4$ nanoparticles was dropped on a carbon-coated copper grid and then dried naturally before recording the micrographs. FTIR spectra of the samples capped with olyl amine were performed on a 170SX spectrometer in the range of 500–4000 cm^{-1}. Magnetic properties of the products were characterized at room temperature with a Lake Shore 7304 vibrating sample magnetometer (VSM). Temperature and field dependences of the samples were recorded on a Quantum Design MPMS-XL superconducting quantum interference device (SQUID). ZFC/FC measurements were carried out in the temperature range of 4–330 K with an applied field of 100 Oe.

RESULTS AND DISCUSSION:

The X Ray Diffraction (XRD) of the samples A,B and C is shown in Figure 1. All the observed peaks showed the formation of pure phase $CoFe_2O_4$. As the quantity of Olyl amine and sodium oleate decreases the particle size increases.

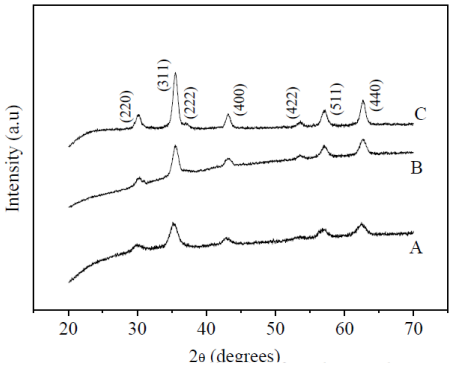

Fig. 1: X - Ray Diffraction of sample

As the quantity of Olyl amine and sodium oleate decreases the capping decreases. Hence the particles grow to bigger sizes. It also shows that the peaks obtained are very broad which is signature of nanocrystallinity.

The average grain size as calculated from the scherrer formulae for sample A, B and C are ~8 ± 2nm, ~16 ± 2 nm and ~24 ± 2 nm respectively.

Figure 2 shows the HRTEM images of sample A. Figure 3 shows the particle size distribution of sample A having a narrow size distribution. The HRTEM images reveal that the particles were nearly spherical and monodisperse. The average particle size is ~ 8 nm. The average particle size obtained is also in agreement with that obtained from the scherrer formulae. It is observed that the particle size as well as shape varied with the variation in concentration of Olyl Amine and Sodium Oleate.

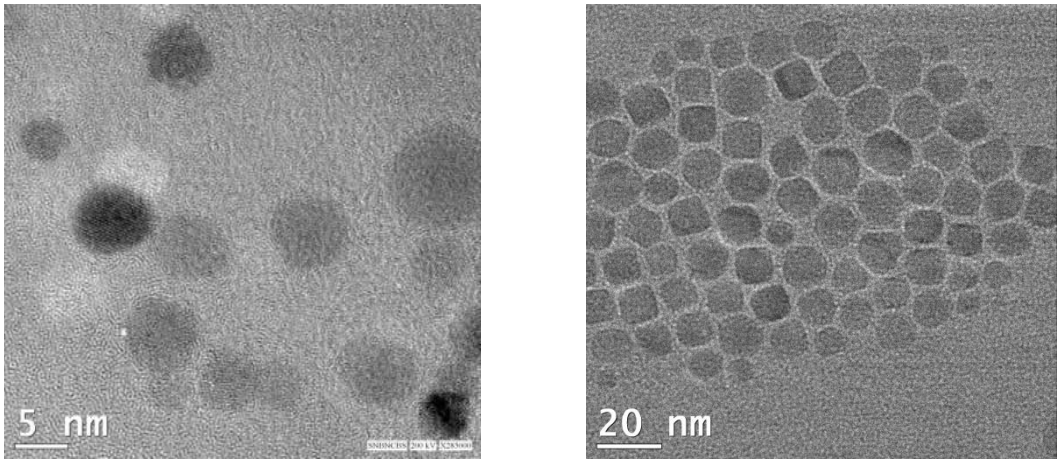

Fig. 2: HRTEM of the $CoFe_2O_4$ particles (Sample A)

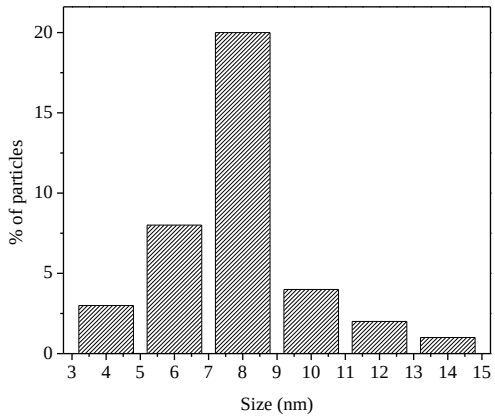

Fig. 3: Particle size distribution of the sample A

Figure 4 shows the Zero Field Cooled (ZFC) and Field Cooled (FC) plots of the sample A. The temperature corresponding to the peak value of the ZFC curve is considered as the blocking temperature, T_B of the sample above which it behaves as a superparamagnetic material. The ZFC M–T curves merge with the FC curve beyond T_B. For a single nanoparticle, ZFC magnetization increases with T as the small thermal fluctuations help orienting the direction of magnetization towards the field direction. Beyond a certain temperature T_B, called blocking temperature, the thermal energy is more than the anisotropy energy and because of the random thermal fluctuations, magnetization decreases with the increase in temperature. For FC measurement, magnetization continuously decreases with the increase in T. In this case, the magnetization was initially oriented along the direction of H and higher thermal fluctuations at higher T reduces the component of magnetization along the direction of H [10].

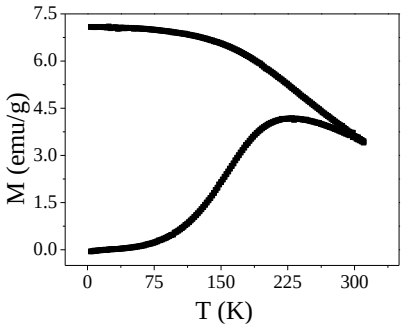

Fig.4 : Zero Field Cooled (ZFC) and Field Cooled (FC) curves of sample A

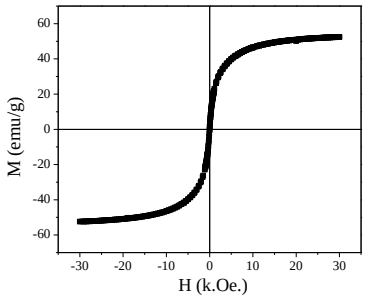

Fig.5: Hysteresis loop of the sample at 300K

The room temperature hysteresis loop of the sample is shown in Figs. 5. The sample does not show any measurable coercivity, H_c and remanence, M_r indicating the superparamagnetic behaviour at room temperature. At a finite temperature and in absence of any magnetic field, the ferromagneticallyalligned magnetic moments within these single-domain particles fluctuate between their two energetically degenerate ground states on a time scale given by [11,12]

$$\tau = \tau_0 \exp\left(\frac{K_{eff} V_p}{k_B T}\right) \qquad (1)$$

Where, τ is the relaxation time, τ_0, a constant estimated to be between 10^{-9} and 10^{-13}s and $K_{eff}V_p$, the total anisotropy energy E_A of the particle. In case of $k_BT > K_{eff}V_p$, no hysteresis is observed if the characteristic time of the measuring instrument, τ_m is higher than τ. This is the

reason for not observing any measurable coercivity in our sample. Theblocking temperature T_B of a particle is the temperature at which $\tau = \tau_m$, the measurement time of the instrument. For $\tau < \tau_m$ the system behaves as a superparamagnet. For $\tau > \tau_m$ thesystem behaves as a ferromagnet.

Temperature dependence of coercivity (H_c) of the particles of sample A is shown in Fig. 6. The coercivity H_c increases with the decrease in temperature. For an assembly of monodispersed, non-interacting, ferro- or ferrimagnetically ordered single-domain particles, the temperature dependence of coercivity$H_c(T)$ can be expressed as [12]:

$$H_c = H_c(0)\left[1-\left(\frac{T}{T_B}\right)^{\frac{1}{2}}\right] \qquad (2)$$

$H_c(T)$ is plotted against $T^{1/2}$ in Fig. 7. Linear dependencyof H_C on T_B is also an evidence of monodispersed noninteracting, ferromagnetically ordered single domain particles.

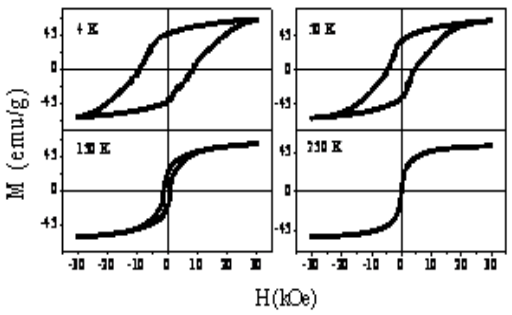

Fig. 6: Hysteresis loop of the sample A at 4K, 50K, 150K and 250K

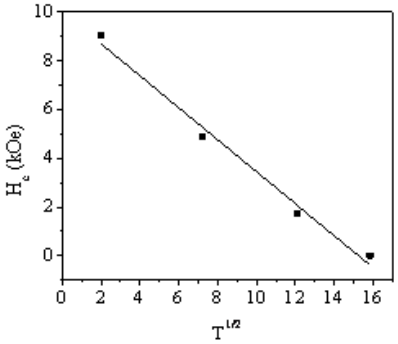

Fig. 7: Coercivity vs $T^{1/2}$ plot

The FTIR spectra of sample A performed in the range of 500 cm^{-1} to 4000 cm^{-1} has been shown in Fig. 8. The peak at 587.4 cm^{-1} is due to the ferrite nanoparticles. The peaks at 1443 $cm^{-1}$and 1534 cm^{-1}corresspond to COO^- asymmetric and COO^- symmetric stretch. Oleic acid shows vibration bands at 2920 and 2855 cm^{-1} that are attributed to the CH_2 asymmetric and CH_2 symmetric stretch. The sharp peaks are due to the long hydrocarbon chain of oleic amine. [13]. The peak at 3,037 cm^{-1} is assigned to the stretching of the vinyl group. The peak at 3,432 cm^{-1} is ascribed to the $-NH_2$ group on the surface of $CoFe_2O_4$. Thus the aboveresults proved that oleic acid and olyl amine combined with the surface of $CoFe_2O_4$ nanoparticles.

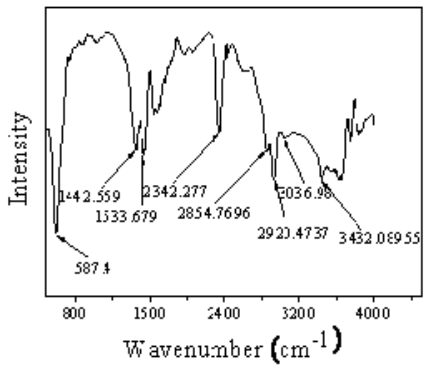

Fig.8: FTIR spectra of the as-synthesized $CoFe_2O_4$(sample A) nanoparticles

CONCLUSION:

Monodisperse, unagglomerated $CoFe_2O_4$ nanoparticles have been successfully synthesized by the hydrothermal technique. The as prepared nanoparticles are found to be superparamagnetic at room temperature. The coercivity vs temperature $^{1/2}$ showed a linear dependence which corroborated the fact that the particles are monodisperse, non-interacting, ferro- or ferrimagnetically ordered single-domain particles. The FTIR measurements proved the coating of Sodium oleate and Olyl amine on the surface of the $CoFe_2O_4$ nanoparticles.

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UPCONVERSION PHOSPHOR MATERIALS FOR BEGINNERS: SYNTHESIS AND APPLICATIONS

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ABSTRACT:

Upconversion is a non-linear optical processes in which inter conversion of low photon energy into high photon energy takes place. The upconverting mechanism is frequently studied since a long 1960s. Since last two decades many applications have been proposed rapidly after tuning the particle size and shape of upconversion materials. In this scenario, many researchers paid their attention towards rare earth doped phosphor materials for real time applications. In this chapter, authors, describe all possible ideas of synthesis to tune the materials' morphology. The different upconversion mechanisms like excited state absorption, energy transfer, ground state absorption, photon avalanche, etc. are described as well in details. The upconverting materials may, however, emit visible spectrum under irradiation of near infra-red photons even at no autofluorescence, a lesser amount of scattering and profound penetration in natural tissues. Therefore, the materials have few charming application such as bio-imaging, photodynamic therapy, latent fingermarks detection, security inks, temperature sensing, etc. All the possible applications under the relevant section are discussed fruitfully.

INTRODUCTION:

The fluorescence light materials often intend the Stroke's law. According to this law, "The energy of incident photons is always higher than that of weak emitting photons," means

efficiency of light emitting materials cannot be more than one (1). Here, Authors are coinciding the discussion only for anti-Stokes emission based upconversion process and its possible applications. In this process the energy of emissive photons is found more than 10 to 100 times of kT (where k and T are Boltzmann's contact and absolute temperature, respectively). The d-ions of transition metal and f- ions of lanthanides when doped /codoped with host matrix (oxide or fluoride form), yields anti-Stokes type of upconversion emission in a large step of excitation/incident sources. For long time, since 1960s the mechanism of upconversion was not too cleared. Only excited state absorption (ESA) the classical absorption rule of photons were efficiently described. This known process is very easy in which one doped ionic system transfers its energy to other systems [1-3]. The process includes as form of Energy Transfer Upconversion (ETU), multi-step excitations via Excited State Absorption (ESA), co-operative energy transfer as well as photon avalanche effect. To understand the upconversion behavior of materials, various mechanisms are likely to be explained here [2].

Energy transfer scheme:

Where emission and absorption phenomena do not occur, the energy transfer takes place between rare earth ions doped/codoped phosphor materials. This character, however, depends on concentration of doped ions. As the concentration increases migration of energy between two centers become start. This kind of energy process takes place without transformation of charge phenomena. Because single f and d ions are having multi-ion process, consequently, an energy transfer phenomenon occurs. On the basis of this argument radiative as well as non-radiative, phonon assisted and energy transfer for resonant case can explicitly be acquainted with. The consequence of consecutive energy transfers between ions at dissimilar sites, ETU takes place. The mutual interaction between ions, however, reside in the ETU process, the optimum concentration of ions is adequate to permit energy migration between two ions. The sensitizer (S) is an ion which is excited first of all and subsequently, energy is transferred to other, called the activator (A). In this chapter, the two ions system however, occasionally called donor and acceptor are considered. Three kinds of well known energy transfer mechanism (a) radiative, (b) non-radiative and (c) phonon assisted of Figure 1 are shown.

When an emitted photon through sensitizer is absorbed by activator, the radiative energy transfer takes place. The larger cross section of sensitizer ion allows immense possibility to transfer more energy to activators. The profile of sensitizer emission depends upon activator

concentration, means this will change based on emission spectra of sensitizer and absorption spectra of activator.

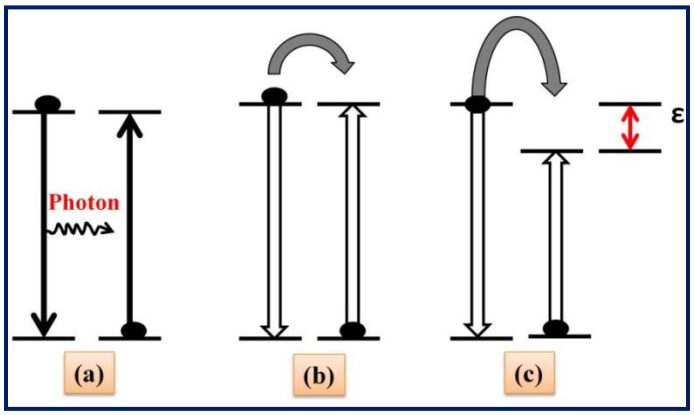

Figure 1. Successive energy transfer mechanism for (a) radiative, (b) non-radiative and (c) phonon assisted. 'ε' stands for energy mismatching

Thus radiative and non-radiative energy transfer phenomena may be discriminated by considering the re-absorption effects. The probability P_{SA} of energy transfer depends upon the function of distance R as given by below equation (1).

$$P_{SA} = \frac{\sigma}{4\pi R^2 \tau} \int g_S(\epsilon) g_A(\epsilon)\, d\epsilon \qquad (1)$$

Where, τ is lifetime of sensitizer, σ is absorption cross section and spectral overlapping shows the integral part. The $1/R^2$ factor is the important factor denotes the distance between two consecutive ions present in concentration. The long range energy distribution between similar ions is caused by such kind of resonant radiative transfer. This resonant radiative energy transfer creates photon trapping effect that was shown in gases many times ago. Due to this effect the observed lifetime increases for triply ionized rare earth doped systems. Now we discuss on two ions system, shown in Figure 1(b). Non-radiative energy transfer between two ions with nearly equal energy is interactions that arise between the ground state and excited state. For non-radiative energy transfer with appropriate interaction among electronic manifolds the excitation escape towards other ion prior to emission of luminescence. In this case the probability P_{SA} of energy transfer belongs to equation (2).

$$P_{SA} = \frac{\left[\frac{R_0}{R}\right]^n}{\tau} \qquad (2)$$

Where, R_0 stands for critical transfer distance (this distance belongs to equal probability of excitation), τ is lifetime of sensitizer while exponent term 'n' is an integer and stands for dipole -

dipole interaction (n=6), dipole- quadrupole interaction (n=8) and quadrupole-quadrupole interaction (n=10). These interactions are calculated by using Judd-ofelt's theoretical model and found elsewhere [4]. Now, we discuss on phonon-assisted energy transfer which also occurs between two ions unlike energy partitions. From equation 1, if the energy integral parts overlap and treated as zero, the probability for energy transfer is minimal consequently, phonon-assisted energy transfer phenomena occurs. The strong probability of phonon-assisted energy can also take place for smaller value of provided energy which is migrated through annihilation as well as production of phonons. In case of rare-earth doped upconversion materials the migrated energy differences is higher at even below the room temperature henceforth multi-phonon process must be well thought-out. Researchers have shown the rate equations for ETU based on power dependence that contains four excited manifolds for Er^{3+} system. Where population inversion is shown by $P_{i,}$ analogous energy transfer coefficient is $R_{i.}$ [5], α and $\boldsymbol{\partial}$ are absorption cross section of donor ion and photon number density, respectively.

$$\frac{dP_1}{dt} = \partial_P \alpha_0 P_0 - 2R_1 P_1 P_1 - R_2 P_1 P_2 - R_3 P_1 P_3 - A_1 P_1 + \beta_2 A_2 P_{2,} \quad 3(i)$$

$$\frac{dP_2}{dt} = R_1 P_1 P_1 - R_2 P_1 P_2 - A_2 P_2 + \beta_3 A_3 P_{3,} \quad 3(ii)$$

$$\frac{dP_3}{dt} = R_2 P_1 P_2 - R_3 P_1 P_3 - A_3 P_3 + \beta_4 A_4 P_{4,} \quad 3(iii)$$

$$\frac{dP_4}{dt} = R_3 P_1 P_3 - A_4 P_4. \quad 3(iv)$$

Where,

$P_0 \cong constant,$

On solving we get the solution of rate equations for large and small upconversion; as

(a) For large upconversion:

The steady state solutions; when $\beta_i = 0$

$$P_i = \frac{1}{2} R_1^{1/2} R_i^{-1} (\partial_P \alpha_0 P_0)^{1/2} \quad where,\ i = 1,2,3 \ldots . p \quad 4(i)$$

$$P_r = \frac{1}{4} \frac{1}{A_n} \partial_r \alpha_0 P_0 \quad 4(ii)$$

(b) For small upconversion:

The steady state solution;

$$P_i = \frac{1}{A_1^i} \prod_{j=2,3,..i} \left(R_{j-1} A_j^{-1}\right) (\partial_r \alpha_0 P_0)^i \quad where\ i = 1,2,3 \ldots . . p, \quad (5)$$

Upconversion process by chronological order:

Before 1966s, the energy transfer mechanism of rare earth ions were used by considering classical laws (i. e. activator ion gets energy from surrounding sensitizer ion) as explained in Figure1. But Auzel, first time explained the quantum mechanical case of each energy transformation by treating the activator ion already existed in excitation state (see Figure 2). At a single ground state activator ion has multi-energy states that is why the photon is summed up over this manifolds by making this consideration. This mechanism was given to explain the laser action of Er^{3+} (sensitized by Yb^{3+}) by energy transfer imperative in a glass host related system [6]. The evidence of this effect was effectively observed for upconverting green emission of Er^{3+} pumped through Yb^{3+} [6, 7].

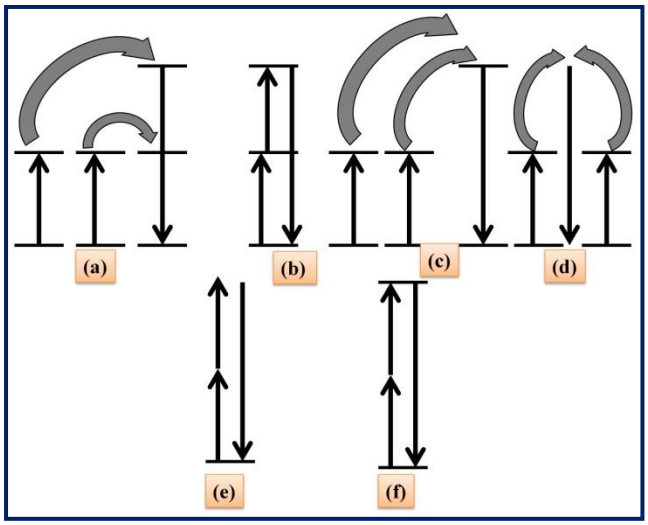

Figure 2: Two photon upconversion mechanism (a) APTE (photon energies by adding transfers) or ETU effect, (b) two steps absorption scheme, (c) co-operative sensitization of large cross sectional ions, (d) co-operative emission process, (e) Second Harmonic Generation, and (f) two photons' absorption excitation

A graphic comparison between ETU effect (a) and two photons upconversion procedure such as two-step absorption (b), co-operative sensitization (c), co-operative luminescence (d), second-harmonic generation (SHG) as well as (e) absorption and excitation of two photons, shown in Figure 2. Solid-state active ions entrenched in a host medium and energy transfers by dipole-dipole interaction by emitting photons for short distance whereas re-absorption for longer distances ions. The dipole-dipole energy transfer takes place in the case of ETU that is first and

foremost of curiosity for laser technology. More details about the ETU may be found elsewhere [8]. For a rare earth doped ion, that is in an excited state, it may decay to a lower state either emitting photons or phonons. The non-radiative emission is explained by treating through energy transfer to other ions. ETU is normally known as an unwanted effect due to non-radiative decay results heating in the applicative systems. Concentration quenching is also consequences of ETU that transpires due to collection of ions in the host matrix.

The concurrent absorption of identical or different energies to excite a molecule from lower to higher excited state two-photon absorption is considered. Two-photon absorption known as a third-order process because of more than a few weaker linear absorption at low photon emission intensity. The two photon absorption process is totally different by linear absorption in which two photon process acts as square of the emission intensity of photon. Therefore, it is a nonlinear ocular method; consequently more effective greater than that of linear absorption of photons at high intensities. A few researchers have demonstrated very fruitful experiment on co-operative upconversion mechanism that was applied for Yb^{3+}-Tb^{3+} co-doped phosphor system [9]. The co-operative luminescence in UV region approaches from two ($^2P_0$) Pr^{3+} excited ions may be found in details [10]. SHG is explained for KDP host matrix and absorption excitation process of two photon for Eu^{2+} doped CaF_2 host matrix is well described by Auzel in 1973 [11]. A detailed energy process with their efficiencies has been summarized in Table 1.

Table 1: Shows various standardize efficiencies for different upconversion route. This Table is reproduced with permission from ref 5 (copyright @ 2004 American Chemical Society)

Matrix	Ions	Process	Order N	Temp (K)	Efficiency $(cm^2/W)^{N-1}$	References
YF_3	Yb^{3+}-Er^{3+}	APTE (ETU)	2	300	$\sim10^{-3}$	11
SrF_2	Er^{3+}	ESA	2	300	$\sim10^{-5}$	11
YF_3	Yb^{3+}-Tb^{3+}	Co-op. sensitiz.	2	300	$\sim10^{-6}$	11
$YbPO_4$	Yb^{3+}	Co-op. lumin.	2	300	$\sim10^{-8}$	12,13
KDP		SHG	2	300	$\sim10^{-11}$	11
CaF_2	Eu^{2+}	Two-phot.	2	300	$\sim10^{-13}$	11

		absorpt.				
YF_3	$Yb^{3+}Er^{3+}$	APTE (ETU)	2	300	2.8×10^{-1}	14
vitroceramics	$Yb^{3+}Er^{3+}$	APTE (ETU)	2	300	2.8×10^{-1}	15
$NaYF_4$	$Yb^{3+}Tm^{3+}$	APTE (ETU)	3	300	3.4×10^{-2}	16
YF_3	$Yb^{3+}Tm^{3+}$	APTE (ETU)	3	300	4.25×10^{-2}	16
vitroceramics	$Yb^{3+}Tm^{3+}$	APTE (ETU)	3	300	8.5×10^{-2}	16
$NaYF_4$, $Na_2Y_3F_{11}$	$Yb^{3+}Er^{3+}$	APTE (ETU)	2	300	10^{-2} to 2×10^{-4}	17
$NaYF_4$	$Yb^{3+}Er^{3+}$	APTE (ETU)	2	300	2.5×10^{-4}	18
$NaYF_4$	$Yb^{3+}Tm^{3+}$	APTE (ETU)	3	300	5.5×10^{-2}	17
$NaYF_4$	$Yb^{3+}Tm^{3+}$	APTE (ETU)	3	300	6.4×10^{-3}	18
fluorohafnate glass	$Yb^{3+}Tm^{3+}$	APTE (ETU)	2	300	8.4×10^{-3}	19
fluorohafnate glass	$Yb^{3+}Ho^{3+}$	APTE (ETU)	2	300	3.5×10^{-1}	19
vitroceramics	$Yb^{3+}Tm^{3+}$	APTE (ETU)	2	300	3.6×10^{-3}	20
vitroceramics	$Yb^{3+}Tm^{3+}$	APTE (ETU)	3	300	2.0×10^{-6}	20
$ThBr_4$	U^{4+}	ESA	2	300	2.0×10^{-6}	21
$SrCl_2$	$Yb^{3+}Yb^{3+}$	Co-op. lumin..	2	100	1.7×10^{-10}	22
$SrCl_2$	$Yb^{3+}Tb^{3+}$	Co-op. sensitize.	2	300	8.0×10^{-8}	22
$SrCl_2$	$Yb^{3+}Tb^{3+}$	Co-op. sensitize.	2	100	1.8×10^{-8}	22

Synthesis techniques:

The upconversion phosphor materials can be synthesized in various shape and size. Therefore, on the basis of its application purposes various methods of synthesis are used time to time. In which solid state method, sol-gel method, polyol method, hydrothermal and thermal decomposition methods are key and most popular these days. The solid state method is most conventional and extremely old method. The powder sample can be synthesized via this method.

However, sol-gel and polyol methods both are useful as well for powder synthesis. The colloidal dispersed sample is being prepared via hydrothermal or thermal decomposition methods. The detailed studies about the different kind of synthesis process have been thrashed out below.

Solid state method:

This is easiest and oldest method of synthesis of upconversion phosphor materials. There is a large number of works reported for persistent luminescence using this synthesis process [23]. This route is very useful technique to synthesize the bulk phosphors material. Thus, prepared particles are generally in µm ranges and surface morphology of sample is not even regular. Such kind of phosphor materials are very suitable candidates for display devices, light emitting devices, persistent luminescence, temperature sensing devices, etc. [23-24]. In this process, first of all the appropriate amount of rare earth and other precursors are taken in agate mortar pestle followed by grinding to get homogeneous mixture of rare earth precursors. Now this mixture is transferred in alumina crucible of 10-15 ml volume then pre fired at lowest temperature range (800 ^{o}C) for 2 to several hours. Now the chosen mixture is again transferred in agate mortar pestle to grind for obtaining more homogeneous mixture. This homogeneous mixture is now annealed at higher temperature 1000 ^{o}C or more than that of, and the required sample is collected for further measurements.

Combustion method:

The combustion method of synthesis is one of easiest chemical rout to synthesize the rare earth doped upconversion materials. There are several reports on upconversion phosphor material through combustion route [25, 26]. Here, we take an example of La_2O_3: Er^{3+}/Yb^{3+} phosphor material reported by Tiwari *et al.* [25]. In this method urea in ethyl glycol (EG) medium used as an organic fuel. The preparatory material of 1 mmol amount was dissolved in nitric acid and heated up to 90 °C. In this solution, 5 ml of EG including 3.5 g of urea was dissolved and kept on magnetic stirrer to get a gel-like solution. Finally, gel was relocated into a crucible and put inside a furnace at 450 °C. After an instant, sample puff up and at once catches fire thus produces voluminous hazy resulted product. Finally, the raw product was squashed and prepared into form of powder for further characterization.

Polymer complex solution method:

Polymer Complex Solution (PCS) synthesized route is a customized combustion technique. In this synthesis process rather than urea, i.e. known as traditional fuel, polyethylene glycol

(PEG) is used as an organic water-soluble polymer [27]. Here, polymer precursor works as chelating agent as well as an organic fuel. In this way PCS provides incorporation of comprising essentials at the atomic level and thus acts as homogeneous agglomeration at little dopant amounts. In very first step an aqueous solution of metal salts and PEG are used. Then, removal of excess irrigates or water forces polymer addicted to closer immediacy, ultimately the structure is found as a resin-like gel after explosion an oxide powder is obtained. Herein, we take an example of Y_2O_3:Er^{3+}/Yb^{3+} phosphor nanoparticle [27]. In short, appropriate stoichiometric amounts of rare earth oxides were mixed into nitric acid. To these solutions, PEG was incorporated in equal ratio. The raw solution was stirred at 80°C and metal-PEG solid complex is obtained and it was further annealed at 800 °C for 2 h in an electric furnace in order to decay the impurities.

Co-precipitation method:

The co-precipitation method is easy and most suitable approach for preparing rare earth doped/codoped upconversion phosphor materials because of easy going reaction circumstances, straightforward synthesizing steps and low cost. Yi *et al.* firstly reported the co-precipitation method to synthesize $NaYF_4$:Yb^{3+}/Er^{3+} phosphor materials with the help of ethylenediamine tetra acetic acid (EDTA) [28]. Here, we describe the preparation step, which was used in co-precipitation method. In this procedure, rare earth EDTA intricate in a NaF solution is formed. Thus formation of α-$NaYF_4$: Yb^{3+}/Er^{3+} upconversion phosphor powder takes place. By changing the concentration ratio of EDTA the size of formed nanoparticles may be nearly controlled. To enhance the upconversion fluorescence intensity an annealing treatment was applied to the sample. Since, after heating, the upconversion materials are liable to agglomerate in higher sizes at higher temperatures that limit their possible applications in bio-imaging and photodynamic therapy.

Sol-gel method

The sol-gel route is very widespread applicable technique to synthesize the phosphor materials. Several reports on this synthesis process have been made till date. Here, we describe one example of this process which was studied by Sivakumar *et al.* [29]. The rare earth oxides in suitable amount were dissolved in doubly de-ionized (DI) water and diluted nitric acid. A bulk hexahydrate nitrate solution of analogous rare earth is created. Certain quantity of citric acid were added and then mixed in nitrate solution. Ammonium hydroxide is incorporated to maintain

the pH of resulting solution around 4. This was continuously stirred at 80 ^{o}C till 2 h until it turned to sticky yellow sol, and the sol was dried at 120 ^{o}C for 24 hr to obtain brown gel. The gel was further dried and the powder thus obtained was kept in dedicator for further characterization purpose.

Polyol method

The polyol is one of good method to synthesize upconversion phosphor materials. With the help of this synthesis technique preparation of oxides and fluorides phosphor material is achievable. Into the current example, authors discuss the synthesis process of $NaYF_4$:Yb^{3+}/Er^{3+} phosphor materials [30]. In this process rare earth chlorides (YCl_3, $YbCl_3$ and $ErCl_3$) were synthesized by dissolving equivalent oxides of rare earth in hydrochloric acid on 80 ^{o}C till the transparent hexahydrated rare earth chloride is obtained. In this preparation process, two types of fluorine resource are used. One is sodium fluoride which was used to get Na^+ ion and F^- ion both in the synthesized phosphor host material. Another kind of fluorine source is NH_4F. To get the sodium ions the fluorine source was used along with NaCl. Here, we describe a wide-ranging approach to synthesize the fluoride phosphors ($NaYF_4$: Yb^{3+}/Er^{3+} nanoparticles). The 40 mL or few relevant of precursors are taken into a 200 or 250 mL round-bottom flask using a reflux condenser; a little weighed amount of NaF is dispersed in the solution. This mixture was further heated upto certain temperature which depends on the kind of solution in an oil bath. Now the freshly prepared hexahydrated rare earth chloride was dissolved in 50 mL of polyol. Then this solution was injected in previously formed combination containing sodium fluoride. The resultant mixture is stirred till 2 h at certain temperature. The precipitated raw material was further collected by using centrifugation to acquire $NaYF_4$: Yb^{3+}/Er^{3+} upconversion nanoparticles.

Hydro/Solvo thermal method

The hydrothermal/solvothermal synthesis is most efficient synthesis processes to prepare the phosphor materials with the desirable shape, controlled particle size. The luminescence intensity for synthesized materials is also extremely good. There are very minute differences between the hydrothermal and solvothermal methods. In the hydrothermal method water is utilized as synthesizing precursor whereas in solvothermal process the water content is not available along with organic precursors [31].

Figure 3: Schematic diagram shows the set up of synthesizing hydrothermal assisted $NaYF_4$: Yb^{3+}/Er^{3+} upconversion phosphor materials

Herein, we provide details of hydrothermal synthesis process of $NaYF_4$: Yb^{3+}/Er^{3+} phosphor materials. All reagents were used without further purification. 1 mmol amount of rare earth oxides with appropriate composition were dissolved into absolute nitric/hydrochloric acid and heat treated at 80 ^oC till a clear transparent solution of hexahydrated rare earth nitrates/chlorides is obtained. In next step, 100 ml Teflon beaker, 2 ml DI water, 8 ml ethanol, 1.2 g amount of NaOH and 15 ml of oleic acid mixed and stared at 1000 rpm. A clear, transparent and homogeneous solution was obtained. Now previously prepared 1 mmol amount of hexahydrated rare earth nitrates and 8 ml portion of 1.0 M NaF solutions are added under the vigorous stirring of 1000 rpm. The whole system was put at constant stirring for another 45 min and the resulting homogeneous sample was relocated into 100 ml Teflon lined autoclave and kept at 200 ^oC over night. After cooling the final raw product was centrifuged at 8000 rpm for 15 min. This final product was washed three times in the presence of excess of ethanol to remove the organic impurities; schematic diagram of each step of synthesis is shown in Figure 3.

Thermal decomposition method

Thermal decomposition assisted phosphor materials are very useful in bio-imaging, photodynamic therapy and security applications. Because a colloidal dispersed phosphor in different solvents is only possible through this synthesis route. This is totally chemical reaction based synthesis process completed in an isolated inert environment [32]. Here, we take example of the synthesis work that was prepared by Mai and his co workers [33].

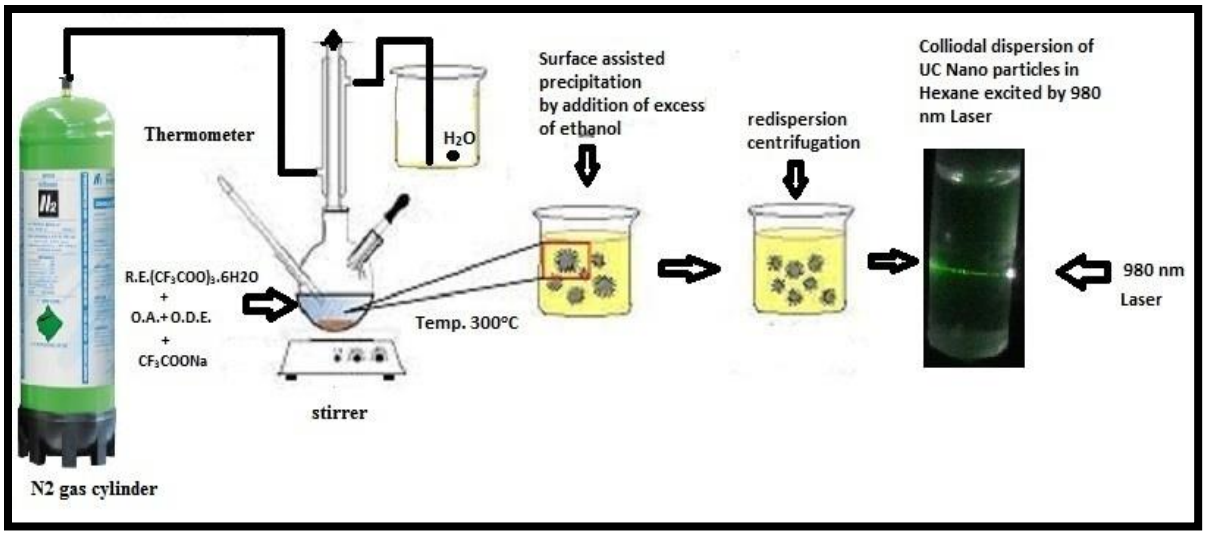

Figure 4: Schematic representation of thermal decomposition assisted colloidal dispersed upconversion phosphor

In this classic synthesis, the sample preparation is followed via two steps. The schematic representation of synthesis process is shown in Figure 4. In the very first step, the appropriate amount of rare earth precursors was acquired and trifloroacetate of all the rare earth oxides were formed by dissolving suitably weighed amounts of rare earth materials in trifloroacetic acid and then heat treated at 80 °C for transparent solution of rare earth trifloroacetate. In next step, 10 mmol of oleic acid, 5 or 10 mmol of oleylamine and 10 or 20 mmol of octadecene (ODE) were mixed homogenously and then hexahydrated rare earth trifloroacetate prepared in first step with appropriate amount of CF_3COONa were added. The whole solution was put in 100 ml of three neck flask. Solution was heated at 150 or 200 °C for 30 min with stirring to eliminate the excess amount of water content. Under the constant flow of N_2 gas temperature was increased gradually by 300 °C. Due to the decomposition of molecules nanoparticles initiate to form. It cools down to room temperature obviously after completion of the reaction. Further, the solution was centrifuged at 8,000 rpm and finally precipitation was collected. The precipitated material was then washed three or four times by ethanol and then dried at 100 °C.

Some more synthesis techniques

Apart from above synthesis process there are some other procedures that have been reported by different research groups. These methods are micro emulsion method [34], Flaming

synthesis [35], electro spanning [36], Microwave synthesis [37], Ionic Liquids-Based synthesis method [38], etc. The brief descriptions of these methods are given below;

The micro emulsion technique has advantages over other like easy action, small size upconversion nanoparticles and controlled morphology as well as the reaction time duration. This technique suffers many confronts like less quantity of phosphor sample production and not easy to separate the impurities.

The Flaming synthesis is a suitable technique for producing phosphor materials. There are five steps to complete this synthesis process. The steps are; precursor reaction, nucleation, growth, polymerization and ion deposition. In this method fine powders are formed while reactions take place into gas-phase. Main disadvantage of this process is to get only oxide phosphors, other kinds of upconversion material, fluoride, phosphate and vanadate are not possible to prepare.

The electro spinning method is the synthesis process of bulk phosphor materials in which precursor is resolved through four steps such as cocoons, stretching, refinement and curing in the presence of high voltage electrostatic field. Dong *et al.* [36] have reported $NaYF_4$/PVP composite nanofibers in range of 300–1000 nm, synthesized via electro spinning technique.

Microwave synthesis process is very eminent method that consist two kinds of process involved in microwave and liquid microwave preparation technique. The previous mixes of rare earth oxides with ammonium fluoride were directly prepared via microwave technique. Later on rare earth materials and fluoride samples are dissolved in a solvent.

Comparing to all methods for synthesis of upconversion phosphor as discussed earlier, the ionic liquids-based synthesis is found as evergreen preparation method because of not necessitating organic solvents, less time requirements for reaction and least annealing temperature [38]. Because of their chemical stability, non-flammability and low vapor pressure upconversion nano materials are synthesized via ionic liquid media. Moreover, the nanoparticles found by this method are having little excellence with unevenness size distribution of particles, lesser monodispersity and non uniformity compared to other techniques, this nature, basically, bounds the utilization of this preparation technique.

APPLICATIONS OF UPCONVERSION PHOSPHOR MATERIALS

Depending upon the structural and optical behavior the upconversion phosphor materials are having potential applications in different sectors as described above explicitly. The more intense phosphor materials (in powder form) are suitable in fabrication of persistent luminescence devices, display devices, lighting devices, LEDs, temperature sensing devices and many more. The colloidal dispersed upconversion phosphor materials are very suitable for security inks and cancer cell imaging applications. Same way high efficient dye sensitized solar cell development is promising by using upconversion phosphor materials as thin film. In the present section we are describing some interesting and important applications of upconversion phosphor materials.

Temperature sensing:

Using the luminescence spectra of rare earth doped upconversion materials one can collect the heating information around materials or environment. In this technique, two thermally coupled level of 4f electronic states are used for temperature sensing. This kind of material is no doubt used as luminescence probe to measure the instrumental temperature [39, 40]. Nowadays, some researchers are trying to improve the sensing ability by synthesizing active shell/active core [41]. Erving *et al.* [41] have proposed multifunctional structures of Nd^{3+} ions to act as sensitizers of Yb^{3+} and Er^{3+} that are, however, being extensively applied for elevated resolution luminescent thermometry with remarkable thermal sensitivities. The intended idea has been pasteurized as shown below, Figure 5. However, researchers are engaged to work on rare earth doped materials for sensing applications but Er^{3+} and Ho^{3+} codoped Yb^{3+} materials has attracted their features more because of high and intense emission in green region. The emission from $^2H_{11/2}$ and $^4S_{3/2}$ is significant studied level of Er^{3+} for sensing in green regime. Researchers also consider the green emitting level $^5F_4$ and $^5S_2$ of Ho^{3+} for temperature sensing probe being a remarkable green color emission. The details sensing application was studied by Kumar *et al.* [40]. They used florescence intensity ratio (FIR = I_{539}/I_{550}) to find out the value of ΔE (energy gap between two thermally coupled level) and further this value was used to calculate the sensor sensitivity [S= (1/FIR)*{d(FIR)/dT}], see Figure 6. The detailed information about this experimental technique may be found in ref [40].

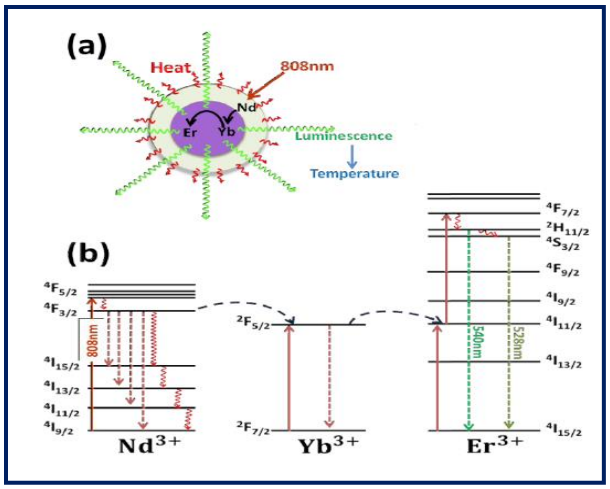

Figure 5: (a) Designed active shell/active core nanoparticles and produces heat when 808 nm laser beam is illuminated. Core provides thermal sensation to shell whereas shell acts as heating chamber, (b) description of energy transfer from Nd^{3+}, Yb^{3+} and Er^{3+} rare earth ions. The image is reproduced with permission from ref [41]. Copyright @ 2013 by Royal Society of Chemistry

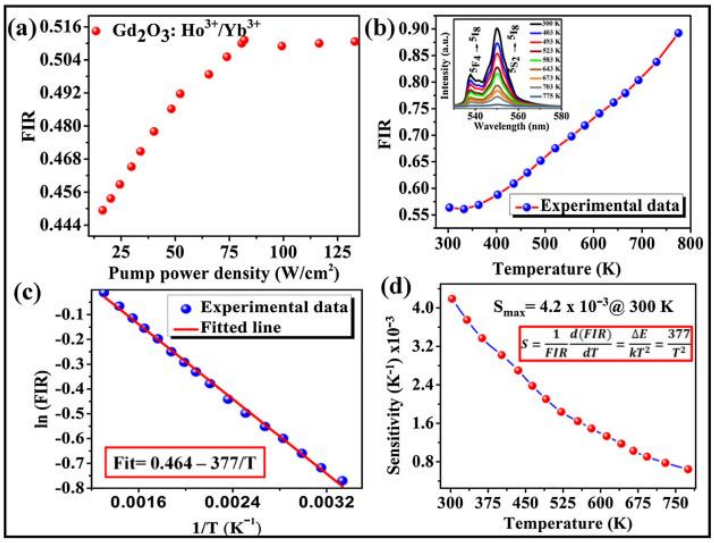

Figure 6: Schematic diagram represents the sensing performance of Ho^{3+}/Yb^{3+} codoped Gd_2O_3 nanoparticles. Figure 6 (a) shows variation of FIR along power density, (b) FIR with temperature, (c) *ln-ln* plot between FIR and inverse of absolute temperature and (d) sensor sensitivity at different temperatures. The image is reproduced with permission from ref 40. Copyright @ 2016 by Elsevier.

Latent fingermark detection

The upconversion materials can be used to detect latent fingermark on several porous, semi-porous and non-porous surfaces. Tiwari *et al.* reported $La_2O_3:Er^{3+}/Yb^{3+}$ phosphor materials for latent fingermark detection on various difficult surfaces, Figure 7. Many techniques have been reported by researchers till now but they are all having a limitations to develop a good contrast image from porous, semi-porous, and non-porous surfaces. Other factor such as the age of the fingermark, composition of the secretions, however, the surface is dry or wet also plays an important role in the proficient detection. New high competent and low attempt technique is searched to overcome on these limitations by crime scene practitioners. The details development of latent fingermarks, recording by a digital camera and etc. may be found in ref [42].

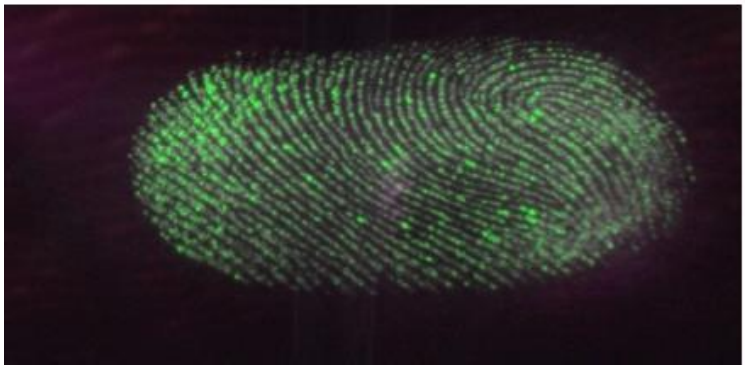

Figure 7: Latent fingermark developed by $La_2O_3:Er^{3+}/Yb^{3+}$ upconversion material on a ply wood. Illumination of 980 nm diode laser is used. Image is reproduced with permission by ref [42]. Copyright @ 2015 by American Institute of Physics

Upconversion materials as cancer cell imaging

Upconversion materials are used as fluorescence targeted imaging *in vivo/in vitro* that is very useful to recognize the tumor cell as well as drug delivery application. In this technique a high autofluorescence background is veiled to the luminescence intensity so highly efficient upconverting materials are needed for this kind of applications. Recently, many researchers [43-45] worked on different host and dopant based phosphor materials to get high luminescence for cancer cell targeting. Xiong *et al.* [46] worked efficiently on high distinction upconversion luminescent nanoparticles targeted for imaging *in vivo* by labeled to nanoparticles, shows in Figure 8. They prepared these nanoparticles by using three steps typical synthesis process. In first step they synthesized upconversion nanoparticles ($NaYF_4$: 20% Yb^{3+}, 1.8% Er^{3+}, 0.2%

Tm^{3+}) by a hydrothermal process. In second step, hydrophilic upconversion nanoparticles are geared up by oleic acid to Lemieux-von Rudloff along with reagent azelaic acid. Third step includes synthesis of PEG-NH_2-Modified upconversion nanoparticles. To make active the surface -COOH groups, EDC and sulfo-NHS are mixed to 2-Nmorpholino ethanesulphonic acid. This mixture is finally, stirred for 12 h and PEG-NH_2-modified upconversion nanoparticles are collected after centrifugation.

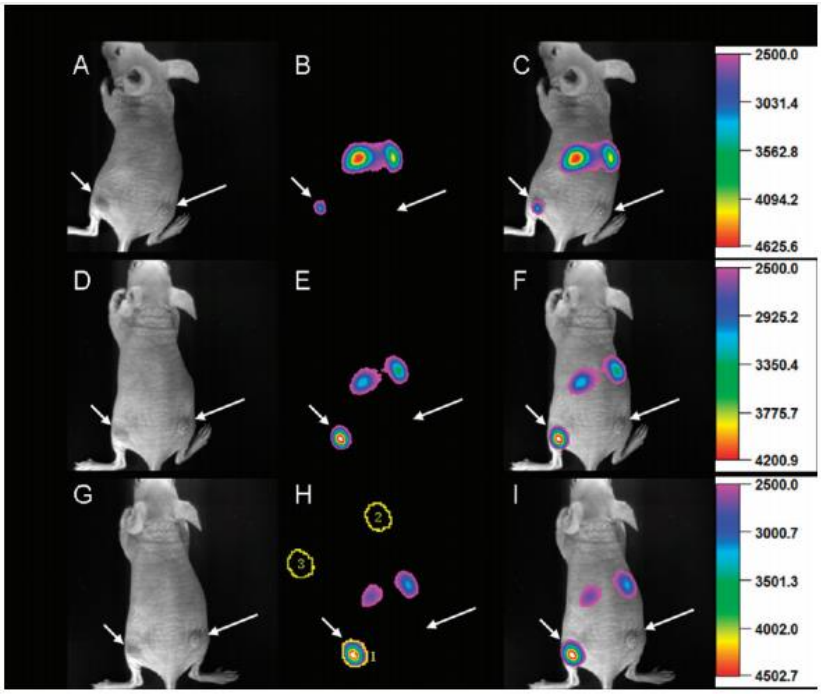

Figure 8: Shows in vivo upconversion imaging of U87MG tumor at left rear leg and implicated by smaller arrows while MCF-7 tumor at right rear leg and implicated by large arrows. Upconversion nanoparticles were injected in naked mice. The laser power was used 80 mW/cm^2 to acquire all images @ 21.5 °C temperature. (H) Shows the calculation of in vivo signal/noise ratio (SNR). The image is reproduced with permission from ref 46. Copyright @ 2009 by American Chemical Society

Further, to get the RGD-Labeled upconversion nanoparticles, authors modify the surface of NH_2 groups with 6-maleimidohexanoic acid N-hydroxysuccinimide ester are mixed with 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid, pH 8.0 restraining the PEG-NH_2-modified upconversion nanoparticles. After stirring at 8 h the sample was centrifuged to get the final product. In this typical experimental programme the MCF-7 (human breast cancer) and U87MG

(human glioblastoma) cell lines are used. MEM modified Eagle's medium is used to grow the MCF-7 cells and MEM supplemented 10% FBS is used to grow the U87MG cells. All the preserved cells are cultured around 37 °C under at 5% CO_2 atmosphere. Figure 4 shows the detailed specific targeting of tumors that is further chronic by *ex vivo* upconversion luminescence imaging of organs [46]. The result of the tissue imaging exposed non autofluorescence signal, however; the penetration depth was almost 600 μm. In this study authors report, high signal to noise ratio almost 24 between interested region of tumor and thus the required examination of the upconverting signals *in vivo* system is exposed.

CONCLUSIONS:

In this chapter authors dealt with different upconversion mechanism, synthesis technique and possible applications of upconversion materials to fulfillment of better understanding of beginners. The final product prepared for application purpose is totally based on selection of appropriate host materials. Every three sections even with suitable images have tried to explain. Many synthesis ideas were discussed in details to get the suitable application of upconversion materials. Different upconversion energy transfer mechanism like classical and quantum mechanical were argued in the respective section of interest. However, the application of upconversion materials cover many more fields of repute like sensing, latent fingermark detection, cancer cell imaging, photo dynamic therapy, solar cell and so forth but only few appropriate applications of upconversion materials have been discussed.

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MODIFIED WET CHEMICAL DEPOSITED SnO_2 THIN FILMS FOR GAS SENSING APPLICATIONS

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ABSTRACT:

Tin dioxide (SnO_2), a wide band gap, n type semiconductor, has been the most premeditated material used in the applications, such as gas sensing, transparent electrodes, dye sensitized solar cells, and liquid crystal displays etc. The present work consists of the synthesis of SnO_2 thin films using successive ionic layer adsorption and reaction technique and its structural, optical, surface morphological and electrical characterization for gas sensing applications for the first time. The synthesized SnO_2 thin films were characterized by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), photoluminescence (PL) and UV-vis spectroscopy. The XRD patterns revealed the formation of SnO_2 with a tetragonal crystal structure. The FESEM micrographs represented micro structured morphology of SnO_2. The SnO_2 thin film sensors were operated in air environment and the hydrogen sulfide gas response was determined.

KEYWORDS: SnO_2; thin film; SILAR; XRD; PL; electrical properties; gas sensor

INTRODUCTION:

Tin dioxide (SnO_2) is a wide band gap (3.6 eV) semiconductor, used in various applications, such as gas sensing, transparent electrodes, and solar cells, etc. [1]. SnO_2 has been applied in semiconductor gas sensors since last sixty years [2]. These sensors are used for

detecting gases like H_2, H_2S, CH_4, LPG, CO, NH_3, NO_2, etc. Among this; hydrogen sulfide (H_2S) is a toxic gas with a characteristic odor of putrid eggs. It is also commonly referred to as sewer gas, stink damp, swamp gas, and manure gas. H_2S is rapidly absorbed by the lungs, once exposed via inhalation [3].

Thin films of SnO_2 can be deposited by a variety of techniques such as physical vapor deposition, pulsed laser deposition, spray pyrolysis, electro-deposition, spin coating etc. [4]. However, deposition of SnO_2 thin films via successive ionic layer adsorption and reaction (SILAR) technique is rarely mentioned in the literature [5, 6]. Unlike many other film deposition techniques, SILAR technique is a simple and relatively cost-effective processing method. The technique involves multiple dipping of a substrate in cationic and anionic precursors. It is an extremely easy technique for preparing films of any composition. SILAR does not require high-quality substrates or chemicals [7].

The present work consists of the synthesis of SnO_2 thin films using SILAR technique and its structural characterization. SnO_2 thin films were prepared from different SILAR cycles with stannous chloride and hydrogen peroxide as the precursors. Characterization of these prepared films using X-ray diffraction (XRD), photoluminescence (PL), UV-visible spectroscopy technique is presented and discussed. Moreover, electrical measurements of as synthesized SnO_2 thin films are presented. Finally, we examined the hydrogen sulfides gas sensing of SnO_2 thin films.

EXPERIMENTAL DETAILS:

EXPERIMENTAL PROCEDURE

SnO_2 thin films were deposited by alternative immersion of glass substrates in 0.05 M $SnCl_4$ and 1% H_2O_2 dissolved in 30 ml double distilled water. The cleaned glass substrates were immersed in the alkaline $SnCl_4$ solution so that tin complex was adsorbed on the substrate surface. The adsorption and reaction time periods were optimized to 25 s. This cycle was repeated successively for the number of times in order to increase the film thickness. The substrates were coated with SnO_2 thin films for different number of SILAR cycles. The SnO_2 films deposited at different SILAR cycles as 40, 60 and 80 are denoted as S1, S2, and S3 respectively.

CHARACTERIZATION TECHNIQUES

The structural properties of the SnO_2 thin films were studied using high resolution X-ray diffraction (XRD) with Ni-filtered Cu-Kα radiation of 1.54056 A.U. (X'pert PRO, Philips, Eindhoven, Netherlands) operated at 45 kV and 35 mA. The surface morphology of the prepared product was recorded by a field emission scanning electron microscope (FE-SEM; S-4700, Hitachi). Optical absorption study of the SnO_2 thin film samples was carried out in the wavelength range of 200–800 nm using UV–Vis–NIR spectrophotometer (Cary 100, Varian, Mulgrave, Australia) at room temperature. The electrical transport properties of the samples were studied by carrying out DC Hall effect measurements (M/N #7707 LVWR, Lake Shore Cryotronics Inc., USA) at room temperature, and electrical resistivity measurements, in darkness, as a function of temperature in the range of 10–310K. For these measurements, fours silver contacts of $1mm^2$ size were deposited at the corners of SnO_2 thin film samples. A home-made gas sensor system was used for the measurement of the gas sensitivity of the SnO_2 thin films. Gas sensing performance was evaluated by measuring changes in resistivity toward various hydrogen sulfide concentrations at different operating temperatures. Conducting silver paste was used to make contacts on both ends of the film. The 1-2 cm large film was mounted on two probe sample holder placed in Borosil glass tube, which was inserted coaxially inside a tubular furnace. The film area was kept constant for all the samples prepared for the measurement of gas sensitivity. A known amount of gas was injected into the system and the change in electrical resistance of the films was measured. After getting constant value, one end of the tube was opened and air was pumped to recover the initial value of resistance in air. The gas response (S [%]) is calculated using following equation:

$$S(\%) = Rg\text{-}Ra/Ra \times 100 \qquad \textbf{(1)}$$

where Ra is the resistance of the film in air and Rg is the resistance of the film after gas exposure.

RESULTS AND DISCUSSION:

In SILAR, deposition of thin films occurs when the ionic product exceeds the solubility product. In our experimental case, the supply of Sn^{4+} and O^{2-} ions in the solution controls the

growth rate of SnO_2 thin films. The cationic precursor solution release Sn^{2+} and/or Sn^{4+} ions, which complexes in alkaline medium. However, due to inert pair effect, Sn^{4+} is more stable than Sn^{2+}, so both oxides (SnO and SnO_2) may be formed in the present study. But, the final product SnO_2 is more stable than SnO. The hydrolysis of H_2O_2 anionic precursor solution gives O^{2-} ions. The formation of SnO_2 thin films using alkaline medium occurs via following steps:

$$nSn^{4+} + 4n(OH)^- \rightarrow [Sn(OH)_2]n \quad \textbf{(2)}$$

$$[Sn(OH)_2]n + nO^{2-} \rightarrow nSnO_2 + 2nOH^- \quad \textbf{(3)}$$

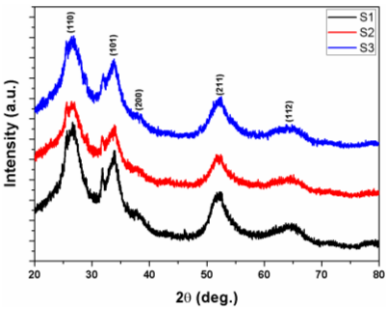

Fig. 1. XRD pattern of SnO_2 thin film samples

Fig. 1 shows the X-ray diffraction patterns of the as deposited SnO_2 thin films samples S1, S2 and S3. The X-ray analysis reveals that samples S1, S2 and S3 are polycrystalline in nature with a tetragonal crystal structure. The deposited SnO_2 thin film shows the diffraction peaks along the (110), (101), (200), (211) and (112) planes at 26.63, 33.80, 38.16, 52.27 and 64.90 degree respectively. The comparison of the observed XRD patterns with the standard (JCPDS data 03-1116) confirms pure phase SnO_2. The mean crystallite size of SnO_2 thin film samples was calculated using the Debye–Scherrer formula as-

$$\text{Crystalline size (nm)} = k\lambda / \text{FWHM} (\cos\theta) \quad \textbf{(4)}$$

where $\lambda = 1.54056$Å, k is the dimensionless constant (0.95), β is the corrected broadening of the diffraction line measured at half of its maximum intensity (taken in radians by multiplying by a factor of $\pi/360$) and D_{110} the diameter of the crystallite and θ is diffraction angle. The crystalline size of the SnO_2 samples S1, S2 and S3 were found to be 50, 58 and 67 nm respectively.

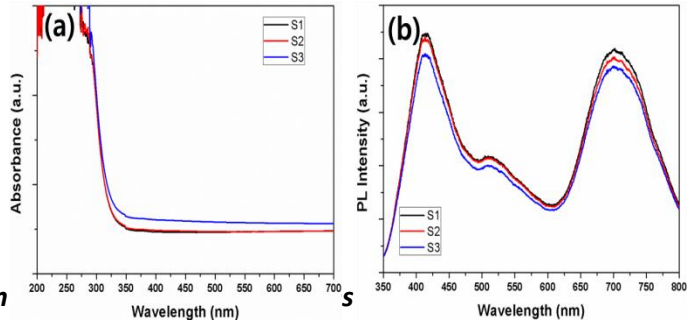

Fig. 2. Optical and PL spectra of SnO_2 thin film samples.

For evaluation of band gap energy and its variation in the film thickness, the spectra of the optical absorption were measured. Fig. 2 (a) shows the room temperature optical absorption spectra of the SnO_2 thin film samples S1 to S3. The onset of the optical absorption is observed at about 320 nm, which is the absorption edge of the SnO_2. At a lower wavelength than 270 nm the optical absorption saturates. The band gap of SnO_2 thin film samples S1, S2 and S3 were found to be 3.82, 3.80 and 3.75 eV, respectively by extrapolating the straight line of the square of absorption coefficient to the intercept of the X-axis of the photon energy (not shown in Fig.). Fig. 2 (b) shows the PL spectra of the SnO_2 thin film samples S1 to S3. Three strong emission bands located at 414, 512 and 703 nm were observed from PL spectra. The broad peaks at ~400 and 700 nm observed in all samples are similar to those reported previously for SnO_2 thin films [8]. The PL peak appeared in the violet region is more prominent than that of the other PL peaks at green and red region. These emission peaks indicates that there probably exist three main defect-related radiative recombination centers inside the SnO_2 thin film. Moreover, the PL intensity is lowered for S3 sample as compare to sample S1. This indicates that, the surface defects are diminished in sample S3 compare with rest of SnO_2 samples [9, 10].

Fig. 3 illustrates the morphologies of the SnO_2 thin films deposited at different SILAR cycles. At the initial of SILAR cycle (Fig. 3 (a1 and a2)), SnO_2 film shows the formation of large islands with complete surface coverage. The close inspection of sample S1 (Fig. 3 (a2)) shows the mirror bright fine-grained granular structure.

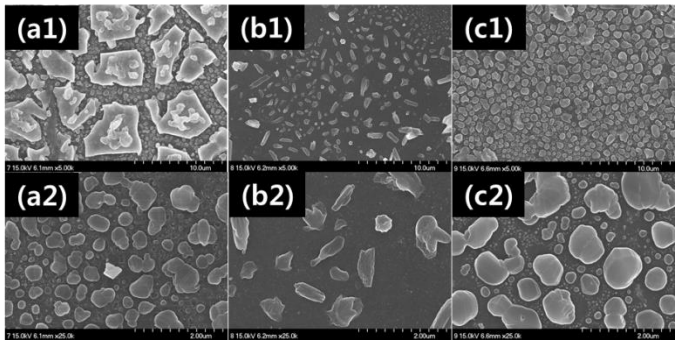

Fig. (3): FESEM images of SnO_2 thin film samples (a1 and a2): S1, (b1 and b2):S2 and (c1 and c2): S3

By contrast, the SnO_2 sample S2 shows the rod like granular, but with closely packed crystallites. Fig. 3 (b2) shows nano-crystalline structures between overgrown rods like micro-grains. Fig. 3 (c1 and c2) shows the SEM micrographs of SnO_2 sample S3. Low magnification SEM image (Fig. 3 (c1)) shows the micro-sized grains over the substrate. The size of grains varies with the SILAR cycles.

In order to further study the electrical properties of SnO_2 thin film deposited on a glass substrate, the carrier concentration, Hall mobility, and electrical resistivity of S1, S2 and S3 samples were obtained by the four probe method using Hall-effect measurement system at room temperature, and the results are given in Table 1.

Table 1. The electrical parameters of SnO_2 thin films

Sample ID	**S1**	**S2**	**S3**
Resistivity (ohm-cm)	6×10^2	3.6×10^2	2.4×10^2
Hall coefficient (cm^3C^{-1})	1.5×10^4	3.6×10^4	5.5×10^5
Carrier Density (cm^{-3})	3.4×10^{13}	7.8×10^{13}	1.2×10^{13}
Hall Mobility ($cm^2V^{-1}S^{-1}$)	4.7×10^2	1.3×10^2	6.7×10^2

The result of the Hall measurement system shows the negative value of the Hall coefficient indicated that all SnO_2 samples are having n-type conductivity. The sample S3 show a high carrier concentration and low resistivity as compared to S1 and S2 samples. The resistance of thin film related with morphology, film thickness, grain size and grain boundaries [11]. The resistance in our case is may be due to the large and compact grains of SnO_2. However, the SnO_2 thin films with large grains are favorable to increase current carrier concentration and improve electron transmission [12]. The electrical properties of the SILAR deposited SnO_2 thin films agree with the requirements for potential applications in thin film gas sensor fabrication.

Due to the superior surface morphological and electrical properties than rest of samples, the gas-sensing test was performed on the SnO_2 thin film sample S3. In general, the gas sensing mechanism of the metal oxide gas sensor is based on a variation in the electrical resistance due to the gas adsorption and desorption on the active surface. The resistivity of SnO_2 based gas sensor

devices decreases after exposing to H_2S gas. Due to the reducing nature of H_2S gas, there is an exchange of electrons from the gas molecules to metal oxide molecules.

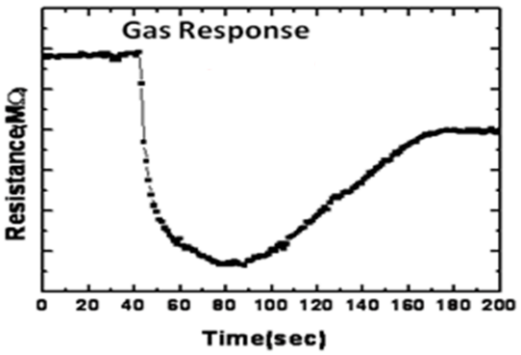

Fig. 4. Gas response of SnO_2 thin film sample S3

Fig. (4) shows the resistance verses time graphs and gas response of the SnO_2 gas sensor for 20 ppm. The resistance of SnO_2 samples was measured under dry air flow to obtain baseline, then the measurement chamber was closed and H_2S gas with different ppm of gas was injected into the chamber. After the sample was exposed to H_2S, the resistances of SnO_2 samples were found to decrease. When the experimental gas was removed with dry air flow, the resistance of the sample was increased slowly and recovers the baseline. Fig. 4 shows the 8% sensitivity for sample S3 for 20 ppm of H_2S gas. The lower value of sensitivity at 20 ppm was attributed to the non-uniform and compact grain growth. The gas response was found increases with the increase in the concentration (in ppm) of H_2S gas. The gas response of metal oxide is found to be increase due to its porous nature. Even though the reported gas sensitivity is low, the detailed underlying mechanism to enhance the sensitivity is a subject for further investigation. However, the route developed here may provide an alternative approach to produce low-cost and effective SnO_2 thin film based gas sensor devices.

CONCLUSIONS:

In summary, SnO_2 thin films have been synthesized by a simple and economical SILAR technique. The structural studies indicate that these films are polycrystalline in nature with tetragonal crystal structure. The optical band gap of as-deposited film was found to be 3.75 eV after 80 SILAR cycles. The crystal structure remains the same for all the samples, while the grain size varies with the variation of the SILAR cycles and it increases with increase in deposition cycle. Moreover, the as deposited SnO_2 thin film can be used for gas sensing applications.

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Mg SUBSTITUTED MANGANESE COBALTITE IS AN EFFICIENT CATALYST FOR DEGRADATION OF RHODAMINE-B

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ABSTRACT:

Powder $Mg_{0.5}Mn_{0.5}Co_2O_4$ sample were prepared by sol-gel technique followed by thermal treatment. The structural, chactrization and photocatalytic degredation of Rhodamine-B has been investigated. The sample were cubic with a spinel structure shown by x-ray diffraction patterns. Diffraction lines were broadened indicating nanocrystalline samples. Increase in temperature caused the change in grain size determined by scanning electron microscopy analysis. The photocatalytic activity increase with decrease in temprerature.

KEYWORDS: X-ray, SEM, EDAX, IR and Photocatalysis.

INTRODUCTION:

The growth of the world's population and industry has increased the demand for water supply [1]. The domestic use and industrial activity especially in developed countries produce large amount of wastewater which is then disposed into natural channels that may lead to high pollution risk. Color in water can be resulted either from natural phenomenon like the presence of humic substances or from artificial phenomenon such as the disposal of dye effluents [2]. Different types of dyes are used in many industries such as textile, paint, ink, plastics and cosmetics. About a half of global production of synthetic textile dyes are classified into azo

compounds that have the chromophore of -N=N- unit in their molecular structure and over 18 % of the textile dyes are lost in wastewater stream during dyeing operation [3]. It is well known that soluble azo dyes when incorporated into the body are split into corresponding aromatic amines by liver enzymes and intestinal flora, which can cause cancer in human [4]. The textile industry produces large quantity of highly colored effluents, which are generally toxic and resistant to destruction by biological treatment methods. Therefore, it is necessary to find effective method to remove color from textile effluents [5]. Mixed metal oxide nanoparticles are technologically important for their wide areas of application such as electrodes in solar cells, lithium ion batteries, electrochemical capacitors, in molten carbonate fuel cells, electro-catalysts, optical limiters and switches and chemical sensors [6-7] etc. Especially now a day their role in photo catalysis is very important to control the water pollution [8].

Photocatalytic degradation by mixed metal oxides a new, effective and rapid technique for the removal of pollutants from water [9]. Rhodamine B is a well known organic dye and is considered as a model of a series of common azo-dyes, used in the industry. The performance of Mn-substituted Mg aluminate nanoparticles for the photocatalytic degradation of Rhodamine B for different hours gives very better result.

EXPERIMENTAL:

Nanocrystaline compound of $Mg_{0.5}Mn_{0.5}Co_2O_4$ were prepared by using simple sol-gel method. The A. R. grade citric acid [$C_6H_8O_7.2H_2O$], cobalt nitrate [$Co(NO_3)_3.6H_2O$], magnesium nitrate [$Mg(No_3)_2.6H_2O$], manganese nitrate [$Mn(No_3)_2.4H_2O$] and ammonia solution [NH_4OH] were used as precursor materials.

The metal nitrate solutions were prepared in double distilled water. Then citric acid as a chelating agent was added to metal nitrate solutions. The molar ratio of citrate to metallic ions in the solution was maintained at 1:1. Citric acid has two different roles, (i)Citric acid as a fuel helps to progress the synthesis at relatively lower temperature, (ii) as a chelating agent binds metallic ions (Mg^{2+}, Mn^{2+} & Co^{3+}) and restricts precipitation of solution during variation in pH. The solutions of metal nitrates were mixed in their stoichiometric ratio followed by agitation using a magnetic stirrer at room temperature for 1h. To increase the efficiency of chelating agent, pH of the solution was adjusted to 9.5 by adding ammonia solution drop by drop. This solution was gelled by heating at 120°C. By further heating the citric acid melts at around 173°C and

converts into aconitic acid and then aconitic acid converts into itaconic acid. The itaconic acid swells with the decarboxylation. Thus the gel was heated at 180°C in an electric oven to get a precursor. The obtained precursor was ground into powder by a pestle and mortar and then calcined in furnace at 500°C to 900°C for 6h with a heating rate of 10°C min^{-1} to obtained desired nanomaterial.

The granulated powders were pressed into pellets of 1cm diameter under a pressure of 8 tons per cm^2 and thickness was adjusted to about 0.3 cm. These pallets were then used for determination of various properties such as, the crystal size, phase identification and lattice constants were determined by using X-ray diffraction studies (Philips PW-1710 X-ray diffractometer with CuKα radiation). The surface morphology of the sample was observed by the use of scanning electron microscopy (SEM Model JEOL-JSM 6360). The elemental analysis was determined using an energy dispersive X-ray spectroscope (EDS). The FTIR spectra were recorded in the range of 350-700 cm^{-1} using KBr pellets (Perkin Elmer FTIR). Photo catalytic degradation of Rhodamine B was studied at different interval of time.

RESULTS AND DISCUSSION:

XRD ANALYSIS:

Powder X-ray diffraction (XRD) was utilized to purity and characterizes the phase of prepared $Mg_{0.5}Mn_{0.5}Co_2O_4$ as shown in Fig.1. XRD pattern shows the characteristic peaks at 31.3°, 36.9°, 44.8°, 55.7°, 59.4°, 65.3° and 76.3° according to JCPDS Card No. 23-1237, which can be indexed to (220), (311), (400), (422), (511), (440) and (533) planes of the cubic spinel with Fd3m space group. The sharp peaks observed in the XRD pattern demonstrate a crystalline phase of the samples. Average crystallite size has been calculated from the full width at half-maximum (FWHM) in the 311 reflection peak applying the Scherrer equation [10].

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

Where λ is the incident wavelength of Cu Kα radiation of the XRD, β is the peak width at mid-height and Θ is the considered angle. The crystallite size increases with increase in temperature. The average crystallite size of the synthesized powders lies in-between 34.62 to 26.21 nm. The value of lattice constant 'a' of the spinel as calculated from XRD data are shown in table 1.

Figure 1. XRD patterns of the system $Mg_{0.5}Mn_{0.5}Co_2O_4$ at different temperature

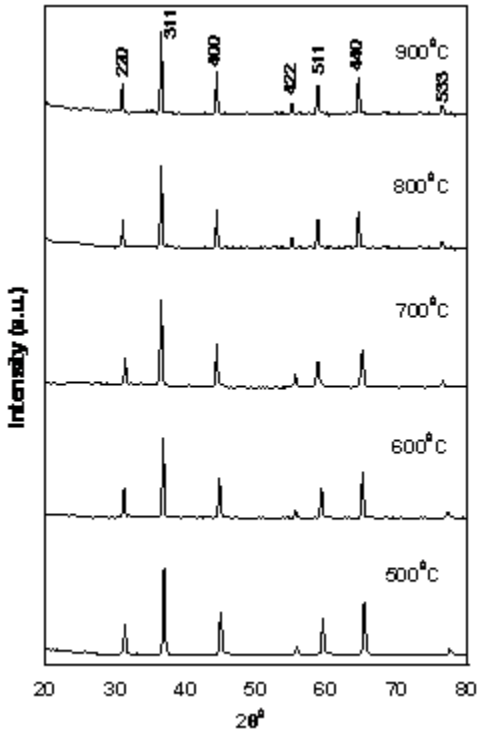


Table 1. Lattice constants, Crystallite size and Porosity for $Mg_{0.5}$ $Mn_{0.5}$ Co_2O_4

Sr.No.	Compound Temp. (°C)	Lattice Constants (Å)	Crystallite Size (nm)	Porosity (P) (%)
1	500	8.216	25.01	13.33
2	600	8.219	27.84	12.79
3	700	8.221	30.49	12.32
4	800	8.222	32.67	11.89
5	900	8.226	34.62	11.21

The lattice constant ‘a’ increases with increase in temperature. The X-ray densities for all samples were calculated using the relation [11].

$$dx = \frac{8M}{Na^3}$$

Where, N = Avogadro's number (6.023 x 10^{23} atom/mole)

M = Molecular weight.

a = lattice constant.

The increase in the dx is considered to be due to change in temperature.

SEM ANALYSIS:

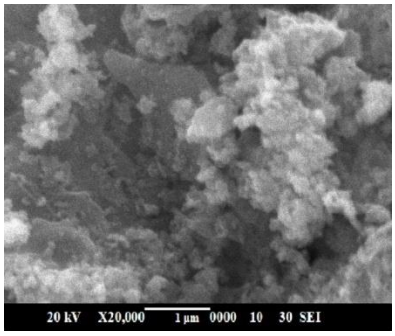
The SEM images of the samples are shown in Fig.2. Aggregate spherical particle morphology was observed. All the SEM images have similar aggregate shape but their sizes are markedly different. Although all the materials are synthesized through parallel procedure changes in morphology was observed, which is due to temperature difference. The temperature increases porosity decreases. The grain size lies in between 1.51 to 2.50 μm calculated by using Cottrell's method [12] which gives the relation between the number of intercepts of grains boundary per unit length (PL) and total number of intercepts (n) as

$$P_L = (n/2\pi r)\, M$$

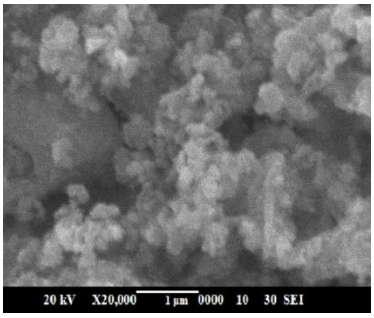
Where 'M' is the magnification at which SEM micrograph was scanned.

'r' is the radius of the circle.

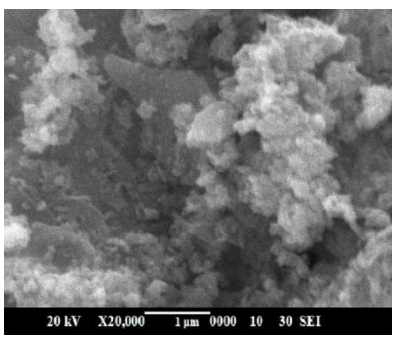
'n' is the number of grains in the circle.



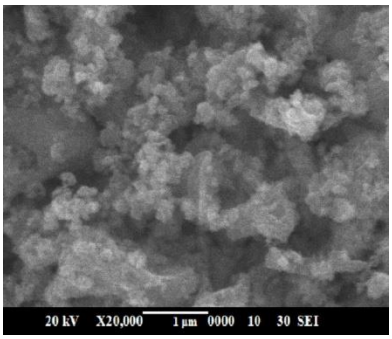
(a)



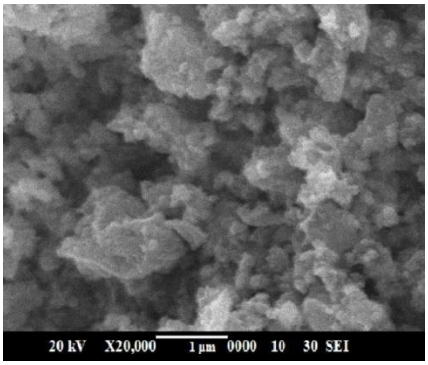
(b)



(c)



(d)



(e)

Fig. 2. SEM Photographs of $Mg_{0.5}Mn_{0.5}Co_2O_4$ a) 500°C, b) 600°C, c) 700°C, d) 800°C and e) 900°C

EDAX ANALYSIS:

EDAX analyses were performed to investigate the chemical composition of the synthesized $Mg_{0.5}Mn_{0.5}Co_2$. The EDAX are shown in Fig.3. According to EDAX analysis Mg, Mn, Co and O were the major constituents of the samples. The theoretical and observed percentage of these metals is match with each other.

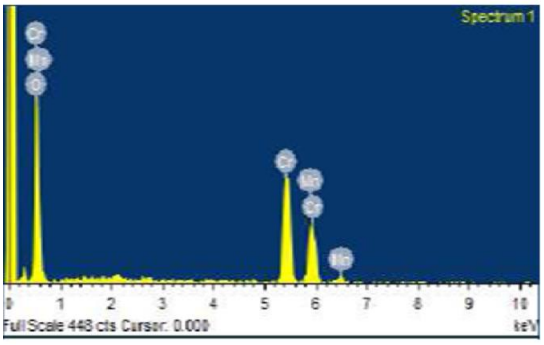
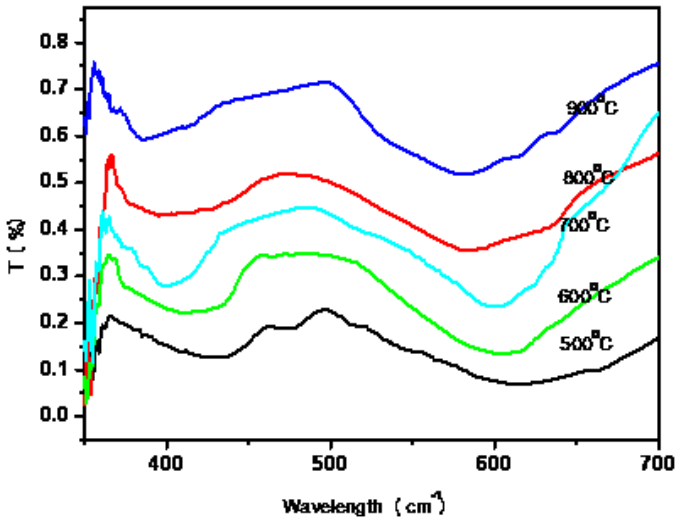


Fig. 3. EDAX pattern of $Mg_{0.5}Mn_{0.5}Co_2O_4$

INFRARED ANALYSIS:

FT-IR spectroscopy is an important tool to identify the stretching and bending vibrations of tetrahedral and octahedral complex of materials. The FT-IR spectra of $Mg_{0.5}Mn_{0.5}Co_2O_4$ measured in the frequency range of 700-350 cm^{-1} are shown in Fig.4. The observed band values of materials are given in table 2. In general, the band around 665-575 cm-1 (υ1) corresponds to intrinsic stretching vibrations of metal cations at the tetrahedral site, while the band around 450-400 cm-1 (υ2) corresponds to metal cations in the octahedral sites. The centre frequency of the bands υ 1 and υ 2 shift slightly towards higher frequency side for series of compositions.

Fig. 4. FT-IR spectroscopy of the system $Mg_{0.5}Mn_{0.5}Co_2O_4$ at different temperature



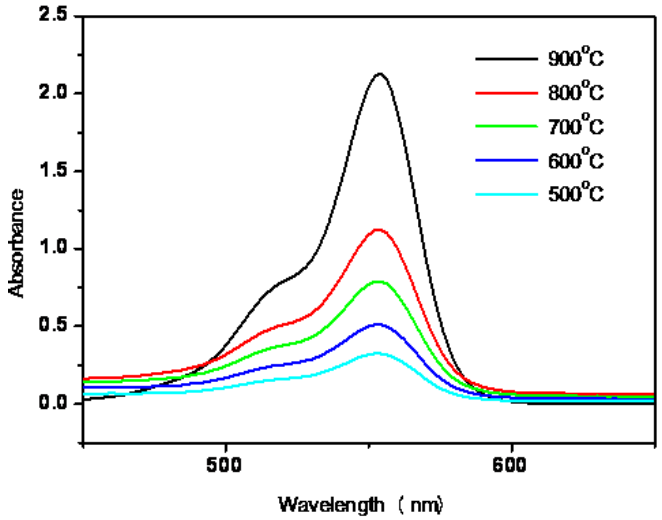
Tableb 2. Data of Positions of IR Absorption Bands $Mg_{0.5}Mn_{0.5}Co_2O_4$ at different temperature

Temperature (°C)	υ_1(cm^{-1})	υ_2 (cm^{-1})
500	576	379
600	579	381
700	583	386
800	598	397
900	611	415

PHOTOCATALYSIS:

Fig.5. show photodecomposition of Rhodamine B with respect to irradiation time for the system $Mg_{10.5}Mn_{0.5}Co_2O_4$. From fig. it is observed that as sintering temperature increases degradation of Rhodamine B decreases also it depents on irradiation time. The photodegradation response of $Mg_{0.5}Mn_{o.5}Co_2O_4$ at 500°C more than 900°C this is due to change in grain size of the material.

Fig. 5. Photocatalytic degradation of Rhodamine B by $Mg_{0.5}Mn_{0.5}C0_2O_4$ at different temperature



CONCLUSION:

The structural, charactrization and catalytic properties of manganese substituted manganese cobaltite have been investigated. The sol-gel autocombution method is successfully used for the synthesis of manganese substituted $Mg_{0.5}Mn_{o.5}Co_2O_4$. The result obtained by XRD pattern dictate that the lattice constant, and crystal size are increases with increaes in temperature. Porosity and degredation increase with decrease in temperature.

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ANALYTICAL INVESTIGATION OF MILK FROM VARIOUS ANIMAL SOURCES AVAILABLE IN SANGLI DISTRICT (M.S.) INDIA

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ABSTRACT:

Food production and safety can be used as a measure of a nation's economic growth and stability as well as the responsiveness of government to the need of its people. In India farmers pets mammalians to utilize the agricultural waste as a cattle feed, instead they get milk which is marked for generation of money as a side business and hence it is required to be legally defined to avoid the health problem instead of its benefits. So its analytical study must be done in relation to physicochemical investigation from the marketing point of view which directly linked with human health and financial benefits. This investigation was carried out for parameters of milk samples of three different species of mammalians buffalo, cow and goat. Milk samples were collected from the different areas of Sangli District of Maharashtra and analyzed for different physiochemical parameters, Physical properties like Turbidity, pH, Density, Specific gravity, Freezing point, Colour, Odour and Chemical properties like Total Solid, Titratable acidity, Ash, Chloride value, Heat stability test, Heat adequacy test, Test of added water, Test of added Buffalo milk in the Cow milk, SNF determination and Seasonal Variation in basic content of milk like Water, fat , Protein, Lactose. After complete analytical investigation, it is concluded that buffalo milk has higher value of all the parameters than the results obtained for milk from sources of cow and goat.

KEYWORDS: Physicochemical parameters, buffalo, cow, goat

INTRODUCTION:

Animals are important resources in India. Animal husbandry and dairy development have an important place in the economy of India. This is an important occupation for the landless and small land holders. In the suburban areas, it is complementary occupation since agricultural production is inadequate. For the people, in the hilly, tribal and drought prone areas, these people domesticate livestock, out of the total production in agriculture; animal husbandry includes 30% of the production. Cow, buffaloes, goats, sheeps, horses, donkey, camels, pigs etc, are the domesticated animals in India. India ranks first in the world for cattle production. Cattle play a major role in the economy of India. as India is an agricultural country.

Milk is the liquid food secreted by mammalians for the nourishment of their new borns. Milk can also be defined as the whole fresh, clean lateral secretion obtained by the complete milking of one or more healthy animals. Milk should be colostrums free and contain the minimum prescribed percentage of milk fat and milk solid not fat. Milk is considered to be the most nearly perfect food for man and hence is one of the most important part of the diet.

A dairy is a place for handling milk and milk products, which deals with processing of milk and the manufacture of milk products on and industrial scale. The rural areas were identified for milk production and the urban centers were selected for location of milk processing plants and products manufacturing factories. In India dairy has been practiced as a rural cottage industries.

A professional in dairy field is incomplete without the fundamental knowledge of Physico - chemical analysis of milk and finished dairy products, which covers the important area of quality management, helps in checking the processing efficiency, thereby proving the need and importance of dairy chemists to maintain hygienic condition of milk, ultimately the health of human beings.

Milk, which is the secretion of the mammary glands, is the only food of the young mammal during the first period of its life. The substances in milk provide both energy and the building materials necessary for growth.Milk also contains antibodies which protect the young mammal against infection [11]. Milk plays a tremendous role in building a healthy society and can be used as vehicle for rural development, employment and slowing down the migration of the rural population[38] .In the year 2013-2014, kadegaon tahshil produced 43,562 million tons of

milk; of which 62.04% was contributed by buffaloes, 34.39% by cows, 1.65% by goats, 0.08% by sheep and 1.83% by camels .Buffalo is the most valuable animal and is being highly liked by the people of the sub-continent. Buffalo milk is preferred more than the cow's milk[7]. Buffalo milk is a valuable nutrient with high content of milk proteins, lipids, vitamin and other biologically active substances[30] .Cow have contributed greatly to human welfare, supplying draft power, milk, meat, hides, fuel and a variety of other products [19].Cow‘s milk has long been considered a highly nutritious and valuable human food and is consumed by millions daily in variety of products[18].

Goats play a special role in the life of smallholder farmers. Their small size makes it possible for farmers to keep a large herd in small area[8] .Goat has been referred as the “poor man‘s cow’’ due to his great contribution to the health and nutrition of the landless and rural poor[13] .Goat milk differs from cow or human milk in having better digestibility, alkalinity and buffering capacity[33] .The aim of present study was to assess and compare the physicochemical parameters of milk samples collected from buffalo, cow, goat and sheep of kadegaon tahshil.

MATERIALS AND METHODS:

Collection of samples:

Thirty fresh milk samples were collected in sterile bottles from three species like buffalo, cow and goat (ten milk samples of each species.) of sangli district. Milk samples after collection were brought to the Laboratory and analyzed.

Physicochemical analysis:

The pH was measured using a digital pH-meter calibrated with pH 4 and 7 buffers. Specific gravity was determined by using pycnometer as described by determined by using pycnometer as described by [4]Titratable acidity was determined by titrimetric method as described by[4] . Total solids content was determined according to the method of [4]. Ash content was determined by gravimetric method using a muffle furnace at 550oC as described by [4]. Fat content was determined by Rose-Gottlieb method as described by [4]. Protein content was estimated by formal titration method [12]. Lactose content was determined by using Fehling’s solution method [45].

Statistical analysis:

The statistical analysis was carried out using SPSS program (Statistical Package for Social Sciences version 16). The significant differences between means were calculated by one-way Analysis of Variance using Turkey range test.

RESULTS AND DISCUSSION:

pH:

pH of milk samples collected from different species was determined at the time of sampling. The values of pH of milk samples of different species are shown in Table. The results showed that pH values were in the range of 6.63-6.75 in buffalo milk, 6.64-6.76 in cow milk,6.55-6.57 in goat milk. pH values of buffalo milk were significantly higher than that of cow. pH values of goat milk were lower than that of buffalo milk at a highly significant level. The results showed that pH values of milk sample collected from cow, goat were non-significantly different from each other.pH values found in buffalo milk were in accordance with the findings of [10] [22]and pH values found in cow milk were in agreement with the findings of [22] and pH values of goat milk were similar to that reported by [40].

Specific Gravity:

Specific gravity of milk samples collected from buffalo, cow, goat and sheep is given in Table. Specific gravity was found in range of 1.033-1.035 in buffalo milk, 1.030-1.036 in cow milk, 1.030-1.032 in goat milk. Specific gravity of buffalo milk was higher than that of cow and goat milk at highly significant level.Specific gravity of sheep milk was also higher than that of cow and goat milk at highly significant level. There was non-significant difference between the specific gravity of buffalo and sheep milk, cow and goat milk. The specific gravity of buffalo milk was similar to the findings of [15] The specific gravity of cow milk was similar that cited by [20] .The specific gravity of goat milk was in accordance with that reported by [21] The specific gravity of sheep milk was quietly similar to that reported by[25] ,[17] .

Total Solid:

The Concentration of total Solid in the milk sample collected from Buffalo, Cow, and Goat is given in table. These result illustrated that the concentration of total Solid was in range of 15.8-16.0% in buffalo milk, 13.5-13.9% in cow milk, 12.9-13.6% in goat milk.The value of total solid in buffalo milk was higher than that in cow and goat milk at highly significant level. The concentration of total solids found in cow milk during this investigation was in line with the finding of ,[14] and [28]. The concentration of total solids found in goat milk was similar to that reported by [22].

Titratble Acidity:

The values of titratble acidity of milk samples collected from buffalo, cow, goat and sheep are given in Table. It was observed from results that the values of titratble acidity were in the range of 0.17-0.26% in buffalo milk, 0.14-0.19% in cow milk, 0.14- 0.18% in goat milk.The values of titratable acidity of buffalo milk were higher than that of cow and goat milk at highly significant level. The values of titratable acidity of sheep milk were also higher than that of cow and goat milk at highly significant level. It was observed that difference in the values of titratable acidity in buffalo and sheep milk was significant. Difference between the values of titratable acidity of cow and goat milk was non-significant. The values of the titratable acidity in buffalo milk were in accordance with the findings **[35]**. The values of titratable acidity in cow milk were in line with that reported by**[14]**,**[28]**. The titratable acidity values of goat milk were similar to the findings of **[40]**. The values of titratable acidity of sheep milk were similar to that reported by **[25]**,**[17]**. Acidity of milk is due the presence of lactic acid, citric acid and phosphoric acid**[11]**.

ASH:

Ash content in milk samples collected from buffalo, cow, goat and sheep is given in Table 5. The results of this study revealed that the ash content was in the range of 0.81-0.90% in buffalo milk, 0.60-0.75% in cow milk, 0.75-0.77% in goat milk. Amount of ash content in cow milk was lower than that in buffalo at highly significant level. There was significant difference between the amount of ash content in cow and goat milk. There was non-significant difference between the amount of ash content in the milk samples collected from buffalo, goat. Amount of ash content found in buffalo milk was in agreement with that reported by **[14,24, 5]**. Amount of ash content found in cow milk was in accordance with that reported by **[14]**. Amount of ash content

found in goat milk during this study was in line with the findings of [6, 23] reported higher ash content in goat milk.

Fat:

Fat content in milk samples collected from buffalo, cow, goat is given in Table. Results illustrated that fat content was in the range of 7.97-9.10% in buffalo milk, 4.00-6.01% in cow milk, 3.97-4.67% in goat milk. The amount of fat content in buffalo milk was higher than that in the milk of other species at highly significant level. There was non-significant difference between the amount of fat content in cow and goat milk. Fat content found in buffalo milk was in accordance with that reported by[24,16] reported lower fat content in buffalo milk than present investigation. Amount of fat content in cow milk was in line with the findings of [22], [37] reported higher fat content in cow milk. Amount of fat content found in goat milk during this investigation was similar to that cited by [42,6].

Metal Level:

1) Na:

In testing specimen under study trace metal of Na,K,Ca& Mg are found to present .However in buffalo milk the range of Na was in between 16.2 to 17.3 gms in buffalo milk 20.4 to21.7 in cow milk and 27.2-28.9 in goat milk.From this it seen that amount of Na in Higher in goat as compare to buffalo and Cow.

2) Ca:

In testing specimen under study trace metal of Na,K,Ca& Mg are found to present .However in buffalo milk the range of Ca was in between 702-752 gms in buffalo milk 680-710 in cow milk and 644-668 in goat milk.From this it seen that amount of Ca in Higher in Buffalo as compare to Goat and Cow.

3) K:

In testing specimen under study trace metal of Na,K,Ca& Mg are found to present .However in buffalo milk the range of K was in between 145-156 gms in buffalo milk 152-155 in cow milk and 113-117in goat milk.From this it seen that amount of K in Higher in buffalo as compare to goat and Cow.

4) Mg:

In testing specimen under study trace metal of Na,K,Ca& Mg are found to present .However in buffalo milk the range of Mg was in between 198-202 gms in buffalo milk 205-226 in cow milk and 139-151 in goat milk. From this it seen that amount of Mg in Higher in Cow as compare to buffalo and Goat.

Table 1. Comparative analysis of various parameters of milk of Buffalo, Cow and Goat

Parameter	Buffalo			Cow			Goat		
	Min	**Max**	**Mean**	**Min**	**Max**	**Mean**	**Min**	**Max**	**Mean**
Physical state	Liquid			Liquid			Liquid		
pH	6.63	6.75	6.69	6.64	6.76	6.70	6.55	6.57	6.56
Specific Gravity	1.033	1.033	1.033	1.030	1.036	1.033	1.030	1.032	1.031
Freezing Point	0.526			0.528			0.512		
Colour	White			Yellowish			White		
Total Solid	15.8	16.0	15.9	13.5	13.9	13.7	12.9	13.6	13.4
Titarble acidity	0.21	0.25	0.23	0.17	0.30	0.24	0.16	0.25	0.20
Ash%	0.81	0.90	0.85	0.60	0.75	0.67	0.75	0.77	0.76
Fat	7.97	9.10	8.53	4.00	6.01	5.01	3.97	4.67	4.32
Metal Level Na	16.2	17.3	16.6	20.4	21.7	20.9	27.2	28.9	27.9
K	145	156	150	152	155	153	113	117	115
Ca	702	752	724	680	710	695	644	668	656
Mg	193	202	197	205	226	215	139	151	145

CONCLUSION:

All the tested parameters were higher in buffalo than and goat milk. Specific gravity, Titratable acidity, pH, total solids, fat in buffalo milk were higher than that of in the cow milk. Comparatively amount of Ca Content was found to be higher in the Milk of Buffalow than other metals. All the tested parameters were similar in cow and goat milk except ash which was higher in goat milk.

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SYNTHESIS, CHEMISTRY AND BIOLOGICAL APPLICATIONS OF 9-SUBSTITUTED DERIVATIVES OF PHENYL PYRIMIDO PYRIMIDINE DIONE USING A PHASE TRANSFER CATALYST

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ABSTRACT:

A simple, most efficient and green procedure has been developed for the synthesis of 9-substituted derivatives of 9-phenyl-5,9-dihydropyrimido[4,5-*d*] [1,2,4] triazolo[1,5-*a*] pyrimidine-6,8(1*H*,7*H*)-dione from a multicomponent one pot three molecule condensation of 3-amino-1*H*-1,2-4-triazole, Barbituric acid and 1-Butyl-3-methyl Imidazolium Chloride ([Bmim]Cl) in water-ethanol with different substituted aromatic aldehydes were screened for their Biological activity.

KEYWORDS: 3-amino-1*H*-1,2-4-triazole, Aromatic Aldehyde ,Barbituric acid , 1-Butyl-3-methyl Imidazolium Chloride ([Bmim]Cl), MCR's.

INTRODUCTION:

Triazolo [1,5-*a*] pyrimidinedione occupies an important position in chemistry and biology. The most of chemist world widespread as growing interest to the development of triazolo [1,5-*a*] pyrimidinedione because of the diverse biological properties as well as pharmacological like, antimicrobial[1], antitumor[2], , analgesic[3], anticancer[4] antifungal activity[5], anti HIV activitiy[6], antibiotics[7]. Moreover, triazolo [1,5-*a*] pyrimidine having binding capacity with metal ions to form a stable complex of coordination chemistry.[8] In

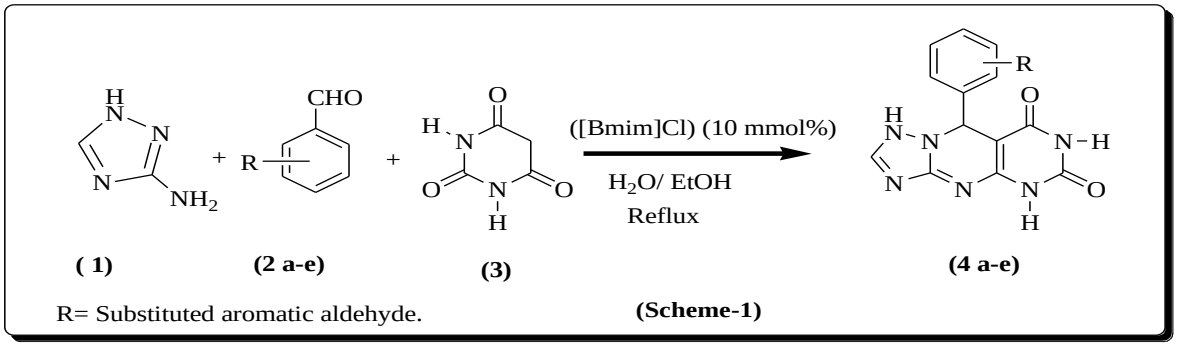
addition, it is used for the formation of the open chain analogs of crown ether, which having medicinal role for transportation function in living cells.[9]

Triazolo [1,5-*a*] pyrimidine synthesis by using reported catalyst like Lewis acid such as Zinc dichloride[10], piperidine[11], dioxane in methanol[12], methanol in hydrochloric acid[13], TBAHS. [14] Some of the method reported above use expensive catalysts, strong acidic conditions, higher temperature, require long reaction time, resulting cumbersome product isolation procedure.

1-Butyl-3-methyl Imidazolium Chloride ([Bmim]Cl), act as a phase transfer catalyst (PTC) and it perform much organic transformation under mild condition. Thus new route utilizing a MCR protocol, for the synthesis of triazolo [1,5-*a*] pyrimidinedione can attacks considerable attention in the search of method for rapid entry of these heterocycles. Consequently, we thought that there is scope for further innovation towards milder reaction condition, short reaction time and better yield in choosing 1-Butyl-3-methyl Imidazolium Chloride ([Bmim]Cl) for this multicomponent reaction (MCRs).

RESULTS AND DISCUSSION:

A mixture of different substituted aldehydes (10 mmol) **(2a-e)**, 3-amino-1*H*-1,2-4-triazole (10 mmol) **(1)** barbituric acid (10 mmol) **(3)** and 1-Butyl-3-methyl Imidazolium Chloride ([bmim]Cl), (10 mmol %) as a catalyst in (10 ml) water and ethanol was refluxed for 2-4 hrs. The reaction mixture was cooled to room temperature and poured in to ice cold water. The precipitate obtained was filtered and washed with water, recrystallized from ethanol to afford the 9-substituted derivatives of 9-phenyl-5,9-dihydropyrimido[4,5-*d*] [1,2,4] triazolo[1,5-*a*] pyrimidine-6,8(1*H*,7*H*)-dione **(4a-e)**. The progress of the reaction was monitored by TLC. These synthesized products **(4a-e)** were completely characterized from IR, ^{1}H-NMR, Mass and ^{13}C-NMR spectroscopic technique and also elemental analysis.



(1) (2 a-e) (3) (4 a-e)

R= Substituted aromatic aldehyde. **(Scheme-1)**

The formation of compounds **(4b)** shows IR spectrum in KBr exhibited stretching band at 3296 cm^{-I} cm^{-I} for the –NH, medium intensity band at 1676 cm^{-I}, 1610 cm^{-I} for conjugated C=O stretching. The ^{1}H-NMR (400 MH_Z, DMSO-d_6) was recorded in DMSO, it shows characteristic singlet peak at δ 6.60 ppm and mass spectra(ESI) shows molecular ion peak at m/z 317 ($M^{+\cdot}$, 100%), 318 ($M^{+\cdot}$,+1), and ^{13}C-NMR (400 MH_Z) in DMSO shows signal at δ 164, 161 ppm for C=O.

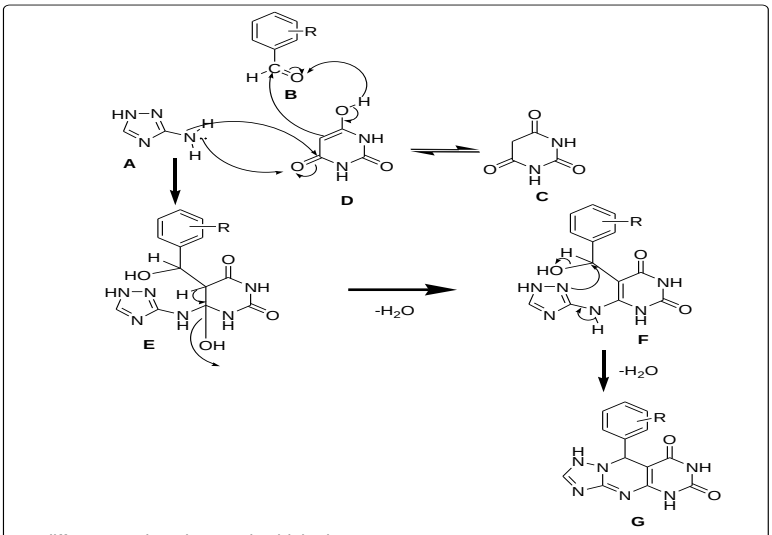
The plausible mechanism involves 1-Butyl-3-methyl Imidazolium Chloride ([Bmim]Cl), catalyzed Knovenagel-Michael addition condensation between an aldehyde **(B)**, barbituric acid **(C**) and 3-amino-1*H*-1,2-4-triazole **(A)**, followed dehydration by cyclization to triazolo[1,5-*a*] pyrimidinedione **(G).**

Table 1. Multicomponent reaction of 3-amino-1*H*-1,2-4-triazole (1), barbituric acid (2), and aromatic aldehyde (2a-e)(4a-4e)

Entry	Subst. Aldehyde (Ar)	Products	Time (Hrs)	Yield%	M.P.^{0}C
1	-C_6H_4	**4a**	3.5	66	234-236
2	4-Cl -C_6H_4	**4b**	4.5	71	241-243
3	2- Cl -C_6H_4	**4c**	5.0	60	232-234
4	4-OCH_3-C_6H_3	**4d**	4.5	73	188-190
5	3,4-diOCH_3-C_6H_3	**4e**	4.0	68	218-220

EXPERIMENTAL:

Open capillary tubes were used for melting points of isolated synthesized compounds and are uncorrected. Perkin-Elmer FTIR spectrophotometer was used for IR (KBr) spectra of compounds. Mass spectral data were recorded on liquid chromatography mass spectrometer (Shimadzu 2010Ev) using ESI probe. The ^{1}H and ^{13}C NMR spectra were recorded on various spectrometers at 400MHz using TMS as an internal standard.



Scheme : Plausible mechanism for the formation of triazolo[1,5-*a*]pyrimidinedione

General procedure for the synthesis of 9-substituted derivatives of 9-(4'-phenyl)-5,9-dihydropyrimido[4,5-*d*][1,2,4]triazolo[1,5-*a*]pyrimidine-6,8(1*H*,7*H*)-dione (4a-e) :

A mixture of different substituted aromatic aldehydes (10 mmol) **(2a-e)**, 3-amino-1*H*-1,2-4-triazole, barbituric acid (10 mmol) **(3)** and 1-Butyl-3-methyl Imidazolium Chloride ([Bmim]Cl), in (10 ml) water-ethanol was refluxed for 3-4 hrs, The progress of reaction was monitored by TLC. The reaction mixture was cooled to room temperature and poured into ice cold water. The solid obtained was filtered, washed with water and recrystallized by ethanol to give **(4a-e)**. The reaction was monitored by TLC.

SPECTRAL ANALYSIS:

9-phenyl-5,9-dihydropyrimido[4,5-*d*][1,2,4]triazolo[1,5-*a*]pyrimidine-6,8(1*H*,7*H*)-dione(4a):

M.P. 234-236^{0}C , Yield 66%. IR (KBr / cm^{-1}) 3230 (-NH), 1710,1630 (2 C=O); ^{1}H NMR (400MHz, DMSO-d$_6$ / ppm) δ 2.90 (s, 1H, =NH), δ 5.30 (s, 1H, =CH), δ 6.4 (s, 1H, -CH), δ 6.7-7.8(m, 5H, Ar-H), δ 11.2 and δ 11.5 (2 bs,2H,-NH); EI-MS (m/z: RA %): 282 ($M^{+\cdot}$, 100%),. Elemental analysis calculated data for $C_{13}H_{10}N_6O_2$; C, 55.32; N, 29.77. Found: C, 55.30; N, 29.75.

9-(4'-chlorophenyl)-5,9-dihydropyrimido[4,5-*d*] [1,2,4] triazolo[1,5-*a*]pyrimidine-6,8(1*H*,7*H*)- dione (4b) :

M.P. 241-243 ^{0}C , Yield 71%. IR (KBr/ cm^{-1}) 3296 (-NH), 1676,1610 (2 C=O); ^{1}H NMR (400MHz, DMSO-d$_6$ / ppm) δ 2.93 (s, 1H, =NH), δ 5.78 (s, 1H, =CH), δ 6.6 (s, 1H, -CH), δ

6.8-7.9 (m, 4H, Ar-H), δ 11.3 and δ 11.5 (2 bs, 2H,-NH); EI-MS (m/z: RA %): 317 ($M^{+\cdot}$, 100%),318 ($M^{+\cdot}$, +1),. ^{13}C NMR (400 MHz, DMSO–d_6/ppm) δ: 164,161, 152, 150, 145, 143, 140, 128, 127,90 ,57, 51, 40, 39, 38. Elemental analysis calculated data for $C_{13}H_9ClN_6O_2$; C, 49.30; N, 26.54. Found: C, 49.28; N, 26.52.

9-(2'-chlorophenyl)-5,9-dihydropyrimido[4,5-*d*] [1,2,4] triazolo[1,5-*a*]pyrimidine-6,8(1*H*,7*H*)-dione (4c) :

M.P. 232-234^{0}C, Yield 60% .IR (KBr/ cm^{-1}) 3250 (-NH), 1707, 1680 (2C=O); ^{1}H NMR (400MHz, DMSO-d_6 / ppm) δ 2.84 (s, 1H, =NH), δ 5.65 (s, 1H, =CH), δ 6.8 (s, 1H, -CH), δ 6.5-7.8 (m, 4H, Ar-H), δ 11.0 and δ 11.2 (2 bs, 2H,-NH); EI-MS (m/z: RA %): 317 ($M^{+\cdot}$, 100%), 318 ($M^{+\cdot}$, +1). Elemental analysis calculated data for $C_{13}H_9ClN_6O_2$; C, 49.30; N, 26.54. Found: C, 49.27; N, 26.53.

9-(4'-methoxyphenyl)-5,9-dihydropyrimido[4,5-*d*][1,2,4]triazolo[1,5-*a*]pyrimidine-6,8(1*H*,7*H*) -dione (4d) :

M.P. 188-190^{0}C, Yield 73%. IR (KBr/ cm^{-1}) 3366 (-NH), 1690,1617 (2C=O); ^{1}H NMR (400MHz, DMSO-d_6 / ppm) δ 3.60 (s, 1H, =NH), δ 3.70(s, 3H, -Ar-OCH_3), δ 5.31 (s, 1H, =CH), δ 5.8 (s, 1H, -CH), δ 6.8-7.8 (m, 4H, Ar-H), δ 10.4 and δ 11.2 (2 bs, 2H,-NH); EI-MS (m/z: RA %): 312 ($M^{+\cdot}$, 100),. ^{13}C NMR (400 MHz, DMSO–d_6/ppm) δ: 164, 162, 159, 156, 155,150, 151, 148, 139,137, 130, 128,125, 115, 113,112, 90, 40, 39, 38. Elemental analysis calculated data for $C_{14}H_{12}N_6O_3$; C, 53.85; N, 26.97. Found: C, 53.83; N, 26.96.

9-(3',4'-dimethoxyphenyl)-5,9–dihydropyrimido[4,5-*d*] [1,2,4] triazolo [1,5-*a*] pyrimidine-6,8 (1*H*,7*H*)-dione (4e) :

M.P. 218-220^{0}C, Yield 68%.IR (KBr/cm^{-1}) 3230 (-NH), 1745,1691 (2C=O); ^{1}H NMR (400MHz, DMSO-d_6 / ppm) δ 3.30 (s, 1H, =NH), δ 3.3 and δ 3.7(2s, 6H, -2Ar-OCH_3), δ 6.63 (s, 1H, -CH), δ 7.89-8.51 (m, 3H, Ar-H), δ 11.08 and δ 11.30 (2 bs, 2H,-NH); EI-MS (m/z: RA %): 342 ($M^{+\cdot}$ +1, 100%),. ^{13}C NMR (400 MHz, DMSO–d_6/ppm) δ: 161, 160 (C=O), 155, 153 (C-4b), 150,147, 131, 128, (Ar-C), 125, (C-9a),116, 115, 111, 55, 40, 39, 38.

Elemental analysis calculated data for $C_{15}H_{14}N_6O_4$; C, 56.75; N, 28.36. Found: C, 56.73; N, 28.34.

BIOLOGICAL ACTIVITY:

Antimicrobial activity:

The synthesized compounds were evaluated for their antibacterial activity against gram positive species ***S. aureus*** and ***B.subtilis*** and gram negative species *E.coli* and S.*typhi* by paper diffusion method. All the synthesized compounds were dissolved in dimethyl sulphoxide (DMSO). The synthesized compounds exhibited zone of inhibition at **07-14mm** in diameter where as standard **Norfloxacin** exhibited zone of inhibition at 14 and 24 in diameter against ***S. aureus*** and ***B.subtilis*** and 20 and 16mm in diameter against ***E.coli*** and ***B.subtilis*** and 20 and 18mm in diameter against ***S. aureus*** and ***B.subtilis*** respectively. Amongst the synthesized compounds **(4b, 4e)** shows higher zone of inhibition against ***S. aureus***. Compounds **(4b, 4d, 4e)** shows higher zone of inhibition against *E.coli*, compounds **(4b, 4e)** shows higher zone of inhibition against ***B.subtilis*** and ***S. aureus*** shows higher zone of inhibition against ***S.typhi*** as compaired to other compounds.

Table 2: Antimicobial activity of compound (4a-4f):

Entry	Compounds	Zone of Inhibition in mm			
		S.aureus	***B.subtilis***	***E.coli***	***S.typhi***
1	4a	06	12	10	10
2	4b	**18**	**20**	**16**	**12**
3	4c	10	10	12	14
4	4d	14	12	**18**	12
5	4e	**16**	**18**	**20**	**14**
7	**Norfloxacin**	**14**	**24**	**20**	**16**
8	**Streptomycin**	**16**	**18**	**20**	**18**

CONCLUSION:

In conclusion, we have synthesized an efficient and facile method for the synthesis of of 9-substituted derivatives of 9-(4'-phenyl)-5,9-dihydropyrimido [4,5-*d*] [1,2,4] triazolo [1,5-*a*] pyrimidine-6,8(1*H*,7*H*)-dione by reaction of corresponding substituted benzaldehydes, 3-amino-

1*H*-1,2-4-triazole and barbituric acid in presence of 1-Butyl-3-methyl Imidazolium Chloride ([Bmim]Cl) in water and ethanol. The product can be easily isolated by simple workup technique, requires ambient reaction condition, short time, less expensive and give good yield. These synthesized compounds show biological activity.

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MODIFICATION OF TITANIUM DIOXIDE FOR HETEROGENEOUS CATALYSIS: - A STRATEGIC OVERVIEW

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ABSTRACT:

Nanoparticles of titanium dioxide with high surface area and mesoporous structure have been largely used to achieve the effective heterogeneous catalysis. This can efficiently accommodate substrates on its surface to interact with each other. Most of the reduction-oxidation type organic transformations, degradation of hazardous organic moieties are feasible at moderate reaction conditions with the help of titanium dioxide nanoparticles due to its ability to form composites with enhanced performance, better metal support interactions, chemical stability, selectivity and presence of reactive acid-base sites on its surface. This article provides a balanced and comprehensive analysis of the more innovative and ambitious strategies for modification of titanium dioxide nanoparticles, by making titanium dioxide based mixed metal oxide nanocomposites. Here attempt is to give brief information about some of the more important titanium dioxide based materials for all those involved in the field of catalysis – researchers, scholars, students etc.

KEYWORDS: Titanium dioxide, Heterogeneous Catalysis, Nanocomposites, Organic Transformation.

INTRODUCTION:

In recent years, semiconductor nanocrystalline oxides have proved to be useful to chemists in the laboratory and industry due to the good activation of adsorbed compounds and reaction rate enhancement, selectivity, easier work-up, recyclability of the supports and the eco-friendly reaction conditions. Also the practical applications of nanocomposite metal oxides as catalysts in organic synthesis have been increased due to their high catalytic activity because of high surface area [1]. Titanium dioxide (TiO_2) nanoparticles are chemically inert, environmental benign in nature, and abundent material.

TiO_2 is used in various applications such as catalysis, energy conversion, optics, sensing, etc. TiO_2 exists in four different forms such as anatase, rutile, brookite and TiO_2 (B). The brookite and TiO_2 (B) phases are unstable at high temperature and therefore practically not so useful. The rutile and anatase phases of TiO_2 are quite stable at high temperature; which having optical band gap is around 3.0-3.2 eV. Anatase TiO_2 is commonly useful for degradation of most of the highly toxic organic moieties in the presence of UV light only. It was also used for antimicrobial activity, purification of air, water disinfection [2-4].

As TiO_2 is electronically semiconducting in nature, two reactions were occurred simultaneously on its surface, i) oxidation reactions due to photogenerated holes on the valence band and ii) reduction reactions due to photogenerated electrons on the conduction band. Different possible reaction pathways for photoactivated TiO_2 are schematically depicted in Figure 1.

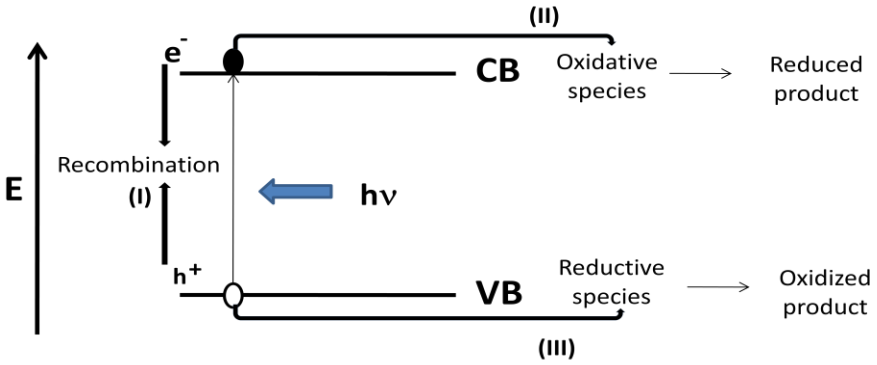

Fig. 1 Different reaction pathways for photoactivated TiO_2

Comparative chart illustrating band gap in eV in different metal oxide semiconductors is as below:

Semiconductor	Band gap (eV)	Wavelength (nm)	Light absorption
TiO_2	3.2	387	UV
SnO_2	3.8	318	UV
ZnO_2	3.2	387	UV
WO_3	2.8	443	Visible
Fe_2O_3	2.2	750	Visible

Loss of small amount of oxygen from lattice sites makes TiO_2 as an n-type semiconductor [5]. Amongst the four different crystal forms: anatase, rutile, brookite and TiO_2 (B) [6], anatase is most important crystal form, in the preparation of coupled M_xO_y/TiO_2 photoactivated nanocomposites. Anatase phase is obtained in the temperature range of 350^{o}C-450^{o}C. On heating, it will be converted into rutile phase above 450^{o}C. Anatase and rutile crystal forms have relatively high band gaps 3.2eV and 3.0eV respectively; this reduces photoactivity of TiO_2 in visible region. Thus, synthesis of visible light active TiO_2 (coupled or bare) requires, engineering the band gap to less than 3.0 eV.

Different strategies have been made to improve reactivity of TiO_2 such as the incorporation of elements or compounds into matrix and post thermal treatments, doping of TiO_2 by metals, non-metals, metal chalcogenides which acts as sink for photogenrated electrons and holes thereby retarding recombination rate, which influences its physicochemical properties [6].

MODIFICATION OF TiO_2 BY MAKING MIXED METAL OXIDE NANOCOMPOSITE:

A nanocomposite is defined as a combination of two or more materials in nanoscale (less than 100 nm) with different physical and chemical properties and distinguishable interphase. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposites will differ markedly from that of the component materials [7-9]. Coupling metal oxide with TiO_2 may result in enhanced optical properties, dielectric properties, heat resistance or mechanical properties such as stiffness, strength and resistance to wear and damage [10, 11].

Making composite with other metal oxide/sulphide is the best strategy found in literature to improve optical response of TiO_2 in the visible range. Usually, TiO_2 is coupled with a narrow band gap material of type M_xS_y or M_xO_y (Where, M= metals like Cd, Zn, Sn, Fe, Co, Ni, Ce etc.). There are various systems related to these composites such as TiO_2/CdS, TiO_2/CdSe, TiO_2/ZnO, TiO_2/WO_3, TiO_2/Fe_xO_y, etc [12-17].

METHODS FOR SYNTHESIS OF MxOy/TiO_2 NANOCOMPOSITES:

The preparation of catalyst with sufficient high specific area is one of the major challenges in front of researchers. Thus, different physico-chemical deposition methods have been used by different workers. These methods include hydrothermal synthesis, chemical vapor deposition, pulsed laser deposition, magnetic sputtering, nitrogen plasma, sol-gel etc. [18-19].

The synthesis of mixed metal oxide nanocomposites will be carried out by using chemical methods. These methods include sol-gel, solvothermal or co-precipitation techniques. In order to prepare proposed nanoparticles fulfilling above mentioned applications, the chemical method is found to be more suitable than other physical techniques such as spray pyrolysis, sputtering, laser ablation etc. because of its easier workup for the synthesis of nanometer sized crystalline powders of high purity at low temperature. During the synthesis, the various preparative parameters such as temperature, concentration of reactants, capping agents will have to be taking into consideration for forming desired structural, morphological, opto-electronic properties of nanocomposites.

Sonosynthesis of N-doped ZnO/TiO_2 core-shell nanocomposite and its deposition on wool fabric were reported by some workers figure 2 [20]. It has been facile one step method workable under ambient pressure and low temperature (75-80^{0}C). Modified fabric with deposition of such novel photocatalyst nanocomposite has wide range of applications in textile industry.

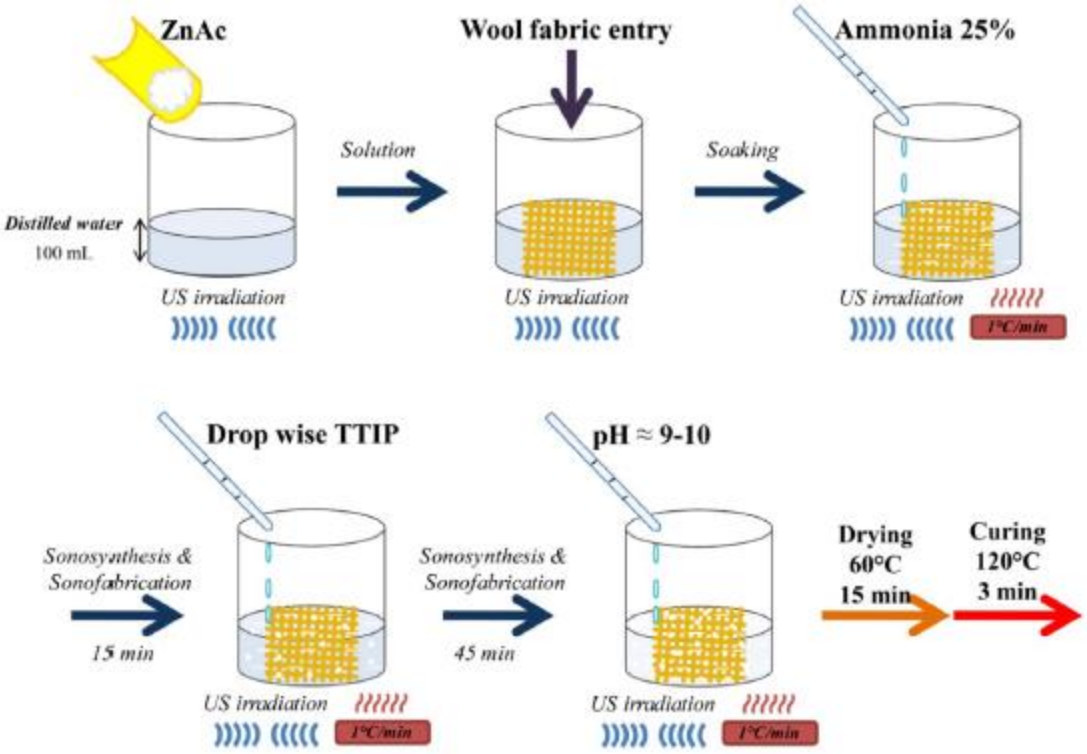

Fig. 2 Preparation procedure for *in situ* sonosynthesis of N-type ZnO/TiO_2 core-shell nanocomposite onto wool fabric [20]

POTENTIALITY OF MxOy/TiO_2 TYPE NANOCOMPOSITES AS HETEROGENEOUS CATALYSTS:

Enhancing the photocatalytic efficiency of TiO_2 to meet the practical application requirements is still a challenge due to low quantum yield because of the rapid recombination of photo generated electrons and holes.The different strategies were developed for improvement of spectral response with catalytic activity of TiO_2 [21-22]. Coupling of TiO_2 nanoparticles with the narrow band gap semiconductors (M_xS_y/TiO_2 or M_xO_y/TiO_2) results into decrease in its band gap as well as tuning optical response in the visible region of electromagnetic spectrum. TiO_2 coupled with metal chalcogenides such as CdS, SnO_2, WO_3, Fe_2O_3, etc was showed improved optical properties under visible irradiation [23-27].

The increase of TiO_2 photosensitization in the presence of others semiconductors (such as CdS, WO_3 etc.) make it more suitable for catalytic and sensing applications. On the other hand, it also makes it potentially significant as promising photocatalyst due to its higher chemical and

physical properties (high oxidation efficiency, non-toxicity, high photo-stability, and chemical inertness, among others).

The photocatalytic studies were suggested that the SnO_2/TiO_2 heterostructures showed enhanced photocatalytic efficiency of Rhodamine B (RB) degradation compared with bare TiO_2 nanofibers under UV light irradiation [28]. TiO_2/WO_3 nanocomposites have a promising prospect in the treatment of wastewater for irrigation. Literature reports demonstrated the catalytic activity of M_xO_y/TiO_2 nanocomposites for preferential oxidation of carbon monoxide in hydrogen-rich stream. Cr_2O_3/TiO_2 mixed oxides, prepared by sol-gel method, show increase in photocurrent in photoelectrochemical cell [29].

From the review of relevant literature, it has been observed that the mixed metal oxide nanocomposites showed good potential in catalyzing various organic reactions like reduction of nitro compounds, oxidation of phenols, alcohols, photodegradation of hazardous organic dyes present in water streams. These composites are also effectively useful in the gas sensing applications. Investigators were also used different metal oxides like ZnO, Bi_2O_3, In_2O_3, ZrO_3, CrO_3 etc. to enhance the photoactivity of TiO_2 [30-31]. Enhancing the rate of chemical transformation reactions by using mixed metal oxide nanocomposites as catalyst is major task for researchers in recent years. Lin et al. [32] prepared sulphated TiO_2 nanotubes and used them as catalysts for the esterification of acetic acid using cyclohexanol. The sulphate groups' modification of ZrO_2/TiO_2 nanocomposites with one-dimensional structure was synthesized by Li et al. [33] and used as catalysts for esterification of organic acid (levulinic acid). Highly efficient oxidation of gaseous benzene on novel Ag_3VO_4/TiO_2 nanocomposite photocatalysts under visible and simulated solar light irradiation was achieved by Jinxiu et al. [34]. Binary metal oxide/titania nanocomposites showed enhanced photocatalytic activity in the decomposition of Rhodamine B (RB) under ultraviolet light [35]. Solvothermal synthesis of CeO_2-TiO_2 nanocomposite for visible light-photocatalytic detoxification of cyanide was reported by some workers [36]. Different facets ({101}, {001}, and {100}) of anatase TiO_2 nanocystals as well as rutile and brookite nanocrystals were obtained by anion assisted synthesis. These different forms of TiO_2 were used for photocatalytic selective reduction of nitrobenzene as well as selective oxidation of benzyl alcohol [37].

CONCLUSION: -

This review highlights the importance of TiO_2 photocatalyst for catalytic applications. As it has been stated that, a number of research studies have focused on the development of a new TiO_2 photocatalyst able to absorb visible light as a main part of solar spectrum. The limitations of pure TiO_2, which require the use of UV light and its high photogenerated electrons and holes recombination rate, can be overcome by introducing foreign species into the titanium dioxide matrix. The coupling TiO_2 with other semiconductors is the major approach that have been reviewed. Till today, the successful applications of TiO_2 photocatalyst under visible light were carried out at the laboratory scale. Future research should be focused on the use of novel TiO_2 photocatalyst (coupled TiO_2 or photosensitized TiO_2) for large scale applications.

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THERAPEUTIC USE OF *WITHANIA SOMNIFERA*: A REVIEW

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ABSTRACT:

In India, it is estimated that around 70,000 plant species, approximately 7500 species have been recorded to have medicinal value. There are estimated to be more than 717,319 registered practitioners of ayurveda, siddha, unani and homeopathy in India and in recent years, the growing demand for herbal products has led to the extinction of many important herbs. *Withania somnifera* (L) Dunal is a well known Indian medicinal plant widely used in the treatment of many clinical conditions in India. It is an important drug commonly known as Asgand, which has been, used either single or in combination with other drugs in Unani as well as Ayurvedic system of medicine for centuries. *Withania somnifera* possess good immunomodulatory anti-inflammatory, anti-tumor, antioxidant, anticancer properties and medicinally important chemicals, they protect the cells from oxidative damage and diseases. Keeping in view the medicinal properties of *Withania somnifera* Dunal (Asgand), an attempt has been made in this review paper we have tried to explore the various dimensions of the drug including phytochemical and therapeutic knowledge about Ashwagandha, which is used to exploit novel medicines.

KEYWORDS: *Withania somnifera*; immunomodulatory; anti-inflammatory; antioxidant and Unani medicine

INTRODUCTION:

According to the World health organization, traditional medicines are widely used in India. Approximately 80% of the population of developing countries depends on traditional medicines for their primary health care needs [1-3]. Plants are one of the most important sources of medicines in world. The medicinal plants are rich in secondary metabolites and essential oils of therapeutic importance. The medicinal plants contain several phytochemicals such as Vitamins (A, C, E, and K), Carotenoids, Terpenoids, Flavonoids, Polyphenols, Alkaloids, Tannins, Saponins, Saponins, Enzymes, and Minerals etc. etc. These phytochemical possess antioxidant activities, which can be used in the treatment of multiple ailments. The important advantages claimed for therapeutic uses of medicinal plants in various ailments are their safety besides being economical, effective and their easy availability [4, 5]. Because of these advantages the medicinal plants have been widely used by the traditional medical practitioners in their day to day practice. In traditional systems of medicine the Indian medicinal plants have been used in successful management of various disease conditions like bronchial asthma, chronic fever, cold, cough, malaria, dysentery, convulsions, diabetes, diarrhea, arthritis, emetic syndrome, skin diseases, insect bite etc. and in treatment of gastric, hepatic, cardiovascular & immunological disorders [2, 6-10].

Withania somnifera Dunal belongs to the family solanaceae. It is a xerophytic plant, found in the drier parts of India, Sri Lanka, Afghanistan, Baluchistan and Sind and is distributed in the Mediterranean regions, the Canaries and Cape of Good Hope. It is found in high altitude ascending to 5,500 feet in the Himalayas medical system for over 3000 years. Numerous studies indicated that ashwagandha possesses antioxidant, antitumor, antistress, anti-inflammatory, immunomodulatory, hematopoetic, anti-ageing, anxiolytic, antdepressive rejuvenating properties and also influences various neurotransmitter receptors in the central nervous system [11].

The researchers revealed that a specific extract from the plant, Withaferin A, was more effective in the inhibition than the common cancer chemotherapy drug, doxorubicin, they used to compare it with [12].

PHYTOCHEMICAL STUDIES:

A review of literature reveals the presence of various chemical constituents in the different parts of the plant which are as follows:

- **Root-**

The roots are reported to contain alkaloids, amino acids, steroids, volatile oil, starch, reducing sugars, glycosides, hentriacontane, dulcitol, withaniol, and a neutral compound. The total alkaloidal content of the Indian roots has been reported to vary between 0.13 and 0.31 percent, though much higher yields (up to 4.3%) have been recorded elsewhere [13,14]. Many biochemically heterogeneous alkaloids have been reported in the roots. Basic alkaloids include cuscohygrine, anahygrine, tropine, pseudotropine, anaferine, isopelletierine, withananine, withananinine, pseudo-withanine, somnine, somniferine, somniferinine. Neutral alkaloids include 3-tropyltigloate and an unidentified alkaloid. Other alkaloids include withanine, withasomnine, and visamine. Withanine is sedative and hypnotic.[15]

- **Leaves-**

The leaves of the plant (Indian chemotype) are reported to contain 12 withanolides, 5 unidentified alkaloids (yield, 0.09%), many free amino acids, chlorogenic acid, glycosides, glucose, condensed tannins, and flavonoids [15]. Withaferin A, a steroidal lactone is the most important withanolide isolated from the extract of the leaves and dried roots of Withania somnifera. It is thermostable and slowly inactivated at pH 7.2. It is insoluble in water and is administered in the form of suspension. For its separation, the leaves are extracted with cold alcohol; the extract is purified and dried, and finally crystallized from aqueous alcohol (yield, 0.18% air dry basis). The yield of this compound from the South-African plants is reported to be as high as 0.86 percent. The curative roperties of the leaves and roots are attributed to Withaferin A [13].

- **Fruit-**

The green berries contain amino acids, a proteolytic enzyme, condensed tannins, and flavonoids. They contain a high proportion of free amino acids which include proline, valine, tyrosine, alanine, glycine, hydroxyproline, aspartic acid, glutamic acid, cystine and cysteine. The presence of a proteolytic enzyme, chamase, in the berries may be responsible for the high content of the amino acid.

- **Shoots-**

The tender shoots are rich in crude protein, calcium and phosphorous, and are not fibrous. They are reported to contain scopoletin.

- **Stem-**

The stem of the plant contains condensed tannins and flavonoids. Bark The bark contains a number of free amino acids [13].

THERAPEUTIC USES *OF WITHANIA SOMNIFERA*:

Withania somnifera is one of the major herbal components of geriatric tonics mentioned in Indian systems of medicine. In the traditional system of medicine Ayurveda, this plant is claimed to have potent aphrodisiac rejuvenative and life prolonging properties. It has general animating and regenerative qualities and is used among others for the treatment of nervous exhaustion, memory related conditions, insomnia, tiredness potency issues, skin problems and coughing. It improves learning ability and memory capacity. The traditional use of 'Ashwagandha' was to increase energy, youthful vigour, endurance, strength, health, nurture the time elements of the body, increase vital fluids, muscle fat, blood, lymph, and semen and cell production. It helps counteract chronic fatigue, weakness, dehydration, bone weakness, loose teeth, thirst, impotency, premature aging emaciation, debility, and convalescence and muscle tension. It helps invigorate the body by rejuvenating the reproductive organs, just as a tree is invigorated by feeding the roots [16-20].

Anti-inflammatory Activity:

Withaferin A exhibits fairly potent anti-arthritic and antiinflammatory activities. Anti-inflammatory activity has been attributed to biologically active steroids, of which Withaferin A is a major component. It is as effective as hydrocortisone sodium succinate dose[15]. It was found to suppress effectively arthritic syndrome without any toxic effect. Unlike hydrocortisone-treated animals which lost weight, the animals treated with Withaferin A showed gain in weight in arthritic syndrome. It is interesting that Withaferin A seems to be more potent than hydrocortisone in adjuvantinduced arthritis in rats, a close experimental approximation to human rheumatoid arthritis. In its oedema inhibiting activity, the compound gave a good dose response in the dose range of 12-25 mg/kg body weight of Albino rats intraperitoneally and a single dose had a good duration of action, as it could effectively suppress the inflammation after 4 hours of

its administration[13, 21]. Asgand (Withania somnifera) has been shown to possess anti-inflammatory property in many animal models of inflammations like carrageenan-induced inflammation, cotton pellet granuloma and adjuvant-induced arthritis .The studies were carried out to investigate the release of serum -1 globulin during inflammation by two models of inflammations viz. primary phase of adjuvant induced arthritis and formaldehyde-induced arthritis. The experiments showed interesting results as most of the APR were influenced in a very short duration and also suppressed the degree of inflammation [22].

Antibiotic Activity:

The antibiotic activity of the roots as well as leaves has recently been shown experimentally. Withaferin A in concentration of 10 g/ml inhibited the growth of various Gram-positive bacteria, a. The antibiotic activity of the roots as well as leaves has recently been shown experimentally. Withaferin A in concentration of 10g/ml inhibited the growth of various Gram-positive bacteria, acidfast and aerobic bacilli, and pathogenic fungi. It was active against Micrococcus pyogenes varaureus and partially inhibited the activity of Bacillus subtilis glucose-6- phosphatedehydrogenase.

Withaferin A inhibited Ranikhet virus. The shrub's extract is active against Vaccinia virus and Entamoeba histolytica[13,15,21]. Asgand showed the protective action against systemic Aspergillus infection. This protective activity was probably related to the activation of the macrophage function revealed by the observed increases in phagocytosis and intracellular killing of peritoneal macrophages induced by Ashwagandha treatment in mice [23]. Antibiotic activity of Withaferin A is due to the presence of the unsaturated lactone-ring. The lactone showed strong therapeutic activity in experimentally induced abscesses in rabbits, the being somewhat stronger than that of Penicillin. It substantiates the reputation of the leaves as a cure for ulcers and carbuncles in the indigenous system of medicine [13].

Anti-oxidant Activity:

Administration of active principles of Withania somnifera, consisting of equimolar concentrations of sitoindosides VII-X and Withaferin A, was found to increase superoxide dismutase (SOD), catalase (CAT) and glutathione peroxidise (GPX) activity in rat brain frontal cortex and striatum. Antioxidant effect of active glycowithanolides of *Withania somnifera* (WSG) may explain, at least in part, the reported anti-inflammatory, immunomodulatory, anti-

stress, antiaging and cognition-facilitating effects produced by them in experimental animals, and in clinical situations [24].

Anti-hyperglycaemic Effect:

Asgand along with other ingredients of a composite formulation (Transina) have been reported to decrease streptozocin (STZ)-induced hyperglycaemia in rats. This anti-hyperglycaemic effect may be due to pancreatic islet free radical scavenging activity because the hyperglycaemic activity of STZ is a consequence of decrease in pancreatic islet cell superoxide dismutase (SOD) activity leading to the accumulation of degenerative oxidative free radicals in islet-beta cells[25].

Anti-stress/Adaptogenic Activity:

Anti-stressor effect of Asgand was investigated in rats using cold water swimming stress test. The drug treated animals showed better stress tolerance [26].A withanolide-free aqueous fraction isolated from the roots of *Withania somnifera* exhibited anti-stress activity in a dose dependent manner in mice [15]. Asgand has been evaluated for its adaptogenic activity. Administration of Asgand with other drugs in experimental animals exposed to a variety of biological, physical and chemical stressors was found to offer protection against these stressors [24, 27].

Antitumor Properties:

To investigate its use in treating various forms of cancer, the antitumor and radiosensitizing effects of WS have been studied. In one study, WS was evaluated for its anti-tumor effect in urethane induced lung adenomas in adult male albino mice [28].Simultaneous administration of WS (ethanol extract of whole plant, 200 mg/kg daily orally for seven months) and urethane (125 mg/kg without food biweekly for seven months) reduced tumor incidence significantly. The histological appearance of the lungs of animals protected by WS was similar to those observed in the lungs of control animals. No pathological evidence of any neoplastic change was observed in the brain, stomach, kidneys, heart, spleen, or testes of any treated or control animals. In addition to providing protection from carcinogenic effects, WS treatment also reversed the adverse effects of urethane on total leukocyte count, lymphocyte count, body weight, and mortality. The growth inhibitory effect of WS was also observed in Sarcoma 180 (S-180), a transplantable mouse tumor [29].Ethanol extract of WS root (400 mg/kg and up, daily for

15 days) after intra-dermal inoculation of 5x105 cells of S-180 in BALB/c mice produced complete regression of tumor after the initial growth. A 55-percent complete regression was obtained at 1000 mg/kg; however, it was a lethal dose in some cases. WS was also found to act as a radio- and heat sensitizer in mouse S- 180 and in Ehrlich ascites carcinoma[29- 31]. Antitumor and radiosensitizing effects of withaferin (a steroidal lactone of WS) were also seen in mouse Ehrlich ascites carcinoma in vivo[32]. Withaferin A from WS gave a radiosensitizer ratio of 1:5 for in vitro cell killing of V79 Chinese hamster cell at a non-toxic concentration of about 2 mM/L.[29-31]. These studies are suggestive of antitumor activity as well as enhancement of the effects of radiation by WS.

Hemopoetic Effect:

Administration of WS extract was found to significantly reduce leukopenia induced by cyclophosphamide (CTX) treatment in Swiss albino mice.[33] Total white blood cell count on the 12th day of the CTX-treated group was 3720/mm3 ; that of the CTX-plus-WS group was 6120/mm3 . In the CTX-plus-WS mice, the cellularity of the bone marrow was significantly increased compared to the CTX-alone treated group (8 x 106/femur). Similarly, the number of alpha-esterase positive cells (1130/4000 cells) in the bone marrow of the CTX-plus-WS mice increased compared to the CTX alone mice (687/4000 cells).The major activity of WS may be the stimulation of stem cell proliferation. These studies indicated WS reduced CTX-induced toxicity and may prove useful in cancer chemotherapy. Further studies need to be conducted to confirm the hemopoetic effect with other cytotoxic agents and to determine its usefulness as an adjuvant in cancer chemotherapy.

Effects on the Endocrine System:

Based on the observations that WS provides protection from free radical damage in the mouse liver, studies were conducted to determine the efficacy of WS in regulating thyroid function.[34- 35] Mice were given WS root extract (1.4 g/kg by gavage, daily for 20 days). The treatment significantly increased the serum levels of 3,3', 5- triiodothyronine (T3) and tetraiodothyronine (T4), while the hepatic concentrations of glucose 6- phosphatase activity and hepatic iodothyronine 5'- monodeiodinase activity did not change significantly. WS significantly reduced hepatic lipid peroxidation and increased the activity of superoxide dismutase and

catalase. The results suggest WS stimulates thyroidal activity and also promotes hepatic antioxidant activity.

Anticonvulsant Activity:

Administration of Asgand root extract was found to reduce jerks and clonus in 70% and 10% animals respectively with dose of 100mg/kg and reduction in the severity of pentylene tetrazole (PTZ)-induced convulsions was evident from EEG wave pattern [36]. Asgand root extract showed reduction in severity of motor seizures induced by electrical stimulation in right basilateral amygdaloid nuclear complex through bipolar electrodes. The protective effect of Asgand extract in convulsions has been reported to involve GABAergic mediation [37].

Anti-ageing Effect:

Double-blind clinical trial carried out to study the effect of plant on prevention of ageing in 101 normal healthy males in 50-59 years age group. Root powder (0.5 g) was given orally three times a day for 1 year. Results showed statistically significant increase in Hb, RBC, hair melanin, and seated stature in treated group in comparison to placebo group. Decrease in serum cholesterol was more in treated group than in placebo group [21].

Neuropharmacological Activity:

Total alkaloidal fraction of root extract showed prolonged hypotensive, bradycardiac and respiratory stimulant activities in dogs. Hypotensive effect was mainly due to autonomic ganglionblocking action and was augmented by the depressant action on higher cerebral centres. The total alkaloids produced a taming and a mild depressant effect (tranquillizer-sedative type) on the CNS in several experimental animals [21]. Systemic administration of Asgand root extract led to differential effects on acetylcholinesterase (ACHE) activity in basal forebrain nuclei. Slightly enhanced ACHE activity was found in the lateral septum and globus pallidus. Asgand root extract affects preferentially events in the cortical and basal forebrain cholinergic signal transduction cascade. The drug induced increase in cortical muscarinic acetylcholine receptor capacity might partly explain the cognition-enhancing and memory-improving effects of extract from *Withania somnifera* observed in animals and humans [38].

CONCLUSION:

Medicinal plants maintain the health & vitality of individuals & also cure disease, without causing toxicity. In the present study, we have discussed the chemical composition, therapeutic uses of Withania somnifera. In the past few years, many promising bioactivities such asanticancer, immunostimulant, Anticonvulsant and anti-oxidant activity of *Withania somnifera* have been reported. The pharmacological and medicinal significance of *Withania somnifera* is gradually increasing. In conclusion, this article provides the therapeutic knowledge about Withania somnifera, which is used by the people all over the world. Also, it is of significance to exploit novel medicines from Withania somnifera.

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A STUDY ON THE INFORMATION AND COMMUNICATION SYSTEM AMONG THE SMALL AND MARGINAL FARMERS OF BHADRAK DISTRICT OF ODISHA

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ABSTRACT:

The present work deals with the study on information and communication system of the small and marginal farmers in relation to agricultural communication and information system in Bhadrak district of Odisha. The objectives of the present work was personal socio-economic characteristics, different sources of information and their credibility, nature and extent of contact with extension personnel, organizations and extension methods and social, economic and organizational constraints in relation to agriculture information and communication system. The study reveals the status of the information and communication system among farmers of Bhadrak District.

KEYWORDS: Information and Communication; Farmers; Bhadrak District

INTRODUCTION:

Information System:

An information system is a collection of message that transforms data into knowledge and methods desired by and useful for individual and group users in organizations and other entities.

Communication:

Leagens says, ”it is a process by which two or more people exchange ideas, facts, feelings or impressions in ways that each gains a common understanding of the message. In essence it is the act of getting a sender and a receiver tuned together for a particular message or series of message

Marginal farmer:

The farmer whose land holdings is 1ha or less (2.5 acre)

Small farmer:

The farmer whose land holdings is 2ha or less (5acre).

Importance ofcommunication:

Paul Leganes has very rightly said that, for development of any nation, three things are necessary, (i) investigation, (ii) interpretation and (iii) administration. Our country India is self-sufficient in investigations i.e. improved technology. Also administration is not posing any problem. But only due to lack of proper interpretation we failed to achieve significant success as compared to developed countries. Interpretation is nothing but communication.

Communication has always been the basis of human endeavor. It has been aptly stated that, communication is a process of social interaction. Communication of farm information is a sine-qua-son for bringing about change in the rural social system. There is a wide gap between knowledge germination and its utilization. It is estimated that not more than 15-20 percent of the available technology reaches our Indian farmers, as against 80-85 percent in some of the developed countries. The scientific knowledge accumulated in the field of research, needs to be continuously communicated to its users. The gap needs to be narrowed down so as to enhance the adoption of specific technology by the farmers.

The development of research in the field of agriculture is quite conspicuous and is capable of meeting the needs of increasing population, if proper infrastructure of communicating these results to the actual users are developed.

The development of useful agricultural information would meet the national goals of self-sufficiency in food, only when the farmers understand, accept and adopt the latest technology

without any undue time lag. Inefficient exploitation of the yield potential is due to the lack of proper understanding of the message communication, which is evident in the partial adoption of these technologies.

Sustained high levels of agricultural production and income are not possible without an efficient agricultural communication service, supported by agricultural research that is relevant to farmers' needs. In India several extension approaches have been implemented to meet the requirements of rural people.

Agriculture occupies the central place in rural life and it is well known that rural life revolves round agriculture any attempt to improve agriculture will usually trigger the rural development. In India, several extension approaches have been adopted for agricultural development. Even in pre-independence days (prior to 1947), a number of disjointed and sporadic attempts were made to stimulate rural development in India.

Channelizing and harvesting local resources and potentialities to the extent possible in right direction. With the primary objectives of increasing the agricultural production, a number of development programmes like, Intensive Agriculture District Programme (IADP-1960) (Package Programme) Intensive Agriculture Area Programme (IAAP-1964), High Yielding Varieties Programme (HYVP_1966) etc. were implemented in our country.

All these extension efforts with some variations, mostly concentrated in Agriculture development work utilizing block extension machinery with provision of more VLWS, Extension officers or Subject Matter Specialists as per the need of the programme. By and large the National Extension Service Pattern, which envisaged multipurpose VLWs and BDO as a coordinator remained in value. However, various constraints were experienced in this system as listed below.

1. Lack of a single line command.
2. Dilution of efforts by assigning multipurpose role to field extension workers.
3. Excessively large areas of operation for VLWs
4. Lack of regular training programmes for updating knowledge of extension workers.
5. Lack of communication networking and support from research.
6. Duplication of services by various agencies involved in the development activities.
7. The working objectives of the system are as follows:
8. Coordinating research, training and extension activities effectively.

9. To make research more effective by catering to the local needs and situation.
10. To evolve an intensive training programme on a systematic basis for extension workers and farmers and to ensure effective supervision and technical support to VAWs/ADOs.

Concept of small and marginal farmers:

It is assumed that the contact farmers must be willing to try out practices, recommended by the extension workers and be prepared to have other farmers, visit their fields. The advice to small and marginal farmers will thus diffuse and spread to other farmers, through the well-knit communication system in the rural area and through the process of dissemination and diffusion.

Small and marginal farmers is one of the farmers who is willing and co-operative in respect of accepting new ideas and in turn be able to transfer the same to his neighbor farmers by dint of his respect in the society. Thus the small and marginal farmers provides the village Agricultural workers with an active means to reach all farmers in the shortest possible time.

Technical advice spreads from the extension agent through small and marginal farmers to a large numbers of farmers mainly by two mechanism. First, outer farmers see what contact farmers try in their fields and results they achieve. This generates interest. Second, each small and marginal Farmers farmer talks about the practices he has been taught, to several friends, relatives or neighbours, and thereby helps them understand and adopt the recommendations. In this way, a larger proportion of farmers can be quickly reached.

SELECTION OF SMALL AND MARGINAL FARMERS:

Small and marginal Farmers are identified by the VAW and Assistant Agricultural Officer AAO with the help of local villagers, especially the village elders. Contact farmers are selected according to the following to the characteristics:

1. They should represent proportionately the main socio-economic and farming conditions of their groups and be regarded by other farmers, as able and worthy of imitation.
2. They should be practicing farmers.
3. They should be willing to adopt relevant agricultural technology on at least a part of their practices and explain the practices to them.
4. They should be able to disseminate information to the fellow farmers.
5. As far as size and composition of farmers, groups permit, they should be dispersed throughout the group area.

The proper identification of small and marginal farmers is extremely important looking to their pivotal role in effective extension. Tenants, share croppers, young farmers and women farmers may be small and marginal farmers, if they possess those characteristics. No major type of farmer should be over or under represented among the small and marginal farmers of a group.

IMPORTANCE OF THE STUDY:

The role of leadership is crucial in enhancing faster diffusion of agricultural innovations. Thus the vital role that the local leaders can play is well recognized. They bring desirable changes in the rural society. Their importance is realized mainly because most of the farmers believe in opinion given by the leaders rather than the extension personnel. The farmers sincerely follow he practices adopted by the local leaders. The success or failure of programme of planned changes ultimately depends upon the ability and co-operation of local leaders at the village level. Thus the success and failure of training and visit system can be measured by assessing the effectiveness of contact farmers influencing other farmers for adoption of improved agricultural technology such as H.Y.V. seeds and seed treatment, agronomic practices, fertilizer management, plant protection measures, improved agricultural implements and post-harvest technology etc.

Obviously, the role of the Small and Marginal farmers are the opinion leaders and act as change agents and proved to be instrumental in bringing about success in agricultural production by transferring the technology to the fellow farmers. So study of communication behavior of small and Marginal a prime need.

Any agricultural innovation that is recommended must be considered not only in terms of its expected productivity but also in terms of its acceptance by the farming community. The latter part cannot be achieved without effective communication. The small and marginal farmers get information from different sources. Therefore, this is a need to know more about different sources of information and their combination through which small and marginal farmers acquire proper skill and knowledge about certain broad groups of agricultural innovations. It is also necessary to determine the credibility enjoyed by different sources as the information agencies.

It is also important to study the relationship between personal socio-economic factors of the small and Marginal farmers and their communication and information system which will

definitely enable the VAW to assess the effectiveness of the small and marginal farmers. Keeping this in view, the present study was designed with the following objectives.

OBJECTIVES OF STUDY:

1. To study the socio-economic characteristics of the small and marginal farmers.
2. To identify various sources of farm information and their credibility among small and marginal farmers.
3. To analyze respondent's nature and extent of contact with various extension personnel, extension organizations, and extension methods.
4. To study the social, economic and organizational constraints in relation to agricultural information and communication system along with their suggestions.
5. To suggest suitable strategies for the information and communication system of small and marginal farmers of Odisha.

RESEARCH METHODOLOGY:

Plan of Work:

Before actual investigation, efforts is made to conduct a detailed survey of all related information and communication system among small and marginal farmers during the course of study. As a part of course curriculum, it is needed to complete the research project within a stipulated academic period. Hence the areas of investigation, sample size, the method of analysis of data etc. is chalked out detail, keeping a number of limitations in view.

Processing and analysis of data:

Statistical measure provides the investigator with the opportunity of expressing the facts in an imperial way. The statistical measurement which had been used in this study were,

(1) Percentage (2) Gap percentage and (3) Critical ratio.

Percentage:

Percentage were used in description analysis for making simple comparison between two responses. For calculating percentage, the frequency of a particular cell was multiplied by 100 and divided by the total number of respondents in the particular category to which the cell belonged.

Percentage = Number of respondents X 100 / Total no. of respondents

Gap (Score gap):

It was the difference between maximum obtainable score and obtained score value for a given variable, when expressed in percentage it was called gap percentage.

Gap percentage (Gap %) = (Maximum score – Obtained Score) /Maximum score X 100

Critical ratio:

This test was carried out to know the significant association between two percentages.

C.R = C.R = P~Q/ PQ(1/N1+1/N2) , P=N1P1+N2P2 / N1+N2,where,

N1=Size of 1st sample,N2=Size of 2nd sample

P1=Percent of 1st sample, P2=Percent of 2nd sample

REVIEW OF LITERATURE:

Gupta (1999) concluded that small and marginal farmer's considerable agricultural Extension officers to be more credible than any other information source for modern agricultural technology. Farmers gave them highest priority & preference. Vaje and Bajaj (2000) reported that occupation was significantly associated with the use of communication media and also social participation.

Mishra (2000) concluded that a negligible correlation ship of the socio- economic variables like family type, family size and annual income with the communication behavior.

The age was highly correlated with the communication behaviour and education as well as occupation. The farm size and the social participation showed a low correlation with the communication behaviour. Wilson and Chaturvedi (2000) reported that extension participation had positive and significant association with adoption behavior of farmers.

RESULTS AND DISCUSSION:

The data obtained in the study were processed, analyzed statistically and presented with the help of tables systematically.

It was evident from the table 1 that, out of 114 small and marginal farmer14.91 percent were of young age group, followed by 53.50 percent who were in middle age group and only 31.57 percent were in old age group category.

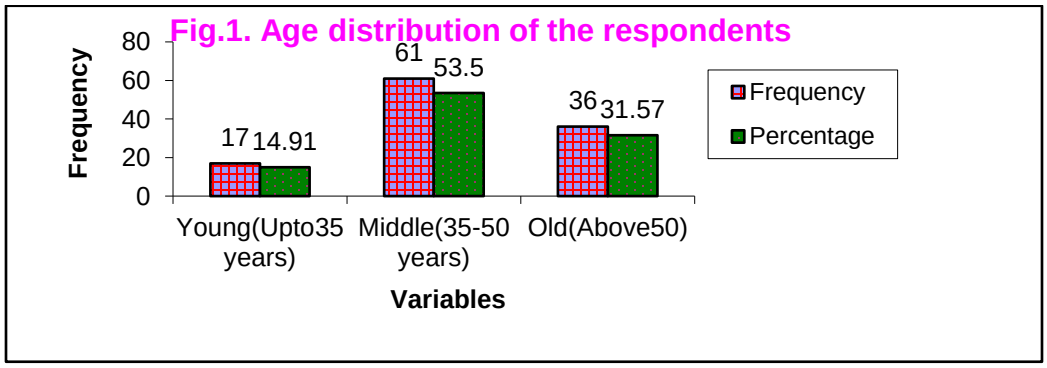
From the above findings, it was observed that most of the small and marginal farmer belonged to middle age category (35-50 year), selected by the V.A.Ws. The reasons might be,

small and marginal farmer of this category were more experienced, active, dynamic and can influence and give advice to the fellow farmers of the community.

Socio- economic characteristics of the small and marginal farmers:

Table 1. Age distribution of the respondents

Sl.No.	Age Category	Frequency	Percentage
1.	Young(Upto35 years)	17	14.91
2.	Middle(35-50 years)	**61**	**53.50**
3.	Old(Above50)	36	31.57



The data compiled in table 2indicated the distribution of educational categories of the small and marginal farmer. Out of the total small and marginal farmer or respondents, 1.75 percent of the respondents were illiterate,whereas 8.77 percent respondents were can sign.name only , 37.71 percent received primarily education 21.92 percent had middle school education, 16.66 percent had high school education and only 13.15 percent had college education.

Education plays a vital role for the development of an individual. The government has launched various programmes to eliminate illiteracy, and to make the illiterates functional literates From the above observation none of the small and marginal farmer were illiterate which is highly satisfactory,because unless a small and marginal farmer is able to read different types of printed materials he will not be able to adopt and disseminate the important agricultural information to his fellow farmers. Also, it was observed that only 16.66 percent of small and marginal farmer received education of high school.

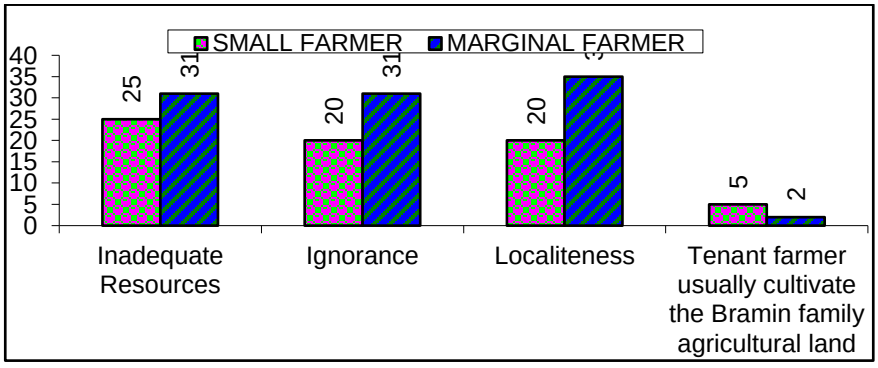
Table 2. Educational level of the respondents (N = 114)

Sr. No.	Educational Level	Frequency	Percentage
1.	Illiterate	2	1.75
2.	Can sign. name only	10	8.77
3.	Primary School	43	37.71
4.	Middle School	25	21.92
5.	High School	19	16.66
6.	College	15	13.15

This is a blatant indication of the fact that those who are getting higher education are reluctant to adopt farming as their prime occupation. Most of the small and marginal farmers belonged to middle age category (35-50year), selected by the V.A.Ws. The reasons might be, small and marginal farmers of this category are more experienced, active, dynamic and can influence and give advice to the fellow farmers of the community .More educated person are now diverting themselves from agriculture to other enterprises.

Table 3. Social constraints in agricultural information and communication system:

Social constraints	Small farmer	Marginal farmer
Ignorance	20(28.16)	31(72.09)
Localiteness	20(28.16)	**35(81.39)**
Tenant farmer usually cultivate the Brahmin family agricultural land	5(7.04)	2(4.65)

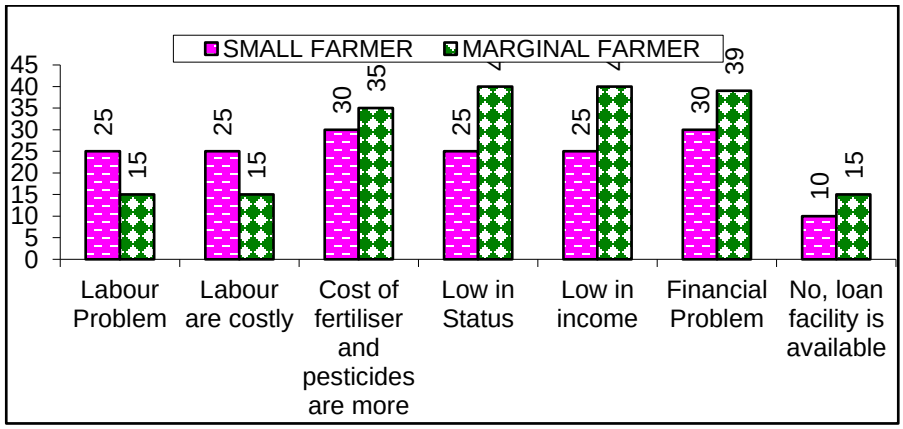


The data presented in Table 3 revealed that localities of the small famers and marginal respondents were 28.16 percent and 35.21 percent respectively because they usually donot go to the agriculture office in their locality.

ECONOMIC CONSTRAINTS

Table – 4 N = 114

Economic constraints	Small farmer	Marginal farmer
Labour Problem	25(35.21)	15(34.88)
Labour are costly	25(35.21)	15(34.88)
Cost of fertilizer and pesticides are more	30(42.25)	35(81.39)
Low in Status	25(35.21)	**40(93.02)**
Low in income	25(35.21)	**40(93.02)**
Financial Problem	**30(42.25)**	39(90.69)
No loan facility is available	10(14.08)	15(34.88)
Inadequate resources	25(35.21)	31(72.09)



The data presented in table 4 revealed that financial problem of the small famers respondents were 42.25 percent. The marginal respondents were 93.02 percent low in status and so low in income.

The data presented in table 5 revealed that the govt. programme do not reach and not getting help from the vetenery officer to the small famers respondents were 100 percent. The govt. programme do not reach to the marginal farmers respondents were 100 percent.

ORGANISATIONAL CONSTRAINTS

Table – 5 N = 114

Organisational constraints	Small farmer	Marginal farmer
No, support from agricultural officer	60(84.50)	34(79.06)
Not available Quality Seeds in time	65(91.54)	36(83.72)
No, help from the vetenery officer	**71(100)**	41(95.34)
Govt. programme not reach to the farmer	**71(100)**	**43(100)**
Not aware of Subsidiary related agricultural implements	64(90.14)	39(90.69)
Officers do not used to come	69(97.18)	20(46.51)
Not getting L.I Point facility	50(70.42)	30(69.76)
Shortage of Electricity supply	50(70.42)	36(83.72)
Monkeys are the main Problem	23(32.39)	20(46.51)
VAW is not sufficient	20(28.16)	19(44.18)
Subsidiary not getting in time	50(70.42)	40(93.02)

SUGGESTIONS:

1. Awareness programme should be conducted: By organizing awareness programme farmers will be aware of new scheme new technology related to agriculture and allied sector.
2. Weekly visit of AAO Officer is necessary: The meetings should be organized and maximum number of farmers should attend themeeting. Helps to know practically oriented scheme. Provide information related to subsidiary in agriculture and allied sector. So thatmost of the Farmers will be benefitted from government agricultural scheme. Government should directly give subsidiary to the farmer. So that maximum numbers of farmers will be benefitted from government policy.

SUMMARY:

1. The gap percentage of kissan call centre of small farmer were 65.72 percent. The gap percentage of kissan call centre of marginal farmer were 66.67 percent. The gap percentage of district level officers of small and marginal farmers were 66.67 percent.

2. The gap percentage of NGO's workers of small and marginal farmers were 66.67 percent. The gap percentage of AAO of small farmers were 64.3 and marginal farmers were 62.78 percent.
3. The gap percentage of OUAT of small farmers were 65.72 percent and marginal farmers were 65.11 percent. The gap percentage of KVK of small farmer were 66.67 percent and marginal farmers were 66.67 percent.
4. The gap percentage of Scientist of small farmers were 66.67percent and marginal farmers were 66.67 percent. The gap percentage of VAW of small farmers were 35.21 percent and marginal farmers were 58.91 percent.

CONCLUSION:

Prosperity of the country is liked with development of agriculture. It is imperative that the socio-economic condition of the farmers be developed through introduction of scientific agricultural innovations. A new strategy for agricultural development was launched to improve the conditions of the farming community of our country by disseminating improved agricultural know-hows by the small and marginal farmers. Under this system, the small and marginal farmers constitute important link in the extension chain for dissemination of agricultural information to the farming community form time to time, to boost up agricultural production.

Majority of the small and marginal farmers were in the medium communication and information group which was not satisfactory. Some of the small and marginal farmers were not even aware of some improved technology and so their dissemination behavior in that area was not eye-catching. Also very few small and marginal farmers adopted demonstration method to disseminate the information to fellow farers, which was not satisfactory to the desired extent. However, the contact farmers were proved to be instruments to carry up-to-date information about scientific agriculture form different information sources to the farming community by virtue of their communication and information system.

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PM_{10} AND $PM_{2.5}$ ASSOCIATED METALS IN AMBIENT AIR OF MINING AND NON-MINING AREAS AND CALCULATION OF THEIR EXCESS CANCER RISK FOR NI, CD AND CR

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ABSTRACT:

The study reports ambient concentration of PM_{10} and $PM_{2.5}$ bound metals in mining and non- mining areas of Dhanbad region, Jharkhand, India. In the study it was found that the concentration of metals associated with $PM_{2.5}$ was higher than PM_{10} bound metals. Enrichment factor of trace metals were find out to access the earth crust relation with ambient metals. Enrichment results indicates high anthropogenic activities from the different sources such as coal mining activities, emission from vehicular exhausts, constructions, industrial activities, earth crust, dust and biomass burning. Cancer risk assessment was done for carcinogenic metals (Ni, Cd, Cr) for both region (mining and non- mining) from the results it is established that the coal mining areas were recodedhigher value for Excess cancer risk (ECR).

KEYWORDS: Excess cancer risk(ECR); Enrichment Value (EV); Particulates; Carcinogenic.

INTRODUCTION:

Particulates are diverse in nature, they are composed by physically and chemically diverse substances these particulate variable in chemical composition, size, formation, concentration and origin. They affect health and directly linked to the cardiovascular, respiratory and premature mortality [1]. Particulatespossess organic and inorganic compounds [5,6].

Emission of metals comes from various natural and anthropogenic sources among anthropogenic, road dust, construction, and vehicular emission, combustion of oil and coal are prominent. [15,7, 16, 2, 8]. These metals directlyaffecthealth system; number of studies has been done on elevated level of metals relation to increased rate of mortality [18, 17]. Studies in coal mining areas [10, 9, 11] showed higher particulates concentration than standard limit.

The aim of our study is to characterizing PM_{10} and $PM_{2.5}$ particles with respect to eight trace metals (Fe, Mn, Pb, Ni, Zn Cd, Cu, and Cr) at four locations in one of the coal mine city of India.Four sampling sites were selected which equally distributed between mining andnon–mining. As per the Central Pollution Control Board (CPCB) research report in collaboration with the Ministry of Environment and Forests, India, Dhanbad is one of the worst polluted city with 13^{th} ranking among 88 industrial areas[19]. Assessment of pollution always been important since ambient air quality has a major effect on mine workers and residents living nearby the area. There are number of pollution sources such as opencast mines, coal based industries, and diesel based vehicular emission. So the monitoring of air quality is the step to identify the condition of air in the study area.

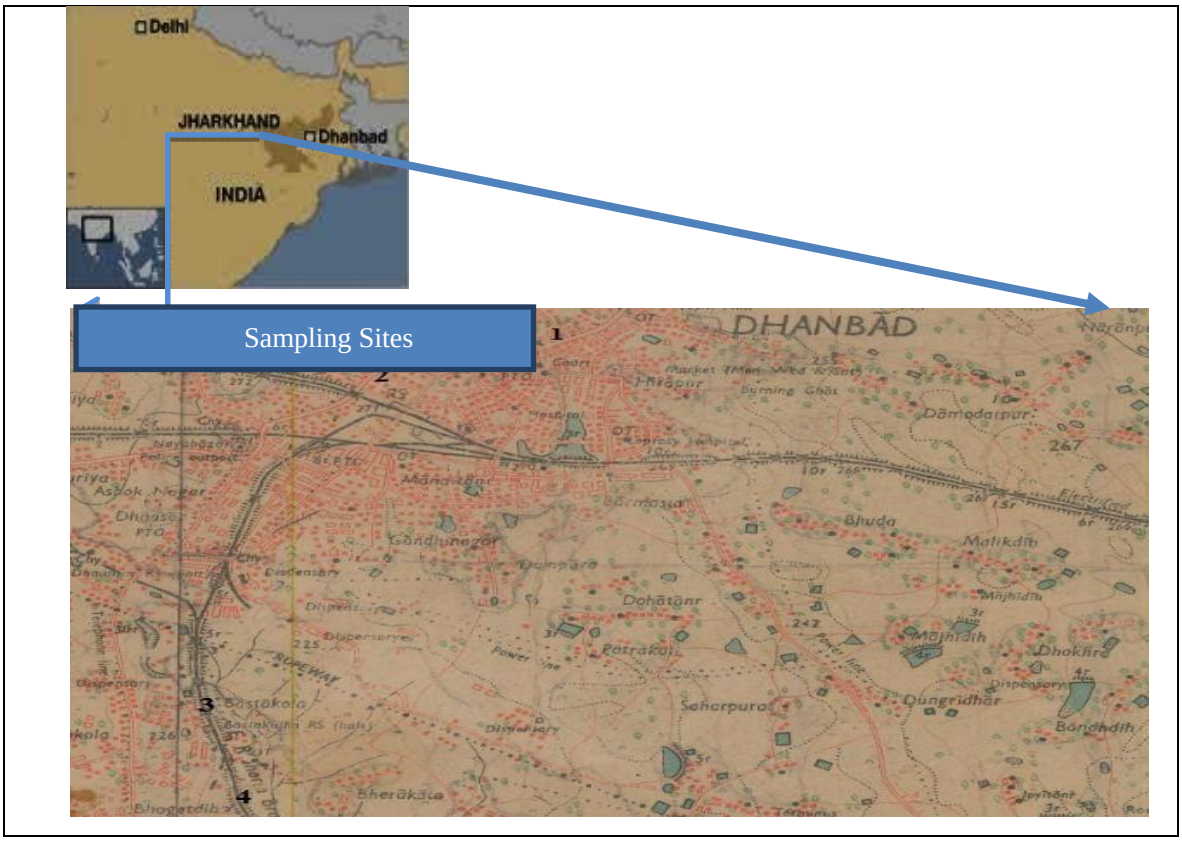

Figure 1. Study area along with sampling sites in Dhanbad, Jharkhand, India

Table 1. Detail Features of sampling sites

	Code	Locations	Remarks
Non-Mining	1	ISM (Main Gate)	Vehicular traffic and other commercial activities.
	2	Court More	Vehicular traffic and other commercial activities.
Mining	3	Bastacola	Mining activities, transportation through paved and unpaved road, domestic coal burning and other ancillary activities.
	4	Dhansaar	

STUDY AREA:

Sampling sites located in Dhanbad which is third largest city of Jharkhand state and famous as a coal capital of India. It lies between 23°37'3" N and 24°4' N latitude and between 86°6'30" E and 86°50' E longitude with the average elevation of 222 m above the sea level. This area fall under sub-tropical climate zone, where winter season start from November and end up to February, while summer start from March and extend until monsoon outbreak in month of June. Dhanbad share boundaries with West- Bengal, Dumka, Giridih and Bokaro. It comes under the plateau of Chota- Nagpur. Dhanbad has been place for companies such as BCCL, Tata Steel, ECL and IISCO which are extensively known for coal mining. Due to coal mining at larger scale, this area always has been concern for environment health problems.The region behind to select this study area was to address particulate bound metals distribution and their associated health risk.

METHODOLOGY:

SAMPLING:

The monitoring was done at 4 locations from April to June 2014 (summer season), total 72 samples were collected. The sampling of PM_{10} and $PM_{2.5}$ was carried out through fine particulate sampler (APM 550 Envirotech India). Samples were retained on PTFE filter (47 mm diameter). In the whole operation flow rate of sampler was maintained 16.7 LPM (liter/minute) and tuned to auto run mode. Filter paper weighted twice in electronic weighing balance before and after the sampling to reduce the error and it was handled carefully with Teflon coated tweezers to avoid

any possible contamination after that filters were wrapped in aluminum foil and stored at 4°C until the analysis.

SAMPLE ANALYSIS:

For trace metal determination acid digestion required, which was carried out in microwave digestion (Milestone Ethos EZ) to reduce the chemical consumption and for better recovery from particles. The samples were dissolved in the mixture of nitric and perchloric acid with 20:2 ratio and the program set to automatic mode. The digested samples were filtered through Whatman 42 and the volume makes up to 50 mL by milli Q waterthen after samples were analyzed for trace metals using ICP-OES (iCAP 6000 series manufactured by Thermo-Scientific).The concentration for each metal was found by deducting the blank value from respective metal of the sample.

The concentration of an element in the atmosphere is obtained from the following relation [20].

$$C\ (\mu g/m^3) = \frac{\text{Concentration of the element in digested sample } \left(\frac{\mu g}{mL}\right)}{\text{Volume of air sample (m3)}} \times \frac{\text{Total volume of the sample (mL)}}{\text{Percent of filter area used for analysis}} \quad \ldots\ldots (1)$$

RESULTS AND DISCUSSION

$PM_{2.5}$ AND PM_{10} CONCENTRATIONS:

From the observed results PM_{10} concentrations varied from the range 241 to 324 $\mu g/m^3$ in mining areas and 184 to 208 $\mu g/m^3$ in non- mining areas whereas the concentrations of $PM_{2.5}$ ranged from 134 to 156 $\mu g/m^3$ in mining and 86 to 105 $\mu g/m^3$ in non- mining. The mean concentration of PM_{10} and $PM_{2.5}$ were 239±28 $\mu g/m^3$ and 145±7.8 $\mu g/m^3$ in mining while it was 192±9 $\mu g/m^3$ and 93±7 $\mu g/m^3$at non-mining locations. Higher concentration of particulates (PM_{10} and $PM_{2.5}$) in mining areas may be due to extensive open cast mining activities, Moreover in the non- mining areasvehicular pollution, construction activities, coal burning for cooking, open biomass burning and dust from pavement due to low pressure develop by the vehicular movement are major sources. However theParticles concentrations in both locations were exceeding the annual mean standard by national ambient air quality 2009.Several other research

has reported fine and inhalable particle concentration to this region for different category such as industrial, commercial, residential areas.

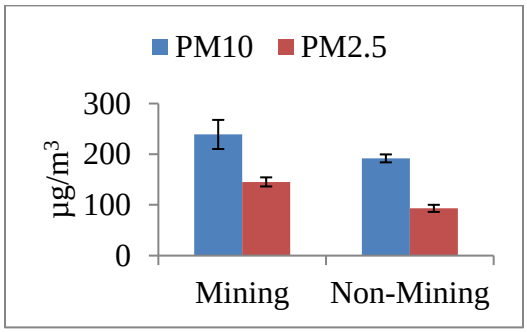

Figure 2. PM_{10} and $PM_{2.5}$ concentration in Mining and Non- Mining regions

ELEMENTAL CONCENTRATIONS:

The mean concentration of PM_{10} and $PM_{2.5}$ associated metals in coal mining and non-mining areas (Pb, Ni, Cr, Cd, Mn, Fe, Cu, Zn) shown in fig.3. From the figure it may be noted that the average concentration of crust metals (Fe, Mn, Cu) in both area were higher than trace and carcinogenic metals while all metals in higher concentration than standard limit.

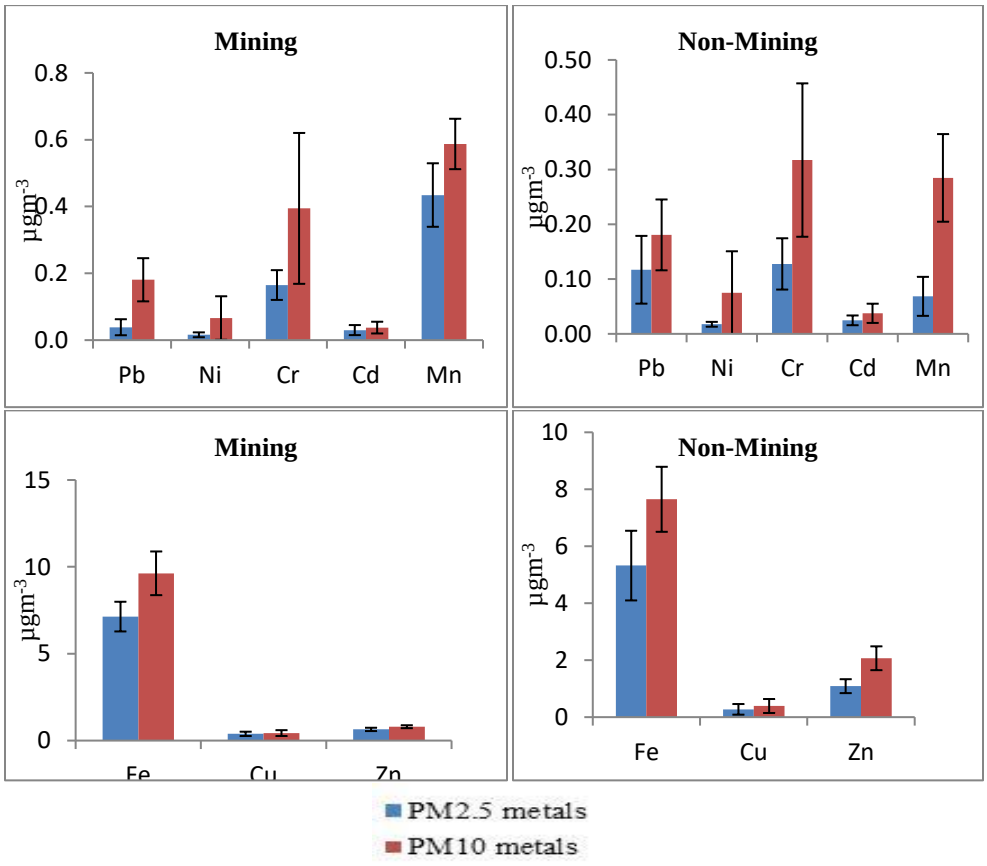

Figure 3. PM_{10} and $PM_{2.5}$ associated metals in Mining and Non- Mining areas

The concentration of Pb showed variation from mining to non- mining it is noted that the concentrations of Pb in non- mining were found higher than the concentration in mining areas it may be due to larger number of diesel and petrol powered vehicles plying on the road and non-mining areas. Pb emission sources would be vehicular pollution although leaded petrol has been phase out by the Indian government in very earlier but there existing concentration in the atmosphere still major issue.From the metals result it is established that respirable particulates have larger concentration of metals than fine particles in both region.

The concentration of Fe was highest among metals which may be due to crustal origin. The concentration of Cr was found highest among the carcinogenic metals Ni and Cd not showed profound difference in both areas. The concentration of Cu found almost similar in both cases. The concentration of PM10 andPM2.5 bound Mn in mining were much higher than the concentration in non- mining whereas Zn concentrationswere higher in non-mining areas.

ENRICHMENT FACTOR ANALYSIS:

The enrichment factor was primarily acquainted by Rahn [12] to determine the origin of metals found in atmospheric air or anticipated their origin from earth crust. The calculation of enrichment factors require metals concentration in atmospheric air with particular reference metal provided that should be crustal origin and not to influence by the anthropogenic activity [14]. There are several metals which have been used as a reference for enrichment factors such as Fe, K, Na, Mg, Al and Mn. Here in the study Fe selected as a reference metal which showed best correlation with other selected trace metals. Fe has been reported as a reference metals in some others studies of this area for enrichment factor like [3]. The calculation of enrichment factor has been done by the equation:

$$EF(x) = \frac{(\mathrm{X/Y})\mathrm{Sample}}{(\mathrm{X/F})\mathrm{Crust}} \quad \ldots\ldots (2)$$

CANCER RISK ASSESSMENT OF TOXIC METAL IN PM_{10} AND $PM_{2.5}$:

In the results cancer risk has been assess for the selected metals Cr, Ni and Cd which are known as highly carcinogenic and possible to create human health problem being exposed to longer. For the study site, assessment was taken in order to find out PM10 and PM2.5 associated

carcinogenic metals (Cd, Cr and Ni) cancer risk factor through inhalation route. The calculation of excess cancer risk was determined by the formula [4].

ECR (inhalation) = ambient concentration of pollutant ($\mu g/m^3$) ×unit risk ($(\mu g/m^3)^{-1}$…… (3)

Table 2. Contamination categories of EF value

EF<2	Deficiency to minimal enrichment
EF=2-5	Moderate enrichment
EF=5-20	Significant enrichment
EF=20-40	Very high enrichment
EF>40	Extremely high enrichment

Table3. EF value in Mining and Non-Mining area

	Mining		**Non-Mining**	
	PM10	**PM2.5**	**PM10**	**PM2.5**
Pb	95.0	88.4	75.5	21.7
Ni	6.6	2.2	4.6	1.5
Cr	22.9	13.2	22.6	12.8
Fe	1.0	1.0	1.0	1.0
Cd	1840	1741	1462	1580
Cu	48.0	48.3	42.1	50.8
Zn	217	164	67	72
Mn	2.2	0.8	3.6	3.6

The unit risk factor for individual metals and information about types of carcinogenicity were taken from the database of USEPA for integrated risk information system. The value of cancer risk for unpolluted ambient air is set at $1x10^{-6}$ for being exposed to life time. In our study the cancer risk for individual metals were found exceeding to the limit.

Table 4. Excess Cancer Risk (ECR) assessment of carcinogenic metals in mining and non-mining area

Seasons	PM size	metals	Concentration µg/m^3	Inhalation unit risk (µg/m$^{3)-1}$	ECR ×10^{-6}
Mining	PM_{10}	Ni	0.07	$1.2x10^{-2}$	794
		Cd	0.04	$2.4x10^{-4}$	9
		Cr	0.39	$1.8x10^{-3}$	710
	$PM_{2.5}$	Ni	0.02	$1.2x10^{-2}$	191
		Cd	0.03	$2.4x10^{-4}$	7.2
		Cr	0.16	$1.8x10^{-3}$	297
Non-Mining	PM_{10}	Ni	0.075	$1.2x10^{-2}$	899
		Cd	0.038	$2.4x10^{-4}$	9
		Cr	0.317	$1.8x10^{-3}$	571
	$PM_{2.5}$	Ni	0.018	$1.2x10^{-2}$	210
		Cd	0.025	$2.4x10^{-4}$	5.9
		Cr	0.128	$1.8x10^{-3}$	230

CONCLUSION:

In the present study, PM_{10} and $PM_{2.5}$ has been characterized for mining and non-mining areas in term of metal concentrations along with its excess cancer risk for human health. The concentrations of metals were found higher in respirable fraction of particles while enrichment factor results indicate anthropogenic origin for Pb, Cd, Cu and Zn. In the risk assessment study fine particles are more susceptible for cancer because it possess greater percentage of carcinogenic metals (Ni, Cd, Cr) while comparative analysis between mining and non-mining risk values. The concentrations of Ni in non- mining areas of both fraction (PM10 and PM2.5) were higher than mining areas. The finding ofthis research may provide a database to createsuitable plan for important mitigative measures for this area.

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BIODEGRADATION OF CHLORINATED HYDROCARBONS AND PESTICIDES, POTENTIAL HEALTH RISKS

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ABSTRACT:

Chlorinated hydrocarbons can be a major source of pollution in groundwater as well as soil. Many people are exposed to these chemicals on daily basis, accidentally or professionally in the laboratory. Organo-chloro pesticides are widely used in our agriculture, especially to save the crops from insect pests. Their presence in ground water or soil can create a hazard to public health and the environment. One of the most common sources for Chlorinated hydrocarbon contamination of soil and groundwater are industrial effluents. In this review, we report about the Chlorinated hydrocarbons and pesticides contaminant, their characteristics and uses, risk to human and environment and removal of the contaminants through bioremediation from the contaminated site.

KEYWORDS: Biodedgradation; Chlorinated Hydrocarbons; Organochloro Pesticides; Enzymes for Bioremediation

INTRODUCTION:

Chlorinated hydrocarbons are organic molecules characterized by the presence of at least one chlorine atom bound to a carbon atom. Numerous companies manufacture or work with

these molecules, also known as chlorocarbons or organochlorides. Chlorinated hydrocarbons are widely used in many industries as a solvent [1]. Ground water pollution or soil contamination is mainly caused by the presence of xenobiotic (man-made) chemicals which comes from application of pesticides, dumping of oil, discharges of industrial and municipal wastes, leachates from landfills, rupture of underground tanks or oil pipeline. Large volumes of chlorinated aliphatic and aromatic hydrocarbons are produced each year for a variety of domestic and commercial purposes [2, 3]. It is also used in laboratory environment. Sediments beneath some industrial sites contain chlorinated hydrocarbons in excess of 1,000 mg/liter [4]. Polychlorinated hydrocarbons such as Trichloroethylene (TCE), Perchloroethylene (PCE) and Trichloroethane are the common contaminants of ground water, both in United States and in developing countries like India and China. The contamination of drinking water supply with TCE is increasing in concentration [5]. A large amount of chloro-compounds enter the soil, ultimately reach into water body and to make the soil and water environment worse. The chlorinated hydrocarbons have potentiality to affect central nervous system. They also cause greater liver and kidney damage compared to other organic solvents. In some cases, these problems may not be readily apparent. As for example, the pesticide DDT, is made with chlorinated hydrocarbons, and while it initially appeared safe to use, scientists later realized that it endangered bird populations by weakening the shells of eggs, making it less likely for embryos to survive to hatching. Chlorpyriphos is an organo-chloro-phosphorus insecticide having broad spectrum property. Organo-chloro-phosphorus compounds are extremely toxic in animal systems such as human. They significantly inhibit the enzyme acetylcholinesterase in synapses of the central nervous system, resulting loss of nerve function [6], affect cardiovascular and respiratory systems [7].

The wide use and discharge of TCE or chloroform, a volatile chloro-hydrocarbon from chemical industry, led to major water pollution in rural areas. In the compounds list, chloroform rank in top few places of US Environmental protection Agency (EPA) and Chinese Environmental Monitoring and Control Priority Pollutants [8]. For these reasons, interest in the microbial biodegradation of chlorinated hydrocarbon has intensified in recent years as humanity strives to find ways to clean up contaminated environments. Bioremediation is one of the eco-friendly means of degrading toxic compounds. Therefore, extensive efforts have been made to study the biodegradation of TCE, Chloroform and other chlorinated pesticides by bacteria. Many

chlorinated organic compounds persists to environmental microbial attack. But sometimes co-metabolism phenomenon has been found where a bacterium can degrade more than one pollutant together [9]. The discharges of toxic effluents from various industrial sources are given in Table 1.

Table 1. Some contaminants potentially suitable for bioremediation:

Class of contaminants	*Specific examples*	*Potential sources*
Chlorinated solvents	Trichloroethylene	Dry cleaners, metal degreasing
Perchloroethylene	Chemical manufacture	
Polychlorinated biphenyls	4-Chlorobiphenyl	Electrical manufacturing
4,4-Dichlorobiphenyl	Power station	
Railway yards		
Chlorinated phenol	Pentachlorophenol	Timber treatment, Landfills

DIFFERENT TYPES OF CHLORINATED HYDROCARBONS:

1. Chloroform:

Chloroform is a colourless, liquid which is most well known compound for its historical used as an anaesthetic agent. It can easily be carried in water, and when it is exposed to oxygen and sunlight, a chemical reaction forms phosgene, a toxic gas. If chloroform is exposed outdoors, the phosgene will break down and ultimately become harmless, but in enclosed spaces, it can be highly poisonous. Usage of modern manufacturing processes, phosgene had a historical use as a deadly chemical weapon in both World War I. In groundwater, chloroform can persist and takes a long time to break down, because it is not readily water-soluble. Today, chloroform is used in a variety of industries including chemical industry. It is also used as a solvent and refrigerant. It is produced by reacting chlorine with ethanol. While relatively stable, it is also toxic and should be handled with care. Excessive exposure to chloroform can cause long term health damage to several major organs.

Chloroform may be released into the environment from its use, production and transport. It is also indirectly formed as a result of the reaction of chlorine with organic compounds [10].

Processes known to contribute to the indirect formation and emission of chloroform include paper bleaching with chlorine and chlorination of municipal water, swimming pools and waste water [11]. Under certain conditions some bacteria can dehalogenate carbon tetrachloride to release chloroform. The majority of chloroform that enters the environment will eventually enter the atmosphere, due to its volatility. The degradation of chloroform involves a reaction with hydroxyl radicals; the half-life for degradation is reported to be approximately 100 – 180 days. Chloroform is a by-product of chlorination of water and is therefore present in drinking water. The drinking water quality guideline for chloroform is 0.2 mg L^{-1} maximum [12].

Chloroform is metabolized in aerobic and anaerobic conditions by some microorganisms. Many aerobic bacteria are able to use chloroform as a sole carbon source and obtain their energy. Some anaerobic bacteria degrade it through reductive dechlorination pathway.

The effects of chloroform on the human body, in addition to induction of anaesthesia, include damage to the liver, kidney and heart. When chloroform touches bare skin, it becomes irritated and forms sores. Chronic exposure of chloroform causes pathological changes in liver, kidney, brain, heart and bone marrow. Respiratory system, exposed to chloroform, damages the lungs and respiratory tract.TCE and chloroform are toxic to the central nervous system, can cause a person to become unconsciousness and even be fatal at high doses. Due to the cytotoxicity of these compounds, their practical applications have been reduced. Chloroform is no longer used as an anaesthetic in operations to make the patient unconscious [13].

2. Trichloroethylene (TCE):

Trichloroethylene (TCE) is a halogenated aliphatic organic compound and widely used as solvent cleaning and metal degreaser. Other than textile cleaning and decaffeination of coffee, U.S. Environmental protection Agency has approved TCE as an alternative for chlorofluorocarbon 113 and methyl chloroform [14]. International Agency for Research on Cancer has classified that TCE is a potent mutagen as well as probable carcinogen. Animal studies also revealed that TCE causes hepatocarcinoma. A great quantity of Chloro-compounds entered into the water body through absorption by soil and made the water environment worse. The wide use and discharge of TCE and Chloroform, both volatile organic Chlorohydrocarbon from chemical industry, led to the major water pollution in industrial as well as rural areas.

It is a suspected carcinogen and is one of the most commonly detected volatile organic contaminant in soil and ground water. Indeed, TCE is considered to be a potentially serious threat to drinking water source. Like many other chlorinated hydrocarbons, trichloroethylene (TCE) has become an important environmental pollutant because of its toxic properties and its wide spread occurrence as a soil, air, and water contaminant.

3. Vinyl chloride (VC):

The largest application of organochloro compounds is in the production of vinyl chloride. The annual production in 1985 was around 13 billion kilograms, which was converted into polyvinyl chloride (PVC) to make water pipes, insulation and other materials. Likewise, chlorinated hydrocarbons are the raw materials for the production of pesticides, solvents and precursors to various industrial processes, coatings, polymers, and synthetic rubber products. Tobacco smoke also contains low levels of vinyl chloride. VC is formed by substances such as trichloroethane, trichloroethylene, and tetrachloroethylene are broken down. It is used to make polyvinyl chloride (PVC). Reductive dechlorination of TCE through natural or catalytic process may result in production of vinyl chloride (VC) which, in contrast to TCE, is a known carcinogen [15]. Drinking water may contain vinyl chloride that released from polyvinyl pipes. Many people are exposed to vinyl chloride in their workplace. Breathing of vinyl chloride for short periods of time may affect dizziness, sleepiness, unconsciousness, and high levels may lead to death. Inhalation of vinyl chloride for long term can cause liver damage, disorder of immune system, nerve damage. FDA administered the level of vinyl chloride in various plastic products. These include plastics that carry liquids and plastics that contact food. Vinyl chloride is recognized as a Group A human carcinogen by EPA.

4. Carbon tetrachloride:

Carbon tetrachloride is a synthetic compound that does not occur naturally. It is a clear liquid with a sweet smell. It is also called methane tetrachloride, perchloromethane, tetrachloromethane. It is most often found in the air as a gaseous compound. It does not dissolve in water very easily. It was used in the refrigerator, propellants for aerosol cans, and as a pesticide, and degreasing agent, in fire extinguishers, and in spot removers. It contaminates soil as well as water. Exposure to high amounts of carbon tetrachloride can damage the liver, kidney,

and nervous system and also cause cancer in animals. It has been found in at least 425 of the 1,662 National Priority List sites, with wide-spread occurrence as identified by the Environmental Protection Agency (EPA) [16]. Because of its harmful effects, these uses are now banned in industrial applications.

5. Chloromethanes:

Most low molecular weight chlorinated hydrocarbons such as chloroform, dichloromethane, dichloroethane and trichroethane are useful solvents. Like Trichloroethylene, Chloromethane and chloroethanes are widely used in metal degreasing and also for textile dry cleaning. Several billion kilograms of chlorinated methanes are produced annually, mainly by chlorination of methane:

$$CH_4 + x\ Cl_2 \rightarrow CH_{4-x}Cl_x + x\ HCl$$

The most important is dichloromethane, which is mainly used as a solvent. Chloromethane is a precursor to Chlorosilane.

6. Ethylene Dichloride:

It is recognized by several other terms, including chlorocarbon. This chlorinated solvent is absorbed by the soil, and then it migrates to groundwater and contaminates drinking water supplies. Exposure to low concentration of ethylene dichloride may cause breathing problem. Inhalation of ethylene dichloride vapour may affect the human nervous system, liver, and kidneys, leading to respiratory distress, cardiac arrhythmia, nausea, vomiting, sleepiness, fatigue, slurred speech, vertigo, disorientation, depression and other problems [3]. These are all contact poisons for human and animals. Due to their insolubility in water, they are not translocated within plants. They have high affinity to fat molecules, and are concentrated in fatty tissues of animals. In varying degrees, chlorinated hydrocarbons are absorbed from the gut and by the lung and skin as well. The chief acute toxic action of the chlorinated hydrocarbons is on the nervous system. It may causes neurological disorder including tremor and involuntary muscular movement, which is due to the prolonged recovery phase of the affected neuron. Interaction of chlorinated hydrocarbons with endocrine receptors, particularly estrogen and androgen receptors is very predominant. Animal model study showed that the function of the endocrine system may be altered by these interactions [17]. Beside these, it may leads to sore nose, sore throat, and

cough. Chronic exposure to chlorinated hydrocarbons cause toxicity including contact dermatitis, neurological problems (headaches, mood changes, loss of memory, difficulty concentrating, decreased attention span, and fatigue), liver damage and kidney damage (weakness, fatigue, polyuria, electrolyte abnormalities).

7. Chloropyrifos:

This is Organo-chloro-phosphorus compound, which is used as broad spectrum pesticides. It is most widely used in large group of insecticides, accounting for more than 36% of the total world market [18]. Among organo-phosphates, Chloro-organo-phosphates [O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate] has been on the market for over 40 years and today is one of the most widely used pest control products for significant crops in diverse countries. The insecticide CP is characterized as moderately persistent with a half-life in soil of 10-120 days, and it has very low solubility in water (2 mg/L). In soil, the degradation of CP can involve a combination of photolysis, chemical hydrolysis and microbial degradation. It is widely used in agriculture but is potentially toxic to humans being. Despite the recent regulatory decision of the United States to eliminate its residential use, CP continues to be widely used in agriculture in other regions of the world including Egypt, Germany, China, India, Bangladesh, Pakistan, and Iraq. CP acts by interfering with cholinesterase, an enzyme that is essential for the proper working of the nervous system of both humans and insects [19]. In general, CP can enter the human body through the skin (dermal exposure), mouth (oral exposure) and lungs (respiratory exposure). However, the transport of CP within the body depends on whether it is absorbed through the skin, lungs or gastrointestinal (GI) tract. CP absorbed through the GI tract, enters the blood stream and reaches the liver, the major site of pesticide metabolism, resulting in liver toxicity. Moreover, CP can also be accumulated in the body tissues, proteins, fats and bones for longer period of time causing additional health hazards [20].

8. Organochlorine Compounds:

CFCs and dichloro-diphenyl-trichloroethane (DDT) all contain chlorinated hydrocarbons. Another chemical class known as polychlorinated dibenzodioxins (PCDDs) are widely used in industries.

Many pesticides contain chlorine, for example DDT, dicofol, heptachlor, endosulfan, chlordane, aldrin, endrin, mirex, Chloropyriphos and pentachlorophenol. Many of these agents have been banned in various countries, e.g. mirex, aldrin, DDT [16]. These hydrophobic compounds accumulate in fat tissues or adipose tissues of animals. They also accumulate in aquatic food chains. Because the body is not able to break down or dispose of these chlorinated compounds which interfere with calcium metabolism in birds, there were severe declines in some predatory bird populations

BIOREMEDIATION:

Polychlorinated hydrocarbons are abundant in nature and they are released either from industries or human sources. Biodegradation a natural process where microorganisms such as bacteria and fungi degrade or convert toxic product to non-toxic compound (i.e. partially oxidized biologically inert compound). Many species of bacteria (*Pseudomonas, Bacillus* etc.), filamentous fungi, cyanobacteria lives in the soil environment and most of them can degrade environmental pollutant. Microorganisms are grown on chlorinated hydrocarbon and obtained nutrition from them, released metabolites into environment. They utilize hydrocarbons as energy source. The degradation is depends upon the biochemical pathway in which microorganism used.

Bioremediation is a most popular clean-up technology and widely used to degrade environmental pollutant. In this process, microorganisms such as bacteria convert toxic chemicals like Chlorinated hydrocarbon, benzene, toluene, polychlorinated biphenyls (PCBs), BTEX compound, and polyaromatic hydrocarbons (PAHs) into non-toxic ones. Naturally occurring microorganisms cannot degrade these compounds efficiently. This capacity has been improved by using genetically modified organisms (GMOs). The history of genetic engineering is strongly based on the bioremediation of oil spill site by *Pseudomonas putida*. In 1971, Prof. A. M Chakrabarty had found that some strains of the common *Pseudomonas* sp. contained plasmids carrying some genes which are responsible for degradation of various hydrocarbons. This was the first biological patent awarded by the US Patent authorities (1980).

The genes encoding the enzymes are located as an extra-chromosomal DNA of *Pseudomonas putida*. This extra-chromosomal DNA is mainly involved in toluene and xylene degradation. This plasmid contained tod operon and referred to as TOL plasmid. The

Pseudomonas putida containing Tol plasmid known as "superbug" that has the capacity to degrade crude oil 10–100 times faster rather than natural strains [21].

The strains can be improved through modification of enzyme specificity. Currently, the biosensor is used for chemical sensing and to reduce toxicity [22].

Bioremediation of Chlorinated hydrocarbons:

Chlorinated solvents are used in large amount for production of chemicals, and many industries like automotive, aerospace, electronic, textile industry and dry cleaning. They are common contaminants of soil and ground water. Chlorinated solvent accumulate on the sub-surface of soil and persist for decades and causes groundwater contamination. These are not degraded naturally, and may be life threaten to human as well as living organisms. The bioremediation process can also applicable to remove the chlorinated solvent. Because bioremediation is one of the eco-friendly means of degrading toxic chemicals compared to other methods, this is the preferred route.

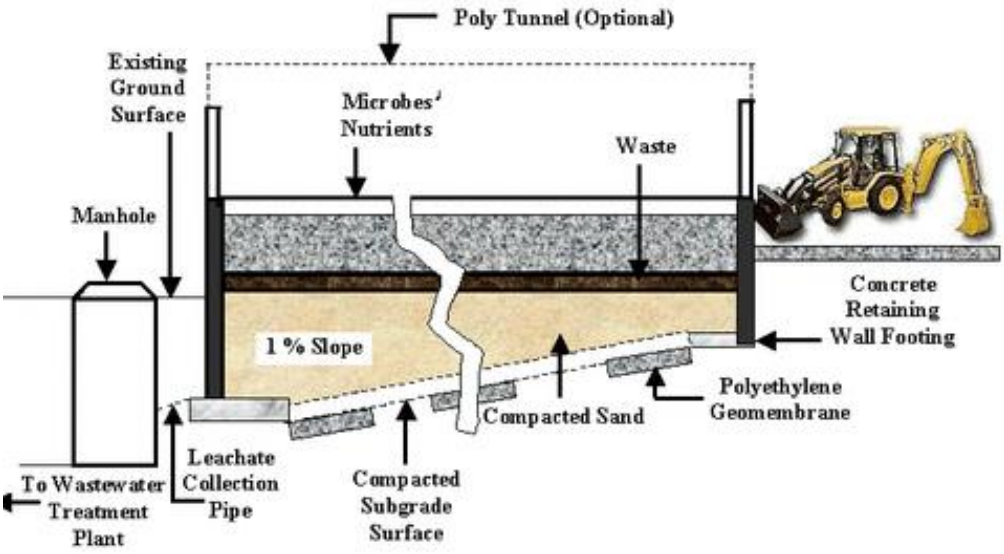


Figure 1: A typical Landfarming unit *(Ex situ bioremediation)*

Many of them are chronic toxins and some of them carcinogens (e.g., polynuclear aromatic hydrocarbons, TCE, vinyl chloride, arsenic). Some innovative technologies have been developed by some environmental protection agencies. Bioremediation involves two methods:

1. Removal of pollutants from a polluted site prior to treatment in another location *(Ex-situ).* This is a rapid technique. It has with minimum input of chemicals, energy, and time. This is

cheapest tool. It involves composting, landfarming and biopiles. Landfarming techniques are widely used from last few decades where large areas are needed but it is the cheapest form of bioremediation (Figure: 1).

2. Another treatment involves removal of pollutant from the environment where they are found *(In-situ).* Bioremediation can be speeded by augmenting natural systems with exogenous biological materials. But it is a time consuming method.

Bioaugmentation:

It is a process in which natural microorganisms or plants grown in large scale in bioreactors. It also involves use of genetically engineered microorganisms (GEMs) developed specifically for the purpose.

Biostimulation:

Biostimulation is a process which involves the modification of the environment to stimulate existing bacteria capable of bioremediation. Polychlorinated hydrocarbons are degredated in soil which can be limited by many factors, including nutrients, pH, temperature, moisture, oxygen, soil properties and contaminant presence [23-25]. This can be improve by adding various nutrients and electron acceptors, such as phosphorus, nitrogen, oxygen, or carbon. The bioremediation technique has developed by using biostimulation and bioaugmentation methods [26, 27]. Some abiotic factors may involve this process. This implicated natural microbial processes that occur without human intervention. Bioremediation depends on some factors as shown in figure 2.

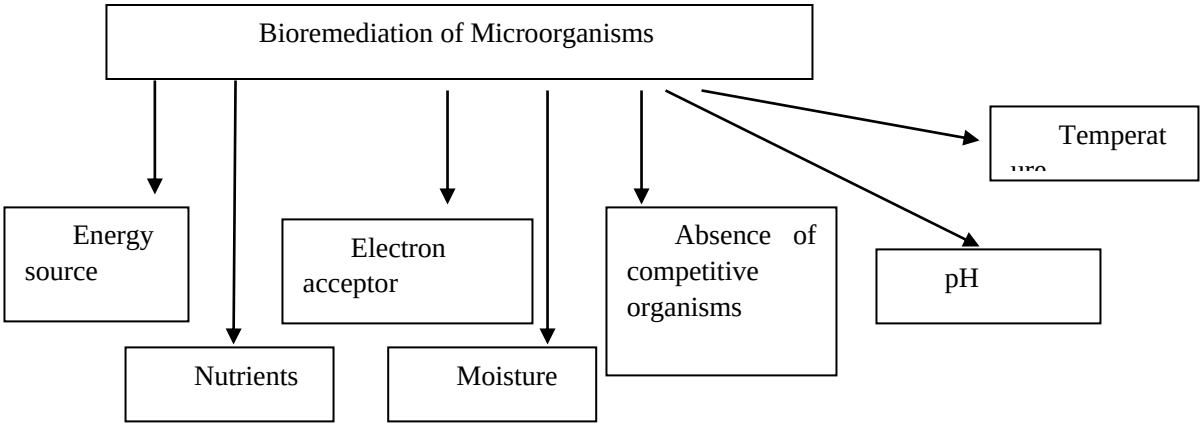


Figure 2: Factors affecting the bioremediation process.

Another innovative technology to treat various sites that have been contaminated with hazardous chemicals is Biofilm.

Biofilms have been shown to serve beneficial purposes in natural environments as well as in some engineered system. It is an accumulation of microbial cells and inorganic components held together in a polymeric matrix and firmly attached to a substratum. Accumulation of biofilms is encountered in many natural and modulated environments. It may be fundamental to process performance i.e., for fixed film biological waste soil treatment, sudden deteriotion of soil as well as water quality and deterioration of substrata.

Biochemical pathway for degradation of chlorinated hydrocarbons:

Microorganisms are capable of degrading pollutants by using a variety of reactions: dechlorination, hydrolysis, cleavage, oxidation, reduction, dehydrohalogenation, and substitution. Dechlorination is the most useful tool to eliminate the chlorinated hydrocarbons.

Dechlorination: — the chlorinated compound becomes an electron acceptor; in this process, a chlorine atom is removed and is replaced with a hydrogen atom.

Dehalococcoides sp. is the most versatile reductive dehalogenators, capable of dehalogenating the chlorinated dioxins, biphenyls, benzenes and vinyl chloride. Mostly anaerobic bacteria degrade the chlorinated hydrocarbons through anaerobic respiration, which results in dechlorination.These dehalorespiring bacterium eliminate chlorinated solvents from the contaminated environments which is suitable for their growth. Dehalorespiration occurs step-wise removal of chlorine atoms from the chlorinated solvent and produces a fully dechlorinated product, for example: trichloroethene (TCE) is converted through cis-1,2-dichloroethene (DCE) and vinyl chloride (VC) to ethene (Figure 2). Figure 3 describes the various anaerobic abiotic pathway that chlorinated aliphatic compounds may degrade from the environment.

Figure 3: Steps of Anaerobic transformation of TCE by dehalorespiring bacterium.

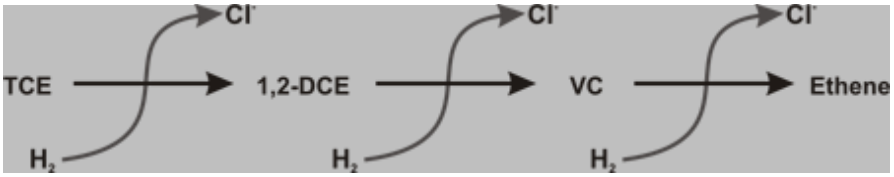
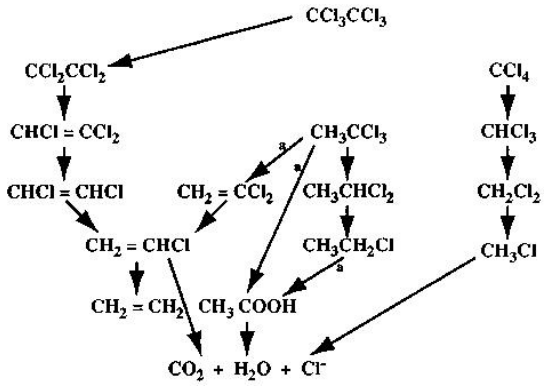


Figure 4: Abiotic (anaerobic) transformations of chlorinated aliphatic hydrocarbons



TOXICITY OF CHLORINATED HYDROCARBONS:

Water is essential for all forms of life and water pollution is a matter of great concern Chlorinated hydrocarbons have been recognized as global threat because of its adverse effects on human, through water contamination

Microbial populations for bioremediation processes*:*

Microorganisms can be isolated from any natural environmental conditions.

Table.2: List of microorganisms that degrade environmental pollutant

Microorganisms	Contaminants
Pseudomonas putida F1	TCE, Toluene
Pseudomonas mendocina KR1	TCE, PCE
Dechloromonas aromatica	Halogenated hydrocarbon
Enterobacter strain B-14	Chlorpyriphos
M. trichosporium OB3b	Chloroform
Pseudomonas sp.	Aldrin, DDT
Trichoderma viride 12	aldrin, endrin, DDT
Dehalococcoides sp.	Vinyl chloride
Burkholderia sp	Chloroform, TCE, Toluene
Methylobacterium extorquens DM4	Dichloromethane

Pseudomonas stutzeri KC	Tetrachloromethane

Microbes are easily adaptable and grow at subzero temperatures as well as extremely hot, desert conditions, in water, and in anaerobic conditions, in the presence of hazardous compounds or on any waste stream. The main requirements are an energy source and a carbon source. Because of the adaptability of microbes and other biological systems, these can be used to degrade or remediate environmental hazards. Many electron donors used as amendments for bioremediation can broadly stimulate many members of the indigenous microbial community, most of which do not have the ability to degrade or completely degrade the contaminants of concern. In the environment, the most significant populations of hydrocarbon and aromatic pollutant degrading microorganisms [27, 28] have been shown to be *Pseudomonas* sp. and methanogens. These microorganisms are shown in Table 2.

GENES AND ENZYMES INVOLVED IN BIODEGRADATION

Oxygenases:

a) Toluene mono and dioxygenase gene (tod gene):

TCE was found to be co-metabolized by some methane and ammonia-oxidizing bacterial species. Some other bacteria are also able to grow on hydrocarbons viz. methane [14] propane [29] and isoprene [30] as a sole carbon source. It was proved that oxygenation reaction by monooxygenase leads to the production of epoxide intermediates [31-33]. In the case of aromatic inducer substrates eg. phenol or initial mono or dioxygenases of the degradative pathways may be responsible for the aerobic TCE degradation. Several aromatic monooxygenase enzymes such as a toluene-4-monooxygenase in *Pseudomonas mendocine* KR-1 [33] are involved in TCE co-oxidation. Some genetically modified strains of *Pseudomonas* sp. (*P. cepacia* G4) have been identified to co-oxidize TCE. To our knowledge, only one aromatic dioxygenases system, the toluene dioxygenase in *Pseudomonas putida* F1 has been shown to be involved in TCE degradation. Toluene dioxygenase enzymes produces formic & glyoxylic acids after metabolism of TCE [9]. Tod operon of *Pseudomonas putida* F1 contains todA, todB, todC1 and todC2 genes (figure 5). The todC gene encodes the toluene dioxygenase enzyme, which was identified as class IIB multicomponent dioxygenase. It comprises the large subunit of the terminal dioxygenase (*todC1*), which is the most important gene for TCE oxidation [34]. Furthermore, Nelson and co-workers used a toluene dioxygenase (*todc1*) mutant strain that could not degrade

TCE in *P. putida* Fl. The oxygenases elicited to attack these substrates contain flavoprotein, heme iron, nonheme iron and as yet undefined prosthetic groups. Later it was reported that Pseudomonas putida (PpFl) degrades toluene through cis-toluene dihydrodiol to 3-methylcatechol. This compound is metabolized by using meta pathway for catechol degradation. Figure 4 shows the genes of tod operon that encodes valuable enzymes for the degradation of toluene. The order of genes in tod operon is: todF, todC1, todC2, todB, tod.A, todD, todE [27].

Table.3: List of different strains corresponded to their enzymes (mono-oxygenase enzymes)

Strain	Toluene mono-oxygenase isoform
Ralstonia pickettii PKO1	T3MO
Burkholderia cepacia G4	T2MO
Pseudomonas mendocina KR1	T4MO
Pseudomonas aeruginosa PAO1	T3MO

Later, Nelson and coworkers [45] and Wackett and Gibson [14] showed that toluene dioxygenase C1 plays a role in the degradation of TCE by using mutants of toluene-utilizing *Pseudomonas putida* Fl. This experiment was done in *Escherichia coli* strain JM109 (pDTG601).

Mammalian liver cytochrome P-450 monooxygenase is involves to detoxify the TCE. Toluene dioxygenase, methane monooxygenase and cytochrome P-450 monooxygenase all have broad substrate specificity. In light of the above observations, there have been extensive efforts to document the biodegradation of trichloroethylene by microbes.

Figure 5 illustrates the role of microorganisms in biodegradation process. Aerobic microbiota has been shown to degrade TCE [42]. Microbial growth on TCE as the sole carbon source has not been reported earlier, we were the pioneer in reporting the microorganisms 2479 and PM102 capable of growing on TCE as the sole carbon source [35, 36]. The bacterium, *Bacillus cereus* 2479 containing *tce1* gene which is the main candidate gene in TCE degradation [37, 38].

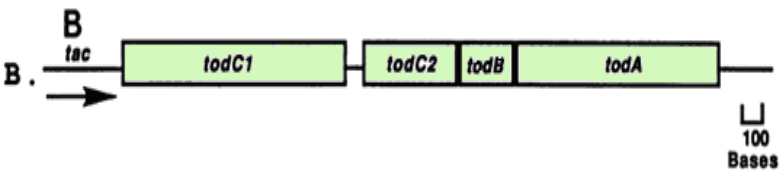


Figure : 5 Diagrammatic representation of recombinant clone pDTG601[34]..

Earlier report showed that three strains of bacteria, *Burkholderia cepacia strain G4, Pseudomonas putida Fl, and P. putida* B5 can catabolize TCE in the presence of toluene [33].

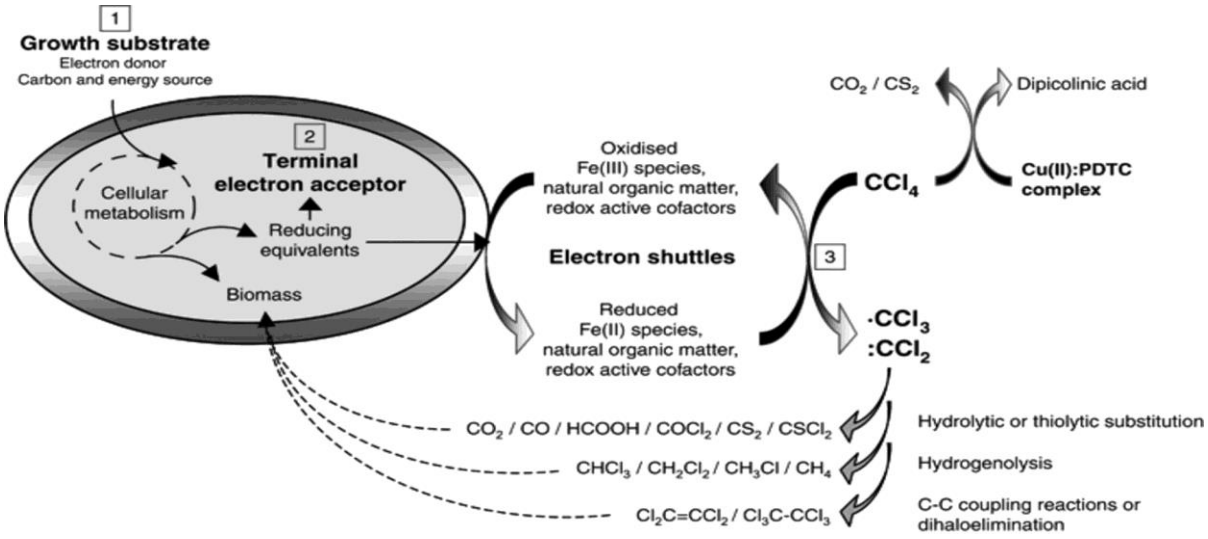


Figure 6 : Role of microorganisms in biodegradation process.

b) Methane Monooxygenase gene (mmo):

Many methanotrophs (methane-oxidizing) bacteria that can grow in aerobic conditions and reported to stimulated TCE degradation by the addition of methane [39-45]. Methane monooxygenase is a powerful oxidizer, thus giving it the capability of oxidizing a wide variety of normally recalcitrant compounds including TCE.

c) Tce1 gene:

Considerable information is available on the biochemistry and genetic regulation of toluene dioxygenase in P. putida Fl [17], making this organism the best choice for making inroads in discovering the molecular basis of bacterial TCE degradation.

Our novel isolate, *Bacillus cereus* strain 2479 was capable of degrading TCE efficiently [30]. The gene for TCE degradation was PCR amplified from genomic DNA of *Bacillus cereus* 2479.The amplified gene was cloned into expression vector pUC I8 in the *E. coli* host XL1-Blue and expressed under the control of lac promoter and nucleotide sequence was determined. The

sequencing results showed that this new gene (designated as *tce1*, GenBank Accession No: **GU183105**) contained 342 bp long ORF encoding 114 amino acids. The novel gene *tce1* showed homology to other known toluene dioxygenase gene on the basis of phylogenetic analysis. This was the first instance when *B. cereus* containing *todC1* gene can degrade TCE efficiently (37). The *tce1* carrying *E.coli* overproduces a polypeptide in the presence of the inducer Isopropyl-β-D-thiogalaocto-pyranoside which reacts immunologically to the antibodies against TCE inducible proteins of the strain 2479. *In silico* analysis showed that molecular weight of protein does not match with the experimental value. The molecular weight of the induced protein from pSM 101 containing *E. coli* was found to be 14.3 kDa. This discrepancy may be due to the expression of *tce1* gene sequence that was partial instead of the full-length coding region. The recombinant *E. coli* could degrade TCE efficiently was analyzed by Fujiwara test. From our study, it can be concluded that the compound, TCE was metabolized by the bacterium *B.* cereus strain 2479. The secondary structure of *TCE1* protein was predicted through internet resources with software, CLC Protein Workbench.

Prediction of local order structure and their sequence from the primary sequence information help to understand folding topology, folding classes and other structural insights. Our analysis of secondary structural properties of the protein provides insightful observation in that the protein predominately composed of alpha-type structure with very little amount of other structures. In this context it was showed that the protein belong in the family dioxygenase whose hydroxylase component was shown to be oligomeric protein constituted either by alpha-type or alpha and beta-type structures.

The present study suggested that cloned gene product (*TCE1*) was capable of degrading TCE as verified chemically (37).

d) Tce 350 gene:

Stenotrophomonas maltophila isolate PM102 in the author's lab was characterized and TCE degrading genes were amplified using the same primers for todC1 gene of *Pseudomonas putida*. This strain was isolated from the soil of industrial belt lining Asansol and Dhanbad, India where the use of TCE is abundant. The author has reported for the first time the TCE degrading ability in *Stenotrophomonas* group of bacteria that could grow on TCE as the sole carbon source. The biotransformation products were analysed by FTIR-spectroscopy [47]. Novel TCE

degrading genes were isolated from strain PM102, cloned into *EcoR*1 site of pGEMT-Easy vector and expressed in *E.coli* DH5α. Two PCR products were obtained with the *todC1* primers using S.maltophila genomic DNA as template of lengths 300 bp. and 350 bp. (GenBank Acc. nos. JX910450 and JX910451). *Tce350* proved to be functional whereas tce300 did not express any protein. 80% homology was seen between tce350 and tce300 sequences showing that the same gene was duplicated with some deletion in coding sequence. The bacterium was also immobilised in calcium alginate to enhance the rate of TCE degradation. *Stenotrophomonas sp*. is widely associated with roots of many plants and thus hold great promise not only for bioremediation but also phytoremediation as far as field studies are concerned. Five TCE inducible proteins were detected, viz. 90.25, 51.61, 38.83, 35.14 and 20.47 kDa in the protein profile of the bacterium *Stenotrophomonas* PM102. Although many bands were seen in the immunoblot with the total antiserum, the preadsorbed antiserum reacted against a single 35.14 kDa band, confirming successful antibody subtraction. TCE induced proteins from the isolate were purified by immuno-affinity column chromatography and found to be homologous to proteins with metabolic activity having oxidoreductase like function by MALDI-TOF-MS. Benzene was found to enhance TCE degradation. The bacterium was found to degrade TCE via epoxide formation [47] from FT-IR studies with TCE metabolic products.

b) Organophosphorus hydrolase (OPH)

Organophosphorus hydrolase (OPH), an important enzyme isolated from bacteria helps in degradation of insecticides and pesticides. *Pseudomonas diminuta* MG and *Flavobacterium* sp. Strain ATCC 27551, exhibited potent hydrolysing property in breakdown of many insecticides [6]. Hydrolysis of organo-phosphorous compounds by OPH enzyme significantly lowers organo-phosphorous compound toxicity [48]. The enzyme exhibited broad spectrum specificity towards the organophosphorus insecticides containing a P-O bond such as chlorpyrifos, parathion and methyl parathion, as well as the organophosphates jointed by a P-S bond such as methamidophos and malathion [49].

ADVANTAGES OF BIOREMEDIATION:

1) Bioremediation is a natural process and is easily adaptable for public and popular waste treatment process for contaminated materials such as soil. Microbes able to degrade the contaminant increase in number when the contaminant is present; when the contaminant

is degraded, the biodegradative microbial population declines. The residues after the treatment are usually harmless products and include carbon dioxide, water and cell biomass.

2) Many compounds that are legally considered to be hazardous can be transformed to harmless products. This eliminates the chance of future liability associated with treatment and disposal of contaminated material.
3) Instead of transferring contaminants from one environmental medium to another, for example, from land to water or air, the complete destruction of target pollutants is possible.
4) Bioremediation can be on site, often without causing a major disruption of normal activities. This also eliminates the need to transport quantities of waste off site and the potential threats to human health and the environment that can arise during transportation.
5) Bioremediation is less expensive method compared to other technologies.

CONCLUSION:

This review summarizes the chlorinated hydrocarbon contaminants, their characteristics and the means to remove them from the environment through bioremediation. According to the definition by the International Union of Pure and Applied Chemistry the term biodegradation is "Breakdown of a substance catalysed by enzymes in vitro or vivo." Bioremediation is a process that uses microorganisms, fungi, plants or their enzymes to return the natural environment polluted by contaminants to its original condition. It has great advantages over other conventional methods, as it is less expensive and microorganisms can be easily grown in normal laboratory condition or in nature. Mutation of any gene in non pathogenic strain of the degrading microbes may lead to increased degradation potential. Degradation rate can also be enhanced by using co-metabolic activity of bacterium from contaminated site. Many genes are responsible for degradation of environmental contaminants viz. toluene, TCE, chlorobenzene acids, xylene and other chlorinated toxic compounds but every compound needs one separate plasmid. One single plasmid is not able to degrade all the toxic compounds of different groups. It is finally concluded that genetically modified strain of bacterium, which is environmentally safe, is more powerful tool for bioremediation than natural organism.

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ENVIRONMENT, BIODIVERSITY CONSERVATION AND MANAGEMENT

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ABSTRACT:

Earth is known to be the only living planet due to the life it supports. Since the human species first became fully conscious of the natural world nature has usually seemed unassessable and abundant with plant and animal life, from mountains, to oceans, to plateaus and grasslands over the course of the twentieth century, however, this view has changed. Man's power over nature, assisted by machines has grown, and human population has increased exponentially. For centuries, nature has been in retreat in face of human settlement, but in the last 50 years, destruction of the natural world has picked up seed as never before. So the purpose of this paper is to aware about biodiversity conservation, understand the threats to biodiversity and to know the ways of conservation and management of biodiversity, another purpose of this paper is also to develop awareness about issues and sustainable development of environment. There is need of concrit work to save environmental.

KEYWORDS: Environment; Biodiversity; Conservation; Management.

INTRODUCTION:

Nowadays there are so many environmental issues. Because of that every one's life is in danger. For getting solution we have to know what is environment?, Biodiversity, need of

conservation of biodiversity and how can we manage safe, clean and sustainable environment. The answer is so simple "Think Globally and ACT Locally".

Because of environmental degradation biodiversity is in danger zone. Environmental degradation is an umbrella concept which covers a variety of issues including: pollution, biodiversity loss and animal extinction, deforestation and desertification, global warming and a lot more. Now its our/current generationsresponsibility to controlenvironmental degradation and save environment. For this purpose author tried a little bit awareness through this paper.

OBJECTIVES OF THE RESEARCH PAPER:

1) To study the concept of biodiversity, value of biodiversity.
2) To study the concept of conservation of biodiversity.
3) To study the management of biodiversity conservation.

SCOPE AND IMPORTANCE OF THE PAPER:

1) Present paper is important for all students and Teachers at primary, secondary, higher secondary and college level.
2) Present paper is important for all human beings.
3) Present paper is limited for the content environment & biodiversity conservation and management.

RESEARCH METHODOLOGY:

For present research paper author used document analysis method.

DATA ANALYSIS & INTERPRETATION:

Biodiversity is refereed to the vast range of life forms, from simple, microscopic, unicellular to the evolved, complex and multi-cellular forms on earth. These include all the living organisrons i.e. millions of plants, animals and micro-organisms. The biodiversity is broadly described in three levels.

1) Genetic diversity –

This is the diversity represented in the organisms in the basic hereditary information units "Genes" within a species, which are passed down to generations. Genetic diversity results in

variations. This diversity gives rise to different 'varieties' of rice or other crops. A large number of varieties in the species can be seen or sensed by colour, taste, flavour but most are invisible such as disease resistance, behavioural patterns. Genetic diversity is important in breeding crops and livestock.

2) Species diversity –

Species is genetically isolated unit of organism which is used to classify millions of different plant and animal forms on earth. As each species is distinct from other species in form and character such as cow and goat. Only similar species can produce fertile offspring.

3) Ecosystem diversity –

'Ecosystem' concept includes living organisms (plants, animals, micro-organisms) and non-living things (air, soil, water, minerals etc.) in a given area, with exchange of material and interaction between them. Ecosystem diversity is therefore the diversity of 'habitals'. Habitat is a place or site where an organism or a population of organisms naturally occur.

Indian Biogeography can broadly be divided into seven prominent regions. Due to bio geographicaldiversity of habitats India represents one of the rich biodiversity. So it is valuable.

Value of Biodiversity:

1) Consumptive Value -

Provides for human needs today and is essential for human survival in the future.

2) Productive Value -

Biodiversity provides the necessary raw material for domestic and industrial use which supports human civilization.

3) Social Value -

A large population depends on local biodiversity for their daily needs and survival. The traditional communities, tribal and local coexist with nature and their cultural richness is a reflection of the biodiversity with which they coexist.

4) Ethical Value –

In the traditional oriental culture, practices and rituals lot of importance is attributed to the ethical value of biodiversity. It is believed that each species is a unique creation of nature and has every right to exist and is to be respected.

5) Aesthetic Value -

Each species and ecosystem adds to this richness of beauty of life on the earth. Once a species is extinct or the ecosystem damaged beyond repairs, it is gone for ever and is impossible to be recreated.

6) Option Value -

Much of the biodiversity is being lost even before knowing its importance to human life, a day is not far when we will realise that we have reduced most of the natural options for food, medicine, row materials etc. This created serious conditions for the future generations who will not be left with many options to cope up with their own new demands for survival and development with the degraded and limited biodiversity.

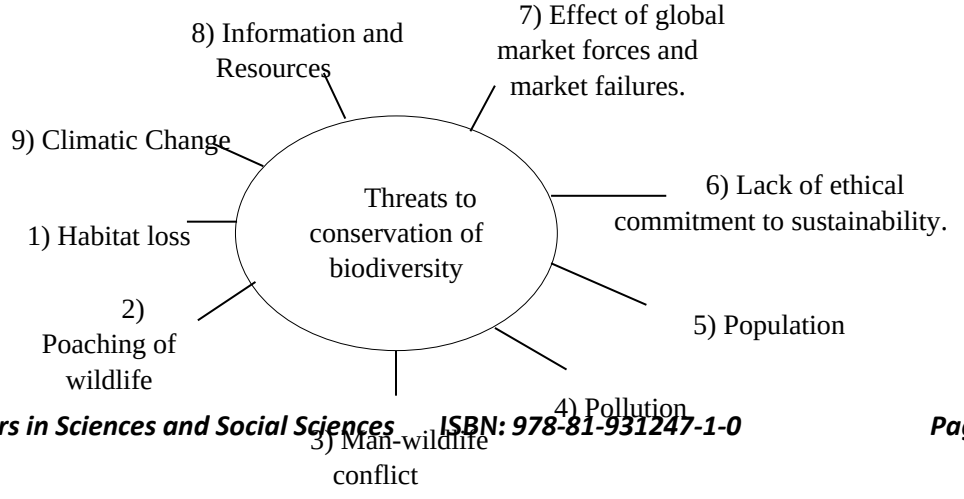
INDIA AS A MEGA DIVERSITY NATION:

India has rich heritage of species and genetic strains of flora and fauna. Out of the 18 biodiversity hot spots in the, world, India has two, the 'Western Ghats' and the 'North Eastern Himalayas'.

Conservation –

The Protection, Preservation, management, or restoration of wild life and natural resources such as forests and water.

Threats to Conservation of biodiversity:



There are different views and priorities about conservation of biodiversity.

Some feel it should be conserved as a matter of principle, others feel it should be protected as a matter of survival, while some feel it should be as a matter of economic benefit.

Management of Biodiversity Conservation:

To conserve biological diversity and ensure sustainable development, the following environmental management aspects are implemented.

1) Conservation of the wild strains of plants.
2) It the ecosystems and the diversity is lost there is emigration of tribal and rural who have lost future and create pressure on the cities. So we have to save or conserve to it.
3) The view has been adopted by the United Nations in the world charter for Nature in 1982.
4) Tourism is one of the largest and fastest growing industries in the world, where nature tourism plays significant role. It provides job opportunities and livelihood to the locals in a number of ways. For this it's our duty to conserve nature.
5) To complete new generation's demands there is no option to save biodiversity. We must have to do it.
6) Need immediate attention for nature conservation.
7) Surface disturbance, rehabilitation and afforestation.
8) Noise monitoring.
9) Solid waste management.
10) Wildlife population studies.
11) Chemical discharge monitoring (waste water, trace elements, gases)
12) Gravity and seismicity studies.

INTERPRETATION:

From above discussion its time need that conservation of the biological diversity, sustainable use of its components, a fair and equitable sharing of its benefits.

CONCLUSIONS:

Conclusions from objectives are:

1) The damage that we cause to the e environment is currently not counted as a cost in economic and social terms.
2) The lack of 'environmental value' has allowed us to over-exploit 'free' natural resources which are of course, not free.
3) We have to change this paradigm of our interaction with the environment.
4) The nature doesn't owe us anything. It is not there for us to 'control' and 'manage' it either.
5) We were born to live in harmony with it indeed, we are a big part of it. And we certainly don't have the right to exploit and destroy it without thinking about the future generations of humans and animals who will be here after us.

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ARBUSCULAR MYCORRHIZAE - A POTENTIAL BIOFERTILIZER

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INTRODUCTION:

Phosphorus is one of the most vital nutrients required in optimum amounts for proper growth of plants. About 98% of Indian soils have inadequate supply of available phosphorus (Gosh & Hassan, 1977). Moreover, due to chemical fixation of phosphatic fertilizers in soil, the efficiency of plants in utilization of phosphorus is of the order 10-15% only (Gaur, 1982).Super phosphate is in short supply and with the diminishing reserves of high quality raw material there is a need to develop sustainable agriculture which requires low fertilizer inputs. Thus depleting natural resources, poor soil fertility, expensive chemical fertilizers and chemical fixation of phosphorus are some of the problems in the present agricultural system. Also indiscriminate use of agrochemicals results in environmental pollution. In this scenario new strategies has to be explored to increase production, as agriculture has greater potential for food security, environmental sustainability and economic opportunity. Sustainable agriculture is an alternative for solving fundamental and applied issues related to food production. Agriculture is sustainable when it is, economically viable, ecologically sound, and based on a holistic scientific approach. As sustaining farming system minimizes the chemical fertilizer there is an urgent need to develop sustainable agriculture that requires low fertilizer inputs. Balanced microbial system contributes sustainability in agriculture and horticulture.

At this juncture, biofertilizers, low cost renewable sources of nutrients that supplement chemical fertilizers, can be utilized to harvest the naturally available biological system of

nutrient mobilization. Biofertilizers , a part of Integrated Nutrient management with growth promoting activities play a crucial role in sustainable global agriculture. Biofertilizers , live preparations containing the latent cells of efficient strains of microbes can be used to accelerate the microbial process to increase the availability of the nutrients that can be assimilated by plants easily. Selected strains of beneficial soil microbes are placed in a suitable carrier and can be used for seed treatment or soil application.

Benefits of Biofertilizers

A. Plays a pivotal role in accelerating beneficial microbial flora in the soil
B. Increases crop yield. Improves the productivity per unit area by consuming only lesser amount of energy
C. Maintains the natural habitat of the soil . Also the soil environment is made congenial for the beneficial microflora, responsible for continuous availability of nutrients from natural resources
D. Converts complex organic material into simple compounds
E. Cost effective to chemical fertilizer. Reliance on chemical fertilizer is not viable because of the cost, both in domestic resources and foreign exchange
F. Improves soil fertility and sustainability
G. Ecofriendly as it is in synergism with nature

Thus biofertilizers can be regarded as a a potential and a promising alternative to chemical fertilizers as they are economical and ecofriendly. Among the biofertilizers *Arbuscular mycorrhiza* (AM), a type of plant-fungal endosymbiosis, is the most ubiquitous underground symbioses on earth. These mutualistic soil fungi are present round the globe and play a crucial role in phosphorus cycling. As these fungi are endowed with the property of mobilizing phosphorus resulting in more efficient use of phosphate fertilizer, these are regarded as a crucial biofertilizer that replaces the chemical fertilizer at least partially. The potential for using AM in agriculture to improve the efficiency of utilization of phosphate from soils and fertilizers has become a major topic in recent research. Their impact in tropical agriculture will be greater than that in temperate regions because, in the tropics, phosphate deficient, phosphate fixing soils are widespread, superphosphate is in short supply and the year round temperature enhance microbial activity (Mikola, 1980) . Also the contribution of this symbiosis to the reduction of fertilizer

requirement is of increasing interest, because of the known world reserves of phosphorus could be depleted in a few decades

***Arbuscular mycorrhiza*:**

*Arbuscular mycorrhiza*l fungi(AMF) , a group of root obligate biotrophs, belonging to phylum Glomeromycota (Schubler et al,2001) colonize the roots of almost all agricultural, and horticultural crops and play an economical and ecological role. The wide range of potential hosts of AM fungi had been responsible for the well worn statement that it is easier to name families and genera which do not form AM than those which do (Gerdemann,1968). These fungi are widely distributed and geographically ubiquitous "The study of plants without their mycorrhizas is the study of artefacts; the majority of plants, strictly speaking, do not have roots—they have mycorrhizas" is the statement of European Bank of Glomeromycota committee (1993). They are considered as natural biofertilizers, since they provide the host with water, nutrient and pathogen protection , in exchange for photosynthetic products (Andrea berruti et al.2016).

The response of inoculation depends on the degree of the mycotrophy of the crop, the activity of indigenous mycorrhizal fungi, the nutrient status of the soil and the effectiveness of the introduced strain. The beneficial aspects of AMF on number of agricultural and horticultural crops are reported from various quarters. Working on mycorrhizas since 33 years and isolated and identified more than 14 species (Ammani, Ph.D thesis). Positive effects of these AMF has been reported on grasses (Ammani1994), cereals and millets (Ammani 1991) in general and rice in particular (Ammani et al., 1985, 1996). Besides crop productivity AM symbiosis has a promising and positive effect on the quality of crop also. These microbes contribute to plant functioning in natural environment, agriculture and reclamation.

The extra matrical mycelium can acquire nutrients from soil volumes that are inaccessible to roots (Smith etal.,2000). This is the greatest advantage as the external mycelium extends the penetration zone of the root fungus system into the soil, thus facilitating an increased efficiency of water and nutrient uptake. The inter connected network of external hyphae , which is extremely variable in structure and density, depending on the specific mycorrhizal fungus, host and soil act as an additional catchment and absorbing surface in the soil beyond the depletion zone that is otherwise inaccessible to plant roots. Further the fungal hyphae are much thinner than the roots and are therefore able to penetrate smaller pores (Allen, 2011). Besides these

direct nutritional advantages, the mycorrhizal fungi increases resistance to disease, drought and salinity (Levy & Kriken, 1980, Auge et al,2015 Pozo & Azcon_Aguilar,2007)

Structure & Diversity of *Arbuscular mycorrhiza*e

The Arbuscular *mycorrhizae* are characterized by the internal colonization of the root without any change in the root morphology. Only in some plants such as onion, tomato, maize or as in some Liliaceae members, the light yellow colour on the freshly harvested roots indicates AM infection. In some cases granular milky appearance in the cortex of transparent young roots also indicates the mycorrhizal infection.

The characteristic structures produced by AM fungi include:

1. External Hyphae:

An external hyphal system with extrametrical mycelium and external vesicles are spores scattered in the surrounding soil (fig 1) The mycelium is dimorphic (Nicolson, 1959; Mosse ,1959), non septate with characteristic, one sided angular projections(Butler 1939) on the main hypha. The amount of external mycelium has been estimated as 80cm per root length in onions (Sanders and Tinker, 1973) and 5% of root weight of heavily infected apple roots (Mosse, 1956). The development and spread of external hyphae thus depend upon the type of soil, plant and fungi

2. Internal Hyphae:

An internal hyphal system is connected to the external network of hyphae through the entry points. The thick walled external hypae on contact with the root surface, swells apically and forms more or less appressorium like structure or the infecting branch may directly penetrate the root hair (fig.3) and may spread intercellularly from the entry point without damaging the integrity of the cells.

3. Arbuscules:

These are intracellular branched dichotomous tree like structures (Fig.3). All the Glomalean fungal species form arbuscules which are, hyphal filled, invaginations of cortical cells that provide intimate contact between the plasmalemma of two symbiotic partners and is the preferential site for fungus plant metabolite exchange (Cox and Sanders, 1974; Cox et al.,1975). Arbuscules are short lived and they remain structurally and functionally intact for a period of 4-15 days (Bevege and Bowen, 1975; cox and Tinker,1976). The presence of arbuscules is a sine qua non to identify a AM infection in root(Bon fonte-Fasolo,1984) and all the genera of

Glomalean fungi form arbuscules. However they are the most labile part of AM infection, strongly dependent on host metabolism and influenced by nutrient supply (Mosse,1973), light (Hayman, 1974) stage of host development (Sutton,1973; Saif and Khan, 1974) and other factors affecting the host

Figure 1 to 7: Characteristic structures produced by AM fungi

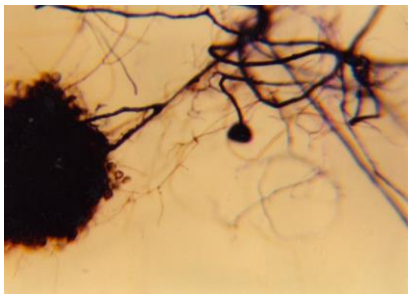
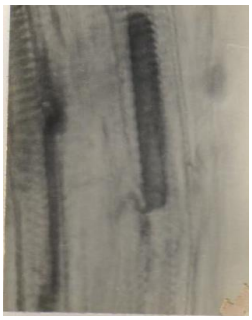


Fig. 1



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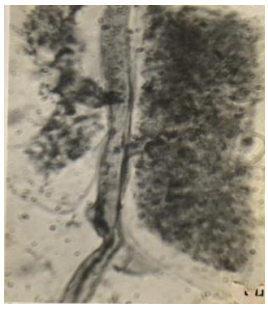

Fig. 3

Fig. 4

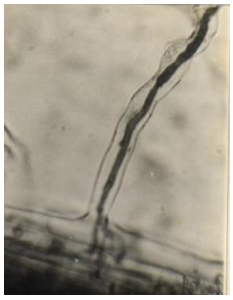

Fig. 5

Fig. 6

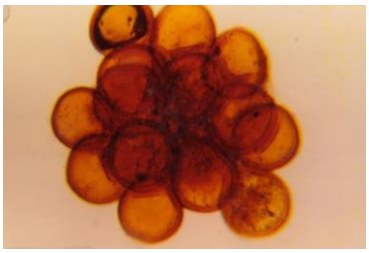

Fig. 7

4. Vesicles:

Vesicles are globose bodies that develop after the arbuscules as terminal or intercalary swellings in the root cortex. These are intercellular or intracellular and differ in their size, shape, number, content and wall structure according to the fungal species involved . In Gigaspora and Scuttellospora vesicles are not produced. Vesicles are spherical, oval, cylindrical to irregular (fig.6).

5. Spores & Sporocarps:

AM fungal spores are chlamydospores or azygospores and are formed singly are in clusters as sporocarps.(fig.7)The spores are variable in size, shape colour.and wall layers. The spore colour varies from hyaline to yellow, brown, orange , reddish brown and black. The spores are spherical, oval, ellipsoid, obovate, reniform, pea shaped or irregularly elongated. The spores may survive in the soil for several months are years. The spore size, colour of the spore, the stalk attachments and the spore ornamentation are some of the important criteria in identifying the spores. The cytoplasm in the spore may be vacuolated or reticulate.

The fungus grows throughout the cortex but it does not invade the endodermis, stele and meristematic region. . However the invasion of the vascular system was reporterd by Taber and Trappe (1982) in *Zingiber officinale.* Pennisetum americanum showed vesicles in the stelar region (fig. 2), a rather rare feature. (Ammani et al., 1990) Ours is the second report.

Ecological diversity of AM fungi:

The recent findings emphasize the ecosystem services of mycorrhiza in agriculture (Gianinazzi et al., 2010). Also they are ecologically important and are predominant in certain areas of broad ecological range. We reported the widespread occurrence of AM in our grasslands forming multiple mycorrhizal associations (Ammani et al.,1994). The amount of external and internal colonization varied and altogether 14 mycorrhizal fungi were identified. Also the development pattern was studied in two selected grass species (Ammani et al.,1994). The distribution of species of AM fungi is affected by climatic and edaphic conditions e.g. *Glomus* is found in acidic soil, *Gigaspora* and *Scutellospora* in tropical soils and *Acaulospora* favours the soil of pH below 5. However the author reported all the genera from our soils (Ammani Ph.D thesis).

Potential role of *Arbuscular mycorrhiza:*

Mycorrhizal fungi are now a days recognized as a natural plant health insurance (Gianinazzi and Gianinazzi – Pearson 1988). .Extensive and tremendous research and the commercial applications emphasizes the sustainable aspects of the use of mycorrhiza (Vosatka and Dodd 2002; Vosatka and Albrechtova 2009; Gianinazzi et al.2010).

Arbuscular mycorrhiza with three main components the root, the fungal mycelia outside and inside the root are mainly implicated in increasing the phosphorus scavenging ability of plants. However with the continuous and current advances in scientific knowledge on mycorrhizal research the multiple roles of mycorrhiza , in addition to the nutritional and non-nutritional effects are brought into lime light. Some of the benefits are discussed below:

1. Uptake of water and nutrients:.

AM fungi colonize plant roots and ramify into the surrounding bulk soil extending the root depletion zone around the root system which transports water and mineral nutrients from the soil to the plant. AM fungi improve the uptake of nutrients such as phosphorus, potassium, calcium, iron, magnesium and zinc. The nutritional aspect, both physiological and molecular have been studied extensively(Harrison et al.,2002; Paskowski et al.,2002; Nagy et al.,2005; Smith and Smith, 2011,2012). It has been elucidated that AMF significantly improve mineral nutrient acquisition , particularly phosphorus ,mainly in low nutrient condition and it has been c. learly established that plant possess a symbiotic Pi uptake pathway (Harrison et al.,2002, Paskowski et al.,2002, Nagy et al.,2005; Smith and Smith, 2011,2012). All The AM colonized plants possess Pi transporters that are specifically expressed in root cortical cells (Bucher 2007, Javot et al.,2007) providing markers for the AM pathway and evidence for the site of P delivery via fungal pathway and the transfer to the plants.

In addition to Pi and N, Sulfur can also be transferred through AM fungi (Allen and Shachar Hill, 2009, Sieh et al.,2013). The sulfur nutritional status of host plant is improved by affecting the expression of plant sulfate transporters (Caiseri et al.,2012, Giovannetti et al., 2014). A sulfate transporter (specifically involved in the uptake from the arbuscule) has been identified. AM fungi also improves the micronutrient concentration of the plants(Lehmann etal.,2014; Lehmann and Rillig,2015). Also iron and manganese nutrition has been observed in herbs.

2. Increased Nitrogen fixation:

The tripartite interaction between nodulating legumes, AM fungi and nitrogen fixing *Rhizobium* frequently result in increased level of nodulation and nitrogen fixation . This synergistic inoculation increases plant production as they promote the plant growth together. Inoculation of *Funnelliformis mossea* not only affected plant growth and nutrition *in Medicago sativa* but also enhanced the activity of *Rhizobium meliloti* (Azcon-Aguilar et al.,1979).

There are several reports also on the interaction between AM and free living nitrogen fixing bacteria. Bagyaraj and Menge (1978) studied the interaction between *Azotobacter chroococcum* and *Glomus fasciculatum* in tomato and reported a synergistic effect on plant growth. The population of *A.chroococcum* was maintained at high level for a longer time. At the same time *A.chroococcum* enhanced the spore production of the mycorrhizal fungus. The author reported triple inoculation of two nitrogen fixing bacteria and a AM fungus on two cereals in pot culture (Ammani, 2002). Triple inoculation with all the three microbes is better than dual or single inoculation for fungal development and plant growth. The compatible combination of microbes plays a crucial role in sustainable agriculture.

3. Soil aggregation and soil stability:

*Arbuscular mycorrhizal*fungi colonize the plant roots and the surrounding soil. The AM hyphae appeared to entangle microaggregates physically and secretes polysaccharides to which the microaggregates firmly adhere. AM hyphae stabilize aggregates of soil through three distinct processes (Miller and Jastrow, 1992)

1. AM hyphae physically entangle particles of the soil
2. Roots and AM hyphae create conditions that enable microaggregates to form in soil
3. Roots and AM hyphae lbind microaggregates and smaller macroaggregates into larger macroaggregates.

In soil under the plants, the macroaggregates are stabilized mainly by roots and AM hyphae (Tisdall and Oades,1982). Bethelenfalvay and Barea (1994) observed a 400% improvement in soil aggregation by inoculating G.mosseae in grey silt loam and 50% increase in yellow clay loam soil. Recently Wright and Upadhyaya (1998) reported that AM fungi produces a insoluble glue like glycoprotein named “Glomalin” in the soil that helps in the aggregate stability

4. Production of plant growth hormones:

The production of growth hormones by mycorrhizal fungi such as IAA ,gibberellin, cytokinin, auxin and growth regulators like Vitamin B have been well documented by many researchers .(Barea, and Azcon-Anguilar, 1982). Also Abscisic acid was found to be more in mycorrhizal plants to that of the non mycorrhizal plants (Danneberg et al.,1992)

5. Increased resistance to root pathogens:

The first attempt to study the interaction of a plant pathogen and AM fungus was by Safir (1968). Since then several reports accumulated to confirm the reduced disease severity. However there are contrasting reports also.. In wheat high levels of AM colonization did not protect the crop from the root pathogens (Ryan et al.,2002). Any way the effects of AMF on disease resistance are somewhat less well understood.

6. Alleviation of Environmental stress:

AM fungi plays a crucial role in alleviating environmental stress. Several researchers studied the influence of AM symbiosis on plant response to abiotic stress such as drought, salinity and flooding . However , the mechanisms responsible for the increased plant tolerance to stress has to be elucidated clearly

7. Reducing emissions of green house gases:

Very recently the influence of AM symbiosis on green house gas (GHG)has been recently investigated (Bender et al., 2014, Lazcano et al., 2014). These fungi could regulate N_2O emission, an important green house gas by enhancing plant N uptake and assimilation, which result in the reduction of soluble N in the soil and consequently denitrification (Bender et al., 2014). AM fungi could have an indirect influence on GHG emissions, and also change the physical conditions of the soil (aggregation, aeration and moisture) all of which influence the production and transport of GHG in soil. Bender et al (2014) demonstrated that AM Fungi could contribute to reducing enmissions of GHG, thus suggesting that they could play a role in the mitigation of climate change

8. Phytoremediation:

Contamination of heavy metals has become a major problem today. AM fungi are known to alleviate heavy metal toxicity in the host plant and also tolerates high metal concentrations in the soil (Lingua etal.,2008, Cornejo et al., 2013; Tamayo et al.,2014, Meier et al., 2015)

9. Rehabilitation and Reclamation of waste land:

Degraded soils are common targets of revegetation efforts in the tropics and the establishment of plant cover is the most important step. As AM fungi has the ability to overcome water stress, drought and nutrient deficiency inoculation with suitable fungi can be a promising tool in restoration and reclamation of waste lands (Pigott,1982).

Commercial inoculum production:

As AMF are obligate biotrophs they cannot be cultured in the lab like rhizobium. The most wide spread of AMF propagation is by using trap plants (pot cultivation) Several alternatives to the use of potted trap plants, such as soilless culture systems aeroponics and hydroponics that give pure clean spores are also available. In Delhi, The Energy and Resource Institute (TERI) has promoted the large scale production and commercialization of mycorrhizal inoculants. They developed mass i*nvitro* cultivation of a consortium of AMF in a semi-synthetic medium

CONCLUSION:

Population growth, soil degradation, increasing cost of fertilizer, indiscriminate use of fertilizers leading to environmental pollution is some of the challenges we are facing today. In this scenario, exploitation of existing soil resources with proper soil microbe management, particularly by using, AM, the biofertilizer is the need of the hour. At this juncture proper management of indigenous AM fungi is essential to exploit the multifarious effects of AM symbiosis. The tremendous progress in both basic and applied aspects in this area should be transferred from the lab to land. Also further research is needed in cultivating the mother inoculum in large scale in a cost effective manner.

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EFFECT OF COW URINE ON GERMINATION AND SEEDLING GROWTH OF SOME AGRICULTURAL CROPS

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ABSTRACT:

The experiment was conducted to study the effect of different concentrations of cow urine on agricultural crops. The experiment was laid out in the laboratory of Botany department, Vivekanand College, Kolhapur. The observations like germination percentage, average root length, average shoot length were recorded up to 30 days. Considering the different cow urine concentrations 0.5 % and 1% concentration were found more effective in these agricultural crops.

KEYWORDS: Cow urine; Seedlings Growth; Crops

INTRODUCTION:

In the past years, inorganic fertilizer was advocated for crop production to make low inherent fertility of soil. However, high cost and scarcity of inorganic fertilizer as well as possible cause of soil acidity and nutrient imbalance pose a constraint to use of inorganic fertilizer. Nutrient imbalance and soil physical degradation hinder sustainable use of inorganic fertilizers in the tropics. There are certain disadvantages of inorganic fertilizers such as Eutrophication, Increased acidity and Loss of Bacteria in Soil. Certain plants are hampered due to excessive dozes of the chemical fertilizers so that they also tend to cease growing and yield of fruits.

In order to sustain soil fertility for a long period of time the use of organic manure is been advocated. This is because the nutrients contained in organic manures are released more slowly and are stored for a longer time in the soil, thereby ensuring a long residual effect, also reported that manures provide a source of all necessary macro- and micro-nutrients in available forms, thereby improving the physical and biological properties of the soil. There are different types of organic manure including cow dung, compost, green and farm yard manure etc.

The cow urine not only used against ailments of diseases as therapeutic agents but also have several other uses as in agriculture and sericulture sectors. It produces best quality of grains, fruits, and vegetables by becoming the best type of manure. Cow urine is a divine medicines and is a pesticide for the crops.

Cow urine also shows a better result in increasing the yield of agricultural crops. Cow urine shows a better growth and increases yield in Paddy [13] and 6% of cow urine foliar spray shows a good result in Soybean [6]. In Floriculture crop Gladiolus shows increasing the growth, flowering and corm production [12]. Seeds can be treated with cow urine. This was found useful in rhizome of turmeric, ginger and sugarcane and they yielded more. Also helps in plant growth and immunity.

It has been experimentally shown that the urine of cow has got agricultural importance in term of control of insect and fungi . Cow urine is shown to control root knot nematodes in tomato [1] and melon aphids and pickle worms in water melon cultivation [3].Cow urine alone or in combination with plants is shown to inhibit a number of phytopathogenic bacteria and fungi [4],[5],[2],[9],[10],[11] and [8].

Application of different rates of cow dung to Okra led to significant increase in growth and yield over the control. Use of cow dung at the rate of 15 to 20 t ha-1 will significantly improve the performance of Okra comparable to use of inorganic fertilizer [7]. Along with combination of NPK and cow urine was found to be best for the growth and increase yield of Paddy [13].

MATERIALS AND METHODS:

Plant material : Cow urine were used in germination test of Soybean (*Glycine max* L. *)* Kidney bean (*Vigna unguiculata* L.), Mung (*Vigna radiata* L.) & Wheat (*Triticum aestivum* L.*)* seedling growth.

Preperation of Cow Urine Concentration :-

Fresh and clean Cow urine taken and filtered with Whatmann No.1 paper and prepare the different concentration like 0.5%, 1%, 2%, 3%,4%. The concentration was prepared with the help of distilled water. The prepared concentration of cow urine were stored and used for treating the seeds of Soybean, Kidney bean , Mung & Wheat.

Petri plate technique was followed for germination studies. Sterilized Whatmann No.1 filter paper was kept in the sterilized petriplates. Seeds were sterilized with 0.1% HgCl2, washed with distilled water for several times and then 10 seeds are kept for germination in petriplates. A control was maintained with distilled water. Germination percentage was calculated after 48 hrs.

RESULTS AND DISCUSSION:

The effect of Cow urine on germination percentage of these some agricultural crops is depicted in table 1.

Table 1. Effect of Cow urine on percentage of seed germination of Soybean , Kidney bean, Mung and Wheat

Crops	Concentration	Germination (%)
Soybean	D/W	50%
	0.5%	90%
	1%	80%
	2%	50%
	3%	50%
	4%	50%
Kidney bean	D/W	90%
	0.5%	100%
	1%	100%
	2%	100%
	3%	100%
	4%	100%

Mung	D/W	90%
	0.5%	100%
	1%	100%
	2%	100%
	3%	100%
	4%	100%
Wheat	D/W	100%
	0.5%	100%
	1%	90%
	2%	90%
	4%	80%
	5%	70%

The study revealed that 0.5 and 1 % concentration of cow urine shows highest germination percentage in all these agricultural crops. As compared to control the germination percentage is increases in all these crops.

The root and shoot length of these crops are presented in table 2.

Table 2. Effect of Cow urine on root and shoot growth (length) on Soybean, Kidney bean, Mung and Wheat at seedling stage

Crop	**Concentration**	**Average root length (cm.)**	**Average shoot length (cm.)**
Soybean	D/W	6.5	19.0
	0.5%	8.0	21.0
	1%	6.8	19.4
	2%	5.8	18.7
	3%	4.9	17.5
	4%	6.2	18.9

Kidney bean	D/W	4.0	18.0
	0.5%	4.5	15.5
	1%	6.0	20.5
	2%	3.8	16.0
	3%	8.3	21.3
	4%	9.2	22.5
Mung	D/W	4.0	16.5
	0.5 %	6.0	13.5
	1%	4.3	15.4
	2%	3.9	15.9
	3%	3.5	19.3
	4%	8.5	22.0
Wheat	D/W	7.6	6.6
	0.5 %	7.2	6.5
	1%	6.1	5.5
	2%	5.8	4.9
	3%	5.5	4.5
	4%	4.4	3.9

It is very interesting to note that the inhabitation is variable, not correlated with concentration. In Soybean and Wheat crops 0.5 % concentration of cow urine shows highest root and shoot length but at 3 % and 4% concentration shows lowest root and shoot length. But in other crops like Kidney bean and Mung 4 % concentration of cow urine shows highest root and shoot length but at 2 % concentration shows lowest root and shoot length.

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MEDICINAL IMPORTANCE OF SOME WEEDS FROM KHED TEHSIL, PUNE DISTRICT, MAHARASHTRA

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ABSTRACT:

The present study expresses an ethno-botanical research work to collect information on the use of some weeds for the treatments of various disorders by the tribes of Khed Tehsil, Pune District, Maharashtra. Tribes of this area have authentic information about to different medicinal plants. They have been using different plant parts like roots, stem bark, leaves, fruits and seeds in the form of juice, paste, decoction and in crude form. The indigenous knowledge of local traditional healers about the weeds used for medicinal purposes was collected by personal interviews during field visits. A field walk with the healers enabled plant collection and documentation relating to the remedial information of weeds used for the treatment of different diseases. In the present investigation, 33 weed species, belonging to 21 different families used by the tribals for the treatments of various disorders are documented.

KEY WORDS: disorder, decoction, ethno-botanical, healers.

INTRODUCTION:

In India, the main traditional systems of medicine include Ayurveda, Unani and Siddha. The traditional healers provide considerable information about the use of many plants or plant parts as medicine. Many of the life saving drugs in present day of allopathic system are obtained

from plant origin. The species which grow on their own, without human efforts can be termed as weeds. They are in general harmful to the crops and generally controlled from crop fields. Many of the weeds are found to be medicinally important. Such weeds can be controlled from crop fields and used for curing the diseases.

The present work deals medicinl importance of some weeds from Khed tehsil, Pune District of Maharashtra.

METHODOLOGY:

STUDY AREA:

Khed tehsil is situated in the Pune District and lies between Lat. 18^0 37' 1"- 19^0 17'4" N and Long.73^0 30' 51" –74^0 3' 5" E on the north –western part of Deccan plateau and is composed of undulating hilly country. It is bounded on the north by Ambegaon tehsil, on the south by Maval and Haveli tehsils and on the east by Shirur tehsil. The western boundary is formed by the range of Sahyadris. Bhimashankar, Vandra, Tambarvadi etc. are some of the areas covered by Sahyadris in the tehsil. The crest of the hills is about 1,060 metres in these areas forming rounded buffs and clear cut ridges while in other places like Khed town, Mahalunga, Alandi, etc., it falls down to 600 to 625 metres above mean sea level. The major hilly belt, the western ghats (known in these parts as Sahyadris) is the most important factor affecting the temperature, climate and consequently the vegetation of the area. From this main line, three major spurs of hills run obliquely eastwards sinking gradually in the plains of Deccan plateau, one running along the northern border of the tehsil comprising of the hills of Bhovargiri, Tokavda, Sherewadi, Bibi, etc., a second one along the southern border of the tehsil comprising of the hills of Bhangarwadi, Gadad, Koliya, Vahagaon, Siva etc., and in between these two a third one comprising of the hills of Shinga, Adgaon, Kondeshwar etc., The area studied possess a rich variety of flora and type of vegetation.

In Khed tehsil total villages are 98. The human population according to the 2001census approximate 3,43,214, and tribals population 38,272 percentage of total population to the tribal population 11.15 %. Tribals are found in large number in this region.

The present study has been conducted in two steps:

Step I- A survey was conducted among the tribal peoples of Khed tehsil to gather information on weed species used for treatment on different disorders as used by them.

Step II- An efforts have been made to collect the weeds which were in flowering and fruiting conditions and were identified by the help of Cooke, T. (1958), Hooker, J.D. (1872-1897), Razi, B.A. (1952), Santapau, H. (1957), Varadpande, D.G. (1966), Shirke, D. R.(1983). The information regarding the medicinal uses of weeds was gathered from the tribals of Khed tehsil to gather information on plant species used for different disorders by them. This information is collected by following Jain, S.K. (1991). Medicinal uses were confirmed by following Nadkarni, A.K. (1927).

RESULTS AND DISSCUSSION:

The present study brought knowledge of tribals for the treatment of different disorders . The collected weed specimens have been identified by the flora, the collected plants species are alphabetically arranged according to their Botanical name, local name, families, parts used and uses.

1. *Achyranthes aspera* L., Family-Amaranthaceae, Local name- Aghada, Part used-Whole plant, Uses- Whole plant is used in toothache. Plant decoction is used in treating rheumatism and joint pain. Leaf paste is useful in skin diseases. Root paste is applied externally on scorpion sting.

2. *Ageratum conyzodies* L., Family- Asteraceae, Local name- Sahdevi, Osadi, Part used-Leaves. Uses- Leaf juice is also used in skin diseases, scabies. Decoction of leaf is applied on cuts, wounds and burns.

3. *Argemone mexicana* L. Family-Papaveraceae, Local name-Pivala dhotra, Part used-Whole plant, Uses- Plant paste applied externally for healing wound, swellings and body pains.

4. *Asclepias currasavica* L. Family- Asclepiadaceae , Local name- Haldi kunku, Part used-Root. Use- Root extract is given to children during night to eradicate intestinal worms.

5. *Boerhhavia* diffusa (L.) Hook, Family-Nyctaginaceae Local name- Punrnava, Part used-Leaves. Uses- Leaf decoction is taken for blood purification, treating kidney stone and urinary troubles.

6. *Calotropis gigantea* (L.) R.Br, Family- Asclepiadaceae, Local name- Rui, Mandar. Part used- Leaves, flowers, Uses- Leaves and flowers are kept on head and massage is given by warmed utensil to reduce headache

7. *Calotropis procera* (Ait.) R.Br. Family-Asclepiadaceae, Local name Aak, Rui, Part used-Leaves, Uses- Dried leaves mixed with jagary are also given for treatment of cough.

8. *Cassia sophera* L. Family-Fabaceae, Local name Chilhar, Part used-Leaves. Use- Leaves half fried in *Sesamum orientale* oil and applied externally over joints in treating arthritic pain.

9. *Cassia tora* L. Family-Fabaceae, Local name –Takla, Parts used-Leaves, root, seed. Uses-Fresh leaf juice is applied for cuts, boils, burns, treating itch, Paste of roots with lemon juice applied externally over ringworm. Seeds are given in stomach disorder.

10. *Catharanthus roseus* Don. Family- Apocynaceae, Local name –Sadaphuli, Part used-Leaves. Use- The juice of leaves taken orally once a day empty stomach for to cure jaundice.

11. *Celosia argentee* L. Family- Amaranthaceae, Local name –Kurdu, Part used-Seed.Use-Seed powder is given in sugar for fever.

12. *Centella asiatica* (L.) Urb, Family- Apiaceae, Local name – Brahmi, Part used-Whole plant,

Uses- The decoction of plant is given in treating urinary burning sensation while urination. The leaves are used to increase memory.

13. *Chenopodium album* L. Family-Chenopodiaceae, Local name -Bathua, chakvat. Part used-Leaves. Use- Leaves used as vegetable for treating anemia.

14.*Clitoria ternatea* L. Family-Fabaceae, Local name -Gokarna. Part used-Whole plant. Use-Plant extract is used for skin itching.

15. *Cocculus hirsutus* L. Family-Menispermaceae, Local name -Vasanvel, Jaljamni, Part used- Leaves. Use- Leaves consumed directly for in enhancing spermatogenesis.

16. *Cuscuta reflexa* Roxb. Family-Cuscutaceae, Local name -Amarvel. Part used-Whole plant. Use- Paste of whole plant applied externally on joint pains, rheumatism and inflammations.

17. *Cyprus rotundus* L.. Family-Cyperaceae, Local name -Nagarmotha. Part used-Whole plant. Use- The whole plant is used for malerial fever, dysentery and vomiting.

18. *Cynodon dactylon* (L) Pers. Family-Poaceae, Local name -Harali. Part used-Whole plant. Use-The whole plant is used in ulcers in stomach.

19. *Datura metal* L. Family-Solanaceae Local name - Kala Dhotra, Part used-Root. Use-Root paste applied externally for pimples.

20. *Eclipta alba* L. Family-Asteraceae Local name - Maka. Part used- Leaves. Use- Leaves curry is eaten to purify blood and also used to treat jaundice.

21. *Euphorbia hirta* L. Family-Euphorbiaceae Local name - Dudhi, Part used-Leaves, Uses-Leaf juice is applied on wounds , treatment for snake bite and scorpion sting. latex applied externally twice a day for warts .

22. *Jatropha gossipifolia* L. Family-Euphorbiaceae, Local name - Erand, Part used-Stem. Use- Stem used as brush for tooth problems.

23. *Justica adhatoda* L. Family-Acanthaceae Local name - Adulsa, Part used-Leaves.Use-The decoction of tender leaves with *Zingiber* used for cough.

24. *Parthenium hysterophorus* L. Family-Asteraceae, Local name - Gajar gavat, Part used-Root

Use-Root extracts about 20-30 ml taken twice a day for two days to cure dysentery.

25. *Phyllanthus niruri* L. Family-Euphorbiaceae, Local name - Bhuiawla, Part used-Whole plant. Use- The extract of fresh entire plant is used to treat jaundice.

26.*Sida acuta* Burm Family-Malvaceae, Local name - Bala, Part used-Whole plant, Uses-Roots useful in treatment of urinary disorders, fever and stomach disorder. Flower paste is used in boils and burns. Leaf is given in gastric disorder and stomach pains.

27. *Solanum surratense* Burm. f. Family- Solanaceae, Local name - Bhuiringini, Part used-Leaves. Use- Leaf paste mixed with turmeric applied to cure itch and ringworm.

28. *Tephrosia purpurea* (L.) Pers. Family- Fabaceae, Local name - Unahali, Part used-Whole plant. Uses- Whole plant powder with curd taken 20-30 ml orally for treating jaundice.The roots are used to cure kidney stone.

29. *Tribulus terrestris* L. Family- Zygophyllaceae, Local name - Sarata. Part used- Fruit. Use-The powder of fruits with one tea cup of milk taken orally to treat urinary problems.

30. *Tridax procumbens* L. Family- Asteraceae, Local name - Ekdandi, Part used- Leaves. Use- Leaf paste used in wounds and cuts.

31. *Urginea indica* (Roxb.) Kunth. Family- Liliaceae, Local name -Janglikanda, Part used-Tuber. Use- 10-20ml decoction of tuber is taken orally once early in the morning to cure cough.

32. *Vitex negundo* L Family-.Verbanaceae, Local name - Nirgudi, Part used- Leaves. Use-Leaf boiled lukewarm water poured over joints in joint pain.

33. *Withania somnifera* (L.) Dunal . Family- Solanaceae, Local name- Ashavaganda, Part used- Root. Use- The powder of root with sugar similar proportion taken orally twice a day as a tonic.

CONCLUSION:

The present research paper is an attempt to enlist the weeds for the treatments of different disorders with the help of tribals. The tribals in the area are dependent on limited agriculture land and local plant products. In this investigation 33 weeds belonging 21families have been documented.

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MEDICINAL PLANTS AS NATURAL WEALTH OF MEDICINE AND INITIATIVES FOR ITS DISEASE CONTROL

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ABSTRACT:

India is well known to have wide range flora of medicinal plants. Near about 54.77% population, belonging to rural and tribal communities depends on plant resources, particularly on medicinal plants. Unfortunately, fungal disease contamination results in destruction of such natural resources.*Adhatoazeylanica* is one of the major medicinal plants used in different formulations in the world of Ayurveda, which suffers from fungal diseases resulting in severe loss of its medicinal values. Therefore, it is our prime duty to avoid and control exploitation of plant wealth by using bio-control agents.Hence, in this present study attemptsare made to find out efficacy of bio-control agents using *P.longifolia*and *D.stramonium*

KEY WORDS: *Adhatodazeylanica;* Acanthaceae; *Datura stramonium;Polialthialongifolia.*

INTRODUCTION:

India has wide range of biodiversity due to variation in physical and climatic conditions. A large population of the country in rural and tribal area depends on forest, particularly on medicinal plants for their livelihood. However, fungal disease incidence is also a major cause of destruction of medicinal plants[2]. *Adhatodazeylanica*is also a one of the major medicinal plant belonging to family Acanthaceae (Plate I). It's leaves are used to cure various diseases like bronchitis, leprosy, blood disorder, asthma, jaundice etc [9]. This plant grows on wastelands, sometimes cultivated as hedge on large scale for commercial purpose [6].But, heavy destruction of this species occurs due to contamination of several fungal pathogens [5].

Therefore, attempts have been made to control the attack of fungal pathogens on leaves by using different biocontrolagents i.e. *Polyalthialongifolia* and*Daturastramonium.*

MATERIALS AND METHODS:

To study to the effect of Bio-control on leaves of *Adhatodazeylanica*, different leaves extracts were prepared by using leaves of *Polyalthialongifolia* and*Daturastramonium*.

PREPARATION OF EXTRACT:

50-gram fresh leaves of *Polyalthialongifolia*were collected, washed and crushed using 50 ml of acetone with the help of mortar and pestle. The extract was filtered by using muslin cloth. Filtrate was then centrifuged at 5000 rpm for 10 min. Supernatant was collected and treated at 100 % i.e. stock solution. Further different concentration of leaves extract were prepared i.e. 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 % by adding 99.5, 99.00, 98.5, 98.00,97.5, 97.00, 96.5, 96 and 95.5 ml and sterile distilled water respectively. In the same way, different leaves extracts concentrations of *Daturastramonium*were prepared.

Further, leaves of Adulsa of same size and age were collected, washed and dipped in different concentration for 15 min. These leaves then kept on filter paper in sterile petriplates by maintaining moisture.[3,4].Then, suspension of 5 mm disc of fungal culture i.e. *Colletotrichumcapsici*(Plate II & III) was applied over leaves with the help of brush and incubated at room temperature for 8 days (Plate-IV).

Plate I-Adhatoda plant

Plate II- *C.capsici* culture

Plate III- mycelia structurePlate

IV-:Activity of bio-control on leaves

Effect of acetone leaves extract was calculated by using following formula

% inhibition = C-T/ CX 100

Where C = Control Reading, T = Treated Reading

RESULT AND DISCUSSION:

It was observed that acetone leaves extract of *Polyalthialongifolia* was most inhibitory at 4.5% concentration and of *Daturastramonium* at 3.0% as shown in (table 1). Khandare and Salve,[7],also reported that leaves extract of *Polyalthialongifolia* was useful in control of various fungal pathogens. Rajamanickamet. al, [8], also screened the effect of biochemical of plant extract i.e.*Polyalthialongifolia*, *Datura metal*., *Azadirachtaindica*on the growth of *Colletotrichumcapsici*.Anjana and Virendrakumar[1], also investigated that acetone extract of *Soracaindica*, and *Daturastromanium*was most effective against fungal pathogen than ethanol and aqueous extracts.

Table 1. Percent inhibition by bio-control activity

Bio control Agent	Incubation Period	% incubation								
		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Polyalthia-longifolia	1st Day	1.81	9.09	20.00	30.90	47.27	64.54	60.00	90.09	100
	8th Day	68.12	86.00	92.12	93.72	94.43	95.25	96.81	98.78	100
Daturastra-monium	1st Day	20.00	45.45	56.36	80.90	92.72	100	100	100	100
	8th Day	87.12	90.68	96.65	98.43	99.53	100	100	100	100

CONCLUSION:

The primary initiative for protection of plant diseases can be done by utilising simple techniques of acetone leaves extract. However, traditional knowledge of local people can also taken into account to conserve and use of natural resources in proper way. People should be make aware regarding limited use of resources.

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TAXONOMICAL SURVEY OF ALGAE FROM PUDDLES, MAHARASHTRA

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ABSTRACT:

During an extensive study on algal taxonomy of Beed district in Maharashtra for the period of three years i.e. January 2006 to December 2008. The algal samples were collected from different habitats such as pools, ponds, cisterns, talaos, dams, streamlets, streams, rivers, polluted water passages, puddles, nursary ponds. A total of 61 taxa under 32 genera were encountered and identified from the puddles during the period of investigation.

KEYWORDS: Algal taxonomy; Beed district; Puddles.

INTRODUCTION:

In the course of studies on algae, the review of literature reveals that, India has a very rich and diversified algal flora. In the present century great advances have been made in the investigations of fresh water algae, marine algae, soil algae and particular attention has been paid to their Taxonomy, Ecology and applied aspects. In Maharashtra tremendous work has been done on algal taxonomy by various workers. In Marathwada region except few reports very rare (Ashtekar 1980, Milind Jadhav 2007, Andhale 2008) attention has been paid towards algal taxonomy, although the climatic conditions are most suitable to grow algae luxuriantly and in diverse form, therefore to fulfill this lacuna present work was carried out. The Beed district is located on Deccan plateau at 16.65º N-74.13º E. The average temperature ranges between 31º c

to 40º c. The average rainfall is 666 mm.

MATERIALS AND METHODS:

The algal samples were collected from different habitats of Beed district. The samples were collected in acid washed collection bottles. The samples were preserved in 4% formalin added with 5% glycerin for further taxonomic investigations. The line drawings were made with the help of mirror type camera Lucida under appropriate magnifications. The algae were identified under light microscope by referring standard literature on algae (Philipose 1967; Prescott, 1951;Desikachary1959; Smith, 1920) The identified taxa are shown in table 1.

RESULTS:

Table 1. Total occurrence of Algal taxa in puddles

Sr. No.	Class	Genera	Species
1	*Chlorophyceae*	20	37
2	*Euglenophyceae*	04	13
3	*Cyanophyceae*	08	11
	Total	32	61

Table 2. List of total occurrence of Algal taxa in puddles

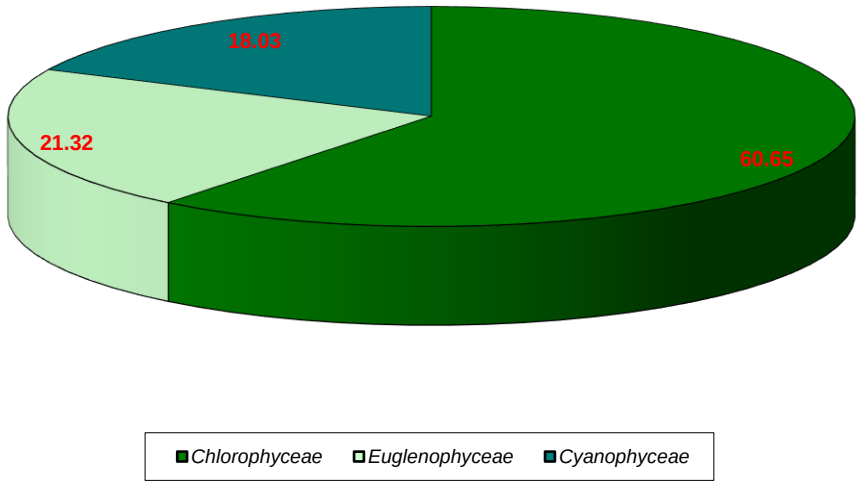
CHLOROPHYCEAE*: Chlamydolomonas angulosa, Eudorina elegans, Sphaerocystis schroeteri, Gloeocystis gigas, Gloeocystis vesiculosa, Protococcus viridis, Oedogonium franklinianum, Oedogonium tapeinosporum, Characium curvatum, Trochiscia reticularis, Pediastrum boryanum, Pediastrum braunii, Pediastrum tetras v. tetradon, Tetraedron limneticum v. gracile, Tetraedron muticum, Tetraedron regulare v. granulata, Tetraedron tumidulum, Oocystis crassa, Oocystis pusilla, Nephrocytium lunatum, Dactylococcus infusionum, Scenedesmus bernardii, Scenedesmus bijugatus, Scenedesmus incrassatulus, Scenedesmus platydiscus, Scenedesmus quadricauda, Scenedesmus quadricauda v. eualternans, Scenedesmus quadricauda v. longispina, Mougeotia bangalorensis, Mougeotia floridana, Zygnema mucigenum, Closterium aciculare, Euastrum spinulosum, Cosmarium laeve, Cosmorium laeve v. acervatum, Cosmorium libogense, Staurastrum quebecense*

EUGLENOPHYCEAE*: Euglena acus, Euglena ehrenbergii, Euglena elongata, Lepocinclis acuta, Lepocinclis glabra, Phacus acuminatus, Phacus acuminatus v. granulata, Phacus*

longicauda, Phacus pleuronectes, Trachelomonas acanthostoma, Trachelomonas hispida, Trachelomonas robusta, Trachelomonas triangularis.

CYANOPHYCEAE: *Chroococcus turgidus, Rhabdoderma gorskii, Rhabdoderma lineare, Myxosarcina burmensis, Oscillatoria princeps, Oscillatoria pseudogeminata v. unigranulata, Phormidium pachydermmaticum, Lyngbya cryptovaginata, Lyngbya dendrobia, Nostoc ellipsosporum, Calothrix geitonos*

Graph 1: Classwise percentage contribution of Algal flora in puddles
(values in percentage)



DISCUSSION:

During present investigation a total of 61 taxa under 32 genera were encountered from the puddles,among which the members of chlorophyceae were found dominantly (37 taxa under20 genera) followed by 13 taxa under 4 genera belonged to euglenophyceae and 11 taxa under 8 genera were belonged to cyanophyceae.The species of *Scenedesmus* were found dominantly and followed by the species of *Pediastrum,Tetraedron* and *Cosmarium* among the chlorophyceae.The species of *Phacus* and *Trachelomonas* were found dominantly and represents the euglenophyceae and the species of *Oscillatoria* and *Lyngbya* are dominantly found from cyanophyceae.

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SCREENING OF SOME PLANT EXTRACTS AGAINST *FUSARIUM OXYSPORUM* F. SP. *CUBENSE* CAUSING PANAMA WILT OF BANANA

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ABSTRACT:

The antifungal activity of five different plants namely *Santalum album* L.,*Tagetes erecta* L.,L*awsonia alba* L. *Syzygium cumuni* and *Gliricidia sepium* Jacq . were tested against *Fusarium oxysporum* f. sp. *cubense*. The plants leaves were extracted with various solvent like Alcohol and aqueous. Among the different plant tested, the 5 % alcoholic leaf extracts of all five plants completely inhibited growth of both the sensitive and resistant isolates of *Fusarium oxysporum* f. sp. *cubense* to benomyl.Whereas the other plant extracts were showed moderate to minimum antifungal activity.

KEYWORDS: Plant extracts; antifungal activity; Fusarium wilt.

INTRODUCTION:

Biological control of plant pathogens is preferred over the hazardous chemical based products. The plants serve as food, medicines, raw product for industry and antifungal sources. The plant extracts serve as ecofriendly and chief antifungal sourse. Banana (Musa spp.) is an important source of human nutrition, providing food & income to millions of people in the world. Banana is cultivated in Asia, Australia, Africa, North and South America [5]. The banana is attacked by many fungal pathogens. Among them Fusarium wilt of banana is most destructive

disease [9],[6]. Panama wilt is caused by *Fusarium oxysporum f.sp. cubense* [7],[8]. In the present investigation alcoholic and aqueous leaf extracts of *Santalum album, Tagetes erecta, Lawsonia alba Syzygium cumuni* and *Gliricidia sepium* were tested for their antifungal activity against *Fusarium oxysporium f. sp. cubense*.

MATERIALS AND METHODS:

Leaves of *Santalum album, Tagetes erecta, Lawsonia alba, Syzygium cumuni* and *Gliricidia sepium* were collected, washed, dried and pulverized to obtain 100g of powder each plant was extracted in 95% alcohol by (1:5 w/v) and condensed to serve as stock extract. The toxicity of stock extract was determined against *Fusarium oxysporum* f. sp. *cubense* sensitive and resistant isolates to benomyl by food poisoning technique [4] at four different concentrations. Plates containing CDA supplemented with plant extracts at four concentrations with three replicates were inoculated with a 6 day old culture of *Fusarium oxysporum* f. sp. *cubense*. 8 mm agar disc of fungal culture was prepared with the help of sterile cork borer and kept upside down on agar plates, incubated at 28 ± 2°C. Plates without plant extract served as control. Linear growth of *F. oxysporum* was measured at different intervals. This procedure was repeated for the water extract of same plants instead of alcoholic extracts. The proportion of water and alcohol was 95:5 respectively.

RESULTS AND DISCUSSION:

Table 1. Antifungal activity of five different alcoholic and aqueous plant extracts against *Fusarium oxysporum* f. sp. *cubense*.

Plant	Conc. In %	Leaf extract	Days							
			1		2		3		4	
			S	R	S	R	S	R	S	R
Santalum album	5	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	17.33	18.33	34.66	34.66	42.00	45.00	54.33	55.66
	10	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	14.66	16.66	34.00	34.33	38.66	44.33	52.66	54.33
	15	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	12.66	15.33	31.33	33.00	37.33	43.33	50.66	53.66

	20	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	12.00	14.33	30.33	32.33	36.33	41.33	50.00	52.00
Control			20.00	21.66	44.00	45.66	58.33	60.00	78.00	80.00
Tagetes erecta	5	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	17.00	18.66	33.66	35.66	41.33	45.33	54.00	55.33
	10	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	16.00	17.33	30.33	34.00	40.66	44.66	52.66	54.33
	15	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	15.33	16.00	28.66	33.33	38.66	41.33	49.33	52.66
	20	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	13.66	14.33	26.66	28.66	34.66	37.33	48.00	50.00
Control			20.00	21.66	44.00	45.66	58.33	60.00	78.00	80.00
Lawsonia alba	5	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	18.33	18.66	36.00	37.00	44.66	46.00	55.00	55.66
	10	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	16.66	17.66	34.33	35.33	42.00	43.33	52.33	54.33
	15	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	13.00	16.00	16.33	17.66	20.33	21.66	24.33	25.33
	20	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	11.00	12.33	14.66	15.33	17.33	18.33	18.33	20.00
Control			20.00	21.66	44.00	45.66	58.33	60.00	78.00	80.00
Syzygium cumuni	5	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	18.33	18.66	35.66	36.66	44.66	45.66	56.33	57.66
	10	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	17.66	18.00	34.33	35.66	41.33	42.66	50.00	51.66
	15	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	13.66	14.33	19.33	21.66	24.66	26.66	34.66	35.66
	20	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	12.00	13.00	15.66	16.66	19.33	21.33	25.33	27.33
Control			20.00	21.66	44.00	45.66	58.33	60.00	78.00	80.00

Gliricidia sepium	5	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	17.33	18.33	34.66	34.66	42.00	45.00	54.33	55.66
	10	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	14.66	16.66	34.00	34.33	38.66	44.33	52.66	54.33
	15	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	12.66	15.33	31.33	33.00	37.33	43.33	50.66	53.66
	20	Alco.	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
		Aque.	12.00	14.33	30.33	32.33	36.33	41.33	50.00	52.00
Control			20.00	21.66	44.00	45.66	58.33	60.00	78.00	80.00

Dunnet multiple comparison test-

Between *Santalum album* conc. F= 42.476

Tagetes erecta conc. F= 44.323

Lawsonia alba conc. F= 38.977

Syzygium cumuni conc. F= 41.449

Gliricidia sepium conc. F= 42.476

P value = P< 0.01

The results are in agreement with other workers [2] observed the leaf extract of *Withania somnifera* had potentiality to control *Aspergillus niger* causing fruit rot of tomato. 10% alcoholic leaf extract of *Semecarpus anacardium*, *Azadirachta indica* and *Commiphora stoksiana* completely inhibited the growth of both the isolates of *Fusarium oxysporum* f. *spinaceae* [1]. According to [3] among the fifteen plants tested for their antifungal activity against *Alternaria solani* causing early blight of tomato.

CONCLUSION:

The 5 % alcoholic leaf extracts of Santalum album L.,Tagetes erecta L., Lawsonia alba L. Syzygium cumuni and Gliricidia sepium Jacq .completely inhibited growth of both the sensitive and resistant isolates of Fusarium oxysporum f. sp. cubense to benomyl. Aqueous leaf extracts of above mentioned plant species were less effective. (Table. 1)

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MEDICINAL PLANTS AS A SOURCE OF ANTIOXIDANTS

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INTRODUCTION:

In the recent years, especially the free radicals and antioxidants have played a great role in the prevention of diseases. Antioxidants are the substances that neutralize free radicals or their actions. Nature has gifted each cell with adequate protective mechanism against any harmful effects of free radicals i.e superoxide dismutase,glutathione peroxidase,glutathione reductase. Vitamin E is an essential nutrient, which functions as a chain- breaking antioxidant that prevents the propagation of free radical reactions in all cell membranes in the human body. Vitamin C is also a part of the normal protecting mechanism. Plants kingdom is treasure house of potential drugs and there has been an increasing awareness about their importance of medicinal plants [1].

ACTION OF ANTIOXIDANTS:

Antioxidants neutralize free radicals at different stages. Antioxidants acts in three ways, prevention, interception and repair. At prevention level, the antioxidants attempt to stop the formation of reactive oxygen species (ROS), which include super oxide that catalyses the dismutation of super oxide to hydrogen peroxide and catalase that break it down to water. At interception level the scavenging of peroxyl radicals is affected. At repair level mainly enzymes are repaired.

BEHAVIOR OF ANTIOXIDANTS:

During a chemical reaction, one reactant loses an electron, which is called oxidant or free radical, while the other gains an electron. Contaminants in the environment and normal metabolism of cell can change molecule into a free radical. Any molecule can become a free radical by either losing or gaining an electron. Once these free radicals are initiated, they get involved in chain reaction with stable types. The compounds thus formed have longer stability in body and increase the potential for cellular damage. Free radicals damage the cell at site of their operation causing serious disorders. Plaque in arteries on oxidation, low density lipoprotein functions as free radical and damage the free artery lining. It may be lead to heart attack. Access free radicals damage DNA, RNA, proteins and enzymes. They lead to formation of tumors and cause cancer. It also causes nervous disorder, cardiovascular diseases, rheumatic and pulmonary diseases.

In living organisms, oxygen in unstable form is the most common free radical; this is called reactive oxygen species (ROS) and is generated during various metabolic activities.

REQUIREMENT OF ANTIOXIDANTS IN THE BODY:

A number of processes are taking place in our body like breathing, breaking up of protein in the body or exposure of body to air pollution or ultra violet radiation leads to the formation of free radicals that aid in the process of oxidation, which further leads to several health problems. If the body is healthy, it is capable enough to break down these free radicals before they become harmful. The free radicals after their formation can damage the cells and tissues. This damage can be counteracted by antioxidants, which prevent the free radical formation. If free radicals are formed then the antioxidants helps to remove from blood stream.

EFFECT OF FREE RADICALS:

All the biological molecules present in our body are being attacked by free radicals. such damaged molecules can impair cell function and even lead to cell death eventually resulting in diseased states.

The membrane lipids present in sub-cellular organelles are mostly susceptible to free radical damage. Lipids when reacted with free radicals responsible for causing direct and indirect effects. Free radicals such as OH react with carbohydrates by abstracting a hydrogen atom from one of the carbon atoms, producing a carbon- centered radical.

ANTIOXIDANTS IN MEDICINAL PLANTS:

Ayurvedic Indian and traditional Chinese systems are living great traditions and have important roles in bio-prospecting of new medicines from medicinal plants, which a rich source of antioxidants. 80% of people in developing country still believe on traditional medicine- based largely on various species of plants and animals for their primary healthcare. Natural compounds derived from dietary sources provide large number of antioxidants. Medicinal plants are the more important therapeutic aid for the alleviating the ailments of humankind [2].

Since long time ago, man has been using plant extracts to protect himself against several diseases and also to improve his health and life style. Many aromatic, medicinal and spice plants contain compounds that possess confirmed strong antioxidant components. The essential oils derived from aromatic plants are not only serve as fragrance and flavor agents but also as dietary antioxidant expected to prevent several diseases caused by free radicals. Currently large number of global population prefers the use of natural products in treating and preventing medical problem. This had influence many pharmaceutical companies to produce new antimicrobial formulations extracted from plants and herbs. Herbs are from natural plants, so they are considered harmless compared with western medicines. Plant species still serve as a rich source of many novel biologically active compounds. However very few plant species have been thoroughly investigated for their medicinal properties. Now a days many medicinal plant species are being screened for pharmacological activities [3] . The phytochemical analysis of the plants is very important commercially and has great interest in pharmaceutical companies for the production of the new drugs for curing of various diseases [4].

Plants absorb sun's radiation and generate high levels of oxygen as secondary metabolites of photosynthesis. Oxygen is easily activated by ultraviolet radiation and heat from the sunlight to produce toxic reactive oxygen species and there by leading to a number of destructive processes causing cellular damage. Plants produce various antioxidant compounds to counteract and detoxify these reactive oxygen species in order to survive. Phenolic compounds are possess

high antioxidant activity and commonly found phytochemical in fruits and leafy vegetables. The antioxidant activity of phenolic compounds is based on their ability to donate hydrogen atoms to free radicals.

Fruits and vegetables are rich source of many food factors including minerals, vitamins and phytochemicals that may act as antioxidants. Thus, a daily consumption of antioxidant rich food provides the body with the essential antioxidants needed to prevent degenerative diseases, premature ageing symptoms, chronic fatigue, so antioxidants are more beneficial for human being.Several epidemological studies suggest that a high intake of fruits and vegetables rich in natural antioxidants increase the antioxidant capacity of the plasma and reduces the risk of some chronic diseases such as cancers, heart diseases and stroke [5]. Fruits and seed latex of *Carissa carandas* are used for treating rheumatoid arthritis, anorexia, indigestion, colic, hepatomegaly, splenomegaly, piles, cardiac diseases, oedema, amenorrhoea, fever and nerving disorder [6].

A BRIEF DESCRIPTION OF COMMON ANTIOXIDANT PLANTS:

Screening of plats is done by measuring the antioxidant activity through variuos in vitro medels like DPPH (2,2-Diphenyl-1-Picryl hydrazyl) method, nitric oxide medel,ORAC method, TBARS assay etc. and via various in vivo method using rats or mices.

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इतिहास शिक्षणातील घटक नियोजनाचे महत्त्व

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सारांश:

इतिहास शिक्षक घटक नियोजन, पाठ नियोजन,वार्षिक नियोजन अशा स्तरावर आपल्या अध्यापनाचे नियोजन करत असतो. त्यातील घटक नियोजन इतिहास शिक्षणाचा महत्त्वपूर्ण पैलू आहे जो अध्ययन सामग्री, अनुदेशनात्मक रणनीती आणि मूल्यांकनासाठी एक संरचित आराखडा प्रदान करतो. हा वैचारिक शोधनिबंध इतिहासाच्या शिक्षणातील घटक नियोजनाच्या महत्त्वाची चर्चा करतो, चिकित्सक विचारांना चालना देण्यासाठी, विद्यार्थ्यांचा सहभाग वृद्धिंगत करण्यासाठी तसेच शैक्षणिक उद्दिष्टे अभ्यासक्रमाच्या मानकांसह संरेखित करण्यासाठी त्याच्या भूमिके वर जोर देतो. शैक्षणिक उद्दिष्टे, शिक्षक व विद्यार्थी कृती,अनुदेशनात्मक रणनीती, अध्ययन सामग्री निवड, मूल्यांकन पद्धती, आवश्यक आशय व प्रश्न निवड, यासारख्या घटक नियोजनाच्या विविध घटकांचे परीक्षण करून हा पेपर इतिहास शिक्षण देण्यासाठी सुसंगत आणि परिणामकारक घटक नियोजनाची आवश्यकता अधोरेखित करतो. चांगल्या घटक नियोजनाद्वारे विद्यार्थ्यांना इतिहासाचे सुयोग्य अनुभव प्रदान करण्यासाठी काही व्यावहारिक शिफारसी सुचविण्यात आल्या आहेत

संशोधन संज्ञा - घटक नियोजन, इतिहास शिक्षण, अनुदेशनात्मक रणनीती, अध्ययन सामग्री निवड, मूल्यांकन पद्धती,

प्रस्तावना:

सद्यस्थितीत घटक नियोजनाचा वापर शिक्षण क्षेत्रात मोठ्या प्रमाणात होऊ लागला आहे. नियोजनाशिवाय कोणतेही कार्य सफलपणे पूर्ण होऊ शकत नाही. प्रभावी अध्यापन करून विद्यार्थ्यांचा सर्वांगीण विकास करण्यासाठी घटक नियोजन करणे शिक्षकास क्रमप्राप्त ठरते. घटक नियोजन ही अल्पकालीन योजना असल्यामुळे तिचा कालावधी सामान्यपणे तीन ते सहा आठवड्यांचा ठेवता येतो, जेणेकरून या कालावधीत तो घटक विद्यार्थ्यांना चांगल्या प्रकारे समजून घेता येईल, विविध कृती त्यांच्याकडून करून घेता येतील, विविध ज्ञानानुभव त्यांना देता येतील, अध्ययनाशी संबंधित विद्यार्थ्यांच्या समस्या सोडवता येतील. विद्यार्थ्यांचे सुयोग्य मूल्यमापन करता येईल व या सर्व प्रक्रियेतून शिक्षकाला स्वतःच्या अध्यापनकार्याची क्षमताही आजमावता येईल. एकंदरीतच प्रभावीपणे अध्यापनाचे नियोजन केले तर विद्यार्थ्यांच्या सर्वांगीण विकास करणे शक्य होईल परंतु घटक नियोजन तयार करणे एवढे

सोपे कार्य नाही त्यासाठी शिक्षकाने मेहनत घेणे आवश्यक असते. विचारपूर्वक केलेल्या नियोजनानेच अध्यापनाची ध्येये व उद्दिष्ट साध्य होऊ शकेल एवढे मात्र निश्चित आहे.

घटक नियोजनाचा अर्थ:

घटक नियोजन अर्थात एखाद्या घटकांचे नियोजन, परंतु घटक म्हणजे नेमके काय? याविषयी विचारवंतांमध्ये मतभेद दिसून येतात बऱ्याचदा 'घटक' किंवा 'युनिट' यास केवळ पाठ्यवस्तूचा अंश असे मानले जाते. मात्र घटक त्यापेक्षाही व्यापक संकल्पना आहे. घटकांचे तात्पर्य ज्ञानानुभवांच्या एकीकृत रूपाशी आहे, असे अनुभव ही जे परस्पर संबंधित असतील व ज्यांना एकत्रितपणे शिकवता येईल ते घटक या संकल्पनेत मोडतात.

प्राध्यापक एच सी मॉरीसन यांनी शिक्षण क्षेत्रात सर्वप्रथम घटक पद्धती ही संकल्पना मांडली वस्तूत 1920 मध्ये शिक्षण क्षेत्रात घटक या संकल्पनेचा वापर होऊ लागला व त्याचे श्रेय हरबार्ट च्या शैक्षणिक विचारात दिसते. त्याने ज्ञानाच्या समग्रतेचे तत्व मांडले व विषय वस्तूच्या परस्पर संबंधांची सांगड घातली. त्यामुळे अभ्यासक्रम निर्मिती करताना विषय वस्तूला महत्त्व दिले गेले याच विषय वस्तूचा एक भाग म्हणजे घटक अशी संकल्पना रूढ झाली. या दृष्टिकोनाचे प्रतिपादन करताना प्रेस्टन यांनी म्हटले आहे "घटक संबंधित विषय वस्तूचे असे विस्तृत क्षेत्र आहे. ज्याचे विद्यार्थी अध्ययन करू शकतील" कालांतराने घटक या संकल्पनेत बदल होत गेला वर्तमान काळात घटक व युनिटचा वापर अभ्यासक्रम निर्मिती व शिक्षण पद्धती या स्वरूपात केला जातो.

सॅमफोर्ड "घटक विषय वस्तूची अशी रूपरेखा आहे जी विद्यार्थ्यांची आवश्यकता व रुची यांच्याशी संबंधित असल्याकारणाने स्वतःचे वेगळेपण दर्शविते." थॉमस एम रिस्क " घटक एखाद्या समस्येशी संबंधित अध्ययन करावयाच्या क्रियांची समग्रता व एकता प्रकट करतो." ई. बी. वेस्ले यांच्या मते " घटक सूचना व अनुभवांच्या त्या संघटनास म्हणतात की जो अध्ययनार्थ्यांसाठी महत्त्वपूर्ण परिणाम निर्माण करू शकेल." अर्थातच घटक हा पाठ्यवस्तूचा एक भाग असून अध्ययन अध्यापन प्रक्रिया अधिक प्रभावी होण्याच्या उद्देशाने शिक्षक या घटकाचे योग्य प्रकारे नियोजन करतो तेव्हा आपण त्याला घटक नियोजन असे संबोधतो.

घटक नियोजनाचे मुख्य घटक व आराखडा

घटक नियोजन									
घटकाचे नाव-						**विषय-**			
उपघटक-						**इयत्ता-**			
एकूण तासिका						**महिना -**			
उपघटक	**पाठ्यमुद्धे**	**तासिका**	**उद्दिष्टे**	**अध्यापन पद्धती**	**शिक्षक कृती**	**विध्यार्थी कृती**	**अध्यापन साधने**	**मुल्यांकन**	**सराव**

घटक नियोजनाचे मुख्य घटक

१. घटकाचे शीर्षक

घटक नियोजनांतर्गत महत्त्वाचा भाग म्हणजे घटकाचे शीर्षक होय. घटकाच्या शीर्षकाचे व्यवस्थित मांडणी करणे, घटकाच्या अंतर्गत येणारे उपघटक वा प्रकरणे लक्षात घेणे गरजेचे ठरते.

२. कालावधी

हा घटक नियोजनाचा महत्त्वाचा भाग होय घटकासाठी तसेच त्या घटकांतर्गत येणाऱ्या विविध उपघटक व प्रकरणी या अनुषंगाने अध्यापन प्रात्यक्षिक कार्य मूल्यमापन सराव यासाठी किती तासिका लागतील याची निश्चिती करावी लागते.

३. अध्ययनाची उद्दिष्टे

घटक नियोजनाचा महत्त्वाचा भाग म्हणजे अध्ययनाच्या उद्दिष्टांची मांडणी करणे होय. ही उद्दिष्टे राष्ट्र व राज्य पातळीवरील प्रशासनाने ठरवून दिलेल्या मानकांची संबंधित असतात. ही उद्दिष्टे विशिष्ट काळात प्राप्त करता येण्यासारखी असावीत, विद्यार्थ्यांनी अर्जित केलेले ज्ञान व क्षमता यांचे मापन करता यावे, अशा प्रकारे उद्दिष्टांची मांडणी केली गेली पाहिजे.

४. उपयुक्त विषय वस्तू व अध्ययन सामग्रीची निवड

विद्यार्थ्यांना अध्ययन अध्यापन प्रक्रियेत योग्य प्रकारे गुंतवून ठेवण्यासाठी तसेच ऐतिहासिक घटकाचे योग्य प्रकारे आकलन होण्यासाठी योग्य त्या आशयाची वा विषय वस्तूची निवड करणे गरजेचे ठरते. आशय हा पाठ्य घटकांवरूप व अचूक असला पाहिजे तसेच त्या अनुरूप साधनांची निवड करणे गरजेचे असते. त्यामध्ये आशयानुरूप प्राथमिक व दुय्यम साधने, परस्पर संवादी वेबसाईट, पॉडकास्ट, चित्रपट, माहितीपट यासारखे बहुमाध्यमे तसेच आवश्यकतेनुसार पाठ्यपुस्तक, चित्र, नकाशा, टाईम लाईन इत्यादी पूरक साहित्याचाही वापर करावा.

५. अनुदेशनात्मक रणनीती

विद्यार्थ्यांपर्यंत माहिती योग्य प्रकारे पोचवण्यासाठी अनुदेशनात्मक रणनीती आवश्यक असतात. विद्यार्थ्यांमध्ये सृजनशीलता, चिकित्सक विचार, अर्थनिर्वचन व विश्लेषण क्षमता, वैज्ञानिक दृष्टिकोन, परस्पर संवाद , परस्पर सहयोग अशा विभिन्न क्षमतांचा विकास करण्यासाठी आधार पद्धती, चर्चा पद्धती, नाट्यीकरण पद्धती, भूमिका पालन पद्धती, प्रकल्प पद्धती, समस्या निराकरण पद्धती, खेळ पद्धती, चौकशी- आधारित शिक्षण इत्यादी अध्ययन अध्यापनाच्या विभिन्न पद्धती, युक्त्या प्रयुक्त यांचा वापर केला जातो जो घटक नियोजनचा अविभाज्य भाग आहे. चांगल्या घटक नियोजना उत्तम अशा अनुदेशनात्मक रणनीतींचा वापर केला जातो.

६. अध्ययन अध्यापन कृती

शिक्षक व विद्यार्थी यांना प्रत्यक्ष अध्ययन अध्यापन प्रक्रिया चालू असताना विविध प्रकारच्या कृती कराव्या लागतात या कृतींचा समावेश यामध्ये केला जातो. जसे शिक्षकाला स्पष्टीकरण करणे, प्राथमिक साधनांच्या आधारे चर्चा करणे, प्रश्न विचारणे, संबोध स्पष्ट करणे इत्यादी विविध कृती करावे लागतात त्याप्रमाणे विद्यार्थ्यांनाही अध्ययन विषयाचे श्रवण करणे, तक्ते वा चित्र यांचे निरीक्षण करणे, प्रश्नांना उत्तरे देणे इत्यादी विभिन्न कृती कराव्या लागतात. या कृतींची योग्य मांडणी शिक्षकाने केली पाहिजे.

७. मूल्यांकनाच्या पद्धती

अध्ययन अध्यापन प्रक्रियेत मूल्यांकनाला महत्त्व आहे. त्याचे प्रतिबिंब घटक नियोजनात पडलेले दिसून येते. एखाद्या घटका अंतर्गत एखाद्या पाठाचे अध्यापन करत असताना शिक्षक जेव्हा विद्यार्थ्यांना स्वाध्याय, गृहकार्य, प्रकल्प देतो तसेच त्या

विषयावर चर्चा घडवून आणतो प्रश्नमंजुषा घेतो यासारख्या उपक्रमातून रचनात्मक मूल्यमापन केले जाते. जे विद्यार्थ्यांना त्वरित अभिप्राय आणि मार्गदर्शक सूचना प्रदान करतात. याउलट संकलित मूल्यमापन हे घटकाच्या अध्यापनाच्या शेवटी घेतले जाते, ज्याचा उद्देश विद्यार्थ्यांनी घटकाच्या अध्ययनादरम्यान प्राप्त केलेल्या ज्ञान, कौशल्य व क्षमतांचे मापन करणे असतो. त्यासाठी विविध प्रकारच्या चाचण्या, निबंध, प्रकल्प दिले जातात. विद्यार्थ्यांच्या प्रगतीचे योग्य मूल्यांकन करण्यासाठी नियम व निकष यांचीही निश्चिती करावी लागते.

८.चिंतनशील सराव

शिक्षकाच्या दृष्टिकोनातून घटक नियोजनाचा महत्त्वाचा भाग म्हणजे चिंतनशील सराव होय. विद्यार्थ्यांचा अभिप्राय आणि अध्ययन निष्पत्ती या आधारे शिक्षक घटक नियोजनातील चांगल्या बाजू व कमतरता लक्षात घेत असतो व पुढील घटक नियोजनात त्याप्रमाणेच योग्य बदल व सुधारणा करत असतो ही प्रक्रिया शिक्षकांना सुधारणा करण्यासाठीची क्षेत्रे ओळखण्यास आणि विद्यार्थ्यांच्या गरजांवर आधारित शिक्षण देण्यासाठी उपयुक्त ठरते. उपरोक्त प्रमुख घटकांचा समावेश करून इतिहास शिक्षक विद्यार्थ्यांमध्ये संरचित, आकर्षक व प्रभावी अध्ययन अनुभव प्रदान करू शकतो. तसेच विद्यार्थ्यांमध्ये सुयोग्य ज्ञान, कौशल्य व क्षमतांचा विकास करू शकतो.

घटक नियोजनाचे महत्त्व:

काळजीपूर्वक व बारकाईने केलेले घटक नियोजन शिक्षकाला अत्यंत फायदेशीर ठरते या घटक नियोजनांचे महत्त्व खालील प्रमाणे

१. शिक्षकांसाठी दिशादर्शक

चांगले घटक नियोजन शिक्षकांसाठी दिशादर्शक ठरते कारण त्यामध्ये विद्यार्थ्यांनी काय शिकले पाहिजे ? व शिक्षकांनी कसे शिकवले पाहिजे? अर्थातच एकंदरीत अध्ययन अध्यापनाची निष्पत्ती काय असली पाहिजे हे स्पष्ट केलेले असते. घटक नियोजनाचे अभ्यासक्रमाच्या मानकांशी केलेले संरेखन शिक्षकाला उद्दिष्टांची निश्चिती, विद्यार्थ्यांचे मूल्यांकन, उपलब्ध सामग्रीचा वापर,सर्वांसाठी गुणवत्ता पूर्ण अध्ययन सामग्रीची उपलब्धता, नाविन्यपूर्ण अध्यापन पद्धती, शिक्षक विद्यार्थी कृती, इत्यादी विविध बाबींसाठी दिशादर्शक ठरते त्यामुळे शिक्षकाचा व्यावसायिक विकास होण्यास मदत मिळते.

२. विद्यार्थी केंद्रित अध्ययन

चांगल्या घटक नियोजनाचे प्रमुख वैशिष्ट्य म्हणजे ते विद्यार्थी केंद्रित अध्ययनावर भर देते. विद्यार्थ्यांच्या गरजा अपेक्षा कुवत सामाजिक पार्श्वभूमी इत्यादी लक्षात घेऊन त्याप्रमाणे अध्ययन अनुभवांची आखणी करण्यासाठी, विद्यार्थ्यांना उचित संधी व अध्ययन अनुभव प्रदान करण्यासाठी, मिळवलेल्या ज्ञानाची व्यवहारात उपयोग करण्याची संधी प्राप्त करून देण्यासाठी, विद्यार्थ्यांमध्ये परस्पर संवाद चर्चा घडवून आणण्यासाठी घटक नियोजन महत्त्वाचे ठरते.

३. परिणामकारक अनुदेशन

चांगल्या घटक नियोजनामुळे शिक्षकाला त्या घटकाची उद्दिष्टे समजतात व या उद्दिष्टानुरूप विद्यार्थ्यांपर्यंत माहिती पोहोचविण्यासाठी कोणत्या परिणामकारक अध्यापन पद्धती युक्त्या, प्रयुक्त्या, तंत्रे यांचा वापर करावा, की जेणेकरून विद्यार्थी सक्रिय राहतील, त्यांच्यात रचनात्मक विकास होईल, विषयाचे सुयोग्य आकलन होईल. अर्थातच त्यामुळे शिक्षकाला समस्या निराकरण पद्धती, आधार पद्धती, प्रकल्प पद्धती यासारख्या नाविन्यकारक पद्धतीने अध्यापन करण्याची संधी प्राप्त होते.

४. कार्यक्षम वेळ व्यवस्थापन

चांगल्या घटक नियोजनाचा फायदा म्हणजे त्यामध्ये अध्ययनाच्या प्रत्येक कृतींसाठी लागणाऱ्या वेळेचे योग्य नियोजन केलेले असते. त्यामुळे प्रत्येक उपघटक, पाठ्य मुद्दे यासाठी किती वेळ द्यावा याची शिक्षकाला निश्चिती करता येते. कार्यक्षमपणे केलेले व्यवस्थापन शिक्षकाला एखादा विषय व महत्त्वाचा मुद्दा अध्यापनातून गाळणे वा घाईघाईने शिकवणे या गोष्टींना प्रतिबंधित करते.

५. चिकित्सक विचारांना चालना

प्रभावी घटक नियोजन विद्यार्थ्यांमध्ये ऐतिहासिक पुराव्यांचे विश्लेषण, अर्थनिर्वचन आणि मूल्यांकनाची क्षमता निर्माण करण्यासाठी प्रोत्साहित करते व त्या माध्यमातून विद्यार्थ्यांमध्ये चिकित्सक विचारांना चालना देते.चौकशी आधारित अध्ययनामुळे त्यांच्यामध्ये तर्क करणे, उच्चस्तरीय विचार करण्याची क्षमता प्राप्त होते.

६. विद्यार्थ्यांच्या प्रगतीचे मूल्यांकन

चांगल्या घटक नियोजनाचा प्रमुख उद्देश विद्यार्थ्यांचा सर्वांगीण विकास हा आहे. संपूर्ण शिक्षण प्रक्रिया या तत्त्वावर अवलंबून असते. घटक नियोजनात शिक्षक विद्यार्थ्यांच्या सर्वांगीण विकासाच्या दृष्टिकोनातून विविध उपक्रमांची मागणी करत असतो. या सर्व उपक्रमातून विद्यार्थ्यांची कितपत प्रगती झाली आहे हे पडताळून पाहणे गरजेचे ठरते.

७. विद्यार्थी व्यस्तता व प्रेरणा

चांगल्या प्रकारे केलेले घटक नियोजन अनुदेशनात्मक रणनीती आणि अध्ययन कृतींना समाविष्ट करते तसेच विद्यार्थ्यांना परस्पर संवादाची सक्रिय सहभागाची संधी देते, त्यामुळे विद्यार्थ्यांना इतिहास विषयांमध्ये रुची निर्माण होते. ते इतिहासातल्या विविध विषयांवर शोध घेण्यास प्रवृत्त होतात त्यामुळे ते इतिहास विषयाशी चांगल्या प्रकारे जोडले जातात. इतिहास शिकण्यासाठी प्रेरणा प्राप्त झाल्यामुळे त्या विषयातील त्यांची प्रगती सुधारते.

८. विद्यार्थ्यांच्या स्वयं अध्ययन प्रवृत्तीच्या विकासासाठी सहाय्यक

चांगल्या घटक नियोजनाचे प्रमुख वैशिष्ट्य म्हणजे विद्यार्थ्यांच्या स्वयं अध्ययन प्रवृत्तीच्या विकासात दिला जाणारा वाव होय. स्वाध्याय, गृहपाठ, लायब्ररीचा वापर याद्वारे विद्यार्थ्यांमध्ये स्वयंअध्ययन प्रवृत्तीचा विकास केला जातो.

९. विद्यार्थ्यांचे उत्तरदायित्व व भूमिका

प्रत्येक घटकाचे अध्यापन करण्यापूर्वी शिक्षकाने त्या संपूर्ण घटकाचे नियोजन विद्यार्थ्यांपुढे मांडावे त्यामुळे विद्यार्थ्यांना त्या घटकाच्या अंतर्गत काय शिकावयाचे आहे? कसे शिकवायचे आहे? तसेच कोणते उद्दिष्ट साध्य करायचे आहेत कोणती कौशल्य अर्जित करावयाचे आहेत याची स्पष्ट कल्पना येते त्यामुळे त्या घटकाच्या परिणामकारक अध्ययन करण्यासंदर्भात त्याची मानसिक तयारी होते व त्याला स्वतःची उत्तरदायित्व व भूमिका याचीही जाणीव होते.

१०.पालकांचा सहभाग

विस्तृत घटक नियोजन विद्यार्थ्यांच्या पालकांसोबत सामायिक केले जाऊ शकते त्यामुळे पालकांना आपल्या जबाबदारीची जाणीव होते. शाळेत इतिहास विषयासंदर्भात चालणारे उपक्रम समजतात. अभ्यासक्रम चांगल्या प्रकारे समजून घेता येतो व त्या अनुषंगाने विद्यार्थ्यांच्या अभ्यासाकडे लक्ष देता येते. घटक नियोजनाप्रमाणे विद्यार्थी शिक्षकाने दिलेली उद्दिष्टे साध्य करत आहे किंवा नाही हे पालकांना समजते त्यामुळे पालक आपल्या मुलांच्या प्रगती प्रति जागृत होतात. तसेच शाळा व पालक यांच्यामध्ये चांगल्या संबंधांची जोपासना होते.

घटक नियोजन दक्षता किंवा शिफारशी

घटक नियोजनाचे उपरोक्त विविध फायदे पाहिल्यानंतर शिक्षकाने घटक योजनात कोणत्या बाबींचे दक्षता घ्यायला पाहिजे ते खालील प्रमाणे.

- सर्वप्रथम ध्येय व उद्दिष्टांची निश्चित मांडणी करावी त्यामुळे विद्यार्थ्यांमध्ये कोणत्या क्षमता ज्ञान कौशल्य यांचा विकास करायचा आहे समजते.
- घटकाच्या अध्यापनाला सुरुवात करण्यापूर्वी शिक्षकाने विद्यार्थ्यांना कोणती उद्दिष्टे व ध्येय साध्य करावयाची याची जाणीव करून द्यावी. त्यामुळे विद्यार्थ्यांना स्वतःची भूमिका समजते.
- पालकांनाही घटक नियोजन संदर्भात कल्पना द्यावी व त्यांचा सहभाग वृद्धिंगत करावा. घटक नियोजनामुळे शाळेत चाललेले उपक्रम पालकांना समजतात व त्याप्रमाणे ते विद्यार्थ्यांच्या प्रगतीकडे लक्ष देऊ शकतात.
- विद्यार्थ्यांचे सर्वांगीण मूल्यांकन करण्याच्या अनुषंगाने वैधतापूर्ण मूल्यमापन योजना तयार करावी हे मूल्यमापन नियमित आणि अंतिम दोन्ही प्रकारचे असावे.
- उपलब्ध साधन सामग्रीची योग्य प्रकारे निवड करावी व त्याच्या उपलब्धतेची खात्री करून घ्यावी व त्या अनुषंगाने नियोजन करावे. शाळेत उपलब्ध असलेली पुस्तके वर्तमानपत्र, मासिके, संदर्भ पुस्तके, ऐतिहासिक वास्तू, शैक्षणिक साहित्य तसेच ग्रंथालय, प्रयोगशाळा, इतिहास कक्ष, भौतिक वातावरण, वस्तुसंग्रहालय यांचा यथोचित वापर करावा.
- घटक नियोजनामध्ये आवश्यकतेनुसार शिक्षकाने विद्यार्थ्यांच्या अभिप्राय जाणून घेऊन व त्यांची प्रगती तपासून दर आठवड्याला सतत सुधारणा करण्याचा प्रयत्न करावा त्यामुळे घटक नियोजन अधिक अचूक होण्यास मदत मिळेल.
- घटक नियोजन करताना इतिहास शिक्षकाने घटक उपघटक वापर करणे, पाठ्य मुद्दे, आशय विचारपूर्वक लक्षात घेऊन प्रत्येकासाठी दिलेल्या कार्यभाराप्रमाणे वेळेचे नियोजन करावे त्यामुळे प्रत्येक बाबीला योग्य न्याय देता येईल.
- घटक नियोजन करत असताना अभ्यासक्रमाची मानके सर्वप्रथम लक्षात घ्यावीत त्यामुळे योग्य रोडमॅप तयार करण्यास मदत मिळते.
- विद्यार्थ्यांच्या गरजा, आवश्यकता, पात्रता, पातळी, सामाजिक संदर्भ लक्षात घेता व्यक्ती भेदानुसार शिक्षणाची योजना तयार करावी.
- घटक नियोजनाद्वारे शिक्षकाने विद्यार्थ्यांना इतिहास शिक्षणात रुची निर्माण करण्यासाठी व पर्यायाने ध्येय व उद्दिष्ट गाठण्यासाठी सतत प्रेरणा द्यावी.
- घटक नियोजनमार्फत विद्यार्थ्यांना स्वयं अध्ययनास प्रवृत्त करावे.

निष्कर्ष:

इतिहास शिक्षकाने अभ्यासक्रमाची मानके, अनुदेशन रणनीती, उचित अध्ययन अध्यापन कृती, पाठ्य घटकाचा भारांशानुसार कालावधी, पालकांचा सहभाग, विद्यार्थ्यांची भूमिका, सतत सुधारणा, निर्दोष व नियमित आणि अंतिम मूल्यांकन

इत्यादी बाबी डोळ्यांसमोर ठेवून घटक नियोजन केल्यास विद्यार्थ्यांमध्ये चिकित्सक विचार, अर्थनिर्वचन व विश्लेषण क्षमता, तर्क क्षमता, सृजनशीलता, प्रयोगशीलता, स्वयं अध्ययन, तंत्रज्ञानाचा वापर इत्यादी विविध क्षमतांचा इतिहास शिक्षणाच्या माध्यमातून विकास करता येतो त्यामुळे अध्ययन अध्यापन प्रक्रिया अधिक आकर्षक व अर्थपूर्ण बनण्यास मदत मिळते.

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ICTHYO-FAUNAL DIVERSITY OF RIVER SIANG IN ARUNACHAL PRADESH, INDIA

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ABSTRACT:

The unique topography of North-East India and watershed pattern is an attractive field for Icthyological studies. This region has already recognized as a global spot of freshwater fish diversity. A great numbers of species have been reported from most of the North-Eastern region states. Siang River is the one of the major river of Arunachal Pradesh. The present study on Icthyofaunal diversity of Siang River in Arunachal Pradesh was carried out from June 2012 to July 2013. Fishes are very important from the biodiversity point of view. The study on River Siang reveals the presence of 90 species of fishes belonging 60 genera under 8 orders and 24 families. Cypriniformes dominates the whole river and found in higher numbers and Beloniformes and Tetradontiformes are found in less numbers; it was due to the because of the favorable conditions *viz.*, physico-chemical parameters and availability of food of fishes for cypriniformes.

KEYWORDS: Fish Diversity; Freshwater; River Siang; Arunachal Pradesh; India.

INTRODUCTION:

Fishes are in variable living components of water bodies. These organisms are important food resource and good indicators of the ecological health of the waters they inhabit. However, the rich biodiversity of the freshwater fish of the Indian region has been rapidly dwindling because of increasing degradation of inland water. Out of a total of 2500 species of fish in India,

930 are in freshwaters and belong to 326 genera, 99 families and 20 orders [1]. India is one of the 12 mega biodiversity hot spots contributing 60-70% of the world's biological resources. India has about 11.72% of total global fish biodiversity. A great number of fish species have been reported from the North - Easter region.

Various important studies have been conducted on the fish diversity. Ghosh and Lipton [2] had reported 172 species with reference to their economic importance from the Assam. Talwar and Jhingran [1] represented 267 fish species belonging to 114 genera under 38 families 10 orders from the northeastern region. Sinha [3] compiled a list of 230 species from the northeastern region. Nath and Dey [4] recorded 131 species of fishes from the drainages in Arunachal Pradesh. Sen [5] reported 806 ichthyospecies inhabiting the freshwaters of India. Kar and Sen [6] worked on the systematic list and distribution of fish biodiversity in Mizoram, Tripura, and Barak Drainages in North- East India. Das *et al.* [7] studied on Habitat Mapping, Spatial analysis of Fish diversity of River Subansiri during winter season in Assam and Arunachal Pradesh (India); they reported 48 species of fishes belonging to 15 families under 7 different orders. Acharjee *et al.* [8] studied Icthyofaunal diversity of Dhansiri River, Dimapur, Nagaland, India they found there 34 fish species belonging to 5 orders and 13 families and 24 genera. Das *et al.* [9] studied Ichthyofauna of Subansiri River in Assam and Arunachal Pradesh, India, they reported a total 87 different fishes were collected under 55 genera; they are classified into 9 orders and 22 families. Das *et al* [10] studied the fish diversity of River Siang in Arunachal Pradesh, India.

STUDY SITE:

The River Siang, is largest river of Brahmaputra river system, originates from Chema Yungdung Glacier near Kubi at 5150 m in Tibet. In Tibet it is popularly known as Tsang-Po, flows in West–East direction. After traversing a distance of about 1625 km river in Tibet and then it takes a turn in south direction, enters the territory of India near Tuting in the Upper Siang district of Arunachal Pradesh and flows through North–South direction in East Siang district towards Assam and finally it merges with Lohit and Dibang in Assam and it becomes the mighty River Brahmaputra [11], [12], [13].

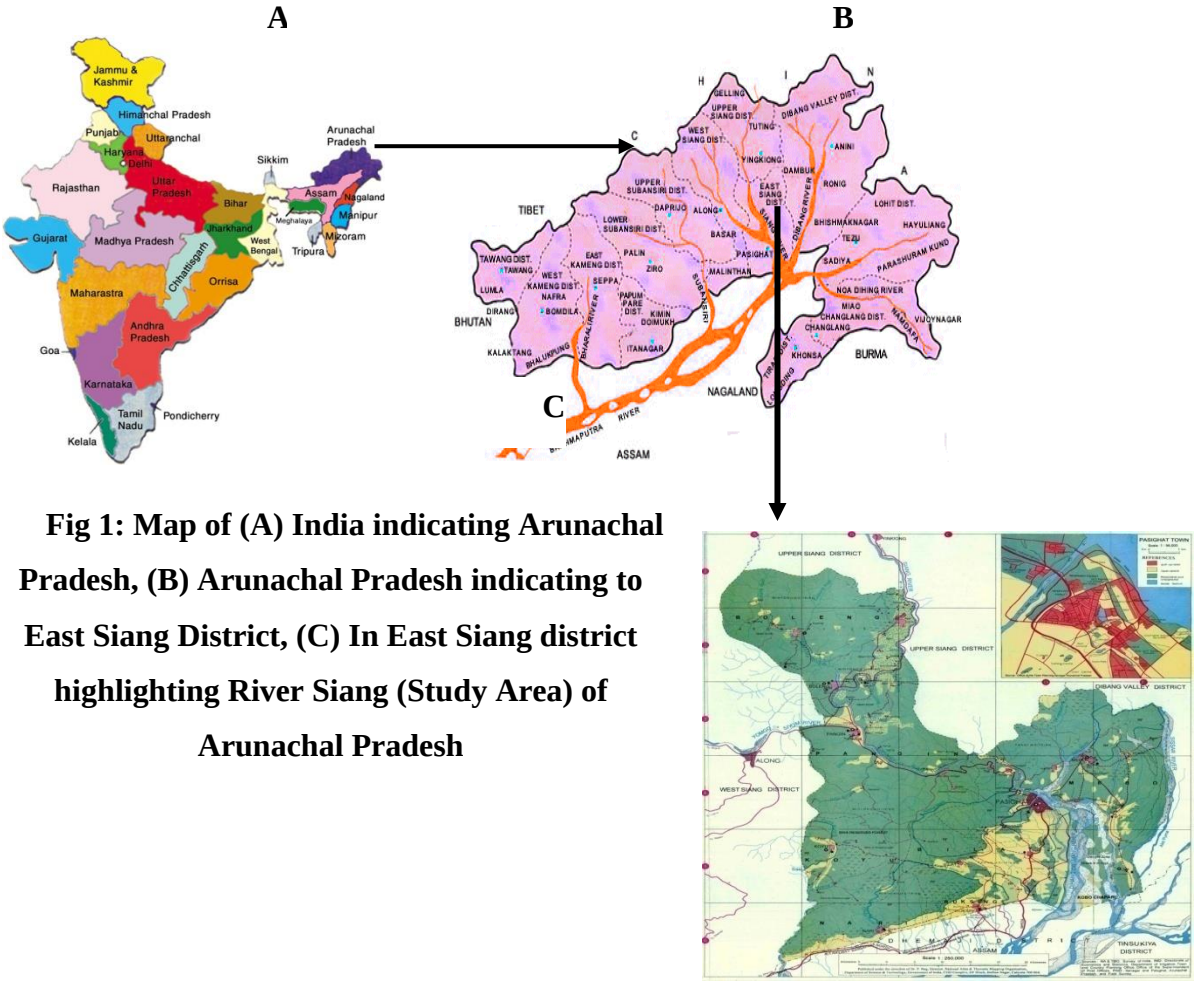

Fig 1: Map of (A) India indicating Arunachal Pradesh, (B) Arunachal Pradesh indicating to East Siang District, (C) In East Siang district highlighting River Siang (Study Area) of Arunachal Pradesh

MATERIALS AND METHODS:

General survey of the fish biodiversity was done using standard procedures [14]. Fish samples were collected from Siang River during June 2012 to December 2013 through experimental fishing; using cast nets (dia.3.7 m and 1.0 m), gill nets (vertical height 1.0 m- 1.5 m; length 100 m -150 m), drag nets (vertical height 2.0 m), triangular scoop nets (vertical height 1.0 m) and a variety of traps and also by hooks and lines. Local people were involved in the netting and also in the fish collection. Fish collecting sites were chooses in the survey area based on micro-habitat types, substrate type, water quality, soil quality and the depth of the river. Fish species have been preserved at first in concentrated (100% formaldehyde) formaldehyde in the field. After that, the fishes were transferred to into a glass container containing 10% formaldehyde for preservations purpose. In the laboratory the fish species have been identified after standard literature by following Talwar and Jhingran [1], Jayaram [15], Kar [16] and Vishwanath [17].

RESULTS:

Fishes depend upon the characteristics of their aquatic habitat which supports all their biological functions. The present study on fish faunal diversity of River Siang of Arunachal Pradesh was carried out from 2012 to 2014 in different seasons throughout the year. The study on River Siang reveals the presence of 90 species of fishes belonging 60 genera under 8 orders and 24 families. Cypriniformes most abundant in the whole river; Beloniformes and Tetradontiformes were found in less abundant during the whole study period. River Siang revealed the presence of 90 species of fishes belonging 60 genera under 8 orders and 24 families (Table 1). The analysis of variance between the fish population within the four seasons of River Siang was found to be statistically significant; as the F critical was less than the F value (F_{crit} 2.429987 < F_{value} 2.628151716; $P < 0.05$, df = 3).

In the present study on fish diversity, it was revealed that the number of fishes was recorded higher in Pre-Monsoon and Monsson seasons in all the studied years. According to IUCN [18] most of the fish species recorded in River Siang were recorded under the category of least concern, as 79% in 2012, 82% in 2013 and 80% in 2014. However, only 3% in 2012, 2013 and 2% in 2014 recorded as the endangered category among the fishes of River Siang. However, in 2012 and 2014, 4% fishes were recorded as the vulnerable category (Figure 2).

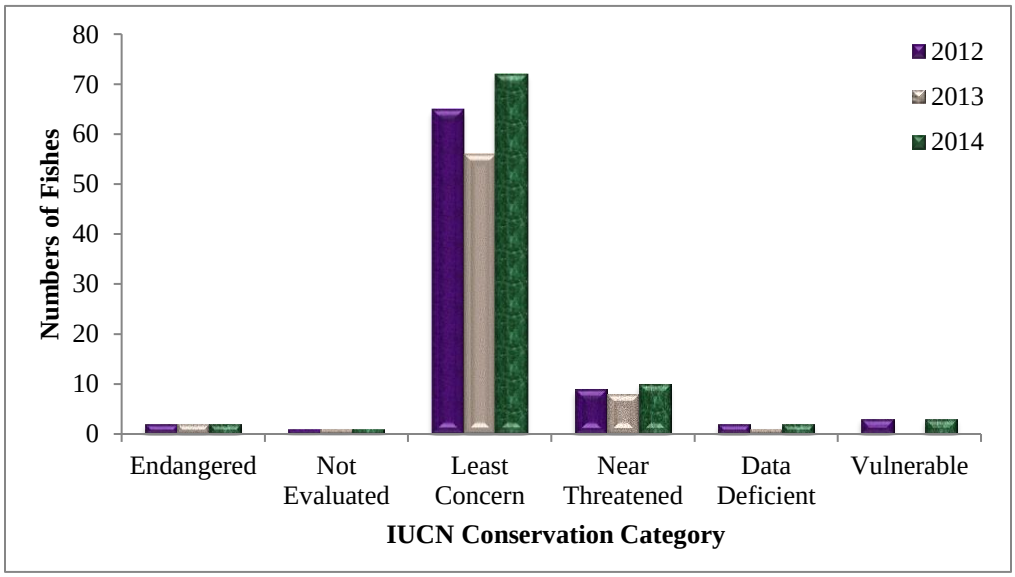

Figure 2: IUCN Conservation Status of Fishes of River Siang in Different Year

According to the CAMP conservation category, 33% in 2012, 34% in 2013 and 34% in 2014 recorded under low risk near threatened category while only 4% in 2012 and 2013 and 3% in 2014 recorded as the endangered category among the fishes of River Siang in Arunachal Pradesh (Figure 3).

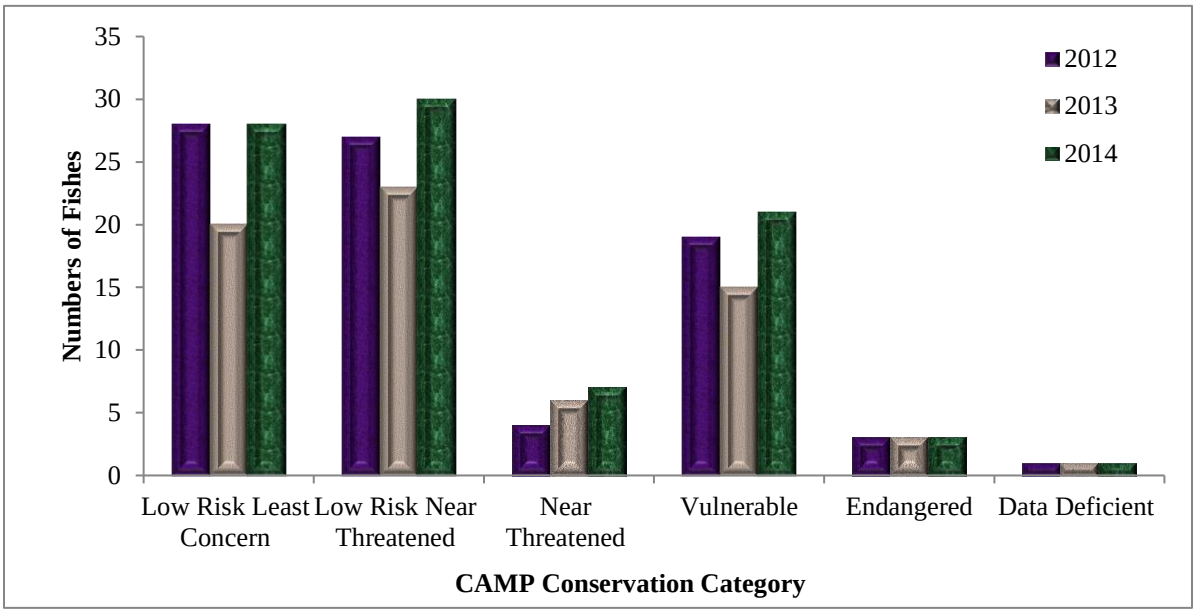

Figure 3: CAMP Conservation Status of Fishes of River Siang in Different year

Table 1: List of Fishes of River Siang

Sr No	Fish Common Name	Fish Scientific Name	Length	Order	Family	Genus	Conservation Status	
							(IUCN)	(CAMP)
1	Reibo	***Aborichthys elongates*** Hora, 1921	4.4 cm	Cypriniformes	Nemacheilidae	***Aborichthys*** Chaudhuri	LC	LRLc
2	Rebio	***Aborichthys kempi*** Chaudhuri, 1913	6.2 cm	Cypriniformes	Nemacheilidae	***Aborichthys*** Chaudhuri	NT	NT
3	Rebio	***Acanthocobitis botia*** (Hamilton-Buchanan, 1822)	7.6 cm	Cypriniformes	Nemacheilidae	***Acanthocobitis*** Peters	LC	LRLc

4	Batasi	***Ailia coila*** (Hamilton-Buchanan, 1822)	12.0 cm	Siluriformes	Schilbeidae	***Ailia*** Gray	NT	NT
5	Tayek	***Amblyceps mangois*** (Hamilton-Buchanan, 1822)	8.9 cm	Siluriformes	Amblycipitidae	***Amblyceps*** Blyth	LC	LRnt
6	Morula	***Amblypharyngodon mola*** (Hamilton-Buchanan, 1822)	17.2 cm	Cypriniformes	Cyprinidae	***Amblypharyngodon*** Bleeker	LC	LRnt
7	Koi	***Anabas testudineus*** (Bloch, 1792)	12.5 cm	Perciformes	Anabantidae	***Anabas*** Cuvier	DD	VU
8	Boriwala	***Aspidoparia jaya*** (Hamilton-Buchanan, 1822)	11.8 cm	Cypriniformes	Cyprinidae	***Aspidoparia*** Heckel	LC	VU
9	Rebio tapio	***Badis assamensis*** Ahl, 1937	6.8 cm	Perciformes	Badidae	***Badis*** Bleeker	DD	NT
10	Khen Ngoi	***Badis badis*** (Hamilton-Buchanan, 1822)	5.0 cm	Perciformes	Badidae	***Badis*** Bleeker	LC	LRnt
11	Mein Lomen	***Bagarius bagarius*** (Hamilton-Buchanan, 1822)	155 cm	Siluriformes	Sisoridae	***Bagarius*** Bleeker	NT	VU
12	Nepura	***Bangana dero*** (Hamilton-Buchanan, 1822)	43 cm	Cypriniformes	Cyprinidae	***Bangana*** Cuvier	LC	LRnt
13	Rebio tapio	***Barilius barna*** (Hamilton-Buchanan, 1822)	15.0 cm	Cypriniformes	Cyprinidae	***Barilius*** Hamilton-Buchanan	LC	LRLc
14	Rebio tapio	***Barilius bendelisis*** (Hamilton-Buchanan, 1807)	19.7 cm	Cypriniformes	Cyprinidae	***Barilius*** Hamilton-Buchanan	LC	LRLc

15	Pan Ngoi	***Botia dario*** (Hamilton-Buchanan, 1822)	15.1 cm	Cypriniformes	Cobitidae	***Botia*** Gray	LC	LRLc
16	Pan Ngoi	***Botia rostrata*** Gunther, 1868	11.3 cm	Cypriniformes	Cobitidae	***Botia*** Gray	VU	VU
17	Boriwala	***Cabdio morar*** (Hamilton-Buchanan, 1822)	12.2 cm	Cypriniformes	Cyprinidae	***Cabdio*** Linnaeus	LC	LRnt
18	Bahu	***Catla catla*** (Hamilton-Buchanan, 1822)	52.4 cm	Cypriniformes	Cyprinidae	***Catla*** Valenciennes	LC	LRnt
19	Keintah Puthi	***Chagunius chagunio*** (Hamilton-Buchanan, 1822)	22.2 cm	Cypriniformes	Cyprinidae	***Chagunius*** H. M. Smith	LC	LRLc
20	Chanda	***Chanda nama*** (Hamilton-Buchanan, 1822)	7.8 cm	Perciformes	Ambassidae	***Chanda*** Hamilton-Buchanan	LC	LRLc
21	Cheng	***Channa gachua*** (Hamilton-Buchanan, 1822)	12.5 cm	Perciformes	Channidae	***Channa*** Scopoli	LC	LRnt
22	Gajar	***Channa marulius*** (Hamilton-Buchanan, 1822)	78 cm	Perciformes	Channidae	***Channa***Scopoli	LC	LRnt
23	Cheng	***Channa orientalis*** Bloch and Schneider, 1801	33.0 cm	Perciformes	Channidae	***Channa*** Scopoli	NE	VU
24	Goroi	***Channa punctata*** (Bloch, 1793)	26.3 cm	Perciformes	Channidae	***Channa*** Scopoli	LC	LRnt
25	Chengeli	***Channa stewartii*** (Playfair, 1867)	17.8 cm	Perciformes	Channidae	***Channa*** Scopoli	LC	VU
26	Shoal	***Channa striata*** (Bloch, 1793)	74.9 cm	Perciformes	Channidae	***Channa*** Scopoli	LC	LRLc

27	Chital	***Chitala chitala*** (Hamilton-Buchanan, 1822)	54.8 cm	Osteoglossiformes	Notopteridae	***Notopterus*** Lacepede	NT	NT
28	Mirika	***Cirrhinus mrigala*** (Hamilton-Buchanan, 1822)	56.9 cm	Cypriniformes	Cyprinidae	***Cirrhinus*** Oken	LC	LRLc
29	Lachim	***Cirrhinus reba*** (Hamilton-Buchanan, 1822)	30.0 cm	Cypriniformes	Cyprinidae	***Cirrhinus*** Oken	LC	VU
30	Magur	***Clarias batrachus*** (Hamilton-Buchanan, 1822)	37.6 cm	Siluriformes	Clariidae	***Clarias*** Scopoli	EN	VU
31	Ngoyou	***Crossocheilus latius*** (Hamilton-Buchanan, 1822)	12.5 cm	Cypriniformes	Cyprinidae	***Crossocheilus*** van-Hasselt	LC	DD
32	Sundori	***Cyprinion semiplotum*** (McClelland, 1839)	37.9 cm	Cypriniformes	Cyprinidae	***Cyprinion*** Heckel	VU	VU
33	Tapo	***Danio dangila*** (Hamilton-Buchanan, 1822)	12.3 cm	Cypriniformes	Cyprinidae	***Danio*** Hamilton-Buchanan	LC	LRLc
34	Darikona	***Danio rerio*** (Hamilton-Buchanan, 1822)	3.8 cm	Cypriniformes	Cyprinidae	***Danio*** Hamilton-Buchanan	LC	LRnt
35	Tapo	***Devario aequipinnatus*** (McClelland, 1839)	12.3 cm	Cypriniformes	Cyprinidae	***Devario*** Hamilton-Buchanan	LC	LRnt
36	Kangon	***Eutropiichthys vacha*** (Hamilton-Buchanan, 1822)	24.3 cm	Siluriformes	Schilbeidae	***Eutropiichthys*** Bleeker	LC	NT
37	Darikona	***Esomus danricus***	13.0 cm	Cypriniformes	Cyprinidae	***Esomus*** Swainson	LC	LRLc

		(Hamilton-Buchanan, 1822)						
38	Tunti	***Erethistes pusillus*** Muller and Troschel, 1849	4.2 cm	Siluriformes	Schilbeidae	***Erethistes*** Muller and Troschel	LC	NT
39	Keyakatta	***Gagata cenia*** (Hamilton-Buchanan, 1822)	12.2 cm	Siluriformes	Sisoridae	***Gagata*** Bleeker	LC	VU
40	Keyakatta	***Gagata gagata*** (Hamilton-Buchanan, 1822)	21.1 cm	Siluriformes	Sisoridae	***Gagata*** Bleeker	LC	VU
41	Ngop	***Garra annandalei*** Hora, 1921	13.9 cm	Cypriniformes	Cyprinidae	***Garra*** Hamilton-Buchanan	LC	LRLc
42	Ngoyou Totum	***Garra gotyla gotyla*** (Gray, 1830)	14.5 cm	Cypriniformes	Cyprinidae	***Garra*** Hamilton-Buchanan	LC	VU
43	Kemp	***Garra kempi*** Hora, 1921	11.3 cm	Cypriniformes	Cyprinidae	***Garra*** Hamilton-Buchanan	LC	VU
44	Nunguga	***Garra lissorhynchus*** (McClelland, 1842)	9.1 cm	Cypriniformes	Cyprinidae	***Garra*** Hamilton-Buchanan	LC	VU
45	Dohjei	***Garra mcclellandi*** (Jerdon, 1849)	13.6 cm	Cypriniformes	Cyprinidae	***Garra*** Hamilton-Buchanan	LC	LRLc
46	Patimutura	***Glossogobius giuris*** (Hamilton-Buchanan, 1822)	35.9 cm	Perciformes	Gobiidae	***Glossogobius*** Gill	LC	LRnt
47	Ngop	***Glyptothorax annandalei*** Hora, 1923	11.5 cm	Siluriformes	Sisoridae	***Glyptothorax*** Blyth	LC	LRLc
48	Ngop	***Glyptothorax cavia*** (Hamilton-Buchanan, 1822)	25.8 cm	Siluriformes	Sisoridae	***Glyptothorax*** Blyth	LC	LRLc

49	Chapila	***Gudusia chapra*** (Hamilton-Buchanan, 1822)	15.8 cm	Clupeiformes	Clupeidae	***Gudusia*** Fowler	LC	LRLc
50	Singhi	***Heteropneustes fossilis*** (Bloch, 1794)	22.2 cm	Siluriformes	Heteropneustidae	***Heteropneustes*** Muller	LC	VU
51	Bata	***Labeo bata*** (Hamilton-Buchanan, 1822)	45.7 cm	Cypriniformes	Cyprinidae	***Labeo***Cuvier	LC	LRnt
52	Kalbasu	***Labeo calbasu*** (Hamilton-Buchanan, 1822)	67.8 cm	Cypriniformes	Cyprinidae	***Labeo*** Cuvier	LC	LRnt
53	Kuri	***Labeo gonius*** (Hamilton-Buchanan, 1822)	127.9 cm	Cypriniformes	Cyprinidae	***Labeo*** Cuvier	LC	LRnt
54	Ghoria	***Labeo pangusia*** (Hamilton-Buchanan, 1822)	78.2 cm	Cypriniformes	Cyprinidae	***Labeo*** Cuvier	NT	LRnt
55	Rohu	***Labeo rohita*** (Hamilton-Buchanan, 1822)	178.6 cm	Cypriniformes	Cyprinidae	***Labeo*** Cuvier	LC	LRnt
56	Remum Poda	***Lepidocephalichthys guntea*** (Hamilton-Buchanan, 1822)	14.9 cm	Cypriniformes	Cobitidae	***Lepidocephalich*** Bleeker	LC	LRLc
57	Tora	***Macrognathus aral*** (Bloch and Schneider, 1801)	54.6 cm	Synbranchiformes	Mastacembelidae	***Macrognathus*** Lacepede	LC	LRLc
58	Tora	***Macrognathus pancalus*** Hamilton-Buchanan, 1822	18.0 cm	Synbranchiformes	Mastacembelidae	***Macrognathus*** Lacepede	LC	LRnt
59	Bami	***Mastacembelus armatus*** (Lacepede, 1800)	67.9 cm	Synbranchiformes	Mastacembelidae	***Mastacembelus*** Scopoli	LC	LRLc
60	Elang	***Megarasbora***	13.3 cm	Cypriniformes	Cyprinidae	***Megarasbora***	LC	LRLc

		elanga (Hamilton-Buchanan, 1822)				Hamilton-Buchanan		
61	Cuchia	***Monopterus cuchia*** (Hamilton-Buchanan, 1822)	78.2 cm	Synbranchiformes	Synbranchidae	***Monopterus*** Lacepede	LC	LRnt
62	Tengra	***Mystus bleekeri*** (Day, 1877)	12.6 cm	Siluriformes	Bagridae	***Mystus*** Scopoli	LC	VU
63	Tengra	***Mystus cavasius*** (Hamilton-Buchanan, 1822)	23.8 cm	Siluriformes	Bagridae	***Mystus*** Scopoli	LC	LRnt
64	Tengra	***Mystus vittatus*** (Bloch, 1794)	16.7 cm	Siluriformes	Bagridae	***Mystus*** Scopoli	LC	VU
65	Tengra	***Mystus tengara*** (Hamilton-Buchanan, 1822)	14.4 cm	Siluriformes	Bagridae	***Mystus*** Scopoli	LC	VU
66	Gadgedi	***Nandus nandus*** (Hamilton-Buchanan, 1822)	22.5 cm	Perciformes	Nandidae	***Nandus*** Valenciennes	LC	LRnt
67	Ngoge	***Neolissochilus hexagonolepis*** (McClelland, 1839)	76.6 cm	Cypriniformes	Cyprinidae	***Neolissochilus*** Rainboth	NT	LRnt
68	Kanduli	***Notopterus notopterus*** (Pallas, 1769)	46.1 cm	Osteoglossiformes	Notopteridae	***Notopterus*** Lacepede	LC	LRnt
69	Pabo	***Ompok bimaculatus*** (Bloch, 1794)	44.7 cm	Siluriformes	Siluridae	***Ompok*** Lacepede	NT	EN
70	Pabo	***Ompok pabda*** (Hamilton-Buchanan, 1822)	30.0 cm	Siluriformes	Siluridae	***Ompok*** Lacepede	NT	LRLc
71	Chanda	***Parambassis baculis*** (Hamilton-Buchanan, 1822)	4.0 cm	Perciformes	Ambassidae	***Parambassis*** Bleeker	LC	LRLc

72	Chanda	***Parambassis ranga*** (Hamilton-Buchanan, 1822)	6.0 cm	Perciformes	Ambassidae	***Parambassis*** Bleeker	LC	LRLc
73	Ngopnogi	***Psilorhynchus balitora*** (Hamilton-Buchanan, 1822)	6.0 cm	Cypriniformes	Psilorhynchidae	***Psilorhynchus*** McClelland	LC	LRLc
74	Puthi	***Pethia ticto*** (Hamilton-Buchanan, 1822)	8.2 cm	Cypriniformes	Cyprinidae	***Pethia*** Hamilton-Buchanan	LC	LRnt
75	Puthi	***Puntius chola*** (Hamilton-Buchanan, 1822)	11.8 cm	Cypriniformes	Cyprinidae	***Puntius*** Hamilton-Buchanan	LC	VU
76	Puthi	***Puntius sophore*** (Hamilton-Buchanan, 1822)	15.6 cm	Cypriniformes	Cyprinidae	***Puntius*** Hamilton-Buchanan	LC	LRnt
77	Ngotabolm	***Raiamas bola*** (Hamilton-Buchanan, 1822)	22.8 cm	Cypriniformes	Cyprinidae	***Raiamas*** Hamilton-Buchanan	LC	LRnt
78	Darikona	***Rasbora rasbora*** (Hamilton-Buchanan, 1822)	13.0 cm	Cypriniformes	Cyprinidae	***Rasbora*** Bleeker	LC	LRLc
79	Ritha	***Rita rita*** (Hamilton-Buchanan, 1822)	127.8 cm	Siluriformes	Bagridae	***Rita*** Bleeker	LC	LRnt
80	Chela	***Salmophasia bacaila*** (Hamilton-Buchanan, 1822)	18.0 cm	Cypriniformes	Cyprinidae	***Salmophasia*** Swainson	LC	LRLc
81	Adoi	***Schizothorax progastus*** (McClelland, 1839)	44.7 cm	Cypriniformes	Cyprinidae	***Schizothorax*** Heckel	LC	LRnt
82	Kadong	***Schizothorax richardsonii*** (Gray, 1832)	32.5 cm	Cypriniformes	Cyprinidae	***Schizothorax*** Heckel	VU	VU

83	Arii	***Sperata seenghala*** (Sykes, 1839)	32.5 cm	Siluriformes	Bagridae	***Sperata*** Wu	LC	LRLc
84	Seni Puthi	***Systomus sarana*** (Hamilton-Buchanan, 1822)	25.7 cm	Cypriniformes	Cyprinidae	***Systomus*** Hamilton-Buchanan	LC	VU
85	Cutcutia	***Tetraodon cutcutia*** (Hamilton-Buchanan, 1822)	8.2 cm	Tetraodontiformes	Tetraodontidae	***Tetraodon*** Linnaeus	LC	NT
86	Ngauch	***Tor putitora*** (Hamilton-Buchanan, 1822)	196.4 cm	Cypriniformes	Cyprinidae	***Tor*** Gray	EN	EN
87	Ngorika	***Tor tor*** (Hamilton-Buchanan, 1822)	167.8 cm	Cypriniformes	Cyprinidae	***Tor*** Gray	NT	EN
88	Kholisa	***Trichogaster labiosa*** Day, 1877	5.1 cm	Perciformes	Osphronemidae	***Trichogaster*** Bloch and Schneider	LC	LRLc
89	Borali	***Wallago attu*** (Bloch and Schneider, 1801)	206.8 cm	Siluriformes	Siluridae	***Wallago*** Bleeker	NT	LRnt
90	Chowki	***Xenentodon cancila*** (Hamilton-Buchanan, 1822)	32.7 cm	Beloniformes	Belonidae	***Xenentodon*** Ragon	LC	LRnt

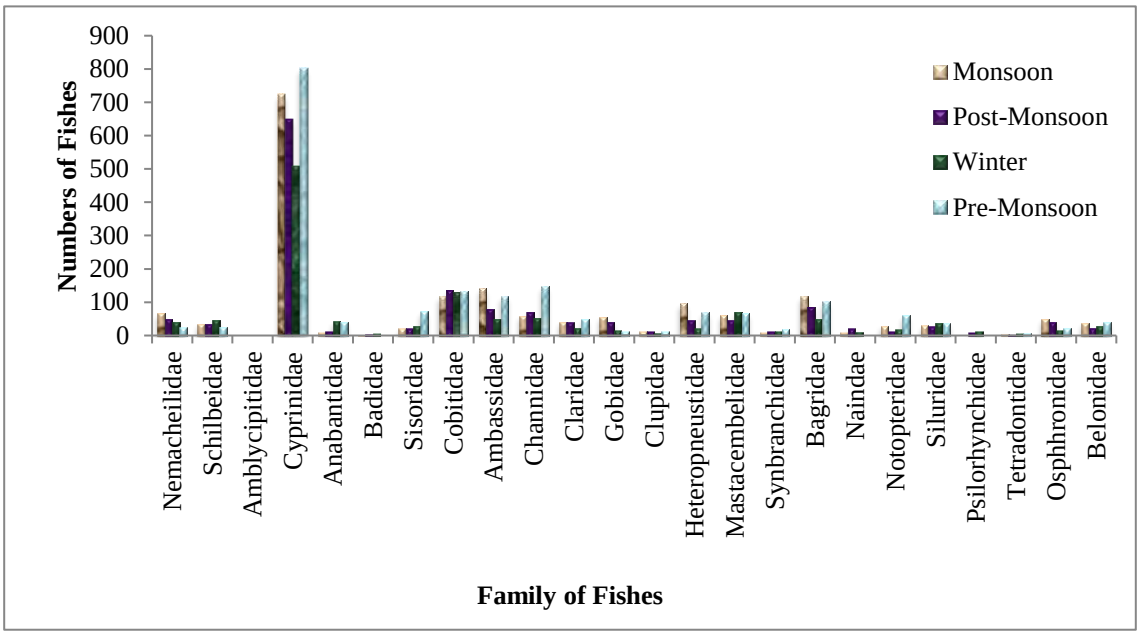

Figure 4: Ichthyodiversity recorded in different seasons in River Siang on basis of Family during 2014

Table 2: Percentage (%) of Fishes (Order wise) of River Siang in different years

Sr. No.	Order	Fish Percentage (%)		
		2012	2013	2014
1	Cypriniformes	49	43	53
2	Siluriformes	14	21	18
3	Perciformes	26	22	18
4	Clupeiformes	1	1	1
5	Synbranchiformes	5	6	5
6	Osteoglossiformes	2	3	2
7	Tetradontiformes	1	1	1
8	Beloniformes	2	3	2

During the year 2013, numbers of individuals of fishes were recorded highest (1197) in pre-monsoon season; while, the lowest (911) was recorded during the winter season. Species richness (S) was highest (62) in monsoon and lowest (57) in post-monsoon. Species diversity index ($H^{/}$) recorded

was between 3.878 and 3.723; maximum in monsoon and minimum in post-monsoon. Simpson index of dominance (D) ranged between 0.02469 and 0.03085, maximum in post-monsoon and minimum in monsoon. Simpson index of diversity (1-D) recorded 0.9792 in post-monsoon and 0.9753 in monsoon season. Evenness (e^H/S) ranged between 0.6964 and 0.7791; maximum in monsoon and minimum in pre-monsoon seasons. Margalef index (D) was recorded between 7.953 and 8.622; maximum in post-monsoon and minimum in monsoon seasons.

Table 3: Species Richness and diversity indices of different seasons

Sr. No	Seasons	Indices						
		Number of Individual	Number of Species (Richness) (S)	Species Diversity ($H^{/}$)	Simpson Diversity Indices		Evenness (e^H/S)	Margalef Index (D)
					Simpson Index of Dominance (D)	Simpson Index of Diversity (1-D)		
1	Winter	911	59	3.783	0.02798	0.972	0.7446	8.511
2	Pre-Monsoon	1197	61	3.749	0.03004	0.97	0.6964	8.466
3	Monsoon	1182	62	3.878	0.02469	0.9753	0.7791	8.622
4	Post Monsoon	1161	57	3.723	0.03085	0.9692	0.726	7.935

DISCUSSION:

The fish fauna of the River Siang drainage exhibit a combination of both hill stream and plain water forms occupying diverse ecological conditions in their distributional ranges. River Siang revealed the presence of 90 species of fishes belonging 60 genera under 8 orders and 24 families (Table 4.4). The results showed that the presence of different sizes (small, medium and large) of freshwater fishes in River Siang. In the present study, the increase in the number of

species with increasing individuals showed an asymptote with no addition of new species. In the present study on fish diversity, it was revealed that the number of fishes was recorded higher in pre-monsoon and monsoon seasons in all the studied years. The year 2014 had recorded a higher diversity of fishes than 2012 and 2013, this was due to the because of the ongoing dam project in the upstream stretches of River Siang, but in the year 2014, the ongoing dam work was fully stopped by local communities for the conservation of the habitat and riverine ecosystem of River Siang. During the whole study period, maximum species richness was reported in monsoon season while minimum recorded in winter season. Species diversity was reported maximum during monsoon and post-monsoon seasons while minimum recorded in winter season during the whole study period.

More than 50% of fish species of River Siang belongs to the order Cypriniformes; whereas, other fishes were represented by the other orders, notably, Siluriformes, Perciformes, Clupeiformes, Synbranchiformes, Osteoglossiformes, Tetradontiformes and Beloniformes. Cypriniformes had been found to be most abundant in the river; while Beloniformes and Tetradontiformes were found to be comparatively less abundant, as observed during the study period. At the same time, the winter had recorded lesser number of fishes as compared to the monsoon and pre-monsoon seasons. In the present investigation it had been observed that the most of the physico-chemical and biological attributes provide congenial environment for the fish growth.

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ORTHOPTERA OF PANDHARPUR TAHSIL

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ABSTRACT:

The present study reports the Orthopteran fauna from the agro-ecological zone and grasslands of Pandharpur Tahsil. In all 23 species of orthopterans were recorded belonging to 23 genera and 05 families viz. Acrididae, Tettigonidae, Gryllidae, Prygomorphidae and Trigonididae.

KEYWORDS: Agro-ecological zone, Grassland ecosystem, Orthoptera, Fauna, Pandharpur

INTRODUCTION:

Order Orthoptera represents small to moderate sized insects with high variation in morphology and species also. These include grasshoppers, locusts, crickets, cave crickets and Katydids. The order Orthoptera is classified into two suborders Caelifera and Ensifera. Among the Class insect, Order Orthoptera is one of the dominant insect order in the tropical region (Nair 2007). It represents 20,000 species worldwide with about 10% ofthe total world species 1,750 species recorded from India (Tandon and Hazra, 1998).

Several inventories were carried out on the different groups of Orthoptera from Indian subcontinent. An important taxonomical work on family Acrididae (Orthoptera) was made by Kirby (1914)in the series ‘Fauna of British India’ and he classified the family Acrididaeinto eight

subfamilies. Uvarov (1921, 1924, 1927, 1942) provided the comprehensive information on the Indian Acrididae. Life wise several accounts are on the hand about orthopteran diversity from the different geographical regions of the country (Agarwala, 1952; Agarwala, 1952; Roonwal, 1956; Tandon, 1975; Julka et al., 1982; Bhowmik, 1985; Shishodia, 1987, Hazra et al., 1993; Shishodia, 1999; Dey and Hazra, 2003; Shishodia, 2010).

Several species of orthopterans are serious pests of agricultural crops and they also acts as primary herbivores in the grassland and forest ecosystem. Visualizing the economic and ecological importance of Orthoptera, intensive surveys were undertaken to find out the Orthopteran complex within agro-ecosystem and grassland ecosystem from Pandharpur Tahsil.

MATERIALS AND METHODS:

Sampling, preservation and identification of specimens:

The routine insect collection material was used during the present study viz. Sweep net, polythene bags, killing jars, and insectlight traps. The collected specimens were brought to the laboratory, cleaned, pinned, spread on spreading/stretching board and oven dried at 60^{o} C for 1 hour. (Drying period is depending on type of specimen). The dry preservation method was followed according to Alfred and Ramakrishna (2004). The identification and confirmation of specimens was made by Dr. Y. J. Koli, Department of Zoology, SantRawoolMaharaj College, Kudal.

Sampling stations:

Faunistic surveys of the Pandharpur Tahsil, especially in the agro-ecological zone and grasslands were conducted between January 2015 to November 2015.The sampling stations selected for collection of grasshoppers areGadegaon, Takali, Mendhapur, Sarkoli, Gursale, OzewadiRanjani, Ambe, Chale and Mundhewadi.

Sampling method and strategy:

The specimens were collected fortnightly during morning hours from 7.00 pm to 9.00. and also in the evening hours from 4.30 to 6.00 pm. The collection of specimens was also made with the help of light trap from 7.00 pm to 8. 00 pm. The collection method of Orthopterans was followed according to (Alfred and Ramakrishna, 2004 and Leather et al., 2005).

STUDY AREA:

Pandharpur tahsil of Solapur district, Maharashtra is geographically situated between 17°30′00″N to 18°05′00″N latitude and75°05′00″E to 75°35′00″E Longitude. The total area of the tehsil is 1303.6 Sq. Km.

The total villages in Pandharpur Tahsil are 103 and for the present study, the agricultural and grassland area of 10 different villages was selected*viz.*Gadegaon, Takali, Mendhapur, Gursale, Sarkoli, Ozewadi, Ranjani, Chale, Ambe and Mundhewadi.

Palkar and Gavade (2013) studied the the land use pattern of Pandharpur tehsil and reported that the land use pattern shows 52% of the land is used for agriculture, 18 % represents fallow land, 17% barren land, 11% grassland and 2% land is occupied by water body.

RESULTS AND DISCUSSION:

The present investigation reports the orthopteran species associated with the agro-ecosystem and grasslands of Pandharpur Tahsil. The agricultural area of the selected villages includes vegetable crops, fruit crops and cash crops. The villages selected for the present study are mentioned in the study area. The patchy grasslands are selected from the nearby area of villages selected as sampling stations.

A total of 23 species were recorded during the study period under 23 genera distributed in 05 families of order Orthopterta viz. Acrididae, Tettigonidae, Pyrgomorphidae, Gryllidae and Trigonidiidae from the Pandharpur Tahsil, district Solapur Maharashtra, India. Table 1 presents the checklist of the orthoptera collected during the study period. Existence of additional species from the Family Tettigonidae, Gryllidae, Pyrgomorphidae andTrigonidiidae is expected, more concentrated efforts are needed to find out the accurate number of species from the study area.

Several records are on hand about Orthoptera of Indian subcontinent. This literature reports the details about species diversity, faunal assessment, richness, pestiferous status of grasshoppers (Kirby, 1914; Dwivedi, 1978; Bhowmik, 1986; Suhail et al., 1999; Shishodia et al., 2002; Chandra, 2003; Paulraj et al., 2009 and Prabhakar et al., 2015). Waghmare et al (2013) studied diversity of Acrididae (Orthoptera) from selected grasslands of Solapur district and

reported 7 species. Bhusnar (2015) studied acrididae of agroecosystemfrom Solapur district and reported 18 species.

Table 1. Orthoptera of Pandharpur Tahsil

Sr. No	Name of species	Family
1	*Dittopternisvenusta* Walker, 1870	Acrididae
2	*Trilophidiaannulata* Thunberg, 1815	Acrididae
3	*Gesonulapunctifrons*Stal, 1860	Acrididae
4	*Phaeobainfumata* Brunner Van Wattenwyi 1893	Acrididae
5	*Acridaturrita* Linnaeus,1758	Acrididae
6	*Hieroglyphusbanian*Fabricius, 1798	Acrididae
7	*Stenocatantopssplendens* Thunberg, 1815	Acrididae
8	*Acridaexaltata* Walker, 1854	Acrididae
9	*Cyrtacanthacristatarica* Linnaeus, 1758	Acrididae
10	*Gastrimargusmarmoratus*Thunberg, 1815	Acrididae
11	*Eyprepocnemisalacrisalacris,*Serville, 1839	Acrididae
12	*Atractomorphacrenulata*Fabricius, 1793	Pyrgomorphidae
13	*Chrotogonustrachypterustrachypterus*Bianchard, 1836	Pyrgomorphidae
14	*Conocephalus maculates* Le Guillous 1841	Tettigoniidae
15	*Mecopoda elongate* Linnaeus, 1758	Tettigoniidae
16	*Holochlora* sp.	Tettigoniidae
17	*Trigonocorpha unicolor* Stall, 1787	Tettigoniidae
18	*Euconocephalusincertaus* Walker,1869	Tettigoniidae
19	*Phonarellus minor*Chopard, 1959	Gryllidae
20	*Gryllodessigillatus* Walker, 1869	Gryllidae
21	*Modicogryllusconfirmatus* Walker,1859	Gryllidae
22	*Telegryllusmitratus*Burmeister, 1838	Gryllidae
23	*Trigonidiumhumbertianum* Saussure, 1878	Trigonidiidae

Plate 1
"Orthoptera of Pandharpur Tahsil"

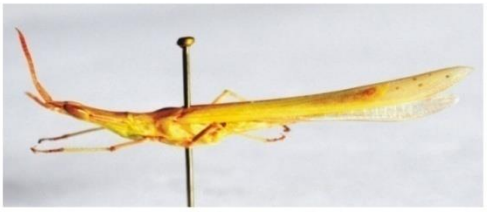
Family Acrididae

Dittopternis venusta Walker, 1870

Trilophidia annulata Thunberg, 1815

Gesonula punctifrons Stal, 1860

Phaeoba infumata Brunner Van Wattenwyi 1893



Acrida turrita Linnaeus,1758

Hieroglyphus banian Fabricius, 1798

Stenocatantops splendens Thunberg, 1815

Acrida exaltata Walker, 1854

Cyrtacanthacris tatarica Linnaeus, 1758

Gastrimargus marmoratus Thunberg, 1815

Plate 2
Family Pyrgomorphidae

Atractomorpha crenulata Fabricius, 1793

Chrotogonus trachypterus trachypterus Bianchard, 1836

Family Tettigonidae

Trigonocorpha unicolor Stall, 1787

Conocephalus maculates Le Guillous 1841

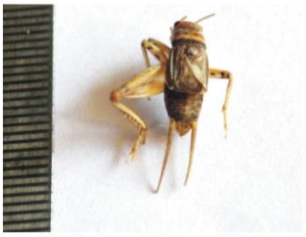
Mecopoda elongate Linnaeus, 1758

Holochlora sp.

Euconocephalus incertaus Walker,1869

Plate 3
Family Gryllidae

Phonarellus minor Chopard, 1959



Gryllodes sigillatus Walker, 1869

Modicogryllus confirmatus Walker,1859

Telegryllus mitratus Burmeister, 1838

Family Trigonididae

Trigonidium humbertianum Saussure, 1878

CONCLSUION:

The agroecosystem and grasslands of Pandharpur Tahasilprovide shelter to great number of Orthopteran species. Orthopterans contribute major part in terms of species diversity and density also in the agro-ecological zone and grasslands of the present study area.

The present study is helpful in the management of pestiferous insects of agro-ecosystem and also helps to understand the primary herbivore complex in the grassland ecosystem. In future, more concentrated efforts are needed to assess food preferences, population density, pacthiness in the agroecosystem and grassland ecosystem ofOrthopterans from this region.

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DIET BREADTH OF BARK AND AMBROSIA BEETLES FROM THE FORESTS OF KOLHAPUR DISTRICT, NORTHERN WESTERN GHATS, MAHARASHTRA

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ABSTRACT:

Based on the observations carried out in the forest area of Kolhapur district, the present paper reports diet breadth of bark and ambrosia beetles. These beetles are well known for their outbreaks in the natural and artificial stands and transmission of plant diseases. In all, 09 species were recorded under 08 genera belonging to 02 subfamilies *viz.* Scolytinae & Platypodinae (Curculionidae: Coleoptera).

KEY WORDS: Insect Herbivores, Food Plant, Beetle, Ambrosia, Western Ghats.

INTRODUCTION:

Herbivore insects are known to feed on almost all types woody mass that is from living healthy tree to furnished wood products. Herbivore insects exhibit rich species diversity, specificity in host plant selection and dispersal with different modes of development.

Among the insect herbivores associated with wood, the bark and ambrosia beetles (Coleoptera: Curculionidae: Scoltynae & Platypodinae) forms most noticeable group of insects exhibiting rich diversity, well developed social organization, specific food, space and feeding habits, concealed life, dispersal, relationship with fungi and diseases.

The beetles from the Scolytinae and Platypodinae (Curculionidae: Coleoptera) recorded in all continents except Antarctica. The majority of the species are found in tropical region but many species are also found in the boreal region [1][2][3][4].

The bark and ambrosia beetles have twofold importance. Several species have been recorded as serious pests of all types of woody material and also known to spread plant diseases. On the other hand they play crucial role in the evolution of natural stand. These beetles kill excess plants in the forest stand when such forest land attain a climax stage and natural outbreaks occur due to high number of over mature trees. After this, the new phase of succession begins with a release of understory. The bark and ambrosia beetles also aid in recycling process which is essential for the maintenance of forest soils and plant succession. These beetles are an important link in food chain. They act as host to number of entomophagous insects, nematodes and rich food resource to birds and small mammals [5][6].

The bark and ambrosia beetles complete their development within wood by preparing galleries and nests. Monophagy and polyphagy have been recorded in many species of Scolytinae and Platypodinae (Curculionidae: Coleoptera). The members of Scolytinae and Platypodinaefind their host plants by the odours of volatile oeleoresins, terpene hydrocarbons, alcohols and other chemical substances released by the injured or recently logged or dying plants or their parts [7].

The symbiotic nature of ambrosia beetles and fungi has been well documented in the recent past[7][8][9][10][11] [12] [13] [14][15][16].Each beetle species has specific fungus whichdevelops in different plant species. Due to this, many species from the Scolytinae and Platypodinae exhibit host specificity [17].

Bark and Ambrosia beetles have been well studied during last century from Indian subcontinent. Earlier studies reports taxonomy, bionomics, their distribution in the Indian subcontinentwith host range, ecological and economic importance of bark and ambrosia beetles [18] [19] [20] [21] [22] [23] [24][25] [26] [27] [28][6].

The Western Ghats of India has rich floral and faunal wealth. As we know that the bark and ambrosia beetles has twofold importance i.e. ecological and economical. With this view, the present work has been carried in the forest area of Kolhapur district to find out the host range of bark and ambrosia beetles from the forest area of Kolhapur district, Northern Western Ghats, Maharashtra.

MATERIALS AND METHODS:

In order to determine the host range of bark and ambrosia beetles, the work was carried out in two phases *viz.* Field Phase and Laboratory Phase during 2011 to 2013.

Materials

Materials used during the study includes a collecting net, forceps, vials containing 70% alcohol and 4% formalin as preserving media, plastic bottles (15 ml) for temporary storage and transportation. Strong field knives used for opening of seed pods, twigs, bark and galls etc. A small fine brush used for picking up small delicate specimens and polythene bags for storing plant material, rearing material, or other samples. Several digging tools were used to collect soil dwelling insects includes long handled spade, ground breakers, mattocks, sickles.

METHODS:

1. Field Phase

Extensive surveys were carried to find out breadth of diet of bark and ambrosia beetles during the present study. The sampling was done at each station (Table-3) in morning (07.00am to 11.00 am) and evening (05.00pm to 8.00pm). During the sampling, beetle habitats on and within the trees and their associated insect groups were observed and sampled accordingly. Recorded habitats and observed evidences were summarized in the Table 1 & 2.

2. Laboratory Phase

A. Killing, preservation and labeling

The specimens were preserved as per wet preservation method[47].

B. Identification

The specimens were identified by Dr. Jiri Hulcr, Assistant Professor, School of Forest Resources and Conservation, University of Florida.

Table 1. Index of methods applied

Methodology	Topics addressed	Reference
External Examinations of trees for Bark and Ambrosia beetles	Assessment of trees in a stand which may be attacked by wood borers, Identity of beetles, Collections of live specimens for subsequent laboratory studies	[46]
External Examinations of trees for Evidence of damage	Assessment of trees in a Stand which may be attacked Presence of beetles/immature stages within shoots and Stems Region of the trunk or stem infested	
Removing Bark or Splitting shoots and logs	Location of Boring species, Identity of boring species, Collection of adult /immature stages which need to be reared to adulthood (that are difficult to identify accurately).	
Hand sorting and beetles	Searching of beetles in damaged wood/ decayed / dead wood	

Table 2. Major habitats of Bark and Ambrosia beetles and evidences of their activity on different parts of trees

Habitat	Beetle Activity	Reference
Shoots/ Stems	Boring Chewing	[46]
Bark Surface	Bark feeding, Boring	
Bark interior	Boring	

Table: 3. Sampling sites selected for the study

Forest	Amba Reserve Forest	Shivaji University Campus	Chandgad Forest Area	Total
Sampling Stations	A1 A2 A3 A4 A5 A6 A7	S1 S2 S3 S4 S5	C1 C2 C3 C4	
Number of Sampling Stations	07	05	04	16

STUDY AREA:

The forest areas of Kolhapur division lie between latitude 15^0 43' to 17^0 10' north and longitude 73^0 40' to 74^0 42' east. The division has eight forest ranges *viz.* Chandgad, Ajara, Gargoti, Radhanagari, Gaganbawada,Karveer, Panhala and Malkapur [29].

The recorded forest area of the district including sanctuary area is 1,744 km^2 which is 22.70 % of the geographical area of the district. The Kolhapur forest division however has a forest area of 1389.71 km^2 that is spread over 8 forest ranges and all 12 talukas and is 18.08% of the geographical area.As per the State of Forest Report 2005 (SOFR), published by Forest Survey of India, Dehra dun, the actual forest cover of Kolhapur district is 1,657 km^2that is 21.56% of the geographical area out of which very dense forests cover is nearly 6% while moderately dense is 57% of the total forest cover. The open forest cover constitutes 37% of the total area under forest cover. This means about 63% of the actual forest cover within the district is moderately dense to very dense [30]

Thestudy was carried out at three different stations viz. Shivaji University Campus, Kolhapur, Amba reserve Forest Area and Chandgad Forest Area. The sampling sites selected for the study are shown in the table 3.

RESULTS AND DISCUSSION:

The study was carried to find out the host plant range of bark and ambrosia beetles from the forest area of Kolhapur Distric during 2011 to 2013. In all, the study reports 09 species belonging to two subfamilies of Family Curculionidae of Order Coleoptera*viz.* Scolytinae and Platypodinae. The host plants recorded during the study period is presented in table 4.

Plate 1
Bark and Ambrosia beetles from the forest of Kolhapur district

Euwallacea sp.

Xyleborinus andrewesi

Xylosandrus crassiusculus

Wallacellus (*Xyleborus*) *similis*

Coccotrypes sp

Xyleborus perforans

Xyleborus affinis

Treptoplatypus solidus

Euplatypus parallelus

Order Coleoptera

Family: Curculionidae

I. Subfamily Scolytinae

1. *Euwallacea* sp.

Material Examined: Kolhapur district, Amba Reserve Forest, 12. v. 2011, (1 ex.), Coll., Bhawane & Mamlayya

Host Plant in Study Area: The *Euwallacea* sp. feeds on the wood of *Symplocosracemosa*..

Earlier Record of Host Plant: This genus is native to Asia. The species with larger body size generally breed and feed on tree trunks [31]. The species from the genus *Euwallacea* known to feed on the wood of *Albizia, Camellia, Hevea, Populus, Robinia, Shorea, Theobroma, Persea, Citrus, Punica*[32].

2. *Xyleborinus andrewesi* Blandford

Material Examined: Kolhapur district, Amba Reserve Forest, 20. vii. 2011, (1 ex.), Coll., Mamlayya

Host Plan in Study Area: The species feeds on the wood of *Symplocosracemosa and Holigarnagrahamii.*

Earlier Record of Host Plant: *Xyleborinus andrewesi* has been recorded from South Asia, Kenya, Zambia and United States of America. *X. andrewesi* is non-host –specific beetle species [33].Globally, there are 59 recorded hosts belonging to 29 families *viz.*Ampellidaceae; Anacardiaceae; Apocynaceae; Bombaceae; Burseraceae; Caesalpiniaceae; Combretaceae; Dilleniaceae; Dipterocarpaceae; Euphorbiaceae; Fagaceae; Guttiferae; Lauraceae; Leguminosae; Malvaceae; Meliaceae; Mimosaceae; Moraceae; Myristicaceae; Myrtaceae; Rubiaceae; Rutaceae; Sapindaceae; Sapotaceae; Sterculiaceae; Theaceae; Tiliaceae; Urticaceae; and Verbenaceae. [23][33][34][1].

3.*Xylosandrus crassiusculus* Motschulsky

Material Examined: Kolhapur district, Chandgad Forest, 19. xi. 2011, (1 ex.), Coll., Bhawane & Mamlayya

Host Plant in Study Area: The species feeds on the wood of *Symplocosracemosa* and *Memecylonumbellatum*

Earlier Record of Host Plant: The native range of *X. crassiculus* is tropical and subtropical Asia, Tropical Africa and North America **[**35][36][37][38] [39][6]. The female prefers to bore

into twigs, branches and small trunks of weak host plants. *X. crassiusculus* is able to breed in a large number of hosts.). In Indian region, it breeds in 12 different pant species [6].*X. crassiusculus*is known to breed in 124 different host plants [34] belonging to 46 plant families. This beetle is widely distributed in tropics. The common hosts are Australian pine, cacao, camphor, coffee, mahogany, mango, papaya, rubber, tea, and teak. In U.S., it breeds in aspen, beech, cherry, Chinese elm, crape myrtle, dogwood, golden rain tree, hickory, locust, magnolia, maples, mimosa, oaks, peach, persimmon, plus, Prunus spp., redbud, sweet gum, tulip poplar, and walnut [39].

4. *Wallacellus* (*Xyleborus*) *similis* Frerrari

Material examined: Kolhapur Dist., Amba Reserve Forest, 19.v.2012. (1 ex) coll. Gaikwad

Host Plant in the Study Area: The species feeds on the wood of *Hologarnagrahamii*

Earlier Record of Host Plant: Usually *X. similis* attacks weak or dying or dead trees in the natural stands. However in the plantations and reforested areas (mono-species area) *X. similis* is successfully colonized, breeds continuously throughout the year and attained a pest status.

The native range of *X. similis* is from Pakistan to Soloman Islands. It has been recorded from Asia, Africa, U.S.A. *Wallacelus (Xyleborus) similis* is a polyphagous. Browne (1961) reported *X. similis*is reported in the wood of 33 plant families [33]. Another study recorded that this species breeds in the wood of 80 plant species which belongs to 32 families [40].

5. *Coccotrypes* sp. (The identification at species level is under process)

Material examined*:* Kolhapur Dist., Amba reserve Forest, 19.v.2012. (1 ex)coll. Gaikwad

Host Plant in Study Area: The species feeds on the wood of *Albizialebbeck and Holigarnagrahamii.*

Earlier Record of Host Plant: *Coccotrypes* is a large genus represents a total of 129 species distributed throughout world [1]. A total of 24 species have been reported from the Indian region [6].This genus is dominant in the Asian countries. In the extended geographic range, several studies reports occurrence of this genus from tropical region of Africa and America [6].

***6. Xyleborusperforans* Wollaston**

Material examined: Kolhapur Dist. Amba Reserve Forest, 07.ix .2013. (1 ex) coll. Bhawane&Mamlayya

Host Plant in study Area: The species feeds on the wood of *Symplocosracemosa, Albizialebbeck and Terminaliatomentosa.*

Earlier Record of Host Plant: It is distributed throughout the tropical and subtropical areas of the world[1].In India, *X. perforans* is known to infest eight species of plants [23][27].From the Indian region, *X. perforans* has been reported on 42 host plants belonging to 19 plant families [33].

***7. Xyleborusaffinis*Echhoff**

Material examined: Kolhapur Dist., Chandagad Forest, 22.viii.2012. (1 ex) coll. Gaikwad

Host Plant in study Area: The species feeds on the wood of *Symplocosracemosa.*

Earlier Record of Host Plant: The distribution of *Xyleborusaffinis* is similar to *Xyleborussimilis. It* is highly polyphagous and known to breed in 248 plant species, angiosperms as well as gymnosperms [34] [35].

II. Subfamily Platypodinae

1. *Treptoplatypus solidus* Bright & Skidmore

Material Examined: Kolhapur district, Chandgad Forest, 12. ix. 2011, (1 ex.), Coll., Mamlayya

Host Plant in Study Area: The species feeds on the wood of *Albizialebbeck and Erythrinaindica.*

Earlier Record of Host Plant: It is well distributed in India, Sri Lanka, Taiwan, Korea andJapan, Australia and Micronesia [41]. It is reported as polyphgous species [1].

2.*Euplatypus parallelus* Fabricius

Material examined: Kolhapur Dist., Karveer, SUK campus, 12. v. 2012 (1 ex) Coll. Mamlayya

Host Plant in Study Area: The species feeds on the wood of *Albizialebbeck.*

Earlier Record of Host Plant: *E. parallelus* is native to South and Central America but has been introduced in Oriental region, and in few parts of Wallacea and New Guinea [42]. It infests *Pterocarpusindicus, Heveabrasiliens*[43][44]*Anacardiumoccidentale*[45].

Table 4. Host Plants of Bark and Ambrosia beetles

Sr. No.	Family	Subfamily	Name of Species	Name of Host Plant
1	Curculionidae	Scolytinae	*Euwallacea* sp.	*Symplocosracemosa*
2			*Xyleborinusandrewesi*Blandford	*Symplocosracemosa and Holigarnagrahamii*
3			*Xylosandruscrassiusculus*Motschulsky	*Symplocosracemosa*and *Memecylonumbellatum*
4			*Wallacellus* (*Xyloborus*) *similis*Frerrari	*Hologarnagrahamii*
5			*Coccotrypes* sp.	*Albizialebbeck and Holigarnagrahamii*
6			*Xyleborusperforans* Wollaston	*Symplocosracemosa, Albizzialebbeck and Terminaliatomentosa*
7			*Xyleborusaffinis*Echhoff	*Symplocosracemosa*
8		Platypodinae	*Treptoplatypus solidus* Bright & Skidmore	*Albizialebbeck and Erythrinaindica*
9			*Euplatypusparallelus*Fabricius	*Albizialebbeck*

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MIDGUT LIPASE ACTIVITY IN *ANTHERAEA PROYLEI* J.

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ABSTRACT:

Assay of midgut lipase activity in larvae of *Antheraea proylei* revealed an optimum pH 8.0 at optimum temperature 40^0C. The linear period of enzyme activity was found at 50 minutes with km value $2.82 \times 10^{-4.}$ The 50% inhibition at higher temperature (60^0C) was found to be 12 minutes.

KEYWORDS: Midgut; Lipase, *Antheraea proylei.*

INTRODUCTION:

Lipases are lipolytic digestive enzymes. They can be defined as the long chain fatty acid ester hydrolases, with the alcohol moiety of ester being glycerol. They bring out hydrolysis of dietary triglycerides. Lipases are water soluble enzymes and catalysis occurs at the oil water interface and catalytic efficiency dependent on suitable dispersion and stabilization of the oil droplet.

In most of the insect species, the energy required for the transformation is derived from lipid. Mainly reserves of triglycerides and the lipase activity is instrumental in the release of energy (Agrell & Lindquist, 1973; Devakinandan *et al*., 1973). Lipolytic activity in insect tissue and its significance in lipid transport was studied by Gilbert *et al*., (1965).

Very fine work has been done on the lipases in insects (Gilbert, 1967; Radhapant, *et al*., 1978; Radhapant & Suman Kumar, 1979). The pre labeled triglycerides in the fat body are

diglycerides there by implying the presence of extra digestive lipases. The actual presence of lipases, hydrolyzing triglycerides was detected in tissue like flight muscles and fat bodies of moth *Hyalophora cercopia* and the cockroach *Periplaneta americana* (Tietz, 1962; Chino and Gilbert, 1965). The triglycerol hydrolyzing capacity of the tissue homogenate has been investigated for midgut, fat body, thoracic musculature and haemolymph of Americam Cockroach, *Periplaneta americana* (Hoffman & Downer, 1979). The level of lipase activity in tissues of third instar larvae of blowfly, *Calliphora erythrocephala* has been measured by Price (1975).

Lipase activity during embryogenesis, larval growth, metamorphosis and in fat body of *Chrysomya rufifacies* has been studied by Pol & Sawant (1990; 1992). Dipteran larvae are known to accumulate lipids, glycogen & proteins during developmet (Pearineoff, 1960; Wigglesworth, 1972). The reason for storing these constituents in larva is fairly obvious. This material later on used during metamorphosis. The lipid store is then utilized to provide energy for metamorphosis (Rao & Agarwal, 1971). Hence its content is reduced in the pupa (Devakinandan *et al*., 1973).

The review of earlier investigation on the lipase study point out that there is no information on lipase activity in *Antheraea proylei.* Hence the present work has been carried out for characterization of lipase to identify the role of midgut in digestion.

MATERIAL AND METHODS:

The cocoons of *Antheraea proylei* were procured from Wangbal sericulture farm, Thoubal District, Manipur State, India. The rearing was performed under laboratory conditions as per method of Jolly *et al*., (1979) and larvae were reared on fresh leaves of *Terminalia catappa*.

The fifth instar larvae were dissected in chilled insect ringer. The midgut was homogenized in 0.9% saline. The homogenates were centrifuged at 3000 rpm for 20 minutes and supernatants were used for characterization of lipase. The assay consisted of 0.25 ml emulsion of triolene in appropriate buffer followed by incubation of 40 ^{0} C for 10 minutes. The reaction was terminated by adding 2 ml of ATC (mixture of acetic acid, triethanol amine & copper nitrate in ratio of 1: 9: 10) reagent and then vigorously shaken and allowed to stand for 60 minutes. Then 2 ml of chloroform layer was pipetted out in well stoppered tube. Then add lipase coloring reagent

of 1.5 ml. The free fatty acids in chloroform produce pink colour with coloring reagent, were measured calorimetrically according top Itaya (1977) at 550 nm. The activity was expressed as µg palmitic acid/ µg protein/hr.

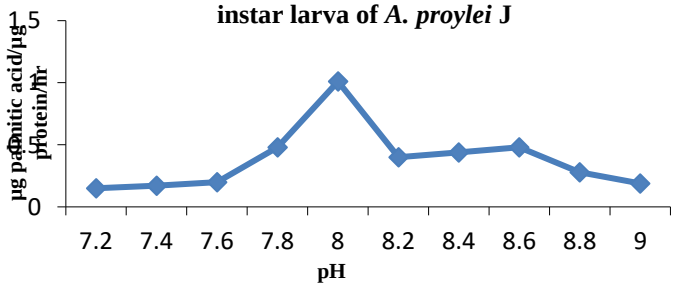
The optimum pH was determined by using appropriate buffers. To determine the optimum temperature, the reaction mixture was incubated for 50 minute at various temperatures ranging from 10 – 60 ^{0}C. To determine thermolability, the enzyme extract was subjected to 60 ^{0}C treatment in water bath for different period of time. One tube of enzyme extract was stored at 5 ^{0}C until needed which served as control. After treatment tubes were cooled in ice cold water. The residual lipase activity was determined as usual. The procedure of Hayashi & Tappel (1970) was used for the determination of lipase activity. The protein concentration of enzyme extract was determined as per Lowry et al., (1951).

RESULTS:

1. pH:

The maximal activity of lipase in midgut occurred at pH 8.0 (fig. 1).

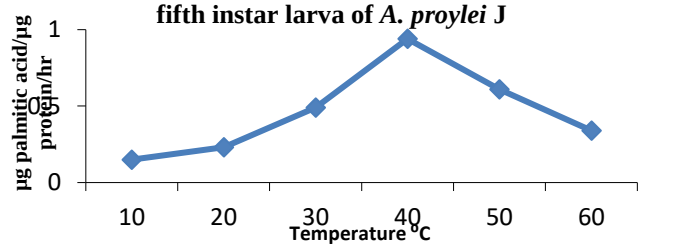
Fig. 1. Effect of pH on midgut lipase activity in fifth instar larva of *A. proylei* J



2. Temperature:

The optimum temperature for mid gut lipase was 40 ^{0}C. (fig. 2).

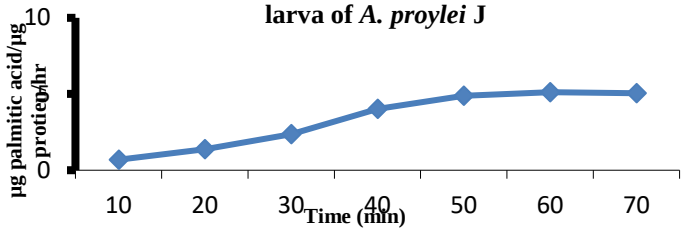
Fig. 2. Effect of temperature on midgut lipase activity in fifth instar larva of *A. proylei* J



3. Time:

A digestion period of 50 minutes was found fit within the linear part of enzymatic activity curve in midgut (fig.3)

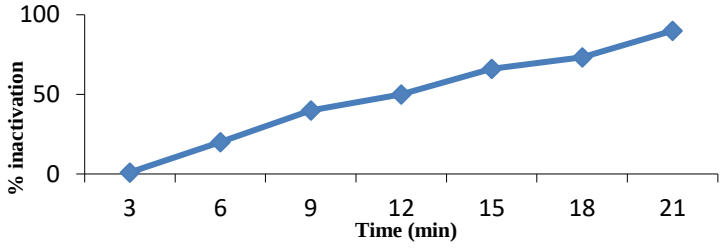
Fig. 3. Effect of time on midgut lipase activity in fifth instar larva of *A. proylei* J



4. Thermolabillity:

The theoretical duration of high treatment at 60 ^{0}C for 50 % loss of activity was found to be 12 minutes. (fig. 4)

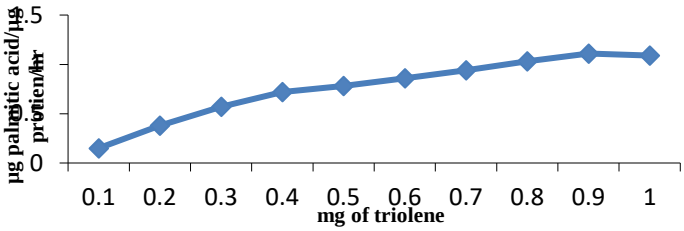
Fig. 4. Thermal inactivation of midgut lipase activity in fifth instar larva of *A. proylei* J

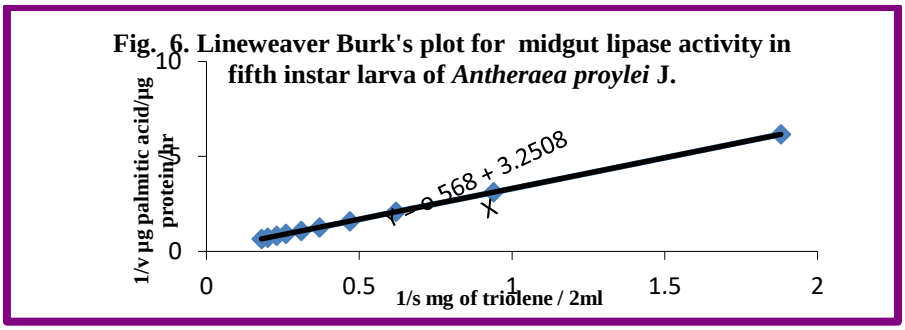


5. Substrate concentration:

The relationship between palmitic acid concentration and rate of hydrolysis was shown in fig. 5. Lineweaver Burk's plot was employed by using regression equation Y = ax + b (fig. 6). The km valur obtained for lipase was found to be 2.82 × 10 $^{-4}$

Fig. 5. Effect of substrate concentration on midgut lipase activity in fifth instar larva of *A. proylei* J





DISCUSSION:

The main site of lipid digestion in insects is the midgut (McFarlane, 1985). Lipids have assumed considerable functional significance during the evolutionary history of the class Insecta. They are essentially structural components of the cell membrane and cuticle and provide a rich source of metabolic energy for periods sustained energy demand. They facilitate water conservation both by formation of water impermeable barrier and by yielding metabolic water up on oxidation and include important hormones and pheromones.

Turunen (1975) showed that renewed synthesis of triglycerides occurs in the larval midgut cells of *Pieris brassicae*. Before being transported from the midgut these triglycerides must be hydrolyzed by an intracellular lipase and diglycerides are released in to the haemolymph. Argell & Lindquist (1975) concluded that lipid possess many metabolic and physiological advantages over other potential reserve materials.

Lipase E.C. 3.1.1.3. plays a significant role in the mobalization of energy (Krysan & Guss, 1975). Most reports on insect digestive lipases described triglycerol – hydrolyzing enzymes (Vonk & Western, 1984). Applebaum (1985) reviewed the processes that are thought to take place in several insect species. After secretion of triglycerol lipase from the mid gut and caecae, free fatty acids are released. These free fatty acids and the SH-2 monoacylglycerols are then SH-2 monoacylglycerol are processes probably occur in most insect species that regularly ingest dietary triglycerol.

Gilmour (1961) concluded that many insect lipases showed the maximal activity in a weakly alkaline medium. It is said that at high pH the fatty acids in the form of soaps help to emulsify the fat and thus promote the action of lipases. However Shinoda (1930) showed that in silkworm, the lipase worked best in a neutral medium although the gut content was highly

alkaline. Wigglesworth (1928) had shown that the cockroach gut lipase was maximally active at alkaline pH.

Assay of lipase activity revealed that optimum pH required for maximum lipase activity is 8.0 in *Antheraea proylei.* Similar results were reported in house cricket *Acheta domesticus* (Teo & woodring, 1988). In *Valanga nigricans* the pH activity curve of the lipase shows an optimal pH at 8.2 (Teo, 1973). In *Onitis philemon* optimum pH is 8.4 (Giakwad *et al*, 1997). In *Chrysomya rufifacies* the optimum pH of the enzyme activity in gut 8.2 to 8.6 (Pol & Sawant, 1995), in *Alphitobius laevigatus* in mid gut is 6.4 (Sio & Teo, 1974/1975). Maximal hydrolysis obtained between pH 7.0 & 9.0 in the mid gut female of *Aedes aegypti* (Feering & Freyvogel, 1975). In 3rd day larva of *Chrysomya rufifacies* optimum pH of 8.4, 8.7 and 8.8 (Pol & Sawant, 1990). Lipase activity was lower at pH range 3 to 8 in gut of 3rd day larvae of the blow fly *Calliphora erythrocephala* (Price, 1975). Only *Periplaneta Americana* is known to have two optimal pH for lipase that is 5.0 and 7.0 (Gilbert *et al*.,1975).

The effect of temperature on the rate of hydrolysis of lipase revealed maximum activity at 40 ^{0}C in *A. proylei.* Similar results were reported in *Onitis philemon* and *Aedes aegypti* (Giakwad *et al*, 1997; Geering, 1975). In *Chrysomya rufifacies* the optimum temperature was 40^{0}C (Pol & Sawant, 1990). In House cricket, *Acheta domesticus* optimum temperature at 55 ^{0}C (Teo & Woodering, 1988). However in *Gryllus rubens* and in *Scapteriscus actetus* the lipase optimum temperature was found to have lower value up to 30 ^{0}C (Thomas & Nation, 1984).

The digestion period of 50 minutes was on the linear part of the enzymatic activity curve in *A. proylei.* In *O. philemon* digestion period was 10 minutes in mid gut and hind gut (Gaikwad *et al*, 1997).

The 50 % inhibition time for lipase was at 12 minutes at 60 ^{0}C in *A. proylei.* In O. philemon 50 % inhibition time was 5-8 minutes at 50 ^{0}C in midgut and in hind gut 12 minutes at 50 ^{0}C (Gaikwad *et al*, 1997). In House cricket, *Acheta domesticus* 50 % inhibition time for lipase was 48 minutes at 50 ^{0}C (Teo & Woodring, 1988).

The km is of considerable importance as it provides a valuable clue to the mode of action of an enzyme catalyzing a reaction (Conn & Stump, 1963). Pol (1984) reported 4×10^{-4} M km value for a mid gut lipase of *Chrysomya rufifacies.* In *Valanga nigricornis* km was 2.68×10^{-2} M (Teo, 1973). The km values for lipase in mid gut and hind gut of *O. philemon* are 3.61×10^{-4} M and 12.56×10^{-3} M respectively (Gaikwad *et al*., 1997).

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MANDIBULAR GLAND IN DIFFERENT RACES OF *BOMBYX MORI* L.

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ABSTRACT:

The structure of mandibular gland studied in three races of *Bombyx mori* L. viz, Pure mysore, Nistari and Kolar gold. The mandibular glands in *Bombyx mori* are the paired tubular gland which opens near the base of each mandible of their respective side in all the races under study. Mandibular gland measures about 6 ± 0.02 mm, 7 ± 0.1mm and 8 ± 0.05 mm in Pure mysore, Nistari and Kolar gold respectively. Histological analysis showed that the mandibular gland is a unicellular epithelial layer with large polyploidy nuclei. Mandibular glands are provided with longitudinal and circular muscles externally and rest upon basement membrane. As the gland is ectadenia due to which very thin intima is also present with luminal border of the epithelial cells. The results are discussed in the light of recent literature.

KEYWORDS: Mandibular gland; Pure mysore; Nistari; Kolar gold.

INTRODUCTION:

The class Insecta constitute dominant group of animal kingdom comprises 9,16,213 species [6] and from India, about 62000 species of insects were described [2]. In the class Insecta, the Lepidoptera is one of the largest and most important orders of insect. The numbers of species includes in the order estimated to be almost 1,50,000 [6]. This order is economically important and beneficial insects like silkworms are included. Nearly 95% of natural silk commodity of

commerce comes from the silkworm *Bombyx mori.* The mulberry silkworm *Bombyx mori* L. (Lepidoptera: Bombycidae) is economically very important for commercial production of silk in sericulture.

The silk proteins are produced in the silk glands of *B. mori*, a pair of tubular structure arising from the labial segment and extending in the length all the way up to the caudal region. A pair of salivary glands arising from the mandibular segment, in addition to the labial silk glands, which are generally considered as modified salivary glands, named as mandibular glands. They may be associated with the mandibles, maxillae or labium [13]. Additionally, silkworm *Bombyx mori* also possess a pair of mandibular gland. This gland serves in the digestion of the enormous quantities of food consumed by the larvae during the developmental stages. Several works was carried out on mandibular gland in insects [1], [12], [5], [4], [11], [3]. The structure or function of the mandibular glands in *Bombyx mori* has not been studied in any detail so far. Parthasarthy and Gopinathan (2005) comparatively analysed the development of the mandibular salivary glands in the mulberry silkworm, *Bombyx mori.* Therefore, in the present study it has been decided to workout in detailed histomorphology of mandibular gland in multivoltine races of *Bombyx mori.*

MATERIAL AND METHODS:

Collection and maintenance of experimental animal:

For the present study three multivoltine races of *Bombyx mori* were used in which one of them was hybrid i.e. Kolar gold (PM x CSR2) and other two were pure races i.e. Pure Mysore (PM) and Nistari. The DFLs of Kolar gold were procured from District Sericulture Grainage Centre, Shahupuri, Dist. Kolhapur, Maharashtra, India. The DFLs of Pure Mysore were procured from Directorate, Sericulture, Govt. Grainage Centre, Ganhinglaj, Dist. Kolhapur, Maharashtra, India. While DFLs of Nistari were procured from Central sericulture Germplasm Resource Centre, Hosur, Krishnagiri District, Tamil Nadu, India

Rearing of all these races were done as per the recommended regimen of Krishnaswami (1978, 1979) in the rearing house of the Department of Zoology, Shivaji University, Kolhapur by providing the fresh leaves of mulberry as food.

Histomorphological study:

The fifth instar larvae of 5th day of all three races viz. PM, Nistari and Kolar gold of *Bombyx mori* were dissected in chilled insect ringer solution under stereoscopic dissecting binocular microscope. The mandibular glands were removed and the measurements were taken for their anatomical study and were fixed into different fixatives. The tissues fixed in Bouin's fixative after 24 hours transfered into 70% alcohol. The tissue fixed in Steives fixative after 24 hours washed in 50% alcohol and then transfered into 70% alcohol containing iodine for varying period of time depending on the tissue. Tissue is then transferred to 70% alcohol for the removal of excess iodine. The numbers of mandibular glands were stored in 70% alcohol for whole mount study while rests of tissues were passed through the alcohol grades, into butanol for complete dehyadaration. The dehydrated tissues were cleared in the xylene then transferred to the mixture of xylene and wax for cold imprrigation treatment and finally it was embedded in paraffin wax (58 ºC -60ºC). The block thus, prepared were trimmed and the sectioned at 5 to 7µm. The sections were stained with haematoxylene-Eosin (Harri's) method and for the whole mout Methylene blue- Wright stain was used. After staining observations were made and microphotography were done.

RESULTS AND DISCUSSION:

In all the races of *Bombyx mori* L. under study, there was presence of a pair of salivary glands known as the mandibular gland derived from the mandibular segment and associate with mandibles. These were tubular glands opens near the base of each mandibles of their respective side in KG (Plate no. 3 fig. no. 1), Pure mysore (Plate no. 1 fig. no. 1), Nistari (Plate no. 2 fig no. 1). In length it measured about 6 ± 0.02 mm in Pure mysore (Plate no. 2 fig no. 2), 7 ± 0.1 mm in Nistari (Plate no. 3 fig no. 2) and to 8 ± 0.05 mm in Kolar gold (Plate no. 1 fig. no. 2). Similar observations were made by Parthasarthy and Gopinathan (2005) in *Bombyx mori.* In *Melipona bicolar* also similar results were found [15]. These mandibular glands were exocrine glands and their secretion helps in the digestion of the enormous quantities of food consumed by the larvae during the developmental stages.

Histologically, the mandibular gland made up from the unicellular epithelial layer which encloses the central lumen in all the races under study. Epithelium contain large polyploidy nuclei rest upon the basement membrane and provided with longitudinal and circular muscle externally. As the gland is ectadenia due to which very thin intima is also present with luminal

border of the epithelial cells. The diameter of mandibular gland was 157.6 ± 4.9 µm in Kolar gold (Plate No. 4 fig. no. 5), 137.3 ± 1.7 µm in Pure mysore (Plate No. 4 fig. no. 1) and 146.8 ± 5.2 µm in Nistari (Plate No. 4 fig. no. 3). The epithelial wall measured were 34.8 ± 0.7µm, 10.7 ± 1.2µm and 32.9 ± 1.4µm in Kolar gold (Plate No. 4 fig. no. 2), Pure mysore (Plate No. 4 fig. no. 4) and Nistari (Plate No. 4 fig. no. 6) respectively having epithelial cells with centrally placed spherical nucleus. In *Scaptotrigona postica*, majority of the secretary cells were spherical and isolated, but were occasionally polyhedric because of compact arrangement of cells [15]. In *Captotermes gestroi*, each mandibular gland was composed of three secretory cells [9], which have a cuticular canal involved in the collection of secretion [3].

ACKNOWLEDGEMENT:

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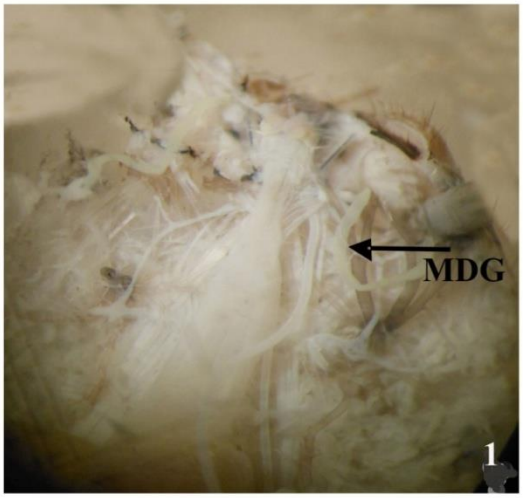
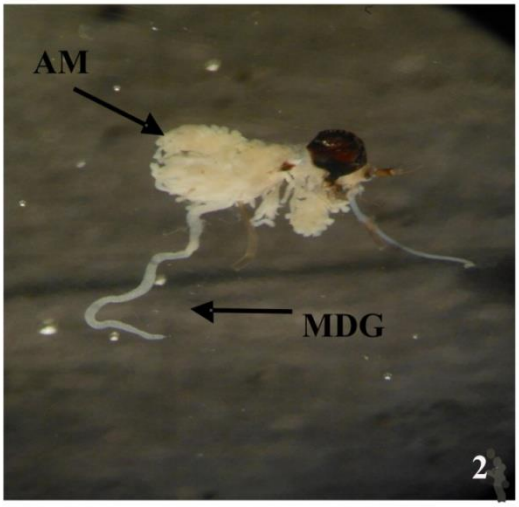
PLATE 1





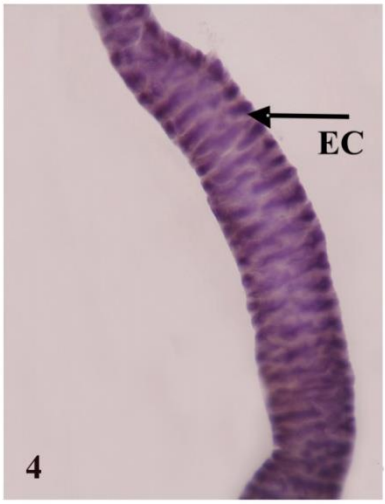


Fig. 1: Whole mount of mandibular gland of Pure mysore race showing the position of gland within larval body

Fig. 2: Whole mount of mandibular gland of Pure mysore race of *Bombyx mori*

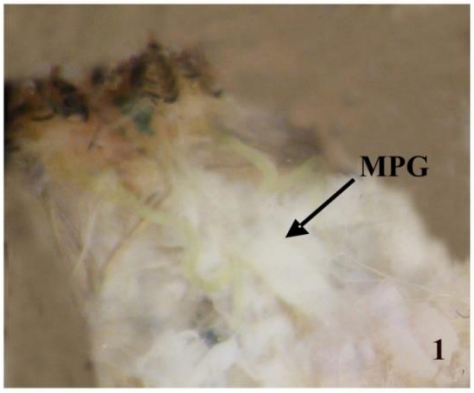
Fig. 3: The mandibular gland stained with Methylene blue-Wright stain

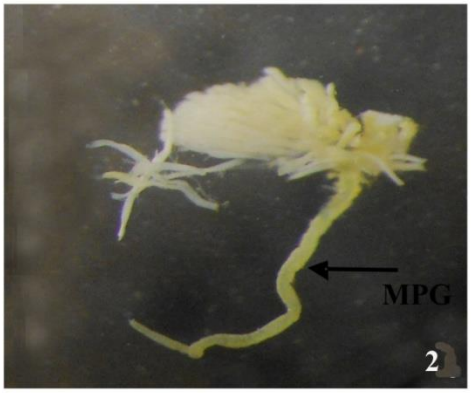
Fig. 4: The mandibular glands showing epithelial cells

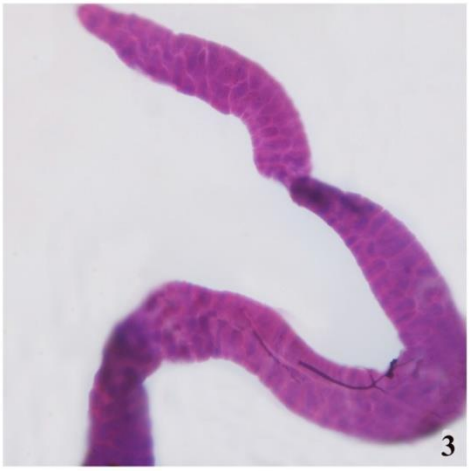
FiG - Fillipis gland MDG - Mandibular gland M - Mandible

EC - Epithelial cells AM - Adductor muscle

PLATE 2







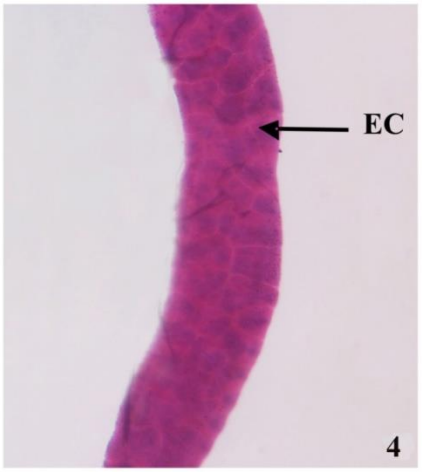


Fig. 1: Whole mount of mandibular gland of Nistari race showing the position of gland within larval body
Fig. 2: Mandibular gland of Nistari race of *Bombyx mori*
Fig. 3: The mandibular gland stained with Methylene blue-Wright stain
Fig. 4: The mandibular glands showing epithelial cells

FiG - Fillipis gland **MDG - Mandibular Gland**
EC - Epithelial cells **AM - Adductor muscle**

PLATE 3

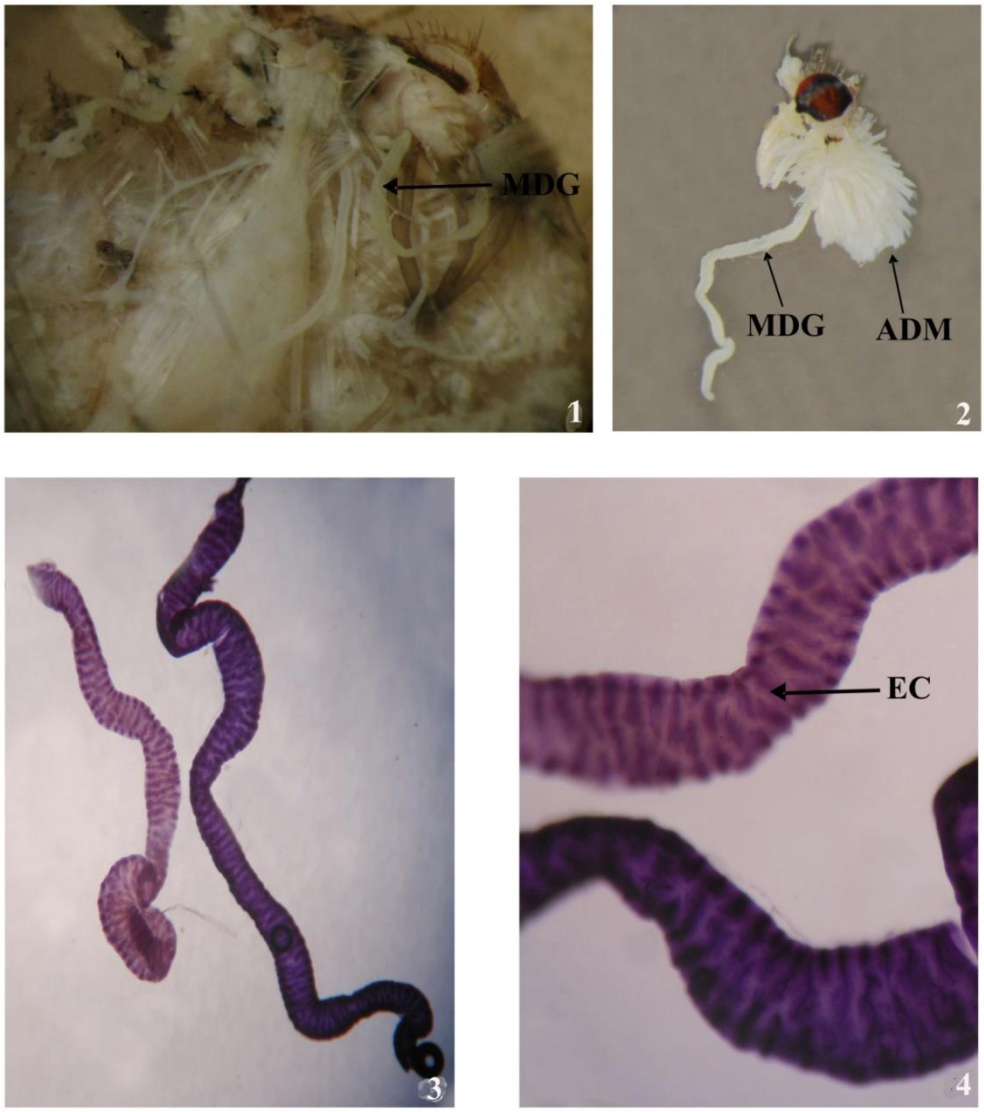


Fig. 1: Whole mount of mandibular gland of Kolar gold showing the position of gland within larval body
Fig. 2: Whole mount of mandibular gland of Kolar gold race of *Bombyx mori*
Fig. 3: The mandibular gland stained with Methylene blue-Wright stain
Fig. 4: Magnified view of mandibular glands showing epithelial cells

FiG - Fillipi's gland **ADM - Adductor muscle**
MDG - Mandibular gland **EC - Epithelial cells**

PLATE 4

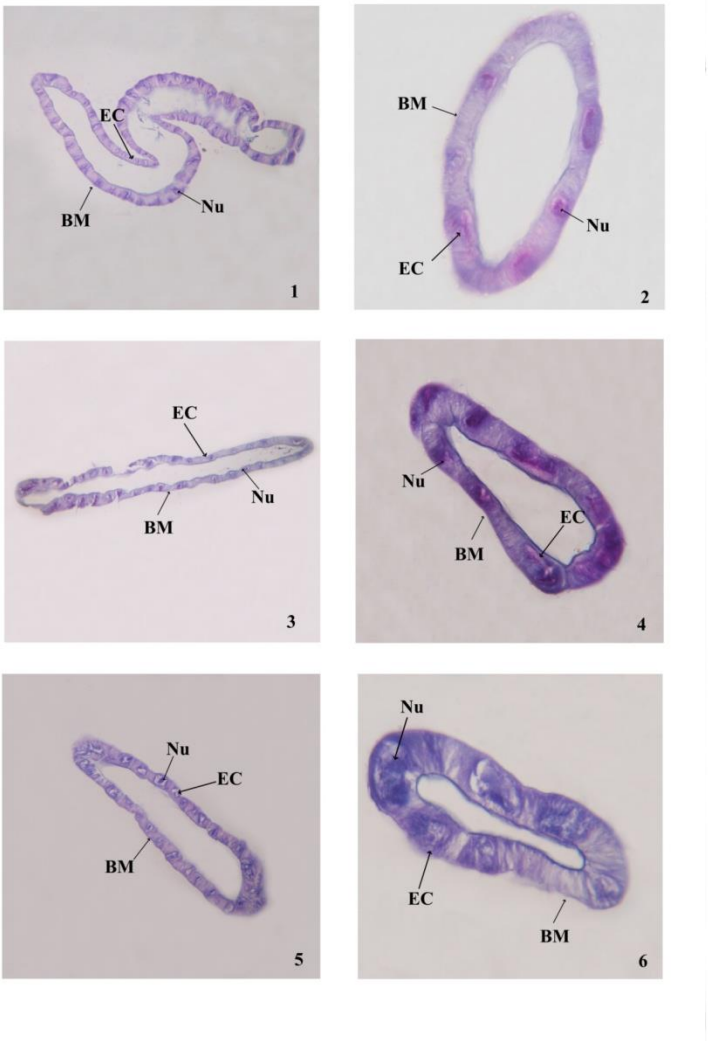


PLATE 4

Fig. 1: Longitudinal section of mandibular gland of fifth instar larvae of Kolar gold race of *Bombyx mori*

Fig. 2: Magnified view of mandibular gland of fifth instar larvae of Kolar gold race of *Bombyx mori* showing epithelial cells with prominent nuclei

Fig. 3: Longitudinal section of mandibular gland of fifth instar larvae of Pure mysore race of *Bombyx mori*

Fig. 4: Magnified view of mandibular gland of fifth instar larvae of Pure mysore race of *Bombyx mori* showing epithelial cells with prominent nuclei

Fig. 5: Longitudinal section of mandibular gland of fifth instar larvae of Nistari race of *Bombyx mori*

Fig. 6: Magnified view of mandibular gland of fifth instar larvae of Nistari race of *Bombyx mori* showing epithelial cells with prominent nuclei

BM - Basement membrane; EC - Epithelial cell; Nu – Nucleus

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