Assessment of bivalves as bioindicator of heavy metal pollution in Girna river at Jamda

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Abstract Heavy metal concentrations in whole body tissue of three fresh water bivalve species, *Parreysia cylindrica*, *Parreysia corrugata* and *Corbicula striatella* was analyzed in sample collected from Girna river at Jamda. The analysis of these animals can give an indication of the status of water environment to which they have been exposed. The bioaccumulation of heavy metals in the bivalve's tissues can be used as environmental bio-indicator. The heavy metal concentration (µg/gm) of Fe, Zn, Cu, Pb, Ni and Cd was analyzed to study the bioaccumulation of heavy metals in three bivalve species and their use as bioindicator of heavy metal pollution.

Key words: Heavy metals, Bivalves, Bioindicator, Girna, Jamda.

Introduction

According to Mason (1991), heavy metal pollution is one of the five main types of toxic pollutants generally present in surface waters. The heavy metals are released into the environment from industrial and many other anthropogenic sources. These heavy metals in higher concentration create harmful effects on some features of the ecological system.

All metals are natural components of the environment and are found in different levels in all ground and surface waters (Martin & Coughtrey, 1982). Some are essential elements that are necessary for the normal metabolism of organisms, while others are non-essential and play no important biological role (Prosi 1979; Cross & Sunda, 1985; Rainbow, 1985; Rainbow & White, 1989; Sanders, 1997). Living organisms require some heavy metals in trace amount. Extreme levels of essential metals can be harmful to the organism. According to Chandran et al., (2005) environmental pollution by metals has become one of the major important problems in the world. Environmental poisoning by heavy metals has increased in the last decades due to wide use of metals in agricultural, chemical and industrial processes, that are becoming hazards to living organisms (Prego and Cobelo-Garcia, 2003; Cheung et al., 2003).

The effect of heavy metals on fresh water environment has become global problem. These metals in that are persistent and therefore once released in the environment remain in the biota for a prolonged time. The heavy metals have been known as serious pollutants of aquatic ecosystems with toxic effect on related organisms, which finally affect the ecological balance. The main environmental pollutants are those that tend to accumulate in organisms, those which are persistent and are readily soluble and therefore environmentally mobile (Sanders 1997).

Aquatic organisms have been generally used in biomonitoring and assessment of safe environmental levels of heavy metals. Huang et al. (2007) reported that during the past few decades, several species have been studied to decide their potential as a biomonitoring organism and mollusca have become a popular selection for heavy metal monitoring.

Bivalve molluscs are well recognized for their biological features of concentrating heavy metals and other materials in their tissues. According to Phillips and Segar (1986) the advantages of the use of bivalve molluscs as biomonitors of trace metal pollution are mostly related to their capacity of concentrating these elements in the tissues, thus providing, in a time-integrated manner, the environmental levels of biologically available pollutants. Heavy metal concentratios in soft bodies of bivalves have been discussed in all of the studies concerned. According to Gundacker (1999), zebra mussels accumulate high amounts of toxic heavy metals and are generally used as bio-monitoring organism. Bivalve molluscs are one of the most appropriate bioindicators because they are sedentary, widespread and have a long life span (Farrington et al. 1983). Bivalves are filter-feeder invertebrates, accumulate heavy metals from food, water and also from the intake of inorganic particulate matters (Huang et al. 2007), therefore fulfilling the criteria as excellent bioindicators. The bioaccumulation of heavy metals in the tissues of bivalve’s can be helpful for the detection of polluted area and can be used as environmental bio-indicator (Langston and Spence 1995). The study of heavy metal in whole soft body tissues of bivalves as bio-indicator gives some information about the level of metal pollution in the environment.

Therefore the present study aims to determine heavy metal pollution level in Girna river at Jamda and use of bivalves as bioindicators of heavy metal pollution.

Materials and methods

Bivalve samples (*Parreysia cylindrica, Parreysia corrugate* and, *Corbicula striatella*) were collected in January 2011, from Girna river at Jamda, 40 Km away from Chalisgaon city (Fig.1).

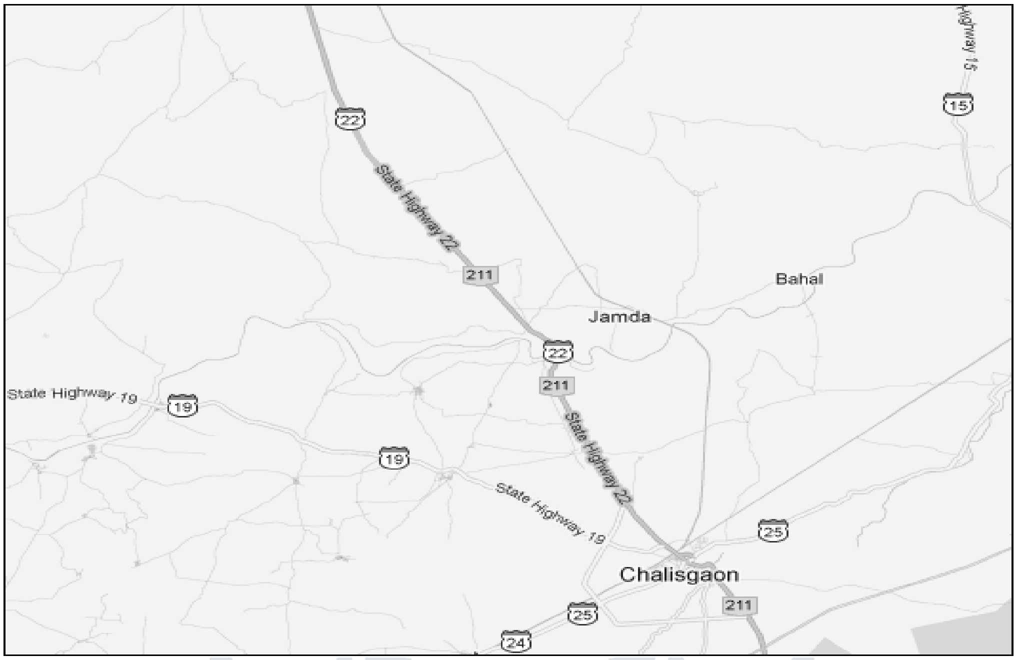

Fig. 1 Map showing sampling location, Jamda from Girna river.

Medium sized 10 specimens were selected from *Parreysia cylindrica*, *Parreysia corrugate* and 30 specimens were selected from *Corbicula striatella* by measuring the length and width of each animal of each species. The bivalves were dissected within 12 hours of collection and their whole body tissues were removed, washed in distilled water and dried separately in oven at about 80^0 C. After complete drying the tissue were powdered. Dry powder of whole soft body tissue of bivalves was digested in 10 mL mixture of Nitric acid: Perchloric acid in (5:1) ratio and sample was prepared for heavy metal analysis. The analysis of heavy metal concentrations in whole body tissue of bivalves was carried out by Atomic Absorption Spectrophotometer. All results are presented on a dry weight basis as µg/gm for heavy metal concentration. The means with standard deviations for heavy metal concentrations of all three species were calculated.

Results and discussion

Heavy metal concentrations in three bivalve species are given in table 1. The Fe and Zn concentrations were highest in bivalves than Cu, Pb, Cd and Ni in all species. Fe concentration was found highest in *Parreysia cylindrica*, Zn, Pb, Ni and Cd concentrations were found highest in *Parreysia corrugata* and Cu concentration was found highest in *Corbicula striatella*. Pb and Ni concentrations were found below detection limit in *Parreysia cylindrica*.

Table 1. Heavy metals concentrations (µg/gm) in *Parreysia cylindrica*, *Parreysia corrugate* and *Corbicula striatella* collected from Girna river at Jamda.

Species	Heavy metal concentrations					
	Fe	Zn	Cu	Pb	Ni	Cd
Parreysia cylindrica	1363.41±13.2	536.64±6.39	57.38±2.63	BDL	BDL	3.62±0.74
Parreysia corrugata	1349.72±10.2	640.91±8.42	37.33±2.37	44.88±2.1	16.05±1.0	6.22±0.93
Corbicula striatella	539.55±7.81	376.71±3.84	103.1±4.85	1.95±0.26	0.79±0.12	2.08±0.31

BDL- Below detection limit, Mean ± SD

The interspecific difference in the metal concentrations is an indication that different organisms show a range of capability for the net accumulation of metals, varying from weak net accumulators of certain elements to very strong net accumulators (Phillips and Rainbow 1989; Phillips 1995; Ruelas-Inzunza and Páez-Osuna 2000). Bivalves exposed to contaminants accumulate various pollutants by their filter-feeding habits (Hamza-Chaiffai et al., 1999), They are capable to accumulate toxic metals in their organs to comparatively high levels without any apparent harmful effects (Hamza-Chaiffai et al. 1999).

Phillips (1980) reported that bivalves were selected for this study because they meet many of the requirements of a good biological monitor. Element concentrations in molluscs vary between different species due to species-specific capacity to accumulate trace metals (Otchere et al., 2003). Different species, within groups like the bivalves, may accumulate very diverse concentrations when exposed to the same atmosphere (Riedel et al 1995). The bivalves of same species and size, class, living in same environment belonging to same age class shows same metal accumulation. While the species of different size and different class living in different environments shows different metal bioaccumulation (Ravera, 1964). Hence in the present investigation animals belong to same size were used to analyse metal concentration. According to Shulkin and Presley (2003) physiological processes of the organism and environmental factors influence the rate of bioaccumulation in bivalves. The accumulation of heavy metals into cells of organisms is mainly dependent on their capacity to pass through the cell membrane, even though the entry route of metal (Connell et al, 1999).

Consequently linear relationship between environmental and tissue metal level are generally expected within a definite range but beyond certain environmental concentrations, metals in tissue of organisms tends to reach asymptotic level (Wang et al 1997). This relationship can be modified by various environmental and physiological factors (Phillips, 1997;

Muhaya et.al., 1997). These natural variables may influence observed differences in bioaccumulated metals.

Furthermore, in the present study, it was observed that the heavy metal bioaccumulation of Fe, Zn, Cu, Pb, Ni and Cd in *Parreysia cylindrica*, *Parreysia corrugata* and *Corbicula striatella* was use to indicate the heavy metal pollution of Girna river at Jamda and their use as a pollution indicator in freshwater.

Acknowledgment : I am thankful to Principal shri.v.s. Naik Arts, Science and Commerce College, Raver, Dist-Jalgaon for providing laboratory facilities.

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Ultrasonic velocity, density measurements of Clobetasol propionate in 10% sodium chloride At 303 k

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Abstract

The acoustical properties have been investigated from the ultrasonic velocity and density measurements of **Clobetasol propionate in 10% sodium chloride** at 300K. The measurement have been perform to evaluate acoustical parameter such as adiabatic compressibility (□s), Partial molal volume (□v), intermolecular free length (Lf), apparent molal compressibility (□k), specific acoustic impedance (Z), relative association (RA), solvation number (Sn).

Key word: - *Ultrasonic velocity, viscosity, adiabatic compressibility, apparent molal volume.*

INTRODUCTION

In the recent years, measurements of the Ultrasonic velocity are helpful to interpreted solute-solvent, ion-solvent interaction in aqueous and non aqueous medium [1-6]. Fumio Kawaizumi[5] have been studied the acoustical properties of complex in water. Jahagirdar et. al. has studied the acoustical properties of four different drugs in methanol and he drawn conclusion from adiabatic compressibility . The four different drugs compress the solvent methanol to the same extent but it shows different solute-solvent interaction due to their different size, shape and structure [6]. Meshram et. al. studies the different acoustical properties of some substituted Pyrazolines in binary mixture acetone-water and observed variation of ultrasonic velocity with concentration[7]. Palani have investigated the measurement of ultrasonic velocity and density of amino acid in aqueous magnesium acetate at constant temperature [8]. The ion-dipole interaction mainly depends on ion size and polarity of solvent. The strength of ion-dipole attraction is directly proportional to the size of the ions, magnitude of dipole. But inversely proportional to the distance between ion and molecules. Voleisines has been studied the structural properties of solution of lanthanide salt by measuring ultrasonic velocity [9]. Syal et.al. has been studied the ultrasonic velocity of PEG-8000, PEG- study of acoustical properties of substituted heterocyclic compounds under suitable condition[10].Tadkalkar et.al. have studied the acoustical and thermodynamic properties of citric acid in water at different temperature[11]. Mishra et.al. have investigated ultrasonic velocity and density in non aqueous solution of metal complex and evaluate acoustic properties of metal complex[12].M. Arvinthraj et.al. have determined the acoustic properties for the mixture of amines with amide in benzene at 303K-313K .They also determined thermodynamic parameters[13].S.K. Thakur et.al. have studied the different acoustical parameters of binary mixture of 1-propanol and water [14]. Mirikar et.sal. studied the molecular interaction between liquids.[15]

After review of literature survey the detail study of substituted drug under identical set of experimental condition is still lacking. It was thought of interest to study the acoustical properties of substituted drug under suitable condition.

Experimental

In the present study, the drug Clobetasol propionate was used. The double distilled solvent was used for preparation of different concentration of drug solution. The densities were determined by using specific gravity bottle by relative measurement method with accuracy □ 1×10^{-5} gm/cm^3. The ultrasonic velocities were measured by using ultrasonic interferometer having frequency 3MHz .The constant temperature was maintained by circulating water through the double wall measuring cell, made up of steel.

In the present investigation, different properties such as adiabatic compressibility (□s), apparent molal volume (□$_v$), intermolecular free length (L_f), apparent molal compressibility (□$_□$), specific acoustic impedance (Z), relative association (R_A), solvation number(S_n), limiting apparent molal compressibility (□$^□_□$), limiting apparent molal volume(□$^□_v$) and their constant (S_k, S_v).

Theory

Adiabatic compressibility (βs) is given by:

$$\beta s = \frac{1}{U_s^2 d_s} \qquad (1)$$

Apparent molal compressibility (ϕ_κ) has been calculated by using the relation

$$(\phi_\kappa) = 1000 \text{ x} \left(\frac{\beta s\, d_0 - \beta 0\, d_s}{m x d_s x d_0}\right) + \frac{\beta s \text{ x } M}{ds} \qquad (2)$$

Where βs, d_0 and β0 d_s are the adiabetic compressibility and density of solution and solvent respectively. m is molal concentration of solute ,M is molecular weight of solute.

$$\text{Apparent molal volume } (\phi_v) = \frac{M}{\quad} \text{ x } \frac{(d_0\text{-}ds)\times10^3}{\qquad} \qquad (3)$$

$ds \qquad mxdsxd_0$

Specific acoustic impedance (Z) = Us ds (5)

Intermolecular free length (L_f) = $K\sqrt{\beta s}$ (6)

Relative association (R_A) = $(ds / d_0) \times (U_0 / U_s)^{1/3}$ (7)

Results and Discussion

In the present investigation, different acoustical properties such as ultrasonic velocity (Us), adiabatic compressibility (□s), intermolecular free length (L_f), specific acoustic impedance (Z), are listed in table-1. Partial molal volume (□$_v$), apparent molal compressibility (□$_□$), relative association (R_A), solvation number (Sn) are listed in table-2. It was found that the ultrasonic velocity decreased with the increase in concentration for system (Table-1). Variation of ultrasonic velocity in solution depends upon the increase or decrease of molecular free length after mixing the component. This is based on a model for sound propagation proposed by Eyring and Kincaud[13]. Intermolecular free length increased linearly on increase in concentration of substituted drug. Hence, decreased in ultrasonic velocity with increase in concentration of drug. It happened because there was significant interaction between ions and solvent molecules suggesting a structure promoting behavior of the added electrolyte. The specific acoustic impedance (Z) decreased with the increase in concentration of drug. When concentration of electrolyte was increased, the thickness of oppositely charged ionic atmosphere increases due to decrease in ionic strength. This is suggested by decrease in acoustic impedance with increase in concentration in system. It was seen that the intermolecular free length increased with the increase in concentration in system. The intermolecular free length increased due to greater force of attraction between solute and solvent by forming hydrogen bonding. The adiabatic compressibility increased with the increase in concentration of solution. It happened due to collection of solvent molecule around ions, this supporting weak ion-solvent interaction. This indicates that there is significant solute-solvent interaction.

It was observed that apparent molal volume increased with concentration in system. It indicates the existence of strong ion-solvent interaction. It was found that the value of apparent adiabatic compressibility was increased with the increase in concentration of drug. It shows strong electrostatic attractive force in the vicinity of ions. From the data, we were concluded that strong molecular association was found in drug. The value of relative association increased with the increase in concentration in system. It has been found that there was strong interaction between solute and solvent. There were regular increases in solvation number with the increase in concentration; it indicates the solvent molecule forms strong coordination bond in primary layer. It indicates the increase in size of secondary layer of Solvation.

Table-1 Ultrasonic velocity, density, adiabatic compressibility (□$_S$), Specific acoustic impedance (Z) Intermolecular free length (L_f).

Concentration moles lit^{-1} (m)	Density (ds) kg m-^{3}	Ultrasonic velocity (Us) m s^{-1}	Adiabatic compressibiliy (□$_S$) x10^{-10} m^{2}N^{-1}	Intermolecular free length (L_f) x10^{-11} m	Specific acoustic impedance (Zx10^6) kg m^{-2} s^{-1}
1x10^{-3}	1020.95	1564.92	3.9983	4.0216	1.59819
2x10^{-3}	1021.26	1559.94	4.0230	1.0340	1.59349
3x10^{-3}	1021.52	1550.58	4.0705	4.0577	1.58438
4x10^{-3}	1021.80	1533.78	4.1592	4.1017	1.56569
5x10^{-3}	1022.03	1519.27	4.2376	4.1402	1.55327
6x10^{-3}	1022.38	1496.36	4.3677	4.2032	1.53007
7x10^{-3}	1022.53	1482.96	4.4462	4.2408	1.51664
8x10^{-3}	1022.71	1478.23	4.4738	4.2540	1.51211
9x10^{-3}	1022.92	1450.15	4.6556	4.3396	1.48119

Table-2 Concentration (m), Relative association (R_A), Apparent molal compressibility (□$_□$), Apparent molal volume (□$_v$) , Solvation number (S_n)-

Concentration (m)moles lit^{-1}	Apparent molal volume (-□$_v$) m^{3}mole^{-1}	Apparent molar compressibility (□$_{k□}$□x10^{-10}) m^2 N^{-1}	Relative association (R_A)	Solvation number (S_n)
1x10^{-3}	18.8452	1.8249	1.02306	0.97409
2x10^{-3}	9.3432	1.8357	1.02502	0.97986

3x10^{-3}	6.1599	1.8570	1.02835	0.99123
4x10^{-3}	4.5730	1.8972	1.03425	1.01269
5x10^{-3}	3.6114	1.9326	1.03941	1.03158
6x10^{-3}	2.9895	1.9917	1.04770	1.06313
7x10^{-3}	2.5178	2.0271	1.05258	1.08202
8x10^{-3}	2.1678	2.0394	1.05445	1.08859
9x10^{-3}	1.8987	2.1222	1.06482	1.13279

Conclusion

The present study shows the experimental data for ultrasonic velocity, density and viscosity at 300K for substituted drug in 10% sodium chloride . From experimental data, the acoustical properties were calculated. The solute-solvent interaction and ion-ion / solute-solute interaction existing between drug and solvent were also studied with the help of experimental data. Lastly it has been concluded from the experimental data, that the solute-solvent interaction in drug-solvent systems are weak.

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Studies of acoustic, thermodynamic and additive properties of Eperisone in 10% ethyl alcohol.

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ABSTRACT:-

Acoustical and additive properties have been studied for Eperisone in 10% ethyl alcohol at different temperature. The measurement have been perform to determine acoustical parameter such as adiabatic compressibility (βs), Partial molal volume (ϕ_v), intermolecular free length (L_f), apparent molal compressibility (ϕ_κ), specific acoustic impedance (Z), relative association (R_A), salvation number (Sn) and also studied the molar polarization, polarisability constant and thermodynamic properties like free energy change, enthalpy change, entropy change of system.

KEYWORD: - Ultrasonic velocity, intermolecular free length, relative association, Molar polarization, polarizability constant,

INTRODUCTION:-

Eperisone is used as reduction of myotonia, improvement of circulation, and suppression of the pain reflex. The drug inhibits the vicious circle of myotonia by decreasing pain, ischaemia, and hypertonia in skeletal muscles, thus alleviating stiffness and spasticity, and facilitating muscle movement[1-2].

The thermodynamic properties of solution are important in chemistry and biology. Studies of the viscosities of such solutions were among the earliest in the field of solution chemistry. The activation Gibb's free energy, entropy and enthalpy change by measuring the viscosity of aqueous solution of tetra methyl, tetraethyl, tetra n-propyl, tetran-butyl and tetran-pentyl ammonium cyclohexa sulfamate in the temperature range 293.15 to 323.15 K[3].

Numbers of researcher measurements of the Ultrasonic velocity are helpful to interpreted solute-solvent, ion-solvent interaction in aqueous and non aqueous medium [4-5]. The acoustical properties of four different drugs in methanol and he drawn conclusion from adiabatic compressibility. The four different drugs compress the solvent methanol to the same extent but it shows different solute-solvent interaction due to their different size, shape and structure [6]. The different acoustical properties of some substituted Pyrazolines in binary mixture acetone-water and observed variation of ultrasonic velocity with concentration[7]. The measurement of ultrasonic velocity and density of amino acid in aqueous magnesium acetate at constant temperature [8]. The ion-dipole interaction mainly depends on ion size and polarity of solvent. The strength of ion-dipole attraction is directly proportional to the size of the ions, magnitude of dipole. But inversely proportional to the distance between ion and molecules. The structural properties of solution of lanthanide salt by measuring ultrasonic velocity [9].The ultrasonic velocity of PEG-8000, PEG- study of acoustical properties of substituted heterocyclic compounds under suitable condition[10]. An acoustical and thermodynamic properties of citric acid in water at different temperature[11]. Ultrasonic velocity and density in non aqueous solution of metal complex and evaluate acoustic properties of metal complex [12]. An acoustic properties for the mixture of amines with amide in benzene at 303K-313K .They also determined thermodynamic parameters [13]. The different acoustical parameters of binary mixture of 1-propanol and water [14].

The refractive index is an important additive property for molecular structure of liquid. The extent of refraction depends on –i) the relative concentration of atom or molecule ii) The structure of atom or molecule. So refractive index gives idea about geometry and structure of molecule. Refraction of light is additive property, but also depends on the structural arrangement of atom in molecule. This can some time be used to determine the structure of an unknown compound whose molecular formula is known.

Density and refractive index of binary liquid mixture Eucalyptol with Hydrocarbon at different temperature. Refractivity properties of some homologous series such as n-ethanoate, methyl alkanoates, ethyl alkanoates etc. were measured in the temperature range from 298.15 to 333.15^{0}K [16].

After review of literature survey the detail study of Eperisone under identical set of experimental condition is still lacking. It was thought of interest to study the acoustical and thermodynamic properties of substituted heterocyclic drug under suitable condition.

EXPERIMENTAL:-

The viscometer put in double wall glass cell. For viscosity measurement Ostwald viscometer (10 ml) was used. The constant temperature was maintained by circulating water through the double wall measuring cell, made up of glass. The flow time was also measured by using digital clock (0.01 Sec).The substituted heterocyclic drug (Eperisone) is used in the present study. The density was determined by using specific gravity bottle by relative measurement method with accuracy ± $1x10^{-5}$ gm/cm^3. The ultrasonic velocity was measure by using ultrasonic interferometer having frequency 3MHz (Mittal Enterprises, Model No F-82) .The constant temperature is mentioned by circulating water through the double wall measuring cell made up of steel.

In the present investigation different parameters such as adiabatic compressibility (βs), apparent molal volume (ϕ_v), intermolecular free length (L_f), apparent molal compressibility (ϕ_κ), specific acoustic impedance (Z), relative association (R_A), Solvation number (S_n) were studied.

$$\text{Adiabetic comprressibility}(\beta o) = \frac{1}{Uo^2 do}$$

$$\text{Adiabetic comprressibility}(\beta s) = \frac{1}{Us^2\, ds}$$

$$\text{Apparent molal volume}(\phi_v) = \left(\frac{M}{ds}\right) x\ \frac{(d_o - d_s)x10^3}{m\ x\ d_s\ x\ d_o}$$

$$\text{Apparent molal compressibility}(\phi_k) = 1000x\ \frac{(\beta_s d_o - \beta_o d_s)x10^3}{m\ x\ d_s\ x\ d_o} + \frac{\beta_s M}{d_o}$$

$$\text{Specific acoustic impedance } (Z) = U_s d_s$$

$$\text{Intermolecular free length } (L_f) = K\sqrt{\square} ds$$

$$\text{Relative association } (R_A) = x\,1\left(\frac{d_s}{d_o}\right)^{1/3}$$

$$\text{Solvation number}(Sn) = \frac{\phi_k}{\beta_o \left(\frac{M}{d_o}\right)}$$

$$\eta_r = A.e^{-\Delta G/RT}$$

$$\log\left[\frac{\eta r_2}{\eta r_1}\right] = \frac{\Delta H}{2.303R}[T_2 - T_1]/[T_1 T_2]$$

$$(\Delta G - \Delta H)/T = \Delta S$$

$$\text{Molar polarisation}(Rm) = \frac{(n^2-1)}{(n^2+2)} x \frac{M}{d} = \frac{4\pi N\alpha}{3}$$

RESULTS AND DISCUSSION:-

In the present investigation , different thermodynamic parameters , such as adiabatic compressibility (βs), Partial molal volume (ϕ_v), intermolecular free length (L_f), apparent molal compressibility (ϕ_κ), specific acoustic impedance (Z), relative association (R_A), salvation number(Sn).

From table-1, these found that ultrasonic velocity increases with increase in temperature. Such an increase in ultrasonic velocity clearly shows that molecular association is being takes place in these mixtures. Variation of ultrasonic velocity in solution depends upon the increase or decrease of molecular free length after mixing the component, based on a model for sound propagation proposed by Eyring and Kincaid [17]. It was found that, intermolecular free length decreases linearly on increasing the temperature of solution. The intermolecular free length decrease due to less force of interaction between solute and solvent by forming hydrogen bonding. This was happened because there is less significant interaction between ions and solvent molecules suggesting a structure promoting behavior of the added electrolyte .This may also indicates that increase in number of free ions showing the occurrence of ionic association due to stronger ion-ion interaction. The value of specific acoustic impedance (Z) increases with increase in temperature. The increase of adiabatic compressibility is decrease with increase in temperature may be due to loss of solvent molecule around ions, this supporting stronger ion-solvent interaction. This indicates that there is not significant solute-solvent interaction.

The decrease in adiabatic compressibility following a increase in ultrasonic velocity showing there by stronger intermolecular interaction.

From table-2, it is observed that apparent molal volume increases with increase in temperature indicates the existence of weak ion-solvent interaction. The values of apparent molal volume are all negative values indicate the presence of solute solvent interaction [18] .The value of apparent molal compressibility is decrease with increase in temperature. It shows weak electrostatic attractive force in the vicinity of ions. It can be concluded that weak molecular association is found in solution. The value of relative association increases with increase in temperature of system. It is found that there is strong interaction between solute and solvent.

The Solvation number decrease with increase in temperature due to strong solute-solvent interaction. There is regular decrease in solvation number with increase temperature indicates the decrease in size of secondary layer of Solvation. The Solvation number in all system decreases with increase in temperature indicates the solvent molecule forms weak coordination bond in primary layer.

The rise of the temperature is accompanied by a decrease of the viscosity of the solution. The rise of the temperature is accompanied by a decrease of the density of the solution. The table 1 shows values of viscosity and density at different temperature. The thermodynamic functions of viscous flow were estimated from the dynamic Viscosity values. Flow process is governed by the ability of molecule to move into the prepared hole and the readiness with which the holes are prepared in the liquid.

The values of Gibb's free energy were calculated from the slope of graph by plotting logη Vs 1/T (Fig. 1). The values of Gibb's free energy were determine and are given in table 2. The values of Gibb's free energy are positive. The values of enthalpy change in reaction were determined and are also negative in all systems. From the values of ΔG and ΔH, the reaction is non spontaneous and exothermic in nature. The values of entropy change were determined from equation. The negative value of entropy change indicates the reaction must be non spontaneous process of flipping of molecule over each other. ΔS were positive due the destruction of hydrogen bond in compounds.

Table-1: Ultrasonic velocity, density, adiabatic compressibility (β_S), Specific acoustic impedance (Z) Intermolecular free length (L_f) at different temperature.

Temperature (K)	Density (ds) Kg m-^{3}	Ultrasonic velocity (Us) m s^{-1}	Adiabatic compressibiliy (β_S) x10^{-10}m^{2}N^{-1}	Intermolecular free length (L_f) x10^{-11}m	Specific acoustic impedance (Zx10^6)kg m^{-2} s^{-1}
Eperisone + 10% Ethyl alcohol					
298.15	995.96	1050.22	9.1033	6.06815	1.04598
303.15	995.6	1056.66	8.9959	6.03225	1.052010
308.15	994.73	1060.15	8.9446	6.01502	1.05456
313.15	994.33	1065.70	8.8552	5.6849	1.05966
318.15	993.55	1069.36	8.8016	5.9668	1.62462

Table-2: Relative association (R_A), apparent molal compressibility (ϕ_κ), Apparent molal volume (ϕ_v), Solvation number (S_n) -

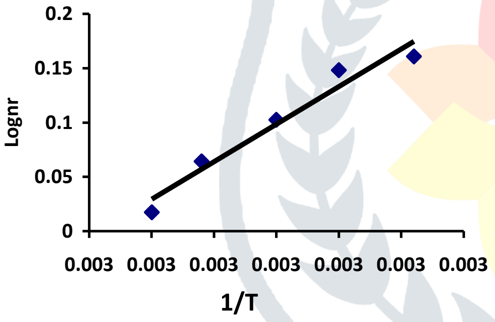
Temperature(K)	Apparent molal volume (-ϕ_v) m^{3}mole^{-1}	Apparent molal compressibility (ϕ_κ)x0^{-10} m^2 N^{-1}	Relative association (R_A)	Solvation number (S_n)
Eperisone + 10% Ethyl alcohol				
298.15	0.24009	2.37734	1.15530	1.2274
303.15	0.24011	2.34847	1.16226	1.1584
308.15	0.24029	2.33609	1.16463	1.1198
313.15	0.24036	2.31245	1.16675	1.0766
318.15	0.24048	2.29871	1.17554	1.0256

Table-3: Viscosity measurement and thermodynamic parameters at different temperature

Temp.(K)	1/T	Density (Kg/M^3)	Time (Sec)	η_r	log η_r	ΔG (JM^{-1}K^{-1})	-ΔH (JM^{-1}K^{-1})	-ΔS (JK^{-1})
Eperisone + 10% Ethyl alcohol								
298.15	0.00336	995.96	204	1..4477	0.16069	939.61	--	--
303.15	0.00330	995.60	176	1.4067	0.14820		10568.7	37.9624
308.15	0.00325	994.73	148	1.2662	0.10251		11868.6	41.5643
313.15	0.00319	994.33	126	1.1594	0.06420		16687.6	56.2899
318.15	0.00315	993.55	97	0.9607	0.01741		12170.5	41.2013

Table-4: The values of molar refraction and polarizability constant at different temperature

Temp.(K)	Density (Kg/M^3)	R.I. (η)	Rmx10^{-6}	α x 10^{-29}
298.15	995.96	1.3584	5.72	2.27
303.15	995.6	1.3563	5.70	2.26
308.15	994.73	1.3551	5.68	2.26
313.15	994.33	1.3430	5.51	2.19
318.15	993.55	1.3490	5.59	2.22



CONCLUSION:-

The experimental data for ultrasonic velocity, density at different temperature for eperisone in 10% ethyl alcohol. From experimental data calculated acoustical parameters and studied to explanation solute-solvent interaction and ion-ion / solute-solute interaction are existing between drug and solvent mixture. From experimental data it can be conclude that weak solute-solvent interaction in all systems. The viscous flow of this substituted heterocyclic drug in ethyl alcohol is thermodynamically spontaneous and exothermic process. Because ΔG and ΔH are negative and ΔS is positive which is indicate the spontaneity of reaction according to thermodynamics.

ACKNOWLEDGEMENTS:-

The Authors is thankful to Principal, V.S. Naik College, Raver(M.S.) for kindly cooperation.

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STUDIES OF STABILITIES OF MANNICH BASE WITH METAL IONS IN MIXED SOLVENT 303.15 K BY PH-METRIC METHOD.

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ABSTRACT

The formation of complexes of mannich base of (N-(3,4-dihydroxyphenyl) (2-oxocyclohexyl)methyl)isonicotinohydrazide) with metal ions at constant ionic strength ($\mu = 0.1M$) in 70% ethanol was investigated at 303.15K by pH-metric titration. The values of proton-ligand stability constant (pK) and metal-ligand stability constant (logK) obtained from the data. It is observed that the metal ions form 1:1 and 1:2 complexes with mannich base of N-(3,4-dihydroxyphenyl) (2-oxocyclohexyl)methyl)isonicotinohydrazide).

Key Words: Stability Constant, pH metry, mannich base.

Introduction: -

The studies of metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport f metal ion in the biological kingdom.

In the earlier number of investigators shows the data base on metal complexes with mannich base was presented. Narwade et.al**[1]** studies the Formation and Stability constant of thorium (IV) complex with some substituted pyrazolines. Mathieu W.A. Steenland et.al.**[2]** studies stability constant of Cu(II) and Ni(II) complexes of trans –dioxopentaaza macrocycles in aqueous solution by different technique. Hong-Wen Gaoet.al.**[3]** has studied the stability constant of Cu (II) and Co (II) complexes with CNBAC in water sample spectrophotometrically. Tuba Sismanoglu **[4]** have studied the stability constant of binary complexes of Nicotinamide with Mn (II) by pH metrically. He also determines change in free energy, change in enthalpy and change in entropy from stability constant at different temperature. Tekade et.al. **[5]** have been studied complex formation of Cu (II) and Co (II) metal ion complex with substituted isoxazolines. O.Yamauchi et.al. **[6]** studied stability constant of metal complexes amino acids with charged side chain by pH–metrically. Hayati Sari et.al.**[7]** studied the stability constant of glyoxime derivative and their Nickel, Copper, Cobalt and Zinc complexes potentiometric and theoretically. Talele**[8]** et. al have been studied the stability constant of Schiff base metal complexes at ionic strength

After review of literature survey the detail study of complex under identical set of experimental condition is still lacking. It was thought of interest to study the chelating properties of mannich base under suitable condition with lanthanide by pH metrically.

Experimental:-

pH measurement were carried out with equip-tronic EQ-610 pH meter (accuracy ± 0.01 units) using combine glass electrode at room temperature. Metal ions solutions prepared in triply distill water and concentration estimated by standard method.**[9]** The solution of drugs prepared in solvent .The pH metric reading in 70% Ethanol – water mixture were converted to $[H^+]$ value by applying the correction proposed by Van Uitert Haas.

The overall ionic strength of solution was constant and calculated by the equation

$$\mu = 1/2 \ \Sigma C_i Z_i^2$$

The concentration of other ion in addition to Na^+ and ClO^-_4 were also taken into consideration.

Result and discussion:-

Substituted heterocyclic drugs may be ionized as acid having replaceable H^+ ion from -OH group. Therefore it is represented as HL i.e.

$$HL \longrightarrow H^+ + L^-$$

The titration data used to construct the curves between volume of NaOH and P^H. They are called acid-ligand titration curves.

It is observed from titration curves for all systems ligand start deviating from the free acid curves at P^H 2.5 and deviating continuously up to P^H=11. The deviation shows that dissociation of proton in drug.

The average number of proton associated with the ligand (n_A) was determined from free acid and acid – ligand titration curves employing the equation of Irving and Rossotti **[10]** . The P^k values were determined from formation curves (n_A v^s P^H) by noting the P^H at which n_A = 0.5. The accurate values of pk were calculated by point wise calculations which are presented in table -1.

Table-1

Determination of proton-ligand stability constant(pK) of AT 0.1M ionic strength.

System	Constant pK	
	Half integral	Point wise calculation
Ligand-1	9.75	8.85

METAL -LIGAND STABILITY CONSTANT (Log k):-

Metal-ligand stability constant of transition metal chelate with some 4-(4-benzhydryloxy-1-piperidyl)-1-(4-tert-butylphenyl) butan-1-one drug were determined by employing Bjerrum calvin P^H metric titration method as adopted by Irving and Rossotti . The formation of complexes between transition metal ions with drug were indicated by the significant separation starting from pH =2.5 for all systems.

The change of colour from colourless to faint yellow colour complex form.

Table-2

Determination of metal –ligand stability constant (logK) of transition metal ions with some ligand at 0.1M ionic strength .

	System	Logk$_1$	Logk$_2$	Logk$_2$ - Logk	Logk$_2$ / Logk$_1$
Ligand	Cu (II)	4.55	8.55	4.00	1.8791
	Zn (II)	4.30	7.15	2.85	1.6628
	Ni (II)	4.70	7.45	2.75	1.5851
	Mg (II)	3.90	6.95	3.05	1.7821
	Fe (II)	4.65	7.10	2.45	1.5269

The result shows the ratio of Logk1 / Logk$_2$ is positive in all cases. This implies that there is little or no steric hindrance to the addition of secondary ligand molecule .The smaller difference may be due to trans structure.

Acknowledgements

The Authors are thankful to Principal and Head of department, D.D.N. Bhole College, Bhusaval for providing necessary facilities.

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Acoustical Properties Analysis of synthesized Schiff Base of Pyrazolone Moiety in Mix Solvent at 303K Using Interferometer

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ABSTRACT

The density and ultrasonic velocity of synthesized Schiff base using (5-hydroxy -3-methyl-1-(2, 4 dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and 2-Amino 3-Hydroxy Pyridine are analyzed using interferometer. Dioxane-water solvent is used for investigation at 303k. Data obtained are used to calculate different Acoustical parameter such as solvation number (Sn).Relative association (RA) specific acoustic impedance (Z), apparent molalcompressibility (ϕk), intermolecular free length (Lf), Partial molal volume (ϕv), and adiabatic compressibility(βs).

KEYWORDS: Schiff base, Interferometry, 5-hydroxy 3-methy 1-[(2, 4-dinitrophenyl) pyrazol 4-yl] (phenyl) methanone, Acoustical parameter.

INTRODUCTION

In aqueous and non-aqueous medium interaction between ions of solute and solvent are studied by using Interferometer. The device interferometer issimple and direct technique to determine ultrasonic velocity with high precision[1-5]. Form recentperiod solvent mixture show anomalously massive impact in determination of the ultrasonic absorption coefficient (Willard, 1941; Willis, 1947; Burton,1948).The information about the physicochemical properties of metal ligand complex solution are very important with the knowledge of theoretical importance for many industries, viz. the fuel,petrochemical etc. These industries involved the process to designing accurate equipment for handling many type of lethal Chemical mixture Viz. hydrocarbons, ketones, Alcohols, aldehydes etc. Itis essential to understand the Ion-solvent interaction[5-8].

Literature review show that the many researchersinvestigate ultrasonic properties of pyrazoline, amino acid and its derivative in mixture of solvent at different concentration and different temperature[6]. Also structural properties of complex are studied by measuring ultrasonic properties and density[7]. The thermodynamic studies also take place with the help of interferometry technique[8].

Butunder the similar investigational condition there is no study are observed for Pyrazolone Schiff base with 2-Amino 3-Hydroxy Pyridine. It draw our interest toward the study of ultrasonic properties of Schiff base of (5-hydroxy-3-methyl-1-(2,4dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and 2-Amino 3-Hydroxy Pyridinein mix solvent and 303k temperature.

EXPERIMENTAL

The ligand of Schiff base was synthesis according to literature process by known technique. Theone pot synthesis are carried out for ligand synthesis by using (5-hydroxy-3-methyl-1-(2,4dinitrophenyl)-pyrazol-4yl)(phenyl) methanone and 2-Amino 3-Hydroxy Pyridineand it will be purified by Vogel's method[9]. Double distilled dioxane solvent use with water for preparation of ligand solution of different concentration. The relative measurement method is use to determine the density is measure with accuracy □ 0.00001gm/cm^3. Ultrasonic properties are determined by using the ultrasonic interferometer, the frequency of instrument is 3MHz.The steel Made double wall cell measurement unit is use and temperature is maintained by circulating water of constant temperature through the cell. In thisinvestigation, the different ultrasonic properties are evaluated such as specific acoustic impedance, apparent molal compressibility, apparent molal volume, relative association, intermolecular free length, adiabatic compressibility, solvation number, apparent molal compressibility, limiting apparent molal volume, and solvation number constant (Sk, Sv) have been evaluated

RESULTS AND DISCUSSION

The investigationaldata of ultrasonic velocity and density are used to determine the acoustical properties and related records reported in table 1-3 at 303K temperature. From this statistical information, we can say that as concentration of solution in system is increase the value of intermolecular free length are decreases while the value of ultrasonic velocity are increase. With concentration the value of specificacoustic impedance also increases in 1,4 dioxane.As the concentration of solution are increase adiabatic compressibility value is decreases, it show that there is solute-solvent interact with each other and this interaction is very strong between solute and solvent molecule in solution. The evidence for strong interaction between ions in solution is also due to apparent molal volume increase as the concentration increases. The decrease in apparent molal compressibility value is observed with increase in Schiff base concentration; it indicates that weak electrostatic attraction force among the close vicinities of ions. Solvation number was a decrease when the concentration of ligand solution increases it is due to the strong coordination bond forms between solventmolecules in primary level layer. The adverse value forSk are observed which indicates the weak interactions between solute and solvent. The positive sign forlimiting apparent molal volume value indicates that the solute-solvent interaction between dioxane andligand of Schiff base shown in table-3.The positive sign for Sv are focusedin the direction to interaction between dioxane and ligand moleculeis strong. The Sv and Skvalue has been detected from fig. 1 and 2.

Table-1 Ultrasonic velocity, density, adiabatic compressibility (□$_S$), Specific acoustic impedance (Z) Intermolecular free length (L_f).

Schiff base of (5-hydroxy-3-methyl-1-(2,4dinitrophenyl)-pyrazol-4yl)(phenyl) methanone and 2-Amino 3-Hydroxy Pyridine + 1,4 Dioxane					
Concentration moles lit^{-1} (m)	Density (ds) kg m-^{3}	Ultrasonic velocity (Us) m s^{-1}	Adiabatic compressibiliy (β_S) x10^{-10} m^{2}N^{-1}	Intermolecular free length (L_f) x10^{-11} m	Specific acoustic impedance (Zx10^6) kg m^{-2} s^{-1}
1x10^{-3}	1019.9	1487.40	4.43252	4.23431	1.5168
2x10^{-3}	1020.04	1492.20	4.4034	4.22038	1.5219
3x10^{-3}	1020.17	1497.60	4.3711	4.20487	1.5276
4x10^{-3}	1020.29	1504.20	4.33228	4.18616	1.5345
5x10^{-3}	1020.4	1511.40	4.2906	4.16597	1.5421
6x10^{-3}	1020.49	1521.00	4.23615	4.13945	1.5520
7x10^{-3}	1020.58	1527.00	4.20255	4.123	1.5583
8x10^{-3}	1020.66	1537.80	4.14337	4.09387	1.5694
9x10^{-3}	1020.72	1545.00	4.10452	4.07463	1.5769

Table-2 Concentration (m), Relative association (R_A), apparent molal compressibility (ϕ_k), Apparent molal volume (ϕ_v), Solvation number (S_n)

Concentration (m) moles lit^{-1}	Apparent molal volume (ϕ_v) $m^3 mole^{-1}$	Apparent molar compressibility (ϕ_k) $x10^{-10}$ $m^2 N^{-1}$	Relative association (R_A)	Solvation number (S_n)
$1x10^{-3}$	0.3069	1.9864	0.9993	0.9933
$2x10^{-3}$	0.3117	1.9715	0.9969	0.9858
$3x10^{-3}$	0.3164	1.9536	0.9948	0.9769
$4x10^{-3}$	0.3212	1.9345	0.9926	0.9673
$5x10^{-3}$	0.3260	1.9097	0.9895	0.9549
$6x10^{-3}$	0.3324	1.8943	0.9877	0.9472
$7x10^{-3}$	0.3369	1.8673	0.9843	0.9337
$8x10^{-3}$	0.3415	1.8495	0.9821	0.9248
$9x10^{-3}$	0.3472	1.8236	0.9787	0.9119

Table-3 Limiting Apparent molal compressibility (□$^{□}_{□}$), Limiting Apparent molal volume(□□v), Sv and Sk

Ligand	Limiting Apparent molal volume (ϕ^0_v) $m^3 mole^{-1}$	Limiting Apparent molal compressibility (ϕ^0_k)$x10^{-10}$ $m^2 N^{-1}$	$S_v m^3 kg^{1/2} mole^{-3/2}$	$S_k m^3 mole^{-2} kg.N^{-1}$
Schiff base of pyrazolone	0.3015	2.0126	5.0475	-20.500

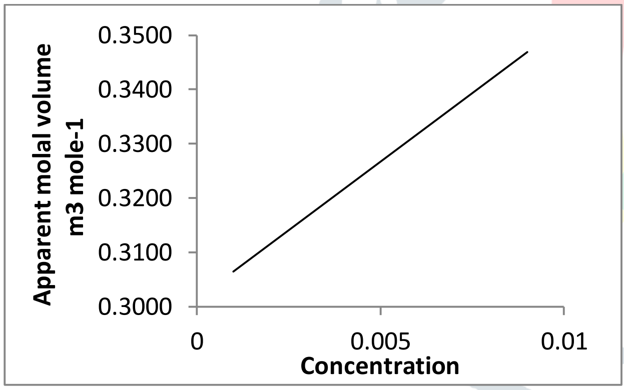

Fig.-1 -Apparent molal volume ($m^3 mole^{-1}$) Vs Concentration (mole lit^{-1})

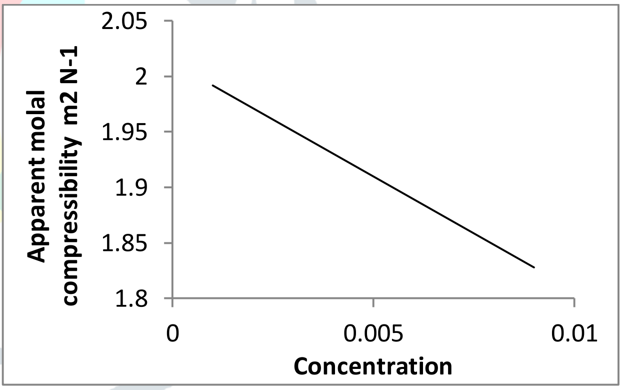

Fig.-2- Aparent molar compressibility10^{-9}($m^2 N^{-1}$) Vs Concentration (mole lit^{-1})

CONCLUSION

In present investigation the ultrasonic properties were evaluated from experimental information, it proves that there are interaction betweenmetal and Schiff base ligand of (5-hydroxy - 3-methyl-1-(2, 4dinitrophenyl)- pyrazol-4-yl)(phenyl) methanone and 4-amino antipyrine in 1,4-dioxane-water solvent. And from the investigational insights it is settled that there are cooperation among the solute and dissolvable particle in Schiff base of benzoyl Pyrazolone and dioxane-water frameworks are solid.

ACKNOWLEDGMENT

We thank Prof. P. R. Chaudhari Principal and Dr. A. K. Patil Head Department of Chemistry TVES's Dhanaji Nana Mahavidyalaya, Faizpur for encouragement. Also Thankful to Dr. P. V.Dalal Principal V. S. Naik College, Raver for providing the facilities for Research.

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EUROPEAN JOURNAL OF BIOMEDICAL
AND PHARMACEUTICAL SCIENCES
http://www.ejbps.com

ISSN 2349-8870
Volume: 6
Issue: 2
383-385
Year: 2019

STUDY THE EFFECT OF SOLVENT ON MOLAR REFRACTION AND POLARIZABILITY CONSTANT OF CLARITHROMYCIN SOLUTION AT 303.15 K.

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Article Received on 11/12/2018 **Article Revised on 01/01/2019** **Article Accepted on 22/01/2019**

ABSTRACT

The molar refraction and molar polarizability constant of substituted heterocyclic drugs Clarithromycin in different solvent like Ethanol, Methanol, Carbon tetrachloride, DMF, Dioxane and THF medium at 303.15 K at different concentrations were studied. The values of molar refraction (Rm) and molar polarizability (α) constant are found to be decreased with decreasing concentration of solute in solvent and drug –solvent interaction in different solvent has been observed.

KEY WORDS: Refractive index, Molar refraction and Molar polarizability constant.

INTRODUCTION

The refractive index is one of a unique and important property of liquid. The measurement of refractive index of organic liquids is of great importance in chemistry. These measurements provide valuable information regarding molecular structure, purity of organic compound and composition of binary mixtures. This study is an important tool for Drug-solvent interactions in medical and pharmaceutical sciences. When a light of beam passes from one substance to another, the beam is bending so that it travels in different direction. If it is passed from less dense to high denser medium it is refracted toward normal to form angle of refraction which is less than angle of incident. The refractive index is the ratio of angle of incident to the angle of refraction. It depends on the temperature and wave length of light. The extent of refraction depends on- i) The relative concentration of atom or molecule ii) The structure of atom or molecule. So refractive index gives idea about geometry and structure of molecule. Refraction of light is additive property, but also depends on the structural arrangement of atom in molecule. Some time, this can be used to determine the structure of an unknown compound whose molecular formula is known. Clarithromycin is most important substituted heterocyclic drug. Clarithromycin is beneficial for treat a number of bacterial infections including pneumonia, Helicobacter pylori, and also alternative to penicillin in strep throat.[1] Tayade et al[2] have been studied the refractometric measurements of 5-o-tolylthiocarbamido-1-naphthol in 55% ethanol-water system at 303 K by Abbe's refractometer. The solvent effects on molar refraction and polarizability of 4-amino-5-chloro-N-(2-(diethylamino) ethyl)-2 methoxybenzamide hydrochloride hydrate solutions at 303 K have been studied by Deosarkar et al.[3] The refractive index, molar refraction and polarizability constant of various compounds were studied by many workers.[4-7] Sangita Sharma[8] has been studied density and refractive index of binary liquid mixture Eucalyptol with Hydrocarbon at different temperature. Oswal[9] has been studied refractivity properties of some homologous series such as n-ethanoate, methyl alkanoates, ethyl alkanoates etc. were measured in the temperature range from 298.15 to 333.15 K. Yangang Liu[10] has studied relationship of refractive index to mass density and consistency of the mixing rule use to calculate these two quantities of multi component mixture like ambient aerosols with the index-density relationship. Yadava[11] has studied refractive indices of binary mixture of bromoalkane and non polar hydrocarbons, also studied molecular interaction between the components of binary mixtures. Sonune[12] has been studied additive properties such as molar refractivity and molar polarizability constant of allopurinal, acenocoumarol, warfarin and amoxicillin in different media. The number of researchers have been studied the molar polarization and polarizability of drugs in different solvent.[13-16]

However, study of molar refractivity and molar polarizability constant of substituted heterocyclic drugs Clarithromycin in non aqueous solvent such as ethanol, methanol, Carbon tetrachloride, DMF, dioxane and THF under identical set of experimental condition. This could cover manifold aspect of solute-solvent interactions scanty. Therefore, the present work is undertaken to make the systematic study of above substituted heterocyclic drugs refractometrically at 25°C.

MATERIAL AND METHODS

All the chemicals used are of good analytical grade (AR). The solutions of various concentrations of substituted heterocyclic drugs were prepared by dissolving required amount of solute in different solvents like ethanol, methanol, and Carbon tetrachloride, DMF, Dioxane and THF. The density of pure solvent and solutions were measured by specific gravity bottle having 10 ml capacity at 303.15 K. The refractive indices of solvent mixture and solutions were measured by Abbe's refractometer at (30 ± 0.1°C). The accuracy of Abbe's refractometer was within ±0.001 units. The constant temperature of theprism box is maintained by circulating water from thermostat at 30°C± 0.1°C. Refractometer was calibrated by using glass test piece of known refractive index supplied with the instrument. The molar refraction of solvent and solution are determined by using Lorentz-Lorentz equation. The calculated values of molar refraction and molar polarizability constant shown in table-1for different system.

RESULT AND DISCUSSION

The measured values of density and refractive index of substituted heterocyclic drugs increases with increase in concentration of ligand in different solvents. The values of molar refraction (R_m) and molar polarizability constant (α) of all ligands are found to be greater in polar protic solvents like ethanol, methanol than polar aprotic solvents like THF, DMF and non polar solvents like dioxane, carbon tetrachloride. This is due to the ability of formation of hydrogen bonding of polar protic solvents may form complex with solute but polar aprotic and non polar solvents does not contains H-bonding and it does not form complex with solute. This may be characteristics to the fact that the dipole in the compound lies perpendicular to the longer axis of the molecule, which shows intermolecular attraction take place. This will be accompanied by increase the value of molar refraction and molar polarizability constant with increasing concentration of solution because of mutual compensation of dipoles. From table-1, it could be seen that molar refractivity and molar polarizability constants decreases with decreasing in the concentration of solution.

Table-1: Molar polarization and polarizability constant (Clarithromycin).

Conc^{n} in Moles/lit.	**Medium**					
	Ethanol		**Methanol**		**CCl_4**	
	$R_m x10^3$ cm^3/mole	**α $x10^{-23}$ cm^3**	**$R_m x10^3$ cm^3/mole**	**α$x10^{-23}$ cm^3**	**$R_m x10^3$ cm^3/mole**	**α$x10^{-23}$ cm^3**
10 $x10^{-3}$	0.2147	8.51	0.2040	8.08	0.1303	5.16
5 $x10^{-3}$	0.1064	4.22	0.1014	4.02	0.0647	2.57
2.5 $x10^{-3}$	0.0527	2.09	0.0503	1.99	0.0323	1.28
1.25 $x10^{-3}$	0.0262	1.04	0.0257	0.99	0.0161	0.64
0.625 $x10^{-3}$	0.0130	0.52	0.0125	0.49	0.0079	0.32

Conc^{n} in Moles/lit.	**Medium**					
	DMF		**THF**		**Dioxane**	
	$R_m x10^3$ cm^3/mole	**α $x10^{-23}$ cm^3**	**$R_m x10^3$ cm^3/mole**	**α$x10^{-23}$ cm^3**	**$R_m x10^3$ cm^3/mole**	**α$x10^{-23}$ cm^3**
10 $x10^{-3}$	0.1648	6.53	0.2062	8.17	0.1904	7.55
5 $x10^{-3}$	0.0819	3.25	0.1026	4.06	0.0949	3.76
2.5 $x10^{-3}$	0.0408	1.61	0.0511	2.02	0.0475	1.88
1.25 $x10^{-3}$	0.0203	0.80	0.0255	1.01	0.0237	0.94
0.625 $x10^{-3}$	0.0101	0.399	0.0127	0.502	0.0117	0.46

ACKNOWLEDGEMENT

The author is thankful to Principal Dr. P. V. Dalal, Shri V. S. Naik Arts, Com. & Science College Raver for kindly cooperation.

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USE OF SOCIAL NETWORKING SITES AMONG THE STUDENTS OF SCIENCE SHRI V. S. NAIK COLLEGE, RAVER: A STUDY

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Abstract

This study was carried out to investigate the use of social networking sites among the undergraduate Science faculty students of Shri V. S. Naik Arts, Commerce and Science College Raver. In the context of today's electronic media, social networking sites have come to mean individuals, using the Internet and web application to communicate in previously impossible ways. This is largely the result of a culture-wide paradigm shift in the uses and possibilities of the internet itself.

KEYWORDS: -ICT, Social Networking Sites, Social Media, Web 2.0

INTRODUCTION

Social networking is an evolutionary development of online participation where people of common interest communicate share and contribute content on the social cyberspace it is a viable tool for cooperation and sharing of knowledge in an open access platform. Social networks are online communities that provide a place for people to connect with friends meet new friends plan their social lives discover new music trends or interests engage with political candidates promote charities and express themselves creatively. There are many social sites like face book, twitter, my space, blogs, wikis, LinkedIn, you tube, what's up weChat etc and many more to stay with all aspects in this challenging time library a library services should also use of this type of social media networking to provide fast and quick respond to its users and promoting of library services effectively to users use of social median networking library services reach to its user in a very less time.

SOCIAL MEDIA/SOCIAL NETWORKING SITES:

Nowadays, there is a great interest in how the Internet and computers can be combined so as to provide higher quality of social communication. The evolution of social media and social networking sites is undeniably one of the most impressive aspects of the internet in recent years. Social media enable human relationships through technology. In other words, social media are the media for social interaction (Canty, 2013). Moreover, social media can be used everywhere from education to business and various other fields. The last decade has seen an increase in the rise of social media sites like Facebook, LinkedIn and Twitter which enable members to share information about themselves, photos and video and to connect to other members of the website (Pfeil, Arjan and Zaphiris, 2009).

SCOPE AND LIMITATIONS OF THE STUDY

The Scope of the Study is limited only Science undergraduate students who perceiving their B. Sc Degree from Shri V. S. Naik Arts, Commerce and Science College Raver.

OBJECTIVE OF THE STUDY

1. To examine the extent of use of social network site;
2. To know the location of browsing SNS;
3. To identify frequency of use SNS;
4. To check the satisfaction level of respondents.

HYPOTHESIS OF THE STUDY

For the present study following hypothesis is used

1. Majority of the respondents are aware about Social Networking Sites;
2. Female respondents is more than male respondents

RESEARCH METHODOLOGY

The present study has adopted survey method for collecting the data in order to collect the comprehensive and related data a structure questionnaire was framed and distributed among 140 Science students of Shri V. S. Naik College, Raver. Out of 140 respondents only 132 filled questionnaires collected from the students. The questionnaire was formulated keeping in view the objective and various facts of the study the questionnaire ware personally distributed and collected with constant personal pursuance the obtained filled in questionnaire ware analyzed tabulated and logically interpreted.

DATA ANALYSIS AND INTERPRETATION

The data was collected by questionnaire methods were analyzed and interpreted and same presented with the help of following parameters:

Gender wise Use of Social Networking Sites

The questions was asked about their Gender, and the responses received were tabulated in Table no. 1

Table No.1: Gender wise use of Social Networking Sites

Gender	Respondents	%
Male	43	32.58
Female	89	70.63
Total	**132**	100.00

The table No 1 shows that 70.63% respondents are female and 32.58% respondents are Male who was using social networking sites.

Time Spend on Social Networking Sites:

The questions was asked regarding time spend for using Social Networking Sites, the response received from the students were presented in Table No.2

Table No 2 Time Spend on Social Networking Sites

Sr.No.	Hours Per day	Respondents	%
1	0-30 min	17	12.88
2	1-2hour	76	57.58
3	2-3 hour	31	23.48
4	3-4 hour	7	5.30
5	More than 4 hours	1	0.76
	Total	**132**	100.00

It can be noted from the table no. 2 that majority 57.58% of the Science students spend their 1 to 2 hours for using social networking sites, 23.48% respondents spend their 2 to 3 hours for social Networking Sites, while 12.88% students spent 0 to 30 minutes and 6.06% students spent their 3 to 4 and more than 4 hours for use of Social Networking Sites.

Place of Browsing Social Networking Sites

The questions was asked about the Place of Browsing Social Networking Sites, the responses received from the respondents were tabulated in Table No. 3

Table No. 3: Place of Browsing Social Networking Sites

Sr. No.	Location	Respondents	%
1	College Library	98	74.24
2	On Mobile	27	20.45
3	Internet Café	7	5.30
	Total	**132**	100.00

It is observed from the Table No.3 that 74.24% respondents using Social Networking Sites in College Library, while 20.45% students used in his/her own mobile for browsing SNS and 5.30% respondents used social Networking Sites at Internet Cafe.

Frequency of Using Social Networking Sites

The questions was asked regarding frequency of using Social Networking Sites, the responses received were presented in Table No.4

Table No. 4: Frequency of Use Social Networking Sites

Sr. No.	Frequency	Respondents	%
1	Daily	129	97.73
2	Sometimes	2	1.52
3	Rarely	1	0.76
	Total	**132**	100.00

The table No 4 shows that the access frequency of social networking sites the respondents indicate their time periods, it’s seem that 97.73% of the respondents were accessing social networking sites daily, only 2.27% respondents was access social Networking Sites Sometimes and Rarely.

Purpose of Using Social Networking Sites

The questions was asked about purpose of using Social Networking Sites, the responses received were tabulated in Table No.5

Table No. 5: Purpose of Using Social Networking Sites

Sr. No.	Purpose	Respondents	%
1	Sharing Important information	63	47.73
2	Sharing video and pictures	36	27.27
3	Instant message (Chat/Communication)	14	10.61
4	To meet new people	6	4.55
5	Seminar/Conferences/Research	10	7.58
6	Other Purpose	3	2.27
	Total	**132**	100.00

The table No. 5 shows the purpose that majority 47.73% of using social media networking sites for sharing important information, 27.27% of the respondents using Social Networking Sites for Sharing video and pictures. While 10.61% of the respondents using for Instant message (Chat/Communication) and only 7.58% respondents using Social Networking Sites for Seminar/Conferences/Research;4.55% respondents for meet new people; and only 2.27% respondents using SNS for others purpose.

Most Used Social Networking Site

The questions was asked about Most Used Social Networking Site, the responses received were presented in Table no.6

Table No. 6: Most Used Social Networking Site

Sr. No.	Popular Site	Respondents	%
1	Facebook	129	97.73
2	WhatsApp	108	81.82
3	YouTube	87	65.91
4	Instagram	20	15.15
5	Twitter	13	9.85
6	LinkedIn	9	6.82
7	WeChat	4	3.03
8	Others	3	2.27

(Multiple Answer were Permitted)

It can be noted from the table no 6 that the most used social networking site is Facebook 129(97.73%), followed by WhatsApp 108(81.82%) and 87 (65.91%) of the respondents used You Tube, while 20 (15.15%) respondents used Instagram; 13 (9.85%) Twitter; 9(6.82%) LinkedIn; 4(3.03%) user used WeChat and only 3 (2.27%) used others SNS.

Problem of Searching Social Networking Sites

The questions was asked regarding problems of searching Social Networking Sites, the responses received from the respondents were tabulated in Table No.7

Table No. 7: Problem of Searching Social Networking Sites

Sr. No.	Problem	Respondents	%
1	Lack of time	59	44.70
2	Slow access/ network problem	31	23.48
3	Difficulty in finding relevant information	24	18.18
4	Privacy	18	13.64
	Total	**132**	100.00

The table No 7 shows that the 44.70% of the respondents were facing problem lack of time for access of Social Networking Sites, and 23.48% respondents stated slow access/ Network Problems, while 18.18% respondents says that difficulty in finding relevant information and only 13.64% respondents stated privacy problems.

Satisfaction Level in Using Social Networking Sites

The questions was asked about Satisfaction Level in Using Social Networking Sites, the responses received from the respondents were presented in Table No. 8

Table No. 8: Satisfaction Level in Using Social Networking Sites

Sr. No.	Satisfaction	Respondents	%
1	Satisfied	123	93.18
2	Not Satisfied	9	6.82
	Total	**132**	100.00

It can be noted from the table No.8 that 93.18% respondents are satisfied with using social networking sites and only 6.82% respondents are not satisfied with using social networking sites.

CONCLUSIONS

The results obtained from this study have shown that a reasonable number of Shri V. S. Naik Arts, Commerce and Science College Raver undergraduate students of Science use the social networking sites. Therefore, the popularity of the social networking sites usage by undergraduate students and the benefits it has on the students have been confirmed from the findings of this study. There are also various purposes for which the students use the social networking sites to achieve and that have been investigated.

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Application of Web 3.0 Technology for Library

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ABSTRACT

The WWW is more and more useful application for application communication. Most people today cannot conceive of life without the internet. Web 3.0 known as a third generation of the web. It refers to a third generation of internet- based services that collectively comprise what might be called the intelligent web such as those using semantic web, micro formats, natural language search, data-mining, machine learning, recommendation agents and artificial intelligence technologies. Purpose of the study is to understand web 3.0 technologies, and how it applicable for to increase to library services.

Keywords: Web 3.0, Web 3.0 features, semantic web, Resource Description Framework (RFD), Artificial Intelligence, Technologies.

INTRODUCTION

Web 3.0 is a word coin by John Markoff of the New York Times in 2006. Basically it is development part of second generation of information technology based on Internet. As called as artificial intelligence, those using semantic web, micro formats, natural language search, data mining, machine learning, cloud computing and artificial technologies which put stress on machine-facilitated understanding of information with a view to providing a more productive and intuitive user experience**.** (Bhattacharya, 2016).

Web 3.0 and its applications is a qualitative leap in the web world. It is new emergence in web for providing better service and facilities in every field. In this situation library needs to develop its services and applications for user's satisfactions. Web 3.0 is about developing services that have the capacity to merge separated uploads into more elaborated pieces of contents. In Library 3.0, library professionals need to adopt themselves according to latest innovations provided by Web 3.0.

WEB 3.0

Web 3.0 refers to a invented third generation of Internet-based services that jointly consist of what might be called 'intelligent Web', such as those using semantic Web, micro formats, natural language search, data-mining, machine learning, recommendation agents and artificial intelligence technologies. (Bhattacharya, 2016).

WEB 3.0 FEATURES:

The main features on web 3.0 these are following

- Convergence of the virtual and physical world- Metaverse
- Access to information anywhere, anytime
- It is mainly driven by the heavy use of smart phones and cloud applications
- It is a web development layer that includes T.V quality open video,
- 3D simulations, augmented reality, human constructed semantic standards and pervasive broad-band, wireless and sensors. Web 3.0 is modern technologies and it can help to the beneficiaries to reach their goals and development.

LIBRARY 3.0

It is a model for modern technology for library automation. it reflect on over all library services. It refers to libraries using technologies such as the semantic web, cloud computing, mobile devices and re-envisioning our use of established technologies such as federated search to facilitate user-generated content and association to support and make library collections accessible. With Library 3.0, library services are frequently updated and evaluated to meet the emerging needs of library users. Library 3.0 is the borderless library; user can access their library collection without going to library physical location. It is a virtual library to physical library spaces and ideally will work seamlessly within established library services and collections.

FEATURE OF LIBRARY 3.0

1. Web OPAC

Web OPAC is most important module for public access to find the sources location in the library. It is a library catalogue using internet. And Users can search the required document by internet like URL of Web OPAC user search location of document anytime during the day and from anywhere in the world. It is programmed to facilitate the library's members to access the OPAC through their own search for the ease of borrowing instead of searching through the card catalogue. library 3.0 is become a part of WEB OPAC of various libraries in visible or invisible web.. Metadata of contents (contents in any format) would be seamlessly accessible and searchable from single user interface.

2. Ontologies:

Ontologies are used for annotating information to the web content and expressing its semantics in a machine-readable manner. These are the techniques to give richer semantic relationships between terms and thoughts of knowledge. These give more standardization in managing web contents instead of merely indexing the terms. Ontology aims at how the information is organized rather than organizing the information. These will be able to give more flexibility in providing semantic description to the content in learning object repositories and at the same time these facilitate automated functions and task delegation to intelligent agents. Ontology deals with questions concerning what entities exist or can be said to exist and how such entities can be grouped, related within a hierarchy and subdivided according to similarities and differences. (Bhattacharya, 2016).

3. Ubiquitous Contents

The ubiquitous computing offers various contents which can be used or reused frequently. The contents of this generation need to be created in various formats and can also be easily shared, transferred and accessible through all modes of communication. Ubiquitous contents are the personal contents of the people persistently stored on the web in the form of movies, blog spots, RSS feeds, wikis, stories, articles, music, games etc. These are always there on the web and it can also available from everywhere over the internet through all mobile and internet accessible devices.

4. Geo Tagging:

This helps users to find specific information located at specific location. It is simply a marking of various media or digital contents like images, photographs, videos, websites or RSS feeds etc. Most of the cell phones and mobile devices have GPS (Global Positioning System) facilities

5. Virtual Reference Service:

Technology is developing very fast in all domains; librarians are more determined to serve the users who are away from the libraries. Libraries are new developed transferable and readable access to the users for collections search as a assistance. Like mobile devices or apps.

6. Semantic Web

The semantic web improves web technologies in order to generate, share and connect content through search and analysis based on the ability to understand the meaning of words. Sharing and organizing information available in every corner of the web which is the main aim of this generation and expected to be achieved with the help of semantic web technologies. It can help to provide effective services to the user. It as tools for accessing and discovering information, collaboration and cooperation with the users.

7. Cloud Computing

Cloud computing is a central remote library which help to maintain data of resources of library which is available on internet. New days it becomes popular because it helps to become repositories, online union catalogue, and access anywhere and anytime without any type of special software and hardware, networks among the library professionals and library users, communicate with each other using social networking sites, also help for library automation.

8. Unique search

Unique search is important advantages of web 3.0. So many databases are available for searching data; these databases want different logins for searching and output. It would be easy for users to find a search result which is displayed in one place and in one way, as a Google Search. New days unique searching is become widespread for libraries because Information technology has intense effect on development and progress of libraries. The advances in science and technology has made a tremendous improvement and changed all activities of library administration.

Much library management software is developed in world and unique searching facilities already in management software, open source software's.

9. Mobile library Catalogues

New day's science and technology has made a tremendous improvement and changed in technology and it's become very small in size using nanotechnology. Mobile is a small size device it uses very far. Like communication, searching, storages, camera etc. Library has own management software for manage all type sources and they have WEB OPAC. It can be provide facilities to their users to access through their phones of other mobile devices.

CONCLUSION

Information technology has intense effect on development and progress of libraries. The advances in science and technology has made a tremendous improvement and changed all activities of library administration. Presently, there is a great influx of the electronic media and the information is available in a variety of formats, which require specialized equipments to read the information inscribed in it. In this era the librarian are very much pertinent in the electronic environment. It became necessary for the librarians to equip and update themselves with the current technologies for providing the appropriate and upto-date information. It is very important for librarian using various technologies these are introduced by the developer for library it can use for to develop their services in the libraries

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Landuse Landcover Change Detection of Dehradun Tehsil Using Landsat Data

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1. Introduction:

The total surface area of the earth is approximately 510 million km^2, of which 7 per cent (361 million km^2) is ocean and 29 per cent (149 million km^2) is land. Land is the basic life support system; it supports all forms of plant and animal life. It is the assemblage of biotic and abiotic components on the earth's surface and is one of the most crucial properties of the earth system (Turner *et al.* 1994). However, there remain remains only few landscapes on the Earth that are still in their natural state. Empirical studies globally have shown that anthropogenic activities are the sole reason that had significantly altered the Earth's surface. Man's presence on the Earth and his use of land has had a profound effect upon the natural environment thus resulting into an observable pattern in the land use/land cover over time.

The landuse and landcover (LULC) pattern of a region is an outcome of natural and socio-economic factors and their utilization by man in time and space. Land is becoming a scarce resource due to immense agricultural and demographic pressure. Hence, information on LULC and possibilities for their optimal use is essential for the selection, planning and implementation of land use schemes to meet the increasing demands for basic human needs and welfare. This information also assists in monitoring the dynamics of land use resulting out of changing demands of increasing population.

LULC change has become a central component in current strategies for managing natural resources and monitoring environmental changes. The advancement in the concept of vegetation mapping has greatly increased research on LULC change thus providing an accurate evaluation of the spread and health of the world's forest, grassland, and agricultural resources has become an important priority. Xiaomei, Y. and Rong Qing, L.Q.Y. (1999) noted that information about change is necessary for updating land cover maps and the management of natural resources. Singh (1998) too stated that change detection is the process of identifying differences in the state of an objector phenomenon by observing it at different times. It is an important process in monitoring and managing natural resources and urban development because it provides quantitative analysis of the spatial distribution of the population of interest. Macleod and Congation (1998) list four aspects of change detection which are important when monitoring natural resources:

a) Detecting the changes that have occurred,
b) Identifying the nature of the change,
c) Measuring the area extent of the change and
d) Assessing the spatial pattern of the change.

2. Remote Sensing and Geographical Information System in LULC Change Detection:

Even since the development of Remote Sensing (RS) techniques and invention of powerful software like Geographical Information System (GIS), data from Earth sensing satellites has become vital in mapping the Earth's feature. In situations of rapid and often unrecorded LULC change, observations of the earth from space provide objective information of human utilization of the landscape. Over the past years, RS and GIS are now providing new tools for advanced ecosystem management. Viewing the Earth from space is now crucial to the understanding of the influence of man's activities on his natural resource base over time. The collection of remotely sensed data facilitates the synoptic analyses of Earth system function, patterning, and change at local, regional and global scales over time; such data also provide an important link between intensive, localized ecological research and regional, national and international conservation and management of biological diversity (Wilkie and Finn, 1996).

3. Statement of the Problem:

Land use is a product of interactions between cultural back ground, state and physical need of the society with the natural potential of land (Karwariya & Goyal, 2011). Mother Nature provided abundant scope for income diversification and choices of livelihood option. Often, however, utilization objectives tend to override the socio-economic and environmental significance of the natural environment. One of the most relevant consequences of unsustainable landuse practice is their incompatibility with the diverse use of the natural environment, thereby adversely affecting the delicate balance between local economic interests, environmental functions and global biodiversity concerns (FAO, 2001). In the recent years, there has been much talked about the rapid denudation of green cover of the geographical area of our land that has threatened the livelihood of millions of poor people (Kotwal *et al.*, 2008). The area under present study (Dehradun Tehsil) witnesses a large scale transformation particularly to the built-up areas since the last two decades. With the declaration of statehood and Dehradun forming the provisional Capital of Uttaranchal (now Uttarakhand), the area has undergone large scale transformation in the landcover. Therefore, the area provides a most suitable condition to study the LULC change detection aided by RS and GIS.

4. Study Area:

Dehradun Tehsil is situated between 29° 56′ 52″ N to 30° 32′ 54″ N latitude and between 77° 33′ 46″ E to 78° 18′ 03″ E longitude. The Tehsil encompasses an area of 1882.22 sq. km. with an average elevation of 682 metres (2237 feet). The entire area can be divided into two distinct tracts, i.e. the montane tract and the sub-montane tract. Towards its north along the Chakrata tehsil the study area consists of entirely of a succession of mountains and gorges. Below the montane tract follows the sub-montane tract, popularly known as Dun Valley bounded by Shivalik hills in the south and outer scarp of the Himalayas in the north. The area experiences wide variety of LULC owing to its vastness in her geographical area as well as physiographic variations. The extreme north is occupied by mountain vegetation of alpine type to thickly forest *sal* (evergreen vegetation) towards the foothills. The southern slopes are mainly settlement areas and agriculture farmland and large tract of dry sands that are ejected by the south flowing rivers and tributaries.

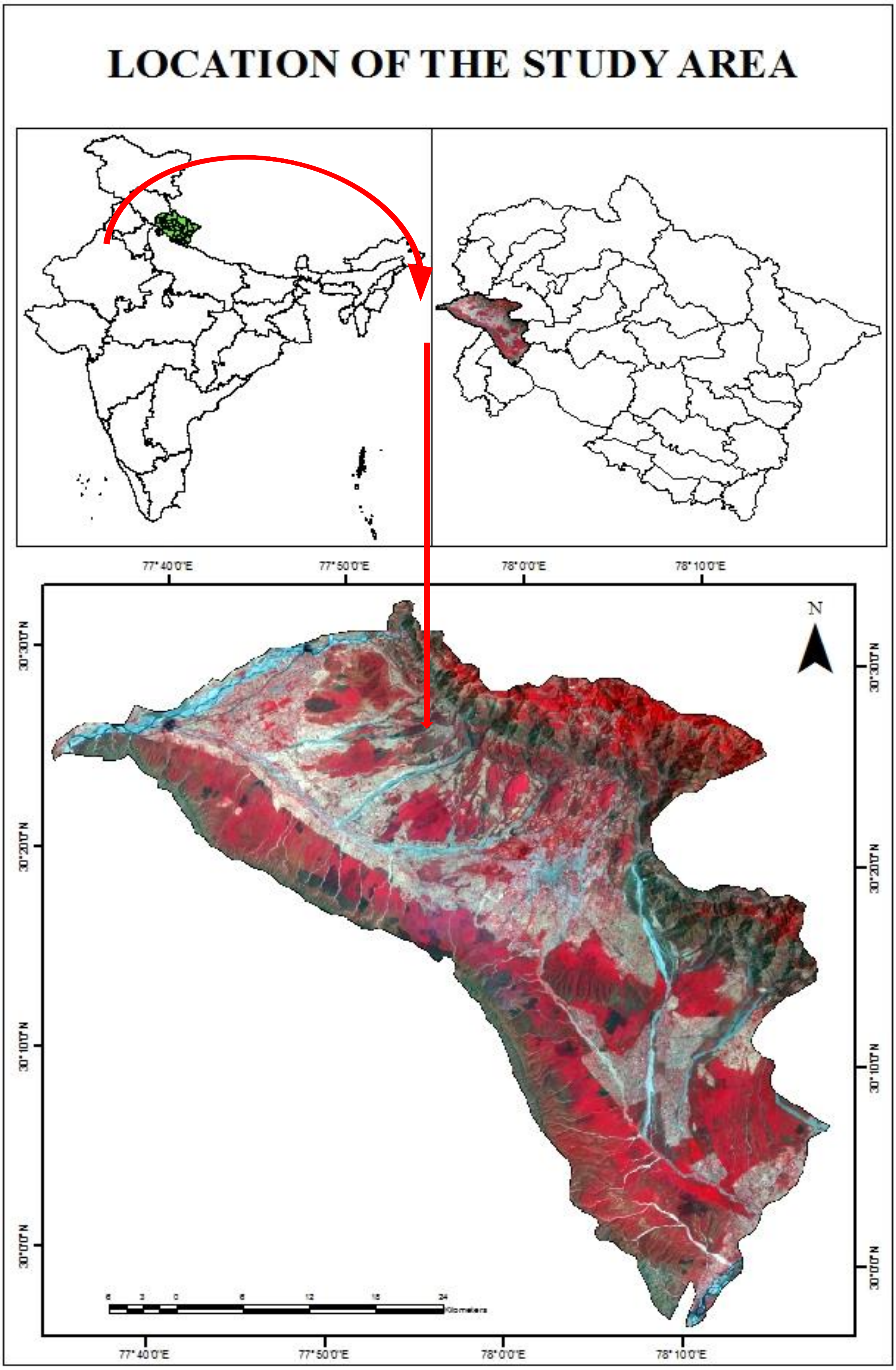


Fig-1: Location of the study area.

5. Objective of the Study:

The main objective of the study is to produce a LULC map of Dehradun tehsil at different temporal scale and to examine and identify the changes that have taken place during those periods. The specific objectives of the study are:

1. To create a landuse landcover map of the study area, and
2. To examine and identify the trend, nature and rate of landuse landcover change.

6. Database and Methodology:

Based on the objective and content of the study requisite, the Landsat satellite imageries for the year 1993, 2003 and 2013 were freely downloaded from the USGS Glovis website http://glovis.usgs.gov/index.shtml. Survey of India toposheet of 1:50,000 scale was used as a baseline map for generation of Area of Interest (AOI). The data specification and methodology performed are discussed in the subsequent paragraphs.

Table-1: Basic Information of the Landsat Satellite Images Used

Sensor	Date of Acquisition	Path/Row	Ground Resolution
LANDSAT-5 (TM)	22-05-1993	146/39	30 Meter
LANDSAT-7 (ETM)	10-05-2003	146/39	30 Meter
LANDSAT-8 (OLI-TIRS)	13-05-2013	146/39	30 Meter

The methodology for the following study is expressed by schematic diagram as given below:

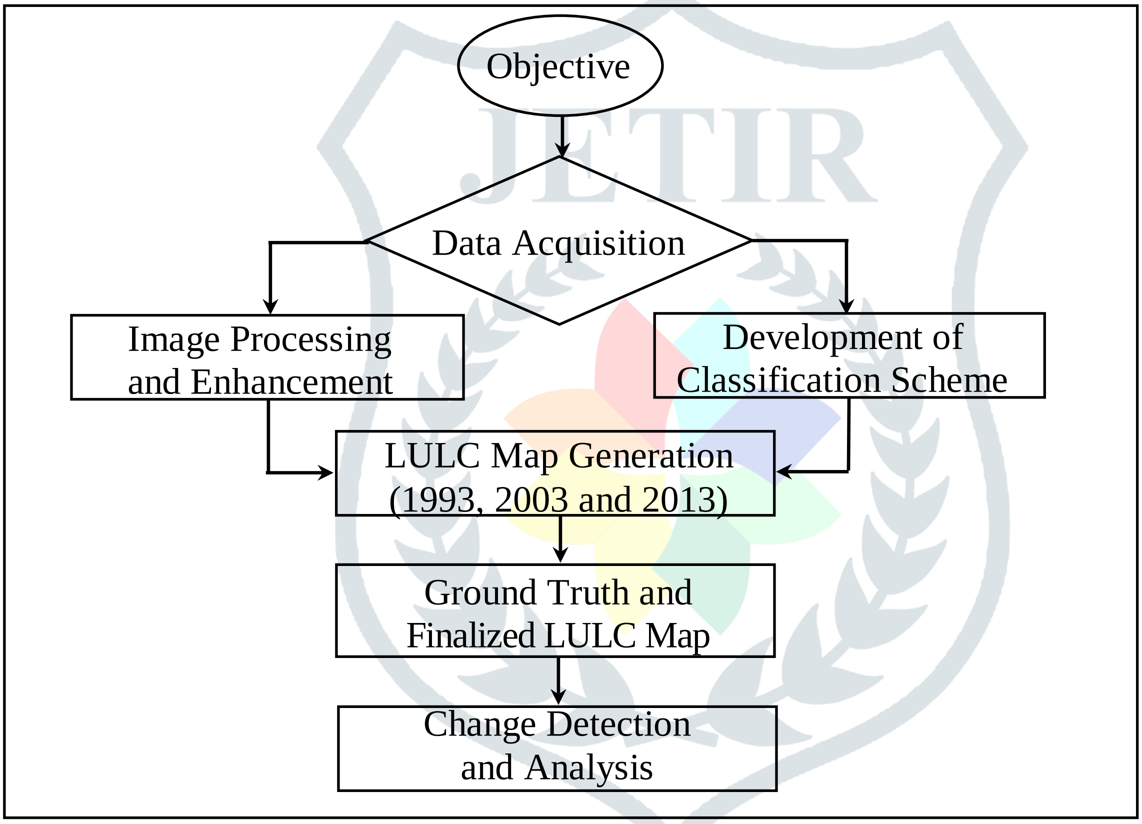


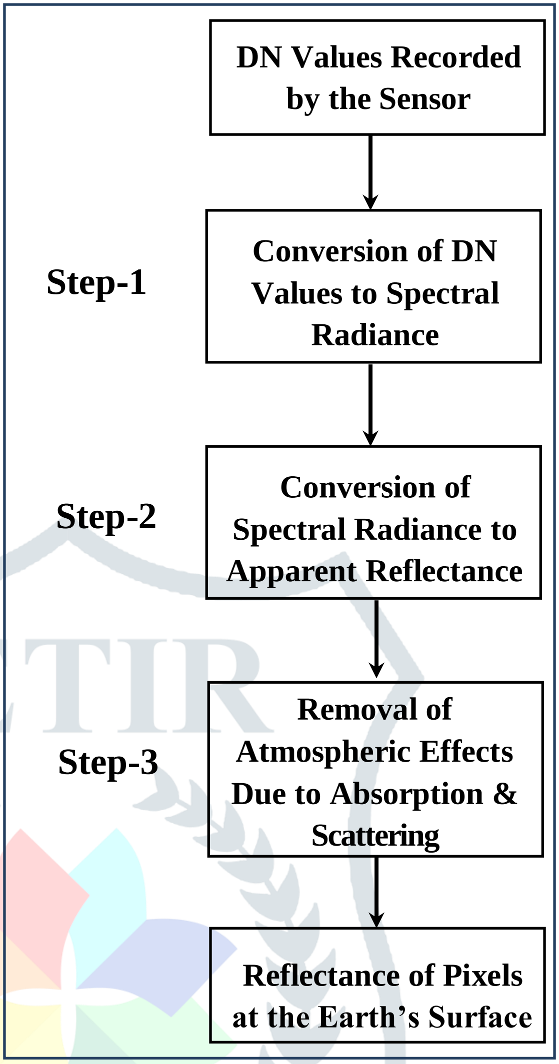
Fig-2: Schematic Diagram of Methodology Followed

Since the study of change detection is being carried out by using multi-temporal Landsat data with coarse resolution, the radiometric and atmospheric correction was felt much essential. Hence, pre-processed of raw data was performed before LULC classification was carried out.

a) Radiometric and Atmospheric Correction:

Digital sensors record the intensity of electromagnetic radiation (EMR) from each spot viewed on the earth's surface as a Digital Number (DN) for each spectral band. The exact range of DN that a sensor utilizes depends on its radiometric resolution. For example, a sensor such as Landsat MSS measures radiation on a 0-63 DN scale whilst Landsat TM measures it on a 0-255 scale and so on. However, the EMR recorded on the sensors are influenced by numerous factors. The corrections of such errors are essential before performing LULC change detection in order to gain more accuracy. Therefore, the radiometric and atmospheric corrections for the three Landsat data were radiometrically and geometrically corrected according to the steps as shown in the Figure-3. The formula used for the conversion of DN to Radiance and Radiance to Reflectance and finally the Haze removal are as shown below:

Fig-3: The Process of Radiometric and Atmospheric Correction



i) DN to Radiance:

The formula used in this process is as follows:

$$L_\lambda = ((LMAX_\lambda - LMIN_\lambda)/(QCALMAX - QCALMIN))*(QCAL-QCALMIN)+LMIN_\lambda$$

Where:

$L\lambda$ is the cell value as radiance
QCAL = digital number
LMINλ = spectral radiance scales to QCALMIN
LMAXλ = spectral radiance scales to QCALMAX
QCALMIN = the minimum quantized calibrated pixel value (typically = 1)
QCALMAX = the maximum quantized calibrated pixel value (typically = 255)

ii) Radiance to ToA Reflectance:

The formula used in this process is as follows:

$$\rho_\lambda = \pi * L_\lambda * d^2/ESUN_\lambda * \cos\theta_s$$

Where:

ρ_λ = Unitless plantary reflectance
L_λ= spectral radiance (from earlier step)
d^2= Earth-Sun distance in astronomical units

$ESUN_\lambda$ = mean solar exoatmospheric irradiances
θs = solar zenith angle.

iii) Atmospheric Haze Removal:

The Haze removal was carried out using a Model Maker in Erdas Imagine using the equation:

EITHER 0 IF ($n3_memory<0) OR $n3_memory OTHERWISE

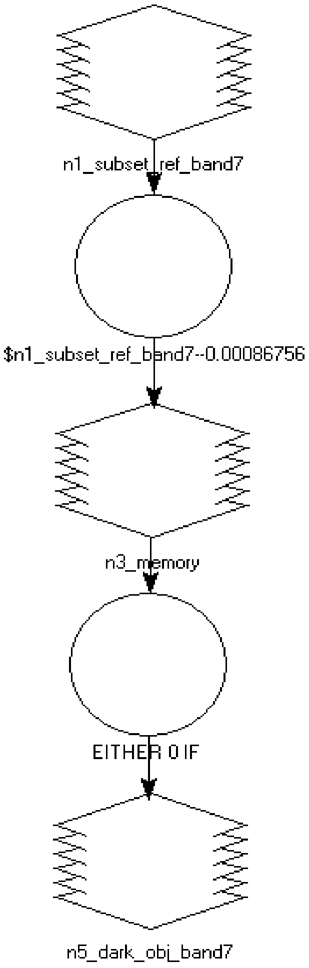


Fig-4: Model Maker for Haze Removal from Landsat Data

The values used for the conversion of DN to radiance and then to reflectance, to generate Top of Atmosphere reflectence for atmospheric corrections are as given below in Table-2.

Table-2: Landsat TM Spectral Range, Post-Calibration Dynamic Range and Mean Exoatmospheric Solar Irradiance ($ESUN_\lambda$)

Landsat TM Sensors (Q_{calmin} =1 and Q_{calmax} =255)

Band Units	Spectral Range µm	Center Wavelength	$LMIN_\lambda$ W/(m^2sr m)	$LMAX_\lambda$	$ESUN_\lambda$ W/(m^2m)
1	0.452-0.518	0.485	-1.52	193.00	1983.00
2	0.528-0.609	0.569	-2.84	365.00	1796.00
3	0.626-0.693	0.660	-1.17	264.00	1536.00
4	0.776-0.904	0.840	-1.51	221.00	1031.00
5	1.567-1.784	1.676	-0.37	30.20	220.00
7	2.097-2.349	2.223	-0.15	16.50	83.44

Landsat-7 ETM Sensors (Q_{calmin} =1 and Q_{calmax} =255)

1	0.452-0.514	0.483	-6.20	293.70	1997.00
2	0.519-0.601	0.560	-6.40	300.90	1812.00
3	0.631-0.692	0.662	-5.00	234.40	1533.00
4	0.772-0.898	0.835	-5.10	241.10	1039.00
5	1.547-1.748	1.648	-1.00	47.57	230.80
7	2.065-2.346	2.206	-0.35	16.54	84.90

Landsat-8 OLI-TIRS Sensors (Q_{calmin} =1 and Q_{calmax} =65535)

1	0.435-0.451	0.440	-63.17	764.98	1969.00
2	0.452-0.512	0.480	-64.42	780.08	1840.00
3	0.533-0.590	0.560	-58.99	714.29	1551.00
4	0.636-0.673	0.655	-49.96	604.96	1044.00
5	0.851-0.879	0.865	-30.31	367.10	225.70
7	2.107-2.294	2.200	-2.48	30.09	82.07

b) Image Classification, Ground Truth and Accuracy Assessment:

The atmospherically corrected images are then classified to generate LULC map. Both supervised and unsupervised classification method were used to have better accuracy. The LULC map was generated for three decadal time period considering the common class-Agricultural Land, Evergreen Forest, Deciduous Forest, Settlement, Water Bodies and Dry River Bed. The results of the classification were then tested for accuracy deriving the results of 72.5 percent for the year 1993, 78 percent for the year 2003 and 88 percent for the year 2013. The classification and LULC map are as shown below:

Fig-5: Landsat Images and the LULC Classified Maps of 1993, 2003 and 2013

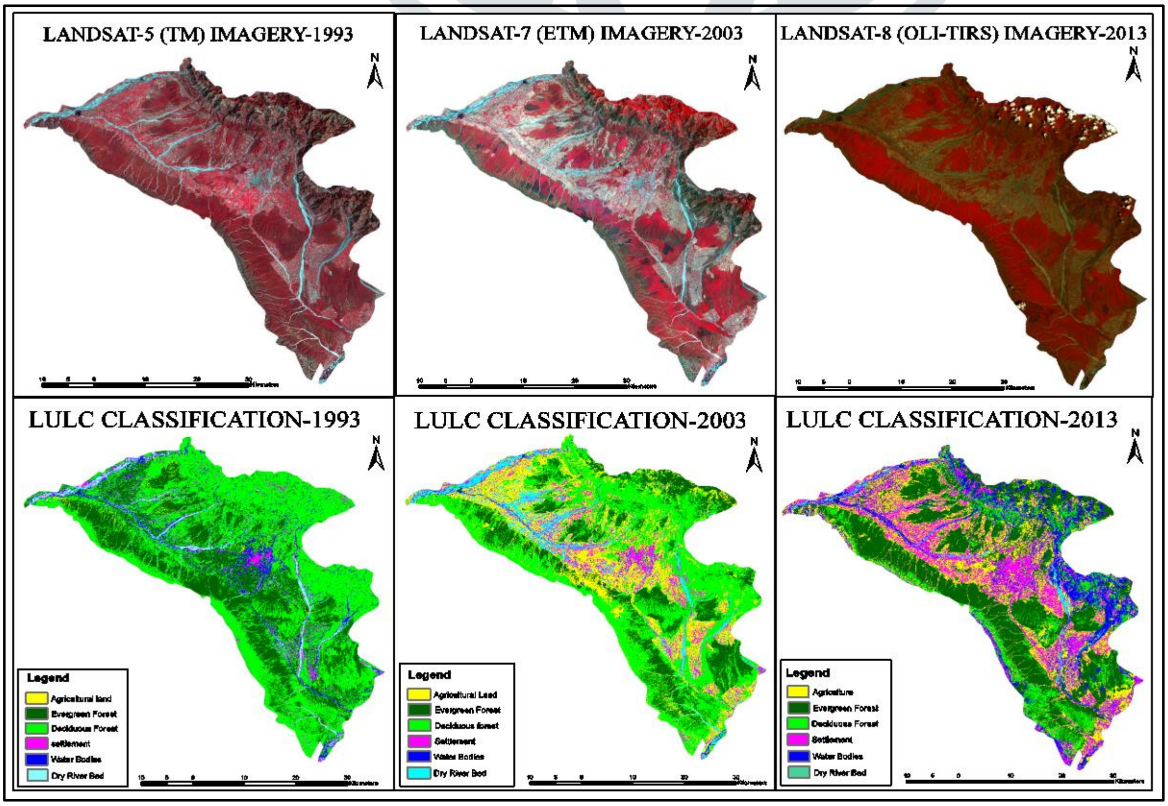
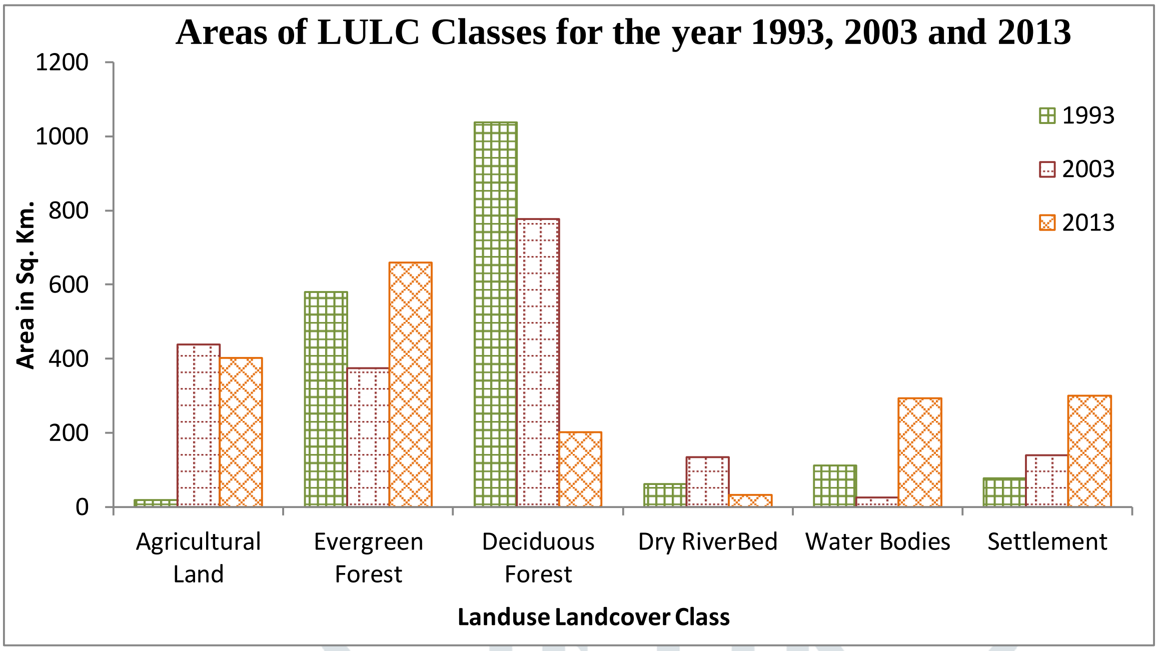


Fig-6: Areas of LULC Classes for 1993, 2003 and 2013 and their Changing Pattern

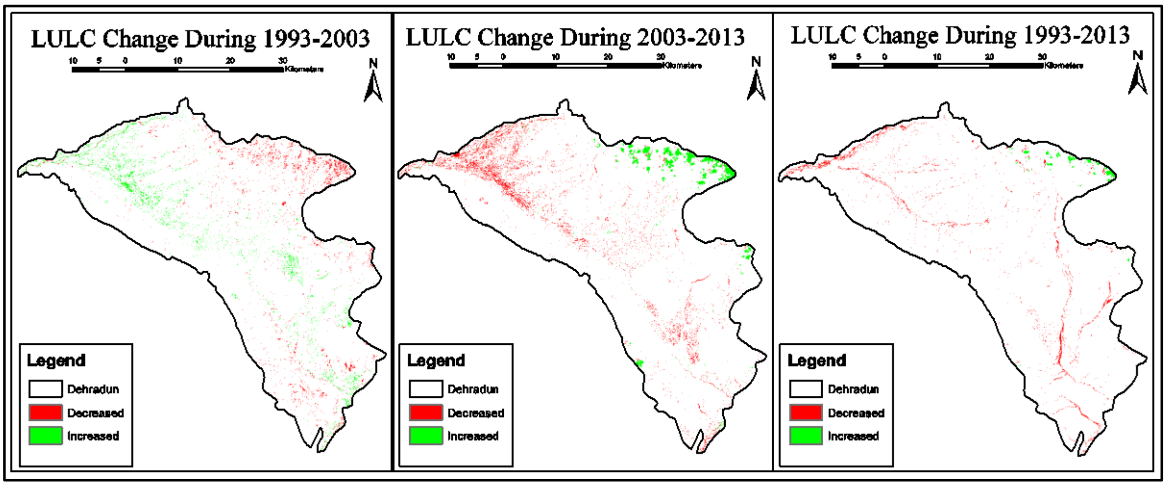


7. Results and Discussions:

Table-3:Comparative change of LULC in Dehradun Tehsil During 1993-2013

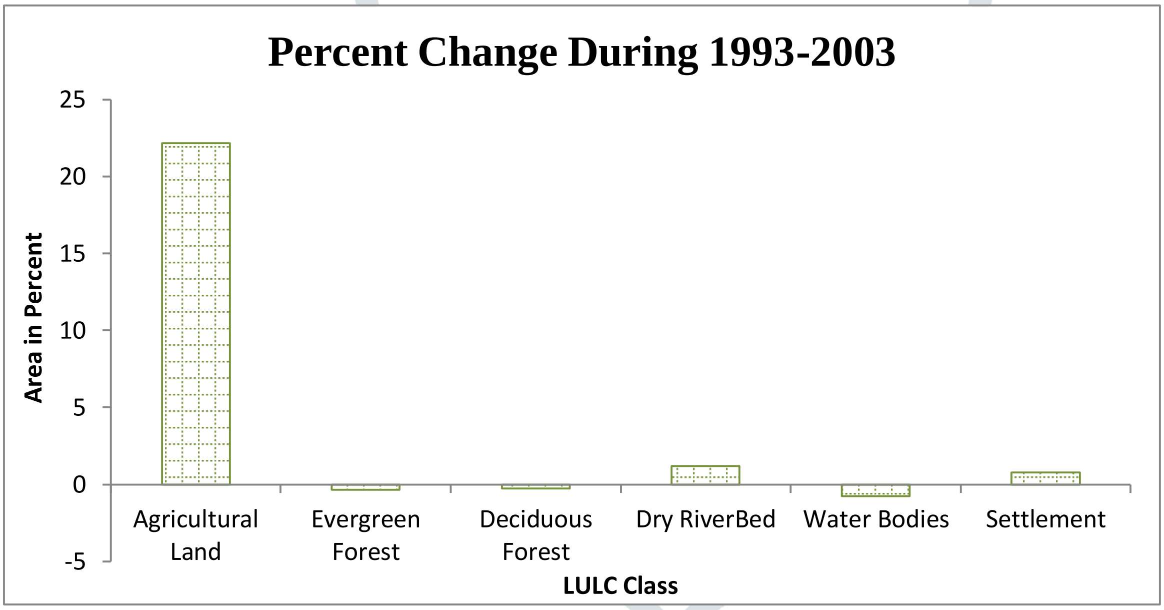
LULC class	Area in sq. Km			Change (in area sq. Km)		Change area in %	
	1993	2003	2013	1993-03	2003-13	1993-03	2003-13
Agricultural Land	18.91	437.99	401.73	419.08	-36.26	22.15	-0.08
Evergreen Forest	580.79	374.38	659.62	-260.40	285.23	-0.35	0.76
Deciduous Forest	1037.52	777.04	201.05	-260.47	-57.59	-0.25	-0.74
Dry RiverBed	61.89	134.95	33.18	73.06	-101.80	1.18	-0.75
Water Bodies	112.09	24.85	292.61	87.24	267.77	-0.77	10.7
Settlement	78.02	140.00	301.02	61.97	161.02	0.79	1.15
Total	1889.25	1889.25	1889.25	20.08	86.40	3.79	1.84

Fig 7: LULC Change during 1993, 2003 and 2013



The attribute data of supervised land use/land cover from the study area between years 1993 and year 2013 with regard to various features indicated significant changes in LULC classes. In the above table it shows that area under agriculture in 1993 was about 18.91 km^2. In 2003 it is showing 437.99 km^2 and In 2013 it reduced to 401.73 km^2.The percentage of agricultural land in 1993-2003 is increasing 22.15 in the reference of total area. But in 2003-13 it decrease -0.08 % of the total area. The decrease of agriculture land could be due to slow and steady growth of urbanization by the way of residential and commercial constructions.

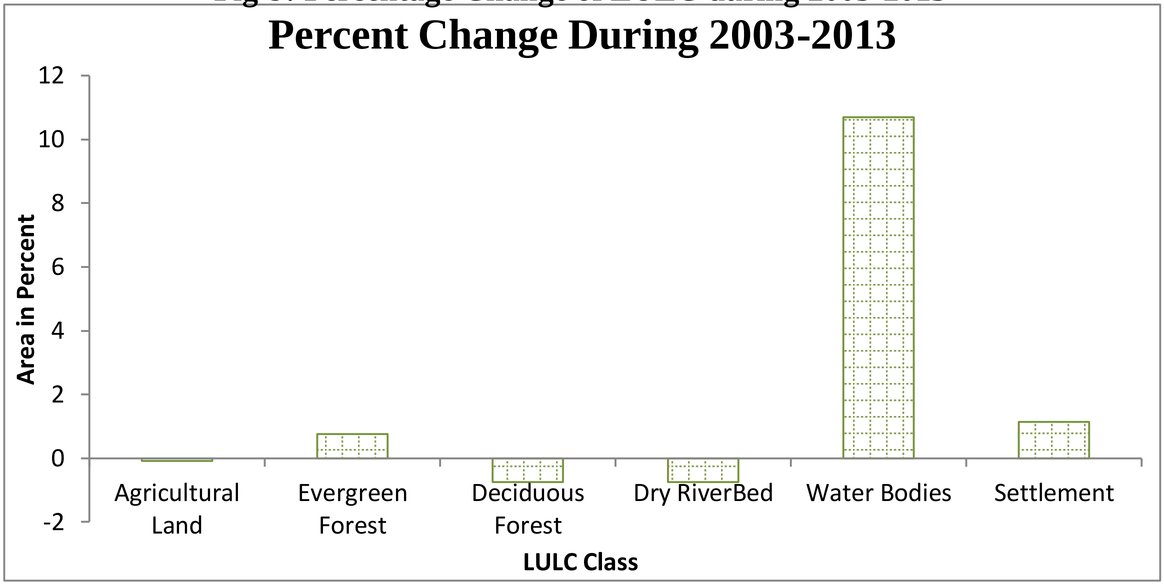
Fig-8:



Percentage Change of LULC during 1993-2003

In the above table it shows that area under Evergreen Forest in 1993 was about 580.79 km^2. In 2003 it is showing 374.38 km^2 and In 2013 it increased to 659.62 km^2.The percentage of Evergreen Forest in 1993-2003 is reducing 0.35 % in the reference of total area. But in 2003-13 it increase 0.76 % of the total area.

Fig-9: Percentage Change of LULC during 2003-2013



The table indicates that area under Deciduous Forest in 1993 was about 1037.52 km^2. In 2003 it is showing 777.02 km^2 and In 2013 it reduced to 201.05 km^2.The percentage of Deciduous Forest in 1993-2003 is reducing 0.25 % in the reference of total area. In 2003-13 it also decreases 0.76 % of the total area.

The above table shows area under Dry River Bed in 1993 was about 61.89 km^2. In 2003 it is showing 134.95 km^2 and in 2013 it reduced to 33.18 km^2. The percentage of Dry River Bed in 1993-2003 is increased to 1.18 % in the reference of total area. In 2003-13, it decreases 0.75 % of the total area.

In the above table it shows that area under water bodies in 1993 was about 112.09 km^2. In 2003 it is showing 24.85 km^2 and in 2013 it increased to 292.61 km^2.The percentage area of water bodies in 1993-2003 is reducing 0.77 % in the reference of total area. But In 2003-13, it increase 10.7 % of the total area.

The table indicates that area under settlement in 1993 was about 78.02 km^2. In 2003 it is showing 140 km^2 and in 2013 it increased to 301.02 km^2. The percentage of Settlement Area in 1993-2003 is increasing 3.79 % in the reference of total area. In 2003-13 it also increases 1.84 % of the total area.

8. Conclusion and Suggestions:

The study of landuse landcover depicts that there are so many spatio-temporal changes are found in the change detection of this study region. Landuse is directly link with human beings. Every change in landuse effects human beings and environment around us. The study reflects that after becoming Uttrakhand new state apart from Uttar Pradesh, Dehradun is the only becoming urban area in state. So our suggestions is that other area of Uttrakhand should also be developed. We should be concentrate on sustainable development for that we should use land in proper. It is therefore suggested that encouragement should be given to people towards the other area of state through the provision and forces of attraction that are available in Dehradun tehsil.

During study period water bodies area tremendously increase hence government should use it for irrigation and hydrological project. In Dehradun institutional and residential space are increasing due to its capital level establishment therefore government should establish institution in other area. In this study 2003-2013 observations are very alarming because dry riverbed area is reducing which may cause of any hazardous disaster. Dry river bed area encroaching by slum dwellers and land developers. Forest area is reducing continue so Government and People should emphasis on the thing that forest should be increase therefore it is suggested that policies aimed at supporting forest products prices provide an incentive to keep forests. It will also a source of revenue for government.

Land is main natural resource for life support system. The land and landcover changes are equally important elements of the larger problem of global and regional environmental changes. Remote sensing technology and satellite data are very helpful for the detection of changes in landuse \landcover between 1993-2013.This Project work demonstrates the ability of GIS and Remote Sensing in capturing spatial-temporal data. Attempt was made to capture as accurate as possible six land use land cover classes as they change through time. Except for the inability to accurately map out water body in 1972 due to the aforementioned limitation, the six classes were distinctly produced for each study year but with more emphasis on built-up land and forest land as it is a combination of anthropogenic activities due to it affects the other classes. However, the result of the work shows a rapid growth in built-up land between 1993 and 2013. The increase in the built up area is because of increasing demand for institutional and residential space for capital level establishments. Beside urban population of the valley has grown and is causing immense pressure for Built up area. The water dry River Bed (seasonal streams) has shown little change area due to encroachment slum dwellers and land developers. The decline in the area of the deciduous forest is due its conversion to farm land and builtup area. It was also observed that change by 2020 may likely follow the trend in 1993/2013 if all things being equal.

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Application of ICT in Higher Education

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Abstract

Higher education in India has made considerable progress in last few decades. Similarly, development in technology brings the terms like e-learning or use of information and communication technology (ICT) in higher education which makes a tremendous change in the education system. It allows learners to study anywhere and at anytime, with effective learning to unlimited number of students. The use of ICT in education itself tends to more student centered learning settings and often this creates a little tension for some teachers and students. However, world moving rapidly into digital media and information, the role of ICT in education is becoming more and more important and this importance will continue to grow. This review article highlights impacts of ICT on contemporary higher education.

Keywords: ICT, Higher education, teaching and learning

Introduction

India has one of the largest higher education systems in the world consisting more than 700 universities according to UGC as on 2016. Besides there are thousands of colleges of higher learning in the country, the number of students enrolled in the universities and colleges has increased since independence, however, this growth does not reveal much improvement in the delivery of higher education in the country.

The higher education system in India is not remarkable due to inadequate access to technology and inequity. However, the application of ICT in higher education has not only brought about diversification in higher education but has also fostered new avenues for international mobility of traditional and non-traditional students (Pegu, 2014). While it is believed that ICT can transform the educational picture in the country, it should tackle the needs and perform multiple roles in higher education. This sense of urgency and also the continuous implementation of ICT in educational activity have led many universities and colleges into a lot of action-oriented adaptation approach (Schmidtlein & Taylor, 2000).

ICTs have a significant impact on educational practice up to date and it is growing considerably in years to come and eventually it will become a strong agent for change among many educational practices. Extrapolating current practices and activities, the consistent use and development of ICT in education will have a strong impact on what and how it is learned; When and where learning takes place (Bala, 2018; Sambyal & Gupta).

What is ICT

Information and Communication Technology (ICT) is referred to the variety of collective technological resources which are useful to communicate. They are also useful in generation, distribution, collection and administration of information. ICT is a logical force that has changed several aspects of the way we live. It consist of the hardware, software, networks, and media for collection, storage, processing, transmission and presentation of information (voice, data, text, images), as well as related services. ICTs can be divided into two components, Information and Communication Infrastructure which refers to physical telecommunications systems and network (cellular, broadcast, cable, satellite, postal), also the services that utilize those (Internet, voice, mail, radio, and television), and Information Technology (IT) that refers to the hardware and software of information collection, storage, processing, and presentation (Sarkar, 2012; Thakare).

Use of ICT in teaching and learning process

ICT has been well tested and used in developed countries to tackle most of these problems associated with teaching and learning process. It can be used in the Indian educational system to teach all subjects like Science, Mathematics including engineering (Kabouridis, 2010). ICT can improve teaching by enhancing an already accomplished knowledge and introducing new ways of teaching and learning process. Transforming teaching is more difficult to achieve. “The changes that take full benefit of ICT will only happen gradually over time, and as long as teachers continue to experiment with new approaches.” (Underwood, et al., 2006).

Use of ICT in higher education

Introduction of use of ICT in the higher education has generated to knowledge creation i.e. field of research and its dissemination and on the other extreme it is feared that there use will further the digital inequity. It is anticipated that their increasing use in education system will also raise issues regarding what kind of technologies, in what quantity, at what level and for what purpose they need to be introduced. The concerns such as who will manage this process develop policy guidelines and strategies also require consideration. Wright (Wright, 2000) pointed out that it will not be wise to ignore the issues related to equity, cultural integrity, and the negative aspects of technology in economic and social development. Nevertheless, the opportunities and challenges raised at different platforms can be categorized as the aspects relating to role of ICT for access and equity in education, role in management and efficiency in education, their role in pedagogy for quality learning and teaching at higher education level and in inducing innovations in approaches and programs (Snehi, 2009).

Use of ICT in research

The steady increases in computing power available have made it possible to conduct complex calculations on large data sets. Communication links make it possible for research teams to be spread across the world instead of concentrated in a single organization. The combination of communications and digital libraries is equalizing access to academic resources, greatly enriching research potential for smaller or remote institutions. Taking full advantage of this trend to form new dynamics in research requires some national policies based on ICTs in higher education and the establishment of joint information systems connecting all higher education institutions.

The application of ICTs in academic research has grown steadily in the past 15 years in both developing and developed countries. The most important use of ICTs in research is in data processing. The unique growth in bandwidth and computing power provide opportunities for analyzing or processing large amount of data and performing complex calculations those are extremely fast, accurate and reliable. Computer data processing not only free researchers from the burdensome task of manually analyzing data but more importantly facilitates quick and accurate analysis of huge amounts of data from national samples or even multi-national samples covering number of respondents. Another important dimension of ICTs in research is the use of online full text databases and online research libraries or virtual libraries which are the direct outcome of the growth in telecommunications networks and technology. These databases and libraries provide researchers the online access to the contents of thousands of books from major publishers, research reports, and peer- reviewed articles in electric journals (Sarkar, 2012).

Benefits of ICT in higher education

ICT enhances higher education in a number of ways with following advantages.

i. Eliminating time barriers in education for learners as well as teachers and geographical barriers for learners to study from anywhere.
ii. It enables the effective storing/sorting of information, and can offer new fast ways of communication;
iii. It enables the reduction of information quantity towards a higher quality and better structure;
iv. It can be integrated into teaching and learning strategies – and used to support relative learning theories; and
v. It can be used to create new types of interactive learning media (computers, Inter and Intranet) for improved quality, equity, and access in higher education (Thomas, 1999).

Challenges of the implementation of ICT

ICTs are powerful tools having potential to transform the educational systems and opportunities for all students including those who are normally excluded by virtue of their special circumstances and special educational needs. Use of ICTs can break down some of the barriers that lead to underachievement, student disaffection and educational exclusion (Swarts, 2006). However, when one looks around, in most of the colleges and universities across the country lack of tackling of this potential is visible. In spite of the fact that planning and implementation of initiatives for enhancing role of technology in education have received priority, analysis of the existing scenario reveals number of factors which have been impeding the integration of ICTs in educational sector (Snehi, 2009). There are several barriers in implementation of ICT in developing countries (Khan, Hossain, Hasan, & Clement, 2012).

1. ICT Supported Infrastructure and Lack of Resources

The development of the ICT infrastructure in a country is depending on the availability of a consistent electricity supply. Moreover, for implementation of ICT demands other resources, such as computers, printers, multimedia projectors, scanners, etc. which are not available in all the educational institutions are also important. Besides, ICT requires up-to-date hardware and software. Using up-to-date hardware and software resources is a key feature in the diffusion of technology (Gülbahar, 2007), but a rare experience in educational institutions. High-speed internet connection is another requirement for integrating ICT into the teaching-learning situation. But unfortunately as shown in table 1 (*Worldwide broadband speed league 2018*) internet access is poor in some countries (Abdullah & Gulzar, 2016).

Table 1. Internet Usage and Broadband Speed (2017-18)

Country	**Broadband speed Mbps**	**Internet Users (%)**
Singapore	60.39	81.00
Japan	28.94	92.00
Taiwan	28.09	79.75
United States	25.86	76.18
Russia	13.51	76.41
China	7.60	53.20
Sri Lanka	5.84	32.05
India	5.19	53.35
Nepal	2.36	19.69
Bangladesh	1.97	65.53
Pakistan	1.32	30.16

2. Insufficient Funds

ICT supported hardware, software, audio visual aids, teaching aids and other accessories demand huge funds (In, 2016). The lack of funds to get the required hardware and software package is one of the reasons that teachers do not use technology in their classes. Efficient and effective use of technology depends on the availability of hardware and software and the equity of access to resources by teachers, students an administrative staff (Afshari, Bakar, Luan, Samah, & Fooi, 2009). These costs are inflated in most cases and cannot be provided by most developing countries.

3. Time and effort constraints

Teachers are normally busy with their daily schedule of lecture sessions, maintaining records, question paper setting, answer sheet correction, interacting with students, conducting seminars, quiz sessions, discussion forums, assignment checking etc. The basic Challenge is that they have to learn the pattern of the operating process initially, then prepare the course content according to the instructions and the various assessment documentations as per the formats compatible to the ICT tool within the available time frame (Mayer, Dumont, Istance, & Benavides, 2010).

4. Teachers' Attitudes about ICT

Teachers’ attitudes are found to be major predictors of the employment of latest technologies in instructional settings (Almusalam, 2001). The successful use of ICT into classroom mostly depends on teachers’ attitudes and belief relating to these. It is found that less technically skilled teachers, who possess positive attitudes towards ICT, require less effort and encouragement to learn the skills required for the implementation of ICT in their design activities into the classroom (Khan, et al., 2012). Similarly, Participants with negative computer attitudes were less skilled in computer use and were therefore less likely to accept and adapt to technology than those with positive attitudes (Harrison & Rainer Jr, 1992).

Although it has numerous advantages reported in literature over traditional learning there are some limitations too. Initially this requires teachers to become more familiar with ICT and which will reduce the interaction with students. Further, those students are more familiar with ICT will get more benefit to learn than who is less which ultimately shifts the driving force of studying core to developing ICT skill. It comparatively more expensive, it may create lack of communication between student and teacher and can reduce the desire of learning in students.

Conclusion

It is believed that the use of ICT in higher education can increase access to learning opportunities. It can help to develop the quality of education with advanced teaching methods, improve learning outcomes and enable reform or improved management of education systems. Availability of course material in education can be shared by means of ICT, can promote better teaching. Moreover, this will increase flexibility so that learners can access the education regardless of time and geographical barriers. Apart from implementation of ICT in higher education, governments and higher education institutions will need to develop strategies for effective ICT deployment and sustainability.

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Nanocomposites thin films as gas sensor application

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Abstract

In present work nanocomposites thin films were prepared by spray pyrolysis technique. As prepared thin films were studied using XRD and FE-SEM and. The film sprayed for composition of WO_3-V_2O_5 (Sample =S2) was observed to be most sensitive (S = 1130) to SO_2 at 350 ^{o}C. The sensor shows quick response (4 s) and fast recovery (8 s) time. The results are discussed and interpreted.

Keywords: Spray Pyrolysis, WO_3-V_2O_5 nanocomposites, SO_2 gas sensing, quick response, fast recovery

1. Introduction

Metal oxide semiconductors are used extensively as a sensing element of different gases and vapors. A depletion region always formed at the surface of metal oxide semiconductor due to adsorption of air oxygen molecules. Then the reaction with the target gas molecule causes reduction of depletion region which results change in conductivity of metal oxide semiconductor. The conductivity may increase or decrease depending on type of semiconductor and type of target gas [1]. The metal oxide-sensing layer (WO_3 or V_2O_5) has been fabricated in different physical forms such as thin film, thick films, and bulk pellets. However, the thin film form is expected to be most effective, because sensing is basically a surface phenomenon of film. Thus, a very few work has been reported for the combination of WO_3/V_2O_5 oxide composite.

In present work efforts was done in the area of SO_2 detection using metal oxide thin films . However, not much attention has been given to the fabrication of nanocomposites structure for detection of SO_2 gas. There has been intensive research on improving the gas sensitivity and selectivity by controlling the particle size, nanostructures, sensing temperature, surface and structure [2].

2. Experimental details

2.1 Preparation of WO_3-V_2O_5 nanocomposites thin films

The starting material used for the preparation of WO_3-V_2O_5 nanocomposites thin films were tungsten hexachloride (WCl_6, Purified Merck) and vanadium (III) chloride (VCl_3), Purified Aldrich). Tungsten hexachloride and vanadium (III) chloride were mixed at various volume ratio such as 30:70, 50:50 and 70:30 as indicated in Table 1.

Table 1: Amounts of spraying solutions and reactant

Sample No.	WCl_6 (cm^3)	VCl_3 (cm^3)	Reactants
S1	30	70	WO_3:V_2O_5
S2	50	50	WO_3:V_2O_5
S3	70	30	WO_3:V_2O_5

The optimized deposition parameters like substrate temperature (350 °C), spray time (10 mn.), rate of spraying solution (8 ml/min.), nozzle to substrate distance (30 cm), quantity of the solution sprayed (30 ml), pressure of carrier gas, and to and fro movement of the nozzle were kept constant. The temperature of the substrate is maintained at a constant value by using a temperature controlled hot plate. The film formation depends upon the droplet landing, reaction and solvent evaporation, which relates to the droplet size. When the droplet approaches the substrate just before the solvent is completely removed, that is the ideal condition for the preparation of the pure WO_3, V_2O_5, and WO_3-V_2O_5 nanocomposites thin film. The as prepared WO_3, V_2O_5, and WO_3-V_2O_5 nanocomposites thin films samples were annealed at 500 °C for 1 h.

3. Results and discussion

3.1. Structural analysis using X-ray diffractogram

Fig. 1 shows the X-ray diffractogram of thin film sample. The observed peak predominates indicating a preferential growth. This means that the grains have *c*-axis perpendicular to the substrate surface. The calculated average crystallite size was found to be 18 nm.

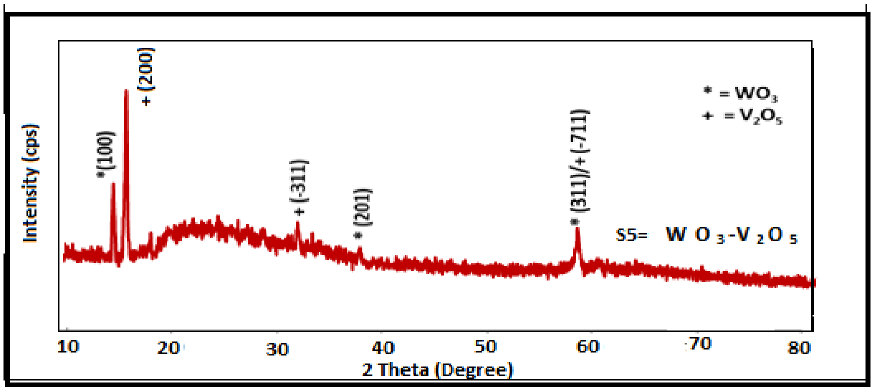

Fig. 1. X-ray diffractogram of most sensitive nanocomposites thin film (sample S2)

3.2. Field emission scanning electron microscope

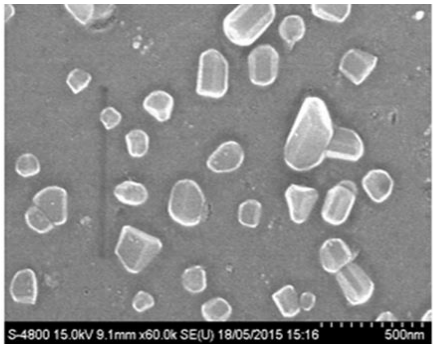

Fig.2. FE-SEM images of most sensitive nanocomposites thin film (sample S2)

FE-SEM images of pure WO_3, V_2O_5, and WO_3-V_2O_5 nanocomposites were represented in Fig.2. Grain size observed to be in the range of 21 - 44 nm.

4. Gas sensing performance of the sensors

4.1. Gas response

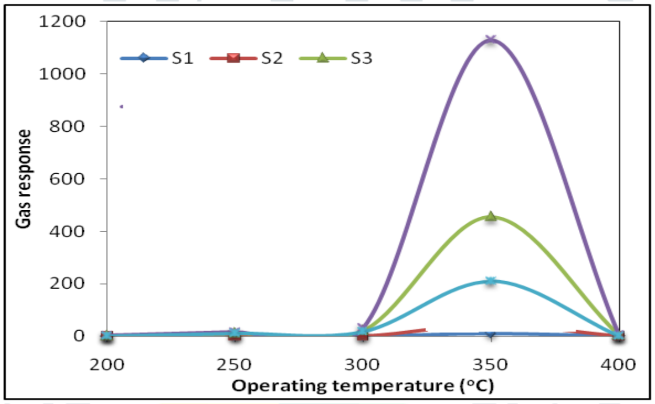

Fig. 3. Gas response of nanocomposites thin films with operating temperature

Fig. 3 represents the response characteristics of the WO_3-V_2O_5 nanocomposite thin films as a function of operating temperature. Among all the films, the sample (S2) film shows the maximum response (1130) at 350 ^{0}C to 500 ppm of SO_2.

4.2. Response and recovery of the sensor with concentration of gas in ppm

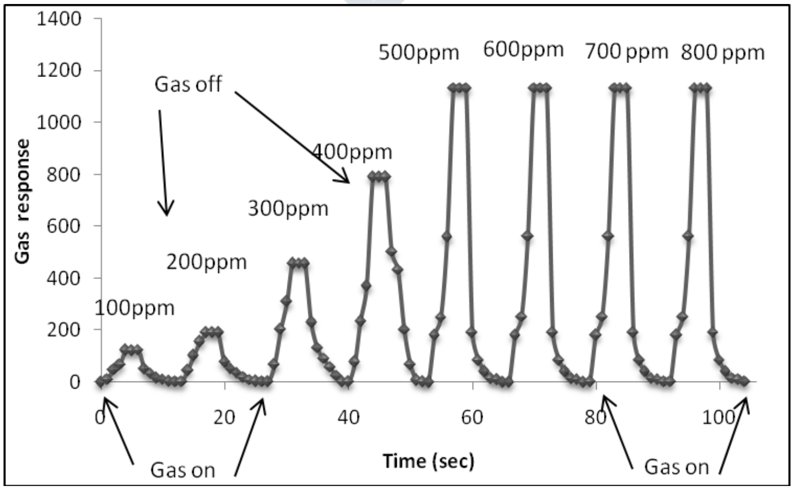

Fig. 4 Response and recovery of the sensor for most sensitive sample (S2).

The response is quick (4 s) and recovery is fast (8 s). The high oxidizing ability of adsorbed oxygen species on the surface nanoparticles and high volatility of desorbed by-products explain the quick response to H_2S and fast recovery [3-5].

5. Conclusion

Nanocomposites thin films were prepared by simple spray pyrolysis technique. The WO_3-V_2O_5thin film of (Sample S2) was most sensitive to SO_2 gas and exhibits the response of S = 1130 to the gas concentration as 500 ppm at the temperature of 350 ^oC. The WO_3-V_2O_5nanocomposites thin films exhibit rapid response–recovery which is one of the main features of this sensor.

Acknowledgements

The authors are thankful to the University Grants Commission, New Delhi for providing financial support. Thanks to Principal, Shri. V. S. Naik A.C.S. College, Raver, for providing necessary infrastructure laboratory facilities for this work. I have also appreciate Prof. Dr. R. H. Bari, Head of Department, Department of Physics, G. D. M. Arts, K. R. N. Com. And M. D. Science College, Jamner for their help. We thanks NMU, Jalgaon for the motivation and encouragement for giving me the opportunity to do this research work as successful one.

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"Study of nanostructured NiO thin film deposition using spray pyrolysis technique"

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Abstract

An attempt was made to deposit NiO thin film on glass substrate at 350 ^{0}C by spray pyrolysis technique (SPT). The structural, elemental, surface morphological properties and semiconducting nature of NiO thin films were investigated. XRD confirms polycrystalline nature with cubic phase. Surface morphology study of NiO deposited films by FESEM reveals nanocrystalline grains of spherical shape. TEM has also confirmed nanocrystalline nature and depicted the size of grain around 17 nm. EDAX analysis have confirmed Ni and O elements in NiO film. Electrical conductivity measurements have confirmed semiconducting nature of deposited films. The nanocrystalline porous spherical shape of grains and semiconducting nature of thin films may offer its applications for sensing and solar cells.

Keywords: *Spray pyrolysis, Nanocrystalline nickel oxide, Thin films, Electrical conductivity.*

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1. Introduction

There has been constant urge for synthesizing nanostructured metal oxid because of their wide applications in solar cells [1]. Especially, nickel oxides have vital applications in solar, semiconducting devices, gas sensing, electrochromic display and optoelectronic devices [2-6]. Nickel oxide is one amongst the other *p* type semiconducting materials with a band gap energy about 3.62 eV to 4.00 eV at room temperature. It has some advantages over the other materials like CdO, In_2O_3, ZnO or Cd_2SnO_4 due to its unique features of interesting properties like non toxicity, good electrical, optical behaviour and piezoelectric behaviour as well as low cost.

Variety of technique have been employed to prepare nickel oxide thin films that involve: vacuum evaporation [7], electron beam evaporation [8], rf-magnetron sputtering [9, 10], anodic oxidation [11], chemical deposition 12–14], atomic layer epitaxy [15], sol–gel [16] and spray pyrolysis technique [17–19]. Among these techniques, spray pyrolysis has proved to be simple, reproducible and inexpensive, as well as suitable for large area applications. Besides the simple experimental arrangement, high growth rate and mass production capability for large area coatings make them useful for industrial as well as solar cell applications. In addition, spray pyrolysis open up the possibility to control the film morphology and particle size in the nanometer range.

In the present investigations, nanocrystalline NiO thin films with different volume of precursor solution were prepared using spray pyrolysis technique. Structural properties were studied using X-ray diffractogram. Surface morphology and microstructure properties were studied using FE-SEM and TEM. Element composition of material was studied using EDAX. Electrical conductivity was measured using two probe method to confirm the semiconducting nature of the deposited material.

2. Experimental details

2.1. Spray pyrolysis set-up:

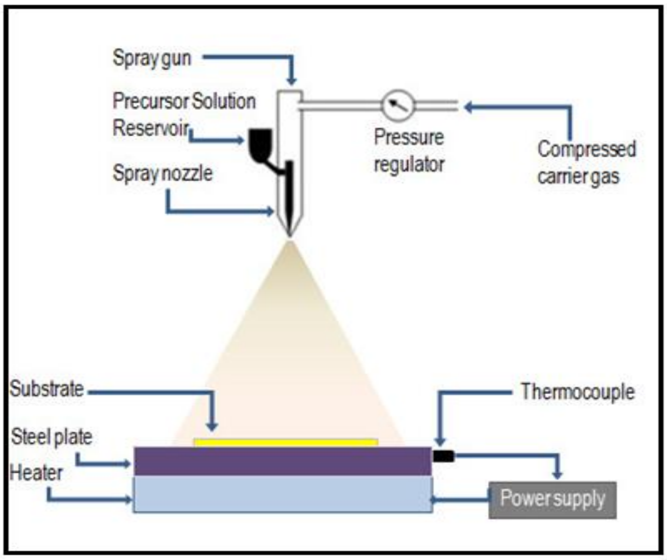


Figure 1: Schematic diagram of spray pyrolysis system for the preparation of nanocrystalline NiO thin films.

The experimental setup of spray pyrolysis system is as shown in Fig.1. It comprises spraying chamber, spray nozzle (gun), carrier gas compressor, heating system with temperature controller. In present work a temperature of 350 ^{0}C was attained by thermocouple with the help of heater before resuming the process of deposition.

2.2 Preparation of precursor and deposition:

Nickel oxide thin film of various thicknesses deposited by varying the spraying volume of solution between 5 to 30 ml. Precursor solution of nickel chloride hexadihydrate having concentration 0.05 M was prepared by dissolving nickel chloride hexadihydrate ($NiCl_26H_2O$) [Merck] in deionized water. The prepared solution was then poured into the spraying chamber. Chemically and ultrasonically cleaned glass substrates are used for deposition. Initially glass substrate was heated up to 350 ^{0}C by keeping it at constant temperature. Various parameters were used to obtain the uniform deposition. The optimized parameters of spray deposited NiO thin film are as shown in Table.1. The deposited thin films are titled as N_1, N_2, N_3 and N_4 for different volume of solution of precursor as 5 ml, 10 ml, 20 ml and 30 ml respectively.

Table 1. Optimized deposition parameters of NiO thin film for spray pyrolysis technique

Sr. No.	**Deposition parameter**	**Optimum value**
1	Substrate temperature	350 ^{O} C
2	Spraying nozzle to substrate distance	30 cm
3	Spray rate of solution	7 ml/ min.
4	Spray time	1 min.
5	Carrier gas	Compressed air
6	Nickel chloride hexadihydrate ($NiCl_2.6H_2O$) concentration in mole	0.20M

.

2.3. Annealing of NiO thin films:

The as prepared nanocrystalline NiO thin film samples N_1, N_2, N_3 and N_4 were annealed at 500 ^{0}C for 1 hrs.

3. Characterizations

The morphology of deposited and annealed NiO thin film was studied using JEOL. JED 6300 and field emission scanning electron microscope (FE-SEM). The elemental analysis was carried out by employing an Energy Dispersive X-ray Spectrometer (EDAX) (JEOL 2300 model, Japan). The structural properties of deposited NiO thin films were investigated using MINIFLEX Model, Rigaku, Japan X-ray diffraction for the range of 10^0 to 80^0,2θ angles. Microstructural properties were carried out by employing CM 200 PHILIPS (200 kV HT) Transmission Electron Microscopy (TEM). The electrical conductivity measurement was studied by using two probe method with SES Instrument Model: PID-210, Model: EHT-11.

4. Results and discussion

4.1. Determination of film thickness:

The variation of nanostructured NiO thin film thickness was studied as a function of volume of sprayed solution. It has been found that the thickness of the films increases with the volume of sprayed solution.

The thickness of the film was measured by using a gravimetric weight analysis method using the following relation given by equation no. (1)

$$t = m/A\rho \text{ ------------- (1)}$$

Where, t is the thickness of the film, m is the actual mass deposited on to the substrate, A is the area of the film and ρ is the density of the material.

The thickness of the thin film samples N_1, N_2, N_3 and N_4 measured by using above equation no. (1) are found to be 450 nm, 789 nm, 833 nm and 978 nm respectively.

4.2. X-ray diffraction analysis

The structural properties of nanostructured NiO thin films were examined by using an X-ray diffractometer. The phase and the orientation of the deposited nanostructured NiO thin films were determined.Fig.2 shows the XRD pattern of NiO thin film samples N_1, N_2, N_3 and N_4.

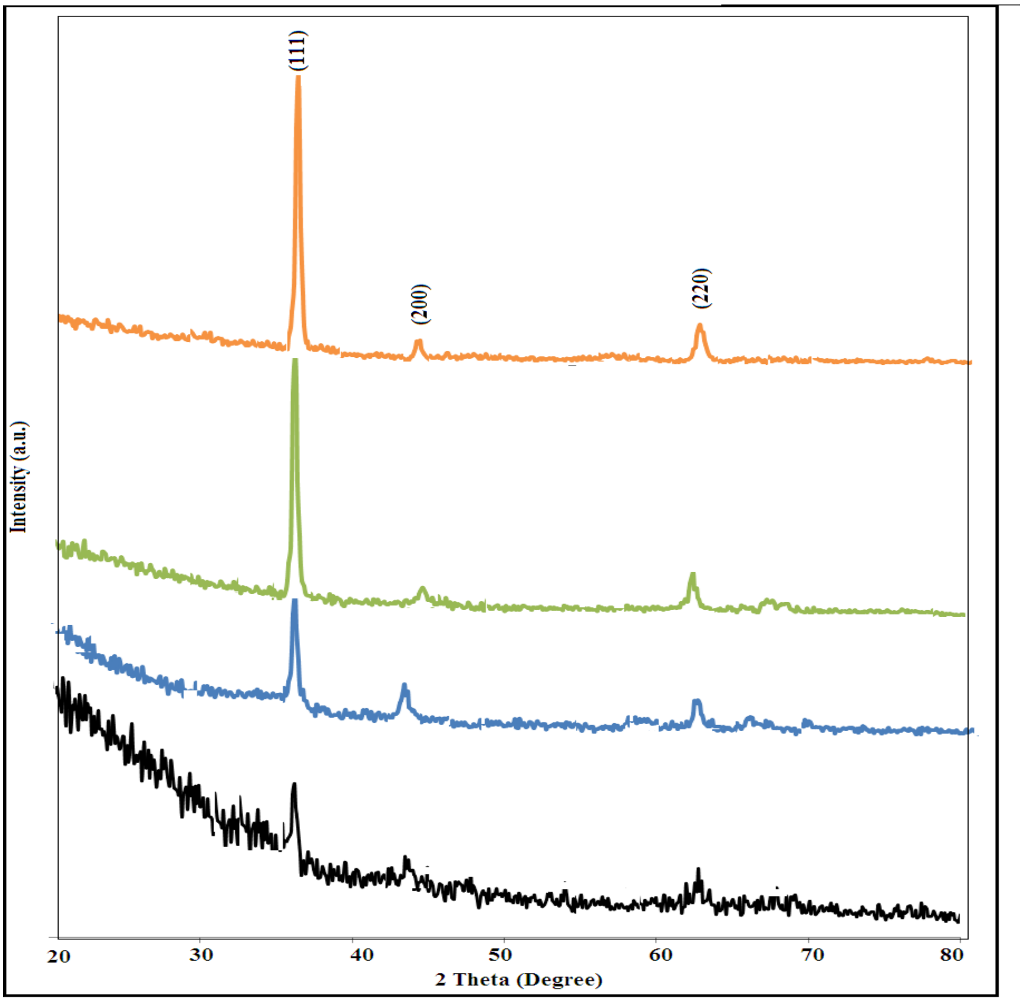


Figure 2:X-ray diffractogram of nanocrystalline NiO thin films samples: N_1, N_2, N_3 and N_4.

For all these samples, the cubic structure characterized with strong reflection plane (111) and there is weak reflection along (220) plane as preferred orientations are well matched with the reported ASTM data of pure NiO [20]. So over all diffraction profile of all these samples illustrate the polycrystalline nature with suitable cubic phase and its formation is independent of film thickness. The average crystalline size of pure NiO thin film samples were obtained using Debye Scherrer formula [21,22] as in equation no. (2).

$$D = 0.9\lambda/\beta cos\theta \text{------------------------} (2)$$

Where, D = Average crystallite size
λ = X-ray wavelength (1·542 Å)
β = Full width at half maximum (FWHM) of the peak (in radians)
θ= Bragg's diffraction angle (Diffraction peak position)

The average crystalline size was found to be in between 14 nm to 19 nm.

4.3. Surface Morphology:

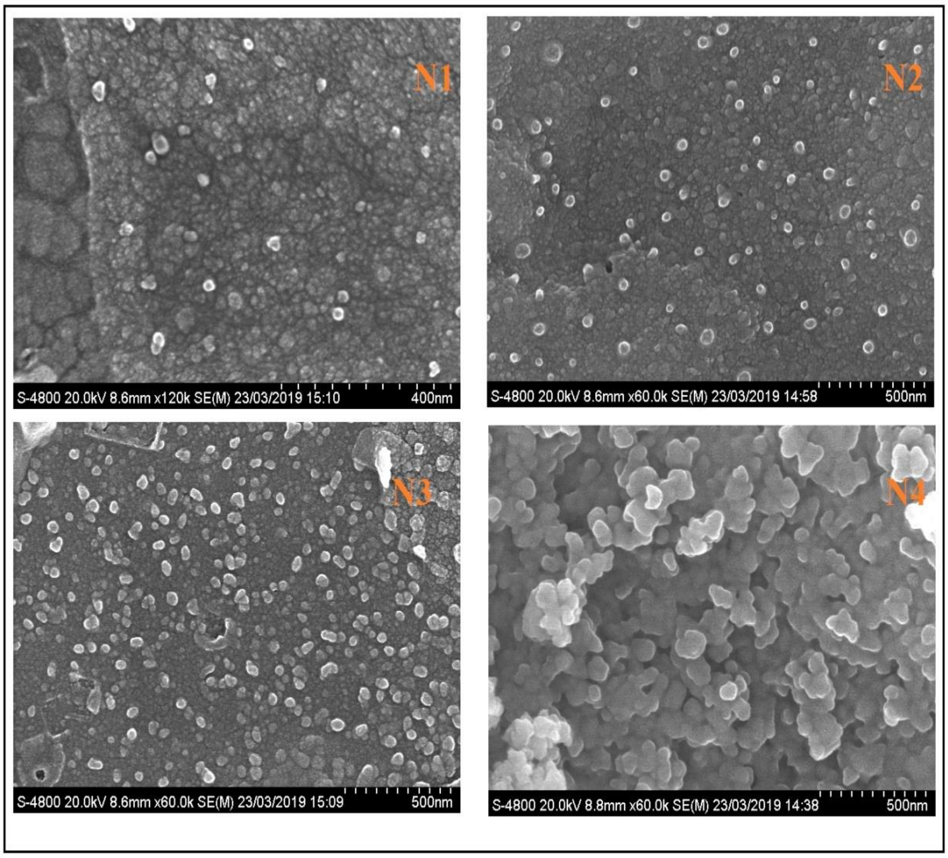


Figure3: FESEM images of nanocrystalline NiO thin film samples: N_1, N_2, N_3 and N_4.

The surface morphology of deposited NiO thin films were studied using a field emission scanning electron microscope (FESEM) analysis. The FESEM images of NiO thin films of different samples N_1, N_2, N_3 and N_4 are shown in Fig. 3 (a to d). It can be revealed from the images that all these films are homogeneous, smooth and well adherent. The microstructures consist of grains, which are roughly spherical in shape, however agglomeration in certain regions can be observed as shown in Fig. 3 (d). The grain size varied from 23 nm to 39 nm as sprayed solution volume utilized from 5 ml to 30 ml. Such kind of morphology is very useful for gas sensing. It is depicted from Table 2 that as the volume of spraying solution increases, the thickness of the deposited thin film goes on increasing with an increase in crystallite size (XRD) and grain size (FESEM).

Table 2: Measurement of volume of sprayed solution, film thickness, crystallite size, and optical grain size.

Sample No.	Volume of sprayed solution (ml)	Thickness (nm)	Crystallite size from XRD (nm)	Grain size from FE-SEM (nm)
N1	5	450	14	23
N2	10	789	16	29
N3	20	833	17	33
N4	30	978	19	39

4.4. Transmission Electron Microscope (TEM):

Microstructural characterization of NiO thin films were carried out using CM200 Philips (200 KV HT) Transmission Electron Microscope (TEM). Fig. 4 shows TEM images of pure NiO thin film (Sample N_3) obtained by scratching the film. The sample was dispersed in ethanol. Copper grid was used to hold the powder. It is clear from TEM images that the grains are nanocrystalline in nature. The size of the nanocrystals are around 17 nm and spherical in shape. The electron diffraction pattern of N_3 sample is as shown in inset of Fig. 4.The pattern is of continuous ring type without any additional diffraction spots and rings of secondary phases, which are revealing crystalline structure of the pure NiO thin film.

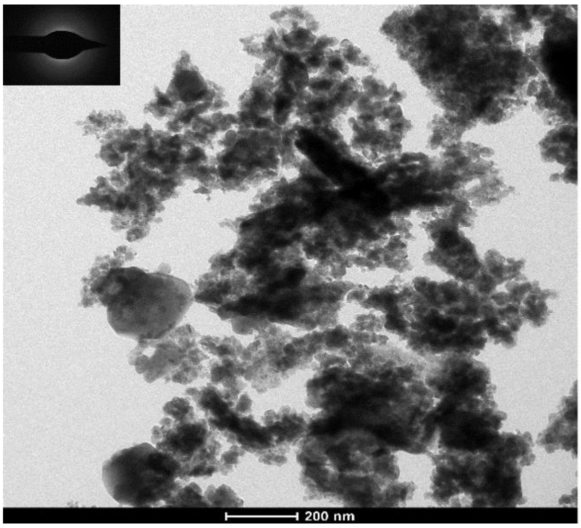
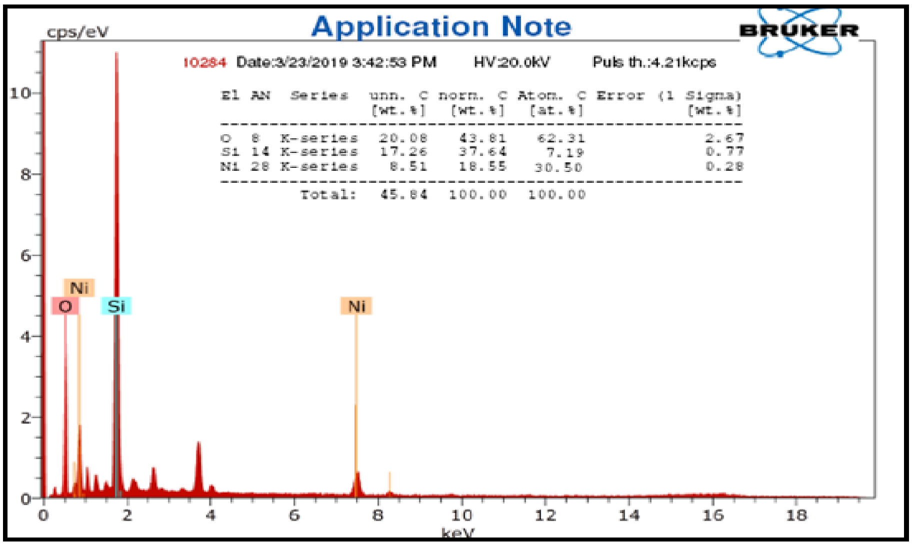


Figure 4: TEM images of nanocrystalline NiO thin film samples (N_3)

4.5. Quantitative element analysis (EDAX):

The quantitative element composition of the nanocrystallineNiO thin film (Sample N_3) was analyzed using an Energy dispersive spectrometer (EDS) as shown in Fig. 5.



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10284 Date:3/23/2019 3:42:53 PM      HV:20.0kV      Puls th.:4.21kcps

El AN  Series   unn. C norn. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
------------------------------------------------------
O   8  K-series  20.08   43.81   62.31            2.67
Si 14  K-series  17.26   37.64    7.19            0.77
Ni 28  K-series   8.51   18.55   30.50            0.28
------------------------------------------------------
         Total:  45.84  100.00  100.00
```

Figure 5: Element analysis of nanocrystallineNiO thin film sample (N_3)

The analysis confirms the presence of Ni and O elements with the better distribution in the ratio 50:50. It is important to note that an additional silicon (Si) element peak was also observed in the EDS spectra which might be due to the presence of Si in glass substrate [23].

4.6 Electrical conductivity

Variation of electrical conductivity with operating temperature and thickness (N_1 to N_4) are as shown in fig. 6. It is seen from the graph that the conductivity increases with temperature and thickness of the sample indicating semiconducting behavior [24]

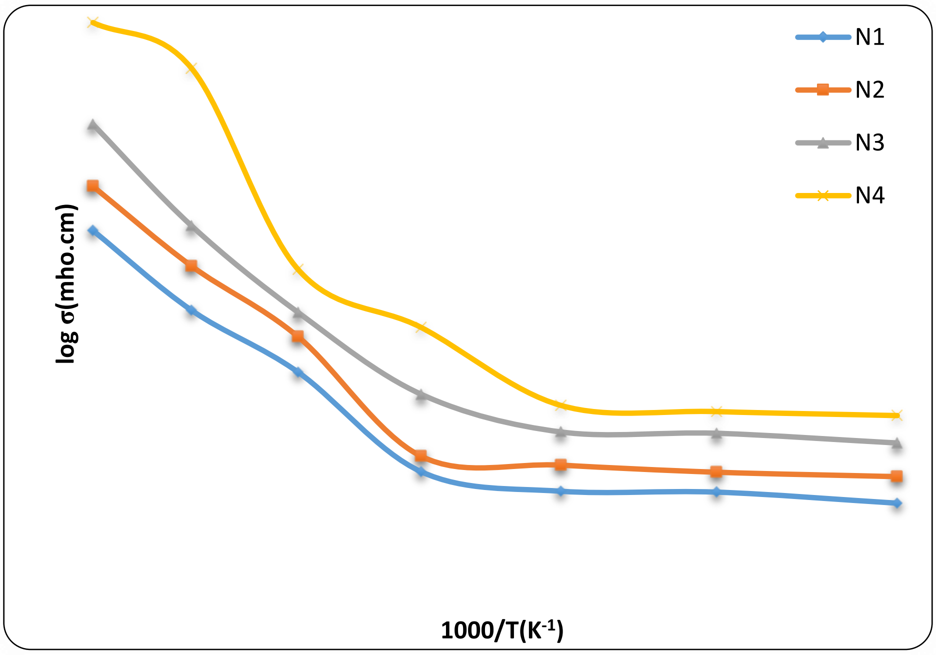

Figure 6: Variation of log (σ) with operating temperature 1000/T (K^{-1}).

5. Conclusions

The overall study shows the successful deposition of nanostructured nickel oxide thin films by spray pyrolysis method. By increasing the volume of the precursor, there is an increase in the thickness and morphological properties of the deposited films. The properties of NiO thin film have been studied using XRD, FESEM, TEM, EDAX and electrical conductivity measurement techniques. The XRD pattern has confirmed the polycrystalline nature with cubic phase. The average crystalline size found in between 14 nm to 19 nm and the porous surface morphology is observed in FESEM images which are useful for gas sensing applications. A variation of electrical conductivity with the operating temperature indicates that the nanocrystalline NiO films are semiconducting in nature. The optimized results may be the answer about the simplicity, low cost, feasibility for mass production and high purity of deposited materials.

6. Acknowledgements

The authors are very thankful to the Principal of Shri. V. S. Naik, Arts Commerce and Science College, Raver for providing necessary infrastructure and laboratory facilities for this work.

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Gas sensing performance of nanostructured NiO thin films

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Abstract:

A simple and inexpensive spray pyrolysis technique was employed to deposit nanostructured NiO thin films from nickel chloride hexadihydrate solution on to the glass substrates heated at 350 °C. The sensing performance of the films was tested for various hazardous gases. The sensor showed high gas response (S = 678 at 250 °C) on exposure of 10 ppm of NO_2. Its response time was short (~8 s) and recovery was also fast (~12 s). The results are discussed and interpreted.

Keywords: Nanostructured NiO, NO_2 gas sensing, response and recovery time.

1. Introduction

Sensors have attracted a great deal of attention for scientists and engineers in the recent years. Even in future it is expected to grain importance in view of the construction subsystems. Nanostructured nickel oxide also possesses excellent chemical and thermal stability [1-2]. Because of its unique properties, Nickel oxide is employed to make device, applicable in different fields of science and daily life. Nanostructured NiO is widely used as for making gas sensors, light emitting diodes acoustic wave filters, UV photo detectors, field effect transistor, intermolecular p-n junction diodes, schottky diodes, photo diodes, optical modulator wave guides. Nickel oxide (NiO) is an interesting chemically and thermally stable n-type semiconductor with large excitation binding energy, large bang gap energy, and high sensitivity to toxic combustible gases.

Nickel oxide (NiO) is the most exhaustively investigated transition metal oxide. It is a NaCl-type antiferromagnetic oxide semiconductor. It offers promising candidature for many applications such as solar thermal absorber, catalyst for O_2 evolution photoelectrolysis and electrochromic device. Nickel oxide is also a well-studied material as the positive electrode in batteries [3].

In this work, nanostructured NiO thin films with different volume of the solution were prepared by spray pyrolysis technique. Crystal structure and grain sizes were studied from X-ray diffraction (XRD) and Transmission electron microscopy (TEM). These nanostructured NiO thin films were tested for sensing different gases and were observed to be most sensitive to NO_2 gas.

2. Experimental details

Nickel oxide thin films of various thicknesses were deposited by varying spraying time of solution between 10 to 40 minutes. The solution was prepared by dissolving Nickel chloride hexadihydrate ($NiCl_2.6H_2O$) [Merck] in deionized water so as to get desired solution concentration (0.05 M). The spray produced by nozzle was sprayed onto the glass substrates heated at 350°C. Various parameters such as solution concentration (0.05 M), spray rate (7 ml/ min), nozzle to and fro frequency (14 cycles/ min), nozzle to substrate distance (30 cm), etc. were optimized to obtain good quality films. The films with different volume of the solutions: 5 ml, 10 ml, min, 20 ml and 30 ml were obtained and were referred to as S1, S2, S3 and S4, respectively. As synthesized NiO thin films were annealed in air at 500°C for 1 hrs.

3. Determination of film thickness

Film thickness was measured by using a gravimetric weight difference (considering the density of the bulk nickel oxide). The films were deposited on clean glass slides whose mass was previously measured. After the deposition the substrate was again weighted, determining the quantity of deposited NiO. Measuring the surface area of the deposited film, taking account of NiO specific weight of the film, thickness was determined using the relation:

$$T = M / A.\rho \quad ----------(1)$$

Where

A is the surface area of the film [cm^2]

M is the quantity of the deposited nickel oxide

ρ is the specific weight of NiO

The measured thickness of the thin film samples S1, S2, S3 and S4 were observed to be 450, 789, 833, 978 nm respectively.

4. Results

4.1 Structural characterization

Fig.1 shows the X-ray diffractogram of nanostructured NiO thin film sample S3. It clear from figure that the films exhibited strong orientation along c-axis (200).The average crystalline size was calculated from Scherer's formula and observed to be 23 nm.

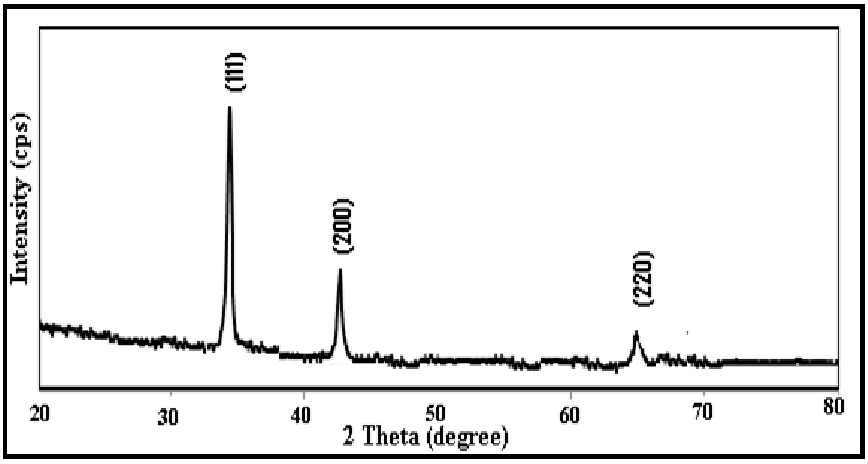


Fig. 1: X-ray diffractogram of most sensitive thin film (Sample =S3)

4.2 Microstructure properties using TEM

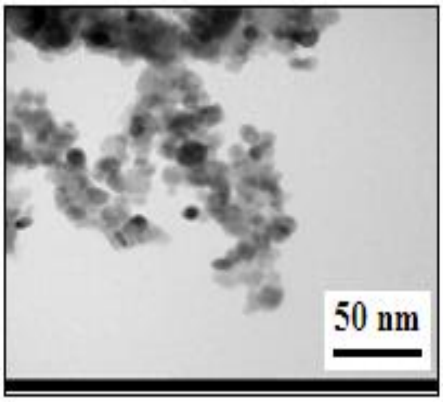


Fig.2. TEM images most sensitive thin film sensor (S3)

Fig. 2 shows the TEM image of most sensitive nanostructured NiO thin film sample S3. The morphology of the grains was spherical in shape. Particle size was observed to be in the range of 10 nm to 16 nm respectively.

5. Sensing Performance of the sensor

5.1 Gas response with operating temperature

Fig.3 shows variation of percentage of gas response with operating temperature of nanostructured NiO thin film samples S1, S2, S3 and S4 on exposure of 10 ppm NO_2. It is clear from Fig.3, that the NO_2 response of sample S3 is higher at 350°C as compared to those of S1, S2, S3 and S4. Due to the greater surface area of nanostructured materials, its interaction with the adsorbed gases is stronger, leading to higher gas response [4].

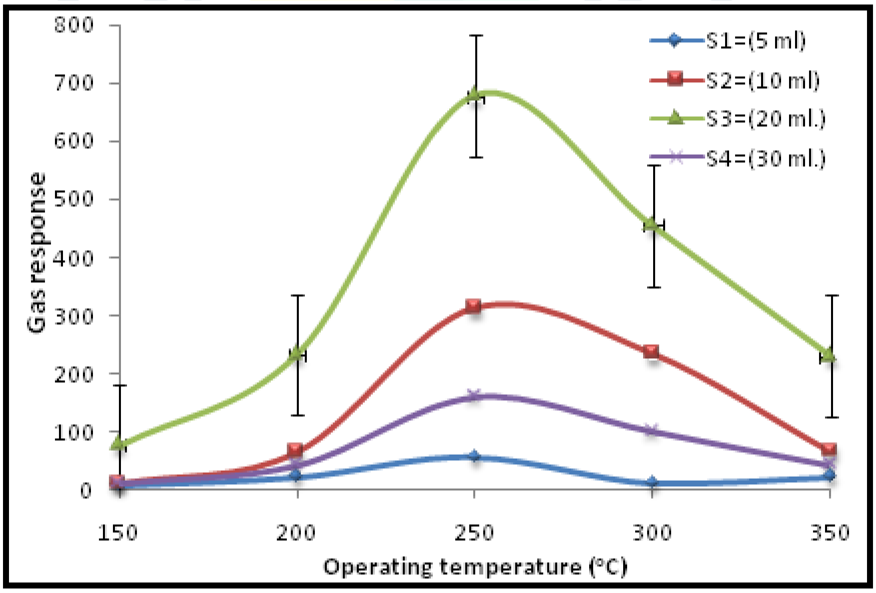
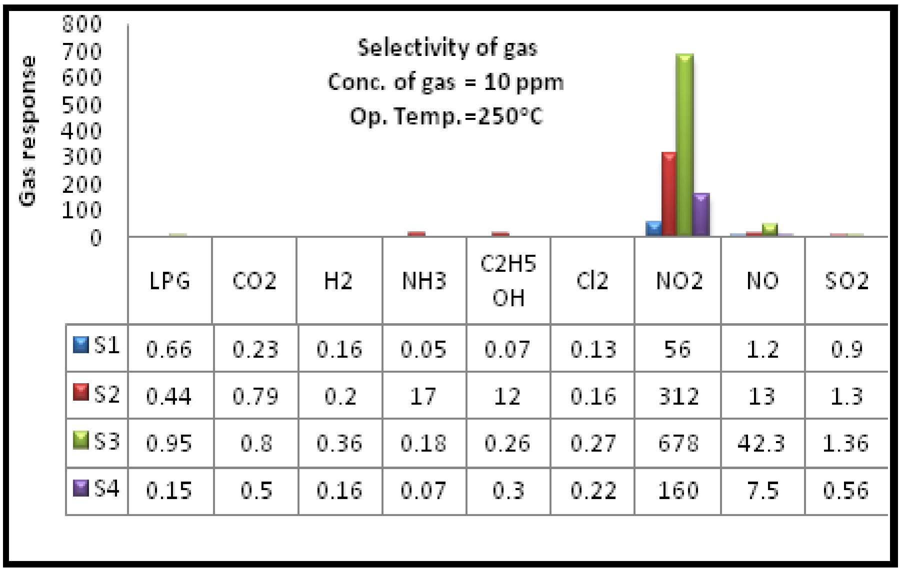


Fig. 3. Gas response of pure nanostructured NiO thin films with operating temperature.

5.2 Selectivity



	LPG	CO2	H2	NH3	C2H5 OH	Cl2	NO2	NO	SO2
🟦 S1	0.66	0.23	0.16	0.05	0.07	0.13	56	1.2	0.9
🟥 S2	0.44	0.79	0.2	17	12	0.16	312	13	1.3
🟩 S3	0.95	0.8	0.36	0.18	0.26	0.27	678	42.3	1.36
🟪 S4	0.15	0.5	0.16	0.07	0.3	0.22	160	7.5	0.56

Fig. 4. Selectivity of nanostructured NiO thin films for different gases.

Fig. 4 depicts the bar diagram to indicate NO_2 selective ability of the sensor as compared to other conventional gases.

5.3 Response and recovery of the sensor

The response and recovery of the nanostructured NiO thin film (sample S3) sensor on exposure of 10 ppm of NO_2 at 350°C are represented in Fig. 5. The response is quick (~8 s) and recovery is fast (~12 s).

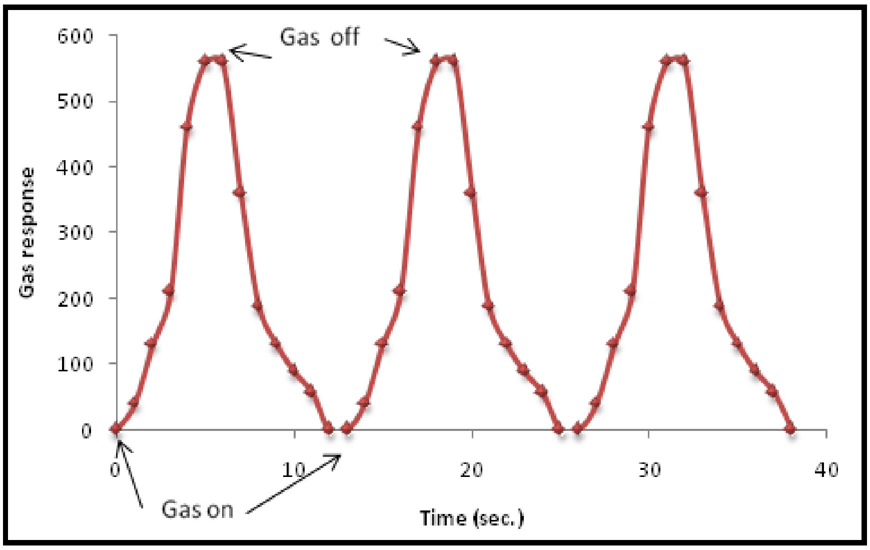


Fig. 5. Response and recovery of the sensor.

6. Conclusions

Nanostructured NiO thin films could be prepared by simple and inexpensive spray pyrolysis technique. Nanostructured grains are found to be important for obtaining enhanced response characteristics. NiO thin film thin film based sensor structure have been designed for the trace level (10 ppm) detection of NO_2 gas at operating temperatures (<250 °C) and exhibit the response of S= 678.The nanostructured NiO thin films exhibit rapid response–recovery which is one of the main features of this sensor

Acknowledgements

The authors are thankful to the University Grants Commission, New Delhi for providing financial support. Thanks to the Principal, Shri. V. S. Naik, Arts, Commerce and Science College, Raver, 425508 for providing laboratory facilities for this work.

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Performance of gas sensors of nanocrystalline thin films

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Abstract:

An attempt is made to focus on the gas sensors which are applicable and used in electronic systems for detection of toxic and harmful gases to date. Among the environmentally hazardous gases namely; NO_2, CO_2, NO, N_2O, H_2S, CO, NH_3, CH_4, SO_2 the CO_2; NO_2 are the most dangerous gases in terms of Threshold Limit Value (TLV) of 3 ppm. Therefore the appropriate gas sensors have been investigated to measure the low concentration limit of each hazardous gas. Semiconducting metal oxides are the good candidates due to their low cost, high sensitivity, fast response, relatively simplicity of use and ability to detect a large number of gases.

1. Introduction:

Semiconducting metal oxides are the good candidates due to their low cost, high sensitivity, fast response and recovery time, simple electronic structure, relatively simplicity of use, low maintenance and ability to detect large number of gases (Choi *et al* 2017) [1]. Applications of chemical sensors include the environmental monitoring, automotive applications emission monitoring, and the aerospace vehicle health monitoring (Vander Wal *et al* 2016) [2].There are two types of metal oxide sensors; n-type (zinc oxide, tin dioxide, titanium dioxide or iron (III) oxide) responding to reducing gases (H_2, CH_4, CO, C_2H_5OH, and H_2S) and p-type (nickel oxide, cobalt oxide) responding to oxidizing gases (O_2, NO_2, and Cl_2) (Pearce *et al* 2015) [3]. Oxide semiconductor gas sensors undergo resistance change upon exposure to reducing gases by the oxidative interactions with the negatively charged chemisorbed oxygen. The gas sensing characteristics such as gas response, responding speed, and selectivity are greatly influenced by the surface area, donor density, agglomeration, porosity, acid-base property of the sensing material, the presence of catalysts, and the sensing temperature (Choi, *et al* 2010) [1]. The gas sensing response of n-type semiconductor to a reducing gas is normally defined as the ratio, ($\Delta R/Rg$), i.e. ratio of the resistance change (ΔR) due to gas introduction to the resistance when the gas is present (Rg), while the response to an oxidizing gas is defined as the ratio ($\Delta R/R_0$), i.e. ratio of the resistance change to the resistance in air (R_0). For p-type semiconductor gas sensor, the definitions are reversed (Wisitsoraat *et al* 2018) [4].

1.1 Sensors:

The sensor is the device, which senses the input signal. Now a day, there is a general opinion in both scientific and engineering communities that there is an urgent need for the development of cheap and reliable sensors for control and measuring systems, for automation of services and for industrial and scientific applications. For the development of the sensors, interest has been increased to study the sensing principles, simulation of systems and the structure investigations of most suited materials and proper choice of technology. The Physical changes in sensor active film may be thick or thin are transduced into electrical signals explained by (Pearce *et al* 2015) [3] as given in Table 1.

Table 1. The physical property and sensor device

Physical Changes	Sensor Devices
Electrical Conductivity	Semiconductor Gas Sensor
Mass	Piezoelectric sensor, Quartz crystal microbalances (QMB), surface acoustic wave (SAW), micro cantilevers.
Optical Parameters: Surface plasmon resonance (SPR), Reflection, Interferometry, Absorption fluorescence, Refractive index, Optical path length	Optical sensor (Fiber optic or thin film)
Work function (electrical Polarization)	MOSFET sensor: diodes, transistors, capacitors
Heat or temperature	Catalytic gas sensors: Seebeck effect, Pellistors, Semistors
Electromotive force or electrical current in a solid state electrochemical cell	Electrochemical gas sensors: Potentiometric

1.2 Need of sensors:

The sensors are required basically for measurement of physical quantities and for use in some controlling systems. Presently, the atmospheric pollution has become a global issue. Gases from auto and industrial exhausts are polluting the environment. The gases like LPG, NH_3, H_2, Cl_2, CH_4, H_2S, No_2 and CO_2 etc. have to be controlled for the healthy survival of the living beings. Thus, there is an increasing concern about minimization of the emission of autointoxication and also to reduce emission of such unburnt hydrocarbons from automobile and industrial exhausts. In order to detect measure and control these gases, one should know the amount and type of gas present in the ambient. Thus, the need to monitor and control these gases has led to the research and development of a wide variety of sensors using different materials and technologies.

1.3 Semiconductor Metal Oxide Sensor:

The principal of operation of semiconductor metal oxide sensors is based on the change in conductance of the oxide on interaction with a gas and this change is usually proportional to the concentration of the gas. There are two types of metal oxide sensors: n-type (SnO_2, ZnO, TiO_2, Fe_2O_3 etc.) which respond to reducing gases and P-type (NiO, Cr_2O_3) which respond to oxidizing gases (G. Korotcenkov *et al* 2017) [5]. The sensors are applicable for air quality control, monitoring and detection of air pollutant hazardous gases. Therefore study of gases is necessary for research. Gases are classified as Inorganic and Organic gases. Inorganic class includes the oxides of carbon, sulfur, nitrogen and other gases like H_2S, NH_3, Cl_2, HF, etc. Organic class includes the hydrocarbons CH_4, C_2H_6, C_3H_8, C_2H_4, C_8H_{18}, formaldehyde, vapors of acetone, alcohols, organic acids etc. Vapours of petrol, diesel, LPG and LNG are gases containing volatile organic compounds. Further they are classified as reducing gas like H_2, CH_4, CO, C_2H_5, H_2S (K. Wetchakun *et al* 2011) [6]. Resistance drops by exposure of these gases on n-type material and increases when exposure on p-type material. P-type sensors responds to oxidizing gases like O_2, NO_2 and Cl_2. It is summarize in Table 2.

Table 2. Type of material, oxidizing gases and reducing gases

Classification	Oxidising Gases	Reducing Gases
n-type	Resistance increase	Resistance decrease
p-type	Resistance decrease	Resistance increase

General reaction mechanism on film surface is summarized by following equations,

$$\frac{1}{2} O_2 + e^- \rightarrow O^- (s) \text{ ------------------------------ } (1)$$

$$R (g) + O^-(s) \rightarrow RO (g) + e \text{ ----------------------- } (2)$$

Where, e is an electron from the oxide.

R(g) is the reducing gas

g and s are the surface and gas, respectively.

2 Environmentally Hazardous Gases:

A summary of physical property, source of emission, toxicity and threshold limit value of environmentally hazardous gases reported by American Conference of Government Industrial Hygienists are shown in table 3. Threshold Limit Value (TLV) is defined as maximum concentration of chemical allowable for repeated exposure without producing adverse health effects.

Gas concentration is also important factor for gas sensors. Concentration levels of typical detectable gas components are summarized as follows.

Table 3. The physical property, source of emission, toxicity and threshold limit value of environmentally hazardous gases.

Gas	Physical property	Source of emission	Toxicity	TLV	References
NO_2	Reddish brown gas with pungent and irritating odor able to form gases nitric acid and toxic nitrates.	Produced by all combustion gas in air produce from the trasportationsector and industrial processes.	Irritating the lungs, respiraratory infection, degradation of rubber, damage tree and crops, resulting insubstantial losses when chemically transform to nitric acid ,irritating eyes ,etc	3 ppm	Air Quality control Ministry of Environment.
H_2S	Colorless, toxic and flammable gas, Smell like rotten eggs.	Occurring naturally in crude petroleum, natural gases, hot spring, produced from bacterial break down of organic matters or waste produced by human and animal etc.	Damage in breathing system.	10 ppm	Kaur et al. [7]
CO	Colorless, odorless, tasteless and non irritating gas.	A byproduct of the incomplete burning gasoline, wood, coal, oil, propene or any other substance that contains carbons, produced whenever combustion occurs.	Preventing oxygen from being absorbed into the blood stream. Without sufficient oxygen in the blood stream, vital organs with stop function.	50 ppm	Hazard fact sheet #1
NH_3	Colorless gas with pungent order	Produced by the heating by the decomposition of animal manures	Irritates the eye at levels in the range of 20-50 ppm	25 ppm	www.en.wikipedia.org/wiki/Ammonia
CO_2	Colorless and odorless gas	All open flame, non vented space, Heater	Can create an oxygen defienceincyand	5000 ppm	www.eoearth.org-article

		also contribute CO_2 to the surrounding air as one of the product of combustion can created	asphyxiation or suffocation		carbondioxide
CH_4	Colorless, odorless gas and combustible gas	Generated by an aerobic digestion of organic material and if stored can be used as a fuel source for internal combustion engines	Non toxic	1000 ppm	www.eoearth.org/article/methane
SO_2	Lighter than air Invisible gas with a nasty sharp smell	Industrial activity as a main source	Irritates the nose throat, and airways to cause coughing, wheezing, shortness of breath etc.	5ppm	Air quality fact sheet

2.1. Measurement of gas sensing performance parameter:

The transducer converts this energy into a useful electrical signal corresponding to analytical change. It further classified into physical and biochemical sensors. In order to characterize sensor performance a set of parameters is used. The most important parameters and their definitions are listed below. (V. E. Bochenkov et al. 2010) [8].

- **Gas response:** It is defined as the change conductance the sample on exposure to gas to the original conductance. It is given by the relation

$$S = \frac{G_g - G_a}{G_a} = \frac{\Delta G}{G_a} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where, Ga is the conductance of sensor in air,

G_g is the conductance of sensor in presence of gas.

- **Selectivity:** The response of the sensor to a specific gas in the mixture of gases is the selectivity.
- **Response time:** The time taken by the sensor to attain the 80% of maximum change in resistance on exposure to the gas is response time.

- **Recovery time:** The time taken by the sensor to roll back to 80 % of its original resistance is the recovery time.
- **Stability:** It is the ability of a sensor to provide reproducible results for a certain period of time. This includes retaining the sensitivity, selectivity, response and recovery time.
- **Detection limit:** It is the lowest concentration of the analyte that can be detected by the sensor under given conditions, particularly at a given temperature.
- **Dynamic range:** It is a analyte concentration range between the detection limit and highest limiting concentration.
- **Linearity:** It is the relative deviation of an experimentally determined calibration graph from ideal straight line.
- **Resolution:** It is the lowest concentration difference that can be distinguished by sensor.
- **Working temperature**: It is usually the temperature that corresponds to maximum sensitivity.
- **Life cycle:** It is the period of time over which the sensor will continuously operate.

All of these parameters are used to characterize the properties of a particular material or device. By Literature review highlights the ideal chemical or other types of sensor would posses high sensitivity, dynamic range, good selectivity and stability, low detection limit, good linearity, fast response and recovery time.

3. Literature review of metal oxide and perovskite:

Tin oxide and Cadmium oxide are both promising materials for their applications as windows and buffer layers in thin film solar cells. They are n-type semiconductor compounds and have good transparency in the visible region (Lewis *et al* 2010 [9]. Recent works have shown that SnO_2 is a promising material for applications as sensors towards various gases. Moon et al reported SnO_2 exhibiting good response towards CO [10]. Patil and co-workers synthesized SnO_2 which gives sensitivity towards H_2 gas [11]. While Jain *et al* 2006 reported Ni doped to be sensitive towards LPG [12]. Most of the researchers have focused on detection of LPG, H_2S, H_2 and NH_3 because of their toxicity, their relation with atmospheric composition or to their high levels in some environments.

The band gap energy of the NiO film between is in between 2.29 and 2.73 eV depending on the growth conditions (Islam *et al* 2008) [13]. NiO thin films have been prepared using various physical as well as chemical deposition methods (Dhawale *et al* 2008) [14]. Among these, deposition of NiO thin films by simple and low cost chemical spray pyrolysis method has been reported by Bhosale [15]. Due to stability of spray method, doping of different materials to improve the conductivity of NiO films for solar cell and gas sensor application has been carried out (Ferro *et al* 1999) [16].

SnO_2 thin film has band gap energy about 3.6 eV (Patil *et al* 2009) [11]. It is expected that the homogeneous alloying of these materials will have intermediate optical properties between those of pure NiO and SnO_2. N-type semiconductor of tetragonal structure are extremely used in gas sensing because of its desirable sensitivity and mainly because of its good stability in adverse environments (Berry *et al* 1999) [17]. However, the physical and sensing properties of semiconductor gas sensors are directly related to their preparation e.g. particle size, sensing film morphology, and film thickness as well as sensing film characteristics.

Wu et al. studied the electrical characteristics of some perovskite oxides such as $NiSnO_3$, $ZnSnO_3$ and $CdSnO_3$ (Wu *et al* 2002) [18]. They prepared $NiSnO_3$ by chemical co-precipitation method and proposed it as a suitable material for detecting ethanol gas. Wang and co-workers studied the conductance versus the operating temperature of $CdSnO_3$ in air between 160^o C and $340\,^o$ C and found a maximum conductance peak at $240\,^o$ C (Wang *et al* 2002) [19].

Conclusions:

Gas sensor films prepared from nanocrystalline thin films, offers grain sizes, where depletion layer has almost the same dimensions as the particle radii, and consequently electrical conduction is predominantly grain controlled. Porous films composed of nanoparticles with diameter between 6nm and 20 nm showed improved sensitivity and high gas selectivity due to increased surface area to volume ratio. Thin films composed of nanoparticles showed a strong dependence of the gas concentration on mobility of charge carriers. Chemisorbed O- species at the surface acts as scattering centers and resist the movement of charge carriers. Adsorption of reducing gas results in the decreased or elimination of these scattering centers. Our aim is to achieve the good characteristic gas sensor.

Acknowledgements:

The authors are thankful to the University Grants Commission, New Delhi for providing financial support. Thanks to the Principal, Shri. V. S. Naik, Arts, Commerce and Science College, Raver, 425508 for providing laboratory and library facilities for this work.

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"भारतीय राजकारणात विज्ञान आणि तंत्रज्ञानाचा वापर"

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सारांश:

स्वतंत्र भारताची लोकशाही 73 व्या वर्षात पदार्पण करत आहे याचा विचार जर केला तर 1952 पासून ते आज तागायत देशांमध्ये लोकसभेच्या व राज्याच्या विधानसभेच्या सार्वत्रिक निवडणुका या मोठ्या प्रमाणात झाल्या। या सार्वत्रिक निवडणुका होत गेल्या तसतशा या निवडणुकीमध्ये सक्रियपणे भाग घेऊन मतदान करण्याचा लोकांचा टक्का सुद्धा वाढत गेला। याचे सर्वस्वी कारण म्हणजे अलीकडच्या काळात विज्ञान आणि तंत्रज्ञानाचा भारतातील प्रमुख राजकीय पक्षांनी आपली भूमिका सर्वसामान्य मतदारांपर्यंत मांडून जाहीरनामा लोकांपर्यंत पोहोचण्याचे काम केले। त्याचबरोबर लोकांनी निवडणूक प्रक्रियेत सहभागी व्हावे व आपला मतदानाचा अधिकार यासाठी व्हाट्सअप, फेसबुक ,आदीच्या माध्यमातून सर्वसामान्य लोकांना आकर्षित करण्याचा प्रयत्न केला खऱ्या अर्थाने या विज्ञान आणि तंत्रज्ञानाची सुरुवात या देशात माजी पंतप्रधान स्वर्गीय. राजीव गांधी यांनी सुरु केली। आणि त्याचाच परिणाम म्हणून आज देशामध्ये निवडणुकीचे प्रचार तंत्र हायटेक झाले आहे। त्याचबरोबर मतपेटीचे जागा आता मशीनन घेतले आहे ज्याला ईव्हीएम इलेक्ट्रिक वोटिंग मशीन असे म्हटले जाते। ज्याद्वारे मतदान करणेही सोपे झाले व त्याच बरोबर मतमोजणी करणेही सोपे झालेल्या पद्धतीमुळे निकाल वेळेस लागण्यास मदत झाली। म्हणजेच जशी लोकशाही प्रगल्भ होत गेली तसतसे लोकशाहीला प्रगल्भ करण्यामध्ये विज्ञान आणि तंत्रज्ञानाने हातभार लावला असे आपल्याला म्हणता येईल.

प्रस्तावना:

भारतीय राजकारणात होणाऱ्या लोकसभेच्या व विधानसभेच्या सार्वत्रिक निवडणुकीमध्ये देशातील सर्वच प्रमुख राजकीय पक्षांनी विज्ञान आणि तंत्रज्ञानाचा उपयोग करायला सुरुवात केलेली आहे। ज्यामुळे राजकीय पक्षांना लोकांपर्यंत पोहोचण्यास खूप मोठ्या प्रमाणात मदत झाली आहे। विज्ञान आणि तंत्रज्ञानामुळे आपल्या पक्षाचा जाहीरनामा लोकांसमोर मांडण्यास मदत झाली। त्यामुळे लोकांना सुद्धा राजकीय पक्षांचा अभ्यास करता आला कोणता राजकीय पक्ष आपल्या राजकीय पूर्तता करू शकेल हा विचार करायला वेळ मिळाला। अशा प्रकारे विज्ञान आणि तंत्रज्ञानामुळे लोकशाही प्रगल्भ होत गेली.

राजकीय पक्ष आणि बदलते प्रचारतंत्र :

पूर्वीच्या काळी निवडणुकीच्या प्रचारासाठी देशातील राजकीय पक्षाकडं प्रचार तंत्राचा वापर करताना ठिकठिकाणी पक्षाचे कट आउट लावले जात होते। गल्लोगल्ली पक्षाच्या कॉर्नर सभा व्हायच्या। त्याचबरोबर मुख्य रस्त्यावरील व दर्शनी भागातील भिंती वरती उमेदवाराचे नाव व त्याचे पक्षाचे चिन्ह हे रंगवले जात होते। त्या माध्यमातून लोकांकडे मतं मागितली जात होती एवढेच नाही तर रिक्षा, हात गाडी, मोटरसायकल या माध्यमातून प्रचार करण्यावर भर दिला जायचा। लोकांना आश्वासने दिली जायची परंतु काळाच्या ओघात जसे विज्ञान आणि तंत्रज्ञान प्रगत होत गेले तसे निवडणुकीच्या प्रचार तंत्रामध्ये सुद्धा बदल होत गेला। म्हणजेच प्रत्यक्ष मतदारांच्या गाठीभेटी घेण्याच्या अगोदर मोबाईलच्या माध्यमातून उमेदवारांना ैडै केले जात. या माध्यमातून उमेदवार कोण आहे? पक्षाचा जाहीरनामा काय आहे? ते थोडक्यात लोकांना

समजावून सांगण्याचा प्रयत्न केला जायचाण आता त्याची जागा फेसबुक ने घेतलीण आता तर प्रत्येक राजकीय पक्षाचे एक स्वतंत्र फेसबुक पेज तयार झाले आहेण त्या फेसबुक पेजवर आतापर्यंत लोकांसाठी राजकीय पक्षांनी केलेली कार्य हे चित्र स्वरूपात व चित्रफितीच्या रूपात मतदारासमोर आणण्याचा प्रयत्न केले जातातण यूट्यूब च्या माध्यमातून काही व्हिडिओसए गाणी लोकांना आकर्षित करण्यासाठी अपलोड केले जातात. त्या माध्यमातून लोकांचे मनोरंजनाबरोबरच आपल्या पक्षाची आवड ती व्यक्ती आपल्याच पक्षाला मतदान कसा करेल याचा विचार केला जातोण तसेच निवडणुकीच्या काळात तर व्हाट्सअप ग्रुपच्या माध्यमातून वेगवेगळ्या सूचनाए पक्षाचे चिन्हए पक्षाचा जाहीरनामाए उमेदवाराच्या बाबत माहिती हे सर्व देण्याचा प्रयत्न केला जातोण व त्यातून सर्वसामान्य विशेषतः सुशिक्षित लोकांना आकर्षित करण्याचा प्रयत्न केला जातो. या सर्व गोष्टीमुळे एक फायदा निश्चितच झाला नव्वदच्या दशकापर्यंत सर्वसामान्यपणे देशातील सुशिक्षित जनता मतदान करण्यासाठी सहजासहजी बाहेर पडत नव्हती व आपला मतदानाचा मूलभूत अधिकार बजावत नव्हती परंतु विज्ञान आणि तंत्रज्ञानामुळे या सुशिक्षित वर्गामध्ये आपला मतदानाचा हक्क बद्दल जनजागृती निर्माण झालीण फेसबुकच्या माध्यमातून उमेदवार एजाहीरनामा याची माहिती मतदारांना झाली व त्यामुळे सहाजिकच या सुशिक्षित वर्गांचा मतदार करण्याकडे कल वाढलाण अशाप्रकारे निश्चितच मतांची टक्केवारी वाढली, वाढलेली टक्केवारी सशक्त व समृद्ध लोकशाही साठी निश्चितच अभिमानास्पद आहे ण

निवडणुका व सोशल मीडियारू

सोशल नेटवर्किंग साधनामुळे ही तंत्रज्ञान क्रांती झालेली आपल्याला दिसून येते. लोकांना एकत्र आणण्याचे एकमात्र साधन म्हणून फेसबुक एट्विटरए व्हाट्सअप ही भूमिका पार पाडत आहेत णभारतामध्ये होत असलेल्या सार्वत्रिक निवडणुका त्यामध्ये सर्वात महत्वाचे म्हणजे 2014ची लोकसभेची सार्वत्रिक निवडणूक ही पहिलीच सोशल नेटवर्किंगच्या माध्यमातून लढलेले निवडणूक होय. निवडणुकांच्या बातम्यांचे त्याच्या प्रचाराचे रंग या निवडणुकीत बदलून गेलेले आपल्याला दिसून येतात. दर पाच वर्षांनी निवडणुकांचा भरणारा कुंभमेळा यामध्ये मध्यमवर्गीयांची संख्या जास्त आहेण पण त्याच वेळेस मध्यमवर्गीयांकडे स्मार्ट फोन आल्यामुळे फेसबुकए ट्विटरए व्हाट्सअप यामुळे सोशल मीडियाचा वापर मोठ्या प्रमाणात होत आहे ण 2014 च्या निवडणुकात देशातील प्रमुख पक्ष भाजपने प्रथमच विज्ञान आणि तंत्रज्ञानाचा मोठ्या प्रमाणात वापर केलाण प्रचारासाठी साधने वापरली त्या माध्यमातून थेट जनतेच्या हृदयात हात घालत नरेंद्र मोदी यांनी स्वप्न दाखविलेण आकडा सांगायचे म्हटले तर 2014 च्या निवडणुकीत 815 दशलक्ष लोक मतदानास पात्र झाले. त्यातील शंभर दशलक्ष लोकांनी अंदाजे प्रथमच मतदान केले. या निवडणुकीमध्ये ग्राफिटी सारख्या वस्तुस्थितीवर बोट ठेवणारा विनोद सर्वांना पसंत पडला. तर काहीनी व्हाट्सअप च्या माध्यमातून अभिव्यक्त व्हायला सुरुवात केलीण ब्छछ ने2014 ची निवडणूकीला सोशल मीडिया निवडणूक मनले.कारण त्यांनी दिलेल्या माहितीनुसार फेसबुक वर मोदींचे तीस लाख अनुयायी आहेत याचा अर्थ ते लोकप्रिय आहेत. त्याचा परिणाम निवडणुकीत दिसून आलाण आणि त्यामुळेच देशाच्या पंतप्रधानपदी नरेंद्र मोदी हे निवडून आलेणतर ठठब ने ही भारतातील निवडणुकींच्या बातम्या व्हाट्सअप वरून दिलेल्या दिसून येतात. भारतात सोशल मीडियाच्या माध्यमातून 2014 च्या निवडणुकीत देशातल्या 543 लोकसभा मतदार संघाच्या निकालाचे विश्लेषण स्पष्टपणे दिले. थोडक्यात निवडणुकीच्या इतिहासात कधी नव्हे तेवढे सोशल मीडिया चे महत्व 2014 च्या लोकसभेच्या निवडणुका पासून निश्चितपणे वाढलेले दिसून येतेण

निवडणुका व घोषणा:

भारतीय राजकारणात लोकसभा विधानसभेच्या सार्वत्रिक निवडणुकीत काळाच्या ओघात विज्ञान आणि तंत्रज्ञानाच्या मदतीने घोषणांचे स्वरूपही बदललेले दिसून येतेण सर्वप्रथम 2004 च्या लोकसभा निवडणुकीवेळी भाजपसारख्या पक्षाने विज्ञान आणि तंत्रज्ञान वर आधारित षशायनिंग इंडियाष व षभारत उदयष अशा नव्या घोषणा पुढे आणल्या तर 2014 ला षडिजिटल इंडियाष षइंडिया कौशल्यष ष मेक इन इंडियाष षहर हर मोदी घर घर मोदीष षअच्छे दिनष यासारख्या नव्या घोषणा विज्ञान आणि तंत्रज्ञानाच्या मदतीने लोकांपर्यंत प्रभावीपणे पोहोचण्याचा प्रयत्न केलाण त्यामुळे त्या निवडणुकात मोठ्या प्रमाणात यश या पक्षाला मिळालेले दिसून येते. याचाच वापर करून राजस्थानए मध्य प्रदेशए छत्तीसगड येथे झालेल्या विधानसभेच्या निवडणुकीत काँग्रेस पक्षाने सुद्धा तंत्रज्ञानाच्या आधारे हायटेक प्रचार करण्यावर भर दिलाण व त्या माध्यमातून तरुण मतदारांना आपल्या पक्षाकडे आकर्षित करण्यात हा पक्ष यशस्वी झालेला दिसून येतोण थोडक्यात काय अलीकडच्या काळात निवडणुका आणि विज्ञान व तंत्रज्ञान हे समीकरणच बनलेल दिसून येते.

निवडणूकपूर्व सर्वेक्षण व राजकीय पक्ष:

अलीकडच्या काळात प्रत्येक राजकीय पक्ष निवडणूकपूर्व सर्वेक्षण करण्यावर भर देतात. अशा प्रकारच्या अंतर्गत पक्ष सर्वेक्षणाच्या माध्यमातून कोणत्या मतदारसंघात कोणत्या लोकांचे प्रमाण जास्त आहे, प्राबल्य जास्त आहे, त्यासाठी कोणता उमेदवार योग्य असेलए कोणाची निवडणूक क्षमता आहेए निवडून येण्यासाठी कोणत्या तंत्राचा वापर करावा लागेलणयाकरीता राजकीय पक्ष आपल्या पक्षाचे विशिष्ट संस्थेच्या माध्यमातून निवडणूकपूर्व सर्वेक्षण करत असतातण म्हणजेच विज्ञान आणि तंत्रज्ञानामुळे तंत्रज्ञानामुळे प्रत्येक राजकीय पक्षाला निवडणुकांना सामोरे जाणे सोपे झालेले दिसून येतेण त्याच बळावर निवडणुका जिंकण्यासाठी सर्वतोपरी प्रयत्न सर्वच राजकीय पक्ष करत असताना दिसून येतात.

निवडणुका आणि मतदान यंत्र:

नव्वदच्या दशकापर्यंत भारताच्या निवडणुकात मतपेटीचा वापर केला जात होताणआता विज्ञान आणि तंत्रज्ञानामुळे काळात मतपेटीचे जागा इलेक्ट्रिक वोटिंग मशीन ने घेतलेली आहेण मतदान करण्याची व मतमोजणी करण्याची प्रक्रिया सुलभ झालेली दिसून येतेण एवढेच नाही तर येत्या निवडणुकीत मतदारांनी कोणत्या उमेदवाराला मतदान केले आहे हे मतदाराच्या लक्षात यावे याकरिता भारतीय निवडणूक निवडणूक आयोगाने ट ट चंट तंत्रज्ञान घेऊन येत आहेण थोडक्यात विज्ञान आणि तंत्रज्ञानाच्या मदतीने भारतातील निवडणुका सोप्या सुलभ व निष्पक्ष करण्याचा पुरेपूर प्रयत्न निवडणूक आयोगाच्या मार्फत केला जात आहेण जेणेकरून लोकशाही व्यवस्थेवरचा सर्वसामान्य भारतीय जनतेचा विश्वास हा वाढण्यास निश्चितच मदत होणार आहे.

निष्कर्ष:

थोडक्यात विज्ञान आणि तंत्रज्ञानामुळे भारतातील राजकारणए नागरिकांच्या राजकीय जाणिवा बदललेल्या दिसून येतातण नागरिकांचा निवडणुकांकडे बघण्याचा दृष्टिकोन निश्चितच बदललेला दिसून येतोण लोकशाहीत नागरिक म्हणून एक चांगले सरकार आपल्या मतदानाचा अधिकार यांच्या माध्यमातून निवडून देणे हे आपले कर्तव्य आहे. हे समजावून सांगण्यात विज्ञान आणि तंत्रज्ञानाच्या साह्याने भारतातील राजकीय पक्ष मोठ्या प्रमाणात यशस्वी झालेले दिसून येतातण त्याचबरोबर नागरिकांचा सुद्धा लोकशाहीवरचा विश्वास अलीकडच्या काळात वाढलेला दिसून येतोण हेच खऱ्या अर्थाने जागतिकीकरणाच्या काळात निर्माण झालेल्या विज्ञान आणि तंत्रज्ञानाचे यश समजता येईल.

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METAL COMPLEX OF BENZIMIDAZOLE CONTAINING QUINOLINONE DERIVATIVE: SYNTHESIS, SPECTROSCOPIC, THERMAL AND ANTIMICROBIAL STUDIES

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Abstract

We have synthesized ligand base approach benzimidazole containing quinolinone compound i.e. 7-hydroxy-4-methyl-1-[(2-thiazol-4-yl)-*1H* benzimidazole-5yl]-quinolin-2-(*1H*)-one and studied their metal complexation with Copper. The synthesized ligand and metal complex were screened for antifungal activity and antibacterial activity against some Gram-positive and Gram-negative bacteria.

Key words: Benzimidazole**,** Thiabendazole**,** Coumarin, Quinolinone and metal complex.

Introduction

Coumarins possess a number of biological activities like anticoagulant, antioxidant and antiviral. Coumarin belongs to a group of benzopyrones in which benzene ring is fused with pyrone. Coumarin also has pharmacological, biochemical and therapeutic applications [1]. Coumarins (2H-1-benzopyran-2-ones) are important oxygen containing fused heterocycles used in drugs and dyes [2,3]**.** Coumarin can be converted into more useful products by incorporation of different groups [4]. Coumarins are also known to have antidiabetic activity [5], as well as antioxidant activity [6].

Cu(II) complexes of some organic drugs have been the subject of a number of studies aimed at establishing the presumed synergy between the Cu(II) ion and the drug [7–10]

In this work, we have prepared a coumarin-derived ligand base compound and their Cu(II) complex and antimicrobial activity of the metal-free ligand and the complex was assessed.

Experimental

Materials/instrumentation

7-hydroxy-4-methyl-1-(2-(thiazol-4-yl)-*1H*-benzimidazole-5-yl) quinolin-2-one (L) ($C_{20}H_{14}N_4O_2S$), The copper chloride dihydrate ($CuCl_2 . 2H_2O$), ethanol, methanol. All reactions were monitored by ascending Thin Layer Chromatography on 0.2 mm silica gel F-254(Merck) plates using UV light (254 and 366 nm) for detection.IR spectra were recorded on an FTIR spectrophotometer [Shimadzu] using KBr disc method in the range 400 to 4000 cm^{-1} at central instrumentation Centre, KTHM College, Nashik.

LCMS spectra were scanned on Instrument Waters UPLC based LCMS Model: Waters, CHA, SQD-2 with H Class UPLC at Sapala Organics Private Limited, Hyderabad. The C, H, N analysis were carried out on elemental analyzer at Sapala Organics Private Limited, Hyderabad.

^{1}H-NMR and CMR spectra of ligand were recorded on JEOL 500-MHz NMR Spectrometer Model: JEOL, JNM-ECZ500R/S1 at Sapala Organics Private Limited, Hyderabad. Experiments of thermogravimetry were conducted at U. D. C. T., K. B. C. N. M. U., Jalgaon.

Synthesis and characterization of Quinolinone-TBZ ligand L

7-hydroxy-4-methyl-1-[(2-thiazol-4-yl)-*1H*-benzimidazole-5yl]-quinolin-2-(*1H*)-one was synthesized and identified by comparing their spectral data with reported values in the literature[11] or their melting point.

Synthesis and characterization of metal complex of ligand L

It involves synthesis of metal complex from 7-hydroxy-4-methyl-1-(2-(thiazol-4-yl)-*1H*-benzimidazole-5-yl) quinolin-2-one (L) by reaction with Copper metal chloride.

Metal Complex reaction scheme

$$L + MX_2 \longrightarrow [MLX_2]$$

Where M: L as 1: 1

L = **7**-hydroxy-4-methyl-1-[(2-thiazol-4-yl)-*1H*-benzimidazole-5yl]-quinolin-2-(*1H*)-one ($C_{20}H_{14}N_4O_2S$)
M = Cu
X = Chloride ion

Synthesis of [Cu ($C_{20}H_{14}N_4O_2S$) Cl_2]

The copper chloride dihydrate ($CuCl_2 . 2H_2O$, 0.400 gm. 2.13 mmol) dissolved in minimum quantity of ethanol was added to 30 ml hot ethanolic solution of L (0.8 gm, 2.13 mmol, 7-hydroxy-4-methyl-1-(2-(thiazol-4-yl)-1*H*-benzimidazole-5-yl) quinolin-2-one). The reaction mixture was refluxed for 5 hours. The precipitate separated overnight as brown colored solid. The precipitate was thoroughly washed with cold ethanol and finally dried under vacuum to give yield 54 %. Melting point was 259-261 ^{0}C

Table 1: Analytical data for metal complex

Comp.	**Molecular Formula**	**Molecular Weight**	**Color**	**Solubility**	**Melting Point (^{0}C)**	**Yield (%)**
CuL	$[Cu(C_{20}H_{14}N_4O_2S)Cl_2]$	508.87	Brown	Insoluble in water, ethanol, methanol, soluble in DMSO.	259-261	54

UV (λ_{max}, DMSO): 209, 280, 319, 489.
IR (KBr): 3248, 3089 (N-H stretch), 1635 (-C=O stretch), 1481(C=N) $_{imidazole}$), 1442υ (C=N) $_{thiazole}$, 1296 (C-S stretch), 999, 813, 759, 694, 617, 540, 439.
Mass: 507.39, 373.33, 255, 215, 154.The mass spectrum of Cu (II) complex shows molecular ions peak of $[Cu\ (C_{20}H_{14}N_4O_2S)\ Cl_2]$ [M+1] at *m/z* 507, $[C_{20}H_{14}N_4O_2S]$ at *m/z* = 373, and other important peaks at 343, $[C_{10}H_8N_4S]$ at *m/z* = 215.
Elemental analysis % found (Calcd.): C, 47.64 (47.21); H, 2.39 (2.77); N, 11.45 (11.01) and Cu, 12.11(12.49).

Results and discussion

Table 2 Comparison of IR frequency of ligand L with its metal complex.

IR Band	**L** cm^{-1}	**CuL** cm^{-1}
N-H stretch	3093	3089
υ $_{(C=N)imidazole}$	1546	1481
υ $_{(C=N)thiazole}$	1481	1442
C-S stretch	1280	1296
-C=O stretch	1639	1635
-OH stretch	3224	3248

The N-H stretch at 3093 remains same for ligand L and metal complex. The IR associated to υ $_{(C=N)\ imidazole}$, andυ$_{(C=N)\ thiazole}$ have remained same in spectra of complex but have shifted slightly as compare to ligand indicating that ligand is coordinated through imidazole and thiazole nitrogens. The C-S stretches have also remained same in lined and its complex compounds hence sulphur does not coordinated to metal. Carbonyls stretching band as well as –OH stretching band also remain same. **(Table 2)**

Table 3 Molar Conductivity and magnetic moment

Metal Complex	Formula	Molar Conductivity in DMSO Λ_M(ohm^{-1}cm^{2}mol^{-1})	Magnetic moment (B. M.) $\mu_{eff.}$
CuL	$[Cu(C_{20}H_{14}Cl_2N_4O_2S)Cl_2]$	45.97	1.66

Molar conductivity values of complex (CuL) of 0.001 molar solution at room temperature in DMSO solution are listed in **Table 3.** For the complex molar conductivity value is less than expected. This indicates that the complex is non-electrolyte. The molar conductivity value was found in range of 30 to 50 ohm^{-1}cm^{2}mol^{-1}

The magnetic moment of copper complex was 1.66 B. M. Its magnetic moment value indicates that presence of one unpaired electron. Thus, copper is paramagnetic in nature.

Thermo gravimetric analysis of metal complex.

The TGA curve indicate that metal complex CuL i.e. $[Cu(C_{20}H_{14}N_4O_2S)Cl_2]$ begins to decompose at 420^{0}C and ends at 650^{0}C. The TGA curve for CuL shows single stage of mass loss within the temperature range 200 to 650^{0}C. For CuL the observed mass loss is 85.46 % corresponding to residue CuO. **(Fig. 1)**Thermal decomposition data for the complex CuL is given in the (**Table No 4**).

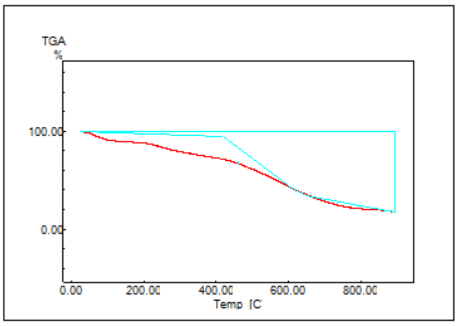

Fig.1 TGA of metal complex CuLi.e. $[Cu(C_{20}H_{14}N_4O_2S)Cl_2]$

Table No 4 TGA data for metal complex CuL, $[Cu(C_{20}H_{14}N_4O_2S)Cl_2]$

Metal Complex	**Stages**	**Temp. range TG (^0C)**	**Mass loss from Thermo gram (%)**		**Decomposition Pattern**
			Expt. loss (%)	**Theor. loss (%)**	
CuL	1	25 to 700	85.46	85.14	Loss of oxides of sulphur, part of ligand and formation of oxide. $[Cu(C_{20}H_{14}N_4O_2S)Cl_2]$ to CuO

Evaluation of antimicrobial activities

Bioassay is an important and crucial role in evaluation of bio-activity of compounds and helpful to establish structure-activity relationship [12-13]. In the present work ligand as well as metal complex was tested for their antimicrobial potency such as antibacterial and antifungal activities against different grampositive bacteria, gram negative bacteria and fungi using

a) Gram positive bacteria (*Staphylococcus aureus, Bacillus subtilis*).

b) Gram negative bacteria (*Pseudomonas aeruginosa, Escherichia coli).*

***c)* Fungi *(Aspergillus niger, Candida albicans, Fusarium moniliforme)*.**

High media antibiotics disk such as Chloramphenicol (10 microgram/disk, Amphotericin-B (100 units/disk) moistened with water are used as standard.

Stock solution of 1000 µg/ml of each sample ligand L and metal complex CuL was prepared in DMSO. Assay is carried out by taking concentration 100 µg/ disc. Chloramphenicol (10 µg/ disc, amphotericin-B (100 units par disc moistened with water are used as standard. A clear zone of inhibition around the disc demonstrated the relative susceptibility of the bacteria or fungi to the synthesized ligand and metal complex. The fungicidal or bactericidal potency is proportional to the diameter (in mm) of the zone of inhibition. One of inhibition was calculated by Vernier Caliper. The experiments were performed in duplicate and average of the measured zone was considered. The results of antimicrobial activity are summarized in (**Table 5).**

Table 5. Results of antimicrobial activities for ligand $L(C_{20}H_{14}N_4O_2S)$ and its Copper metal complex by disc diffusion assay

Sr. No	**Sample Code**	**Zone of inhibition (Diameter in mm)**						
		G^+ bacteria		**G^- bacteria**		**Fungi**		
		S. a.	***B. s.***	***E. c.***	***P. a.***	***C. a.***	***A. n***	***F.m.***
1	L	13.70	18.11	14.84	10.08	-----	-----	
4	CuL	10.22	14.03	8.45	-----	-----	-----	-----
6	A	27.90	20.05	26.91	**14.10**	NA	NA	NA
8	B	NA	NA	NA	NA	21.42	7.98	8.10

CuL $[Cu(L)Cl_2]$ **A** Chloramphenicol **B** Amphotericin B

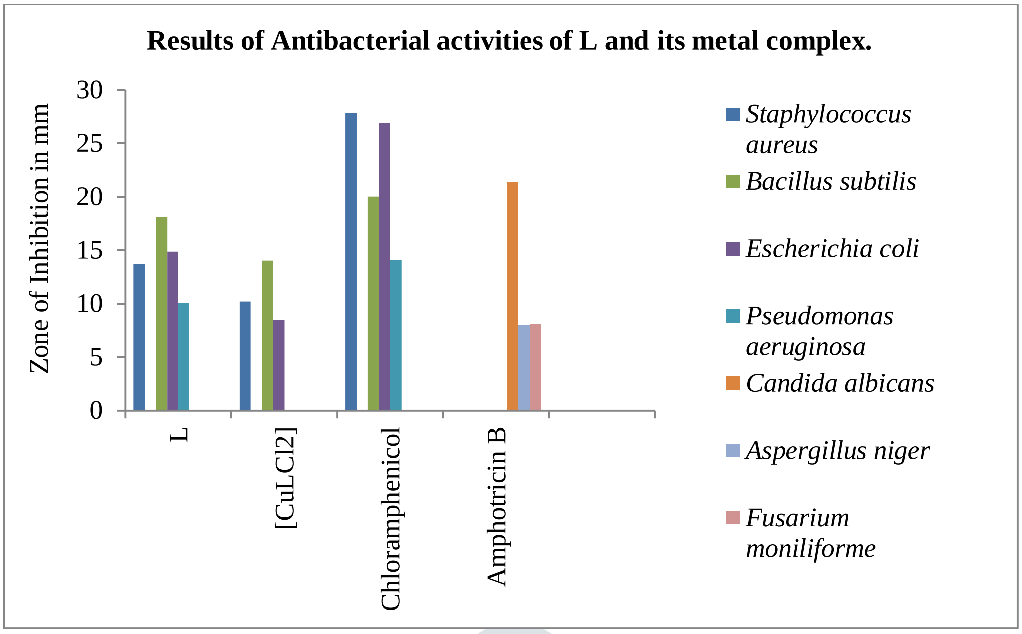

Fig. 2: Antimicrobial activities of L and its metal complex

Antibacterial activity:

Staphylococcus aureus: In antibacterial efficacy against *S. aureus* the ligand L exhibited moderate antibacterial activity. The metal complex CuL i.e. $[Cu(L)Cl_2)]$ shows poor antibacterial activity.

Bacillus subtilis: Metal free ligand L exhibit excellent antibacterial activity against *Bacillus subtilis* with zone of inhibition 18.11 mm compare to standard drug Chloramphenicol is 20.05 mm. The metal complex CuL shows moderate antibacterial activity.

Escherichia coli: Ligand L shows better antibacterial activity against *E. Coli.*with zone of inhibition 18.11 mm. The metal complex CuL metal complex shows poor efficacy against *E. Coli.*

Pseudomonas aeruginosa: Ligand L shows moderate antibacterial activity against *P. aeruginosa*. Metal complex CuL are inactive against *P. aeruginosa*.

Antifungal activity:

Candida albicans: L is inactive against antifungal species *C. albicans*. Metal complex CuL is inactive due to no zone of inhibition.

Aspergillus niger**:** L is inactive against antifungal species *Aspergillus niger*while CuL are inactive**.**

Fusarium moniliforme: CuL is inactive against *F. moniliforme.*

Conclusion

Cu(II) complex of **7**-hydroxy-4-methyl-1-[(2-thiazol-4-yl)-*1H* benzimidazole-5yl]-quinolin-2-(*1H*)-one (L) characterized based on elemental analyses, infrared, magnetic moment, molar conductance, mass spectra, UV-Vis analysis and thermogravimetric analysis (TGA).

From the elemental analysis, it is found that the complex have formula $[M(L)(Cl)_2]$. The molar conductance data reveal that metal chelate is non-electrolytes. From the magnetic and solid reflectance spectra, it is found that the structure of these complex is square planer. The synthesized ligand and metal complex were screened for antimicrobial activity, such a non-toxic compound as might have potential use as a therapeutic agent.

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कृत्रिम बुद्धिमत्ता तंत्रज्ञान व भारतीय अर्थव्यवस्था

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गोषवारा :

तंत्रज्ञान व अर्थव्यवस्था यांचा सहसंबंध धनात्मक स्वरूपाचा आहे. तंत्रज्ञानाचा विकास आर्थिक विकासाला सहाय्यभूत ठरतो.1991 च्या आर्थिक सुधारणा नंतर भारतीय अर्थव्यवस्था वेगाने बदलत आहे. जागतिकीकरणाचा प्रभाव क्षेत्रात भारतीय अर्थव्यवस्थेने आधुनिक तंत्रज्ञान स्वीकारण्यात अनुकूलता दर्शवली आहे. सद्यपरिस्थितीत बहुचर्चित असलेल्या कृत्रिम बुद्धिमत्ता तंत्रज्ञान भारतीय अर्थव्यवस्थेच्या कृषीए आरोग्य सेवा एशिक्षणए रोजगार इत्यादी घटकांना प्रभावित करत आहे. प्रस्तुत शोध निंबधात भारतीय अर्थव्यवस्थेवरील कृत्रिम बुद्धिमत्ता तंत्रज्ञानाचा कृषीए आरोग्यसेवाए शिक्षण व रोजगार या घटकांवरील परिणाम या अनुषंगाने आढावा घेण्यात आला आहे.

संक्षिप्त शब्द रू भारतीय अर्थव्यवस्थाए कृत्रिम बुद्धिमत्ताए तंत्रज्ञानए कृषी क्षेत्र, आरोग्यसेवा, शिक्षणए रोजगार संधी.

प्रस्तावना

1991 च्या आर्थिक सुधारणा स्वीकारल्यानंतर भारतीय अर्थव्यवस्था वेगाने बदलत आहे. 1991 पासून च्या अडीच दशकात भारताने सातत्याने सरासरीने पाच टक्के पेक्षा जास्त आर्थिक वाढ नोंदवली आहे .आज भारत जगाच्या पाठीवरची चीन नंतरची सर्वात वेगाने वाढणारी अर्थव्यवस्था म्हणून गणला जातो. निवळ उत्पन्नाच्या दृष्टीने जगात सहाव्या क्रमांकाचीए क्रयशक्ती समानता तत्त्वानुसार तिसऱ्या क्रमांकाची अर्थव्यवस्था आहे. लोकसंख्या दृष्टीने दुसऱ्या क्रमांकाची तर युवाशक्तीच्या दृष्टीने क्रमांक एक ची अर्थव्यवस्था म्हणून पुढे येत आहे. 1991च्या आर्थिक सुधारणा नंतर भारतीय अर्थव्यवस्थेने अनेक आव्हाने स्वीकारले . खास करून भारताने जागतिकीकरणाच्या वातावरणात वेगाने माहिती तंत्रज्ञान दळणवळण सॉफ्टवेअर क्षेत्रात प्रगती केली. सातत्याने वेगाने बदलणारे तंत्रज्ञान आत्मसात करून स्वतःसाठी संधी निर्माण करण्यात भारत अग्रेसर राहिला आहे .आजच्या काळात जागतिक स्तरावर सर्वाधिक चर्चिला जाणारा तंत्रज्ञानविषयक भाग म्हणजे कृत्रिम बुद्धिमत्ता होय. भारतीय अर्थव्यवस्थेने हे तंत्रज्ञान स्वीकारले आहे. कृत्रीम बुद्धीमत्ता तंत्रज्ञान भारतासाठी एक नवीन संधी आहे .आज जागतिक स्तरावर कृषी आरोग्य सेवा दळणवळण संरक्षण सर्व क्षेत्रात कृत्रीम बुद्धीमत्ता तंत्रज्ञानाचा मोठ्या प्रमाणात वापर करण्यात येत आहे. प्रस्तुत शोधनिबंधात कृत्रिम बुद्धिमत्ता तंत्रज्ञानाचा भारतीय अर्थव्यवस्थेवरील परिणामांचा आढावा घेण्यात आला आहे.

कृत्रिम बुद्धिमत्ता तंत्रज्ञान म्हणजे काय ह

कृत्रिम बुद्धिमत्ता या तंत्रज्ञानाची ओळख जगासाठी नवीन नाही मागच्या 70 वर्षाच्या कालखंडापासून या संदर्भात सातत्याने क्रमिक विकास होत आहे परंतु माहिती तंत्रज्ञानाच्या युगात कृत्रीम बुद्धीमत्ता तंत्रज्ञान नवीन रूपाने समोर येत आहे. साधारणपणे 1950 पासून कृत्रीम बुद्धिमत्ता संगणक शास्त्रातील महत्त्वाचा विषय बनला आहे. एलन टुरींग यांना या संकल्पनेचा जनक म्हणतात.

कृत्रीम बुद्धीमत्ता तंत्रज्ञान म्हणजे एखाद्या यंत्राला मानवसदृश्य उच्च दर्जाची बुद्धिमत्ताए माहितीचे मानवी बुद्धिमत्ता पातळीवर वर्गीकरण करण्याची क्षमता देणे होय.

मानवी तर्कए निष्कर्षए भाषा आकलनए प्रतिक्रियाए संवाद या मानवी बुद्धिमत्तशी विविध अंगाने जुळणारे यंत्र म्हणजे कृत्रीम बुद्धीमत्ता होय (सरकार, २०१८).

कृत्रिम बुद्धिमत्ता या तंत्रज्ञानाचे आर्थिक व सामाजिक फायदे जगाच्या लक्षात येत आहेत. जगाच्या पाठीवरील सर्व देशात भविष्यात या तंत्रज्ञानाच्या माध्यमातून मोठ्या प्रमाणात आर्थिक व सामाजिक फायदे उचलण्याच्या तयारीत आहेत.

कृत्रिम बुद्धिमत्ता व भारत

भारत जागतिक बदल सकारात्मक दृष्टीने स्वीकारत आहे .कृत्रीम बुद्धिमत्ता भारतासाठी विकासाच्या नवीन आशा निर्माण करत आहे. खास करून उत्पादन क्षेत्रात ए कृषिक्षेत्रातए संरक्षणए आरोग्य क्षेत्रातए पर्यावरण क्षेत्रातए सामान्य प्रशासनए शासकीय योजना इत्यादी ठिकाणी भारताच्या संदर्भात आर्थिक बाजूने कृत्रीम बुद्धिमत्ता तंत्रज्ञानाचा वापर महत्त्वाचा ठरतो (नीती आयोग, २०१८).

भारत जागतिक स्तरावर डिजिटल अर्थव्यवस्था म्हणून पुढे येत आहे. भारत माहिती तंत्रज्ञान क्षेत्रात आघाडीवर असून भारतीय अर्थव्यवस्था व कृत्रिम बुद्धिमत्ता तंत्रज्ञानाच्या मदतीने आर्थिक प्रगती करता येवू शकते. अनेक प्रकारच्या उत्पादन वाढीचा वेग वाढवता येतो. अशा परिस्थितीत अधिक दर्जेदार उत्पादन करण्यासाठी कृत्रिम बुद्धिमत्ताचा वापर होत आहे. कृत्रिम बुद्धिमत्ता तंत्रज्ञान भारतासाठी वरदान ठरू शकते निती आयोग कृत्रिम तंत्रज्ञानाच्या बाबतीत राष्ट्रीयस्तरावर धोरण तयार करत आहेप कृत्रिम बुद्धिमत्ता तंत्रज्ञान सरकारी तथा खाजगी दोन्ही क्षेत्रात महत्वपूर्ण कार्य पार पाडू शकतेप भारत माहिती तंत्रज्ञान खास करुन सॉफ्टवेयर क्षेत्रात आघाडीवर असूनदेखील कृत्रिम बुद्धिमत्ता तंत्रज्ञानात भारताने फारशी आघाडी घेतलेली दिसुन येत नाही असे असले तरीही एक उदयोन्मुख अर्थव्यवस्था म्हणुन भारताला कृत्रिम बुद्धिमत्ता क्षेत्रात खूप संधी व आशा आहेतप

भारताची आर्थिक वृद्धी व कृत्रिम बुद्धिमत्ता

तंत्रज्ञानाच्या मदतीने वेगाने आर्थिक प्रगती करता येते हे एक एतिहासिक सत्य आहेप अनेक प्रकारच्या शोधामुळे उत्पादन वाढीचा वेग हजारोपटींनी वाढला आहे अशा परिस्थितीत अविरत व अधिक दर्जेदार उत्पादन करण्याच्या दृष्टीने कृत्रिम बुद्धिमत्ता

वरदान ठरू शकतेʊ उत्पादनाच्या अनेक यंत्रकुलमधे आता रोबोटिकच्या सहाय्याने उत्पादन होत आहेʊ उत्पादन क्षेत्रात भारताने स्टार्ट अप इंडिया आणि मेक ईन इंडिया हे महत्वाकांक्षी उपक्रम हाती घेतले आहेतʊ या उपक्रमांना कृत्रिम तंत्रज्ञानाची जोड मिळाली तर ते वेगाने यशस्वी होऊ शकतातʊ 1991 च्या सुधारणांनंतर भारत सातत्याने दुहेरी विकास दर आकड्यांचे स्वप्न पाहत आहेʊ निश्तीच कृत्रिम बुद्धिमत्ता तंत्रज्ञानाचा वापर भारताचे हे स्वप्न पुर्ण करु शकतोʊ

भारतीय कृषी क्षेत्र व कृत्रिम बुद्धिमत्ता तंत्रज्ञान

भारत ही कृषीप्रधान अर्थव्यवस्था आहेʊ आजही भारतात कर्त्यालोकसंख्येपैकी 49: लोकसंख्या कृषी संबंधी क्षेत्रात काम करते (Economic Survey, 2018). परंतु मागील काही दिवसांपासून सातत्याने राष्ट्रीय उत्पादनातील वाटा घटत आहे त्यामुळे कृषीमध्ये अनेक समस्या राष्ट्रीय स्तरावर निर्माण झाल्या आहेतʊ निश्चितच कृषी विकासासाठी आधुनिक शेती करने आवश्यक बनले आहे आणि शेती तंत्रज्ञानाचे आधुनिकीकरण करण्यात कृत्रिम बुद्धिमत्ता तंत्रज्ञान महत्वाची भूमिका पार पाडू शकतेʊ आज मोठ्या प्रमाणावर भारतात स्मार्टफोनचा वापर वाढला आहेʊ स्मार्टफोन व कृत्रिम बुद्धिमत्ता तंत्रज्ञानाची सांगड घालून शेतीचे आधुनिकीकरण करता येऊ शकतेʊ पीकआरोग्यए निरीक्षणए मातीपरीक्षणए जलव्यवस्थापनए पीक जनुकीय विकासए किडींचे नियंत्रण ई क्षेत्रात कृत्रिम बुद्धिमत्ता तंत्रज्ञान बहुमोल कामगिरी पार पाडत आहेʊ

भारतीय आरोग्य क्षेत्र व कृत्रिम बुद्धिमत्ता

कुठल्याही देशाचा आर्थिक विकास हा मानवी भांडवलाच्या दर्जामध्ये नसतो सहाजिकच मानवी भांडवलाचा दर्जा ठरविणे मध्ये आरोग्यसेवांची भूमिका महत्त्वाची असते वाढत्या लोकसंख्येबरोबर भारतातील आरोग्य क्षेत्रात झपाट्याने वाढ होत आहे परंतु आजही ग्रामीण निमशहरी भागांमध्ये आरोग्य सेवेचा वानवा आहे आरोग्य क्षेत्रात बुद्धिमत्ता भारतात योगदान देऊ शकते भारतात दर हजार माणसांमागे डॉक्टर चे प्रमाण एक टक्क्यापेक्षा (0.76) कमी आहे (निती आयोग, २०१८). तसेच डॉक्टर ग्रामीण व आदिवासी भागात काम करण्यास फारसे उत्सुक नसतात त्यामुळे ग्रामीण भागात डॉक्टरांची कमतरता जाणवते या समस्येवर कृत्रिम बुद्धिमत्ता तंत्रज्ञानात करू शकते रुग्णांची परिचारिकांची माध्यमातून कृत्रिम बुद्धिमत्ता यंत्राच्या साह्याने तपासणी करता येऊ शकते व त्यावर निदान होऊ शकते या तंत्रज्ञानाने भारतातील ग्रामीण व आदिवासी भागातील डॉक्टरांची कमतरता भरून काढता येऊ शकतेʊ

भारतीय शिक्षण प्रणाली व कृत्रिम बुद्धिमत्ता

देशाचा आर्थिक प्रगती अवलंबून असते आणि भांडवलाच्या दर्जामध्ये शिक्षणाची भूमिका महत्त्वाची आहे मानव विकास निर्देशांकामध्ये साक्षरता महत्वाचा आहे बनवण्यासाठी शिक्षण प्रसार व शिक्षणाचा दर्जा यावर भर देणे आवश्यक आहे या कामी भारतामध्ये कृत्रिम बुद्धिमत्ता तंत्रज्ञान शिक्षण प्रणाली विद्यार्थी गळतीचे प्रमाण लावलेले आहे शैक्षणिक गुणवत्ता शिक्षकांचा अभाव आधुनिक साधनांचा वापर इत्यादी समस्यांनी ग्रस्त

आहे वापर करून या समस्यांवर मात करता येऊ शकते बुद्धिमत्ता तंत्राचा वापर वरील समस्या सोडवण्यात बऱ्यापैकी यश आले आहे

रोजगार संधी व कृत्रिम बुद्धिमत्ता

यांत्रिकीकरणामुळे रोजगार संधी कमी होतात अशी चर्चा केली जाते अगोदर भारतासारख्या मुबलक व स्वस्त असलेल्या देशात यामुळे रोजगार संपत आहेत अशी चर्चा होते परंतु भारतात संगणकाचा वापर सुरुवात झाली तेव्हा देखील अशीच चर्चा झाली आहे उलटपक्षी संगणक वापरणे रोजगाराच्या संधीत वाढ झाली आहे याचे उत्तम उदाहरण म्हणजे भारतीय बँकिंग क्षेत्र संगणकीकरणामुळे भारतीय बँकेचा व्यवसाय झपाट्याने वाढला त्यामुळे रोजगार संधी पुरवण्यात भारतीय बँक आघाडीवर असल्याचे दिसून आले हिच बाब कृत्रिम बुद्धिमत्ता तंत्रज्ञानाला लागू होईल. कृत्रिम बुद्धिमत्ता वापरामुळे उत्पादन व सेवा क्षेत्र वेगाने वाढले तसेच अर्थव्यवस्थेचा आकार वाढून रोजगार संधी देखील वाढतील. लोक नवीन कौशल्य आत्मसात करतील व निम्न उत्पन्न नोकऱ्यांकडून उच्च उत्पन्न नोकऱ्यांकडे व खासकरून बौद्धिक क्षमता असलेल्या रोजगार संधीकडे वळतील (सरकार, २०१८).

सारांश

आज भारत जगात वेगाने वाढणाऱ्या अर्थव्यवस्था पैकी एक आहे. निश्चितच भारताला आर्थिक विकास वेगाने घडवून आणायचा असेल तर नियोजनबद्ध पद्धतीने भारताने सर्वच क्षेत्रात कृत्रिम बुद्धिमत्ता तंत्रज्ञान वापरण्यासाठी पावले उचलणे गरजेचे आहे. आधुनिक तंत्रज्ञानाची सांगड घातल्याशिवाय आर्थिक प्रगती साध्य केली जाऊ शकत नाही हे जागतिक स्तरावरील सत्य भारताने स्विकारले असुन भारत सरकार कृत्रिम बुद्धिमत्ता वापराच्या दिशेने योग्य पाउल टाकत आहे. निती आयोगाने यादृष्टीने कृती आराखडा तयार करण्यास सुरुवात केली आहे.

संदर्भ

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2द्ध सरकारए अविक ;एप्रिल 2018द्धए भारताच्या विकासाला गती देणारी कृत्रिम बुद्धिमत्ता. योजना मासिक चचण 48.53

Role of Coriander (*Coriandrum sativium L.*) on Accumulation and Depuration of Mercury in *Bellamya bengalensis(L.)*

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Abstract:

Present study aimed to examine the usefulness of Coriander (*Coriandrum sativium L.*) extract for elimination of heavy metal bioaccumulated in the whole body tissue of the experimental model animal gastropod snail *Bellamya bengalensis (L.)* The accumulation and elimination of mercury (Hg) was examined by exposing the snail *Bellamya bengalensis(L.)* to 0.173ppm ($HgCl_2$) mercuric chloride with and without Coriander (*Coriandrum sativium L.)* extract for 7, 14, 21 days. After 21 days treatment the snails were allowed to cure naturally in normal water and with coriander extract up to 21 days separately. The whole body tissue samples were taken out after every 7 days for metal analysis. There was a gradual increase in heavy metal content with increase in exposure period for mercury. The concentration of mercury during depuration was found to be decreased with increase in period. However the recovery was faster in those which are treated with coriander extract as compaired to those which are allowed to cure naturally in normal water. The aim of present study was to highlight the antioxidation, heavy metal detoxification, elimination and chelating aspects of coriander.

Key words:

Coriander, Heavy Metal, Mercury, Bioaccumulation, Depuration, Gastropod, *Bellamya bengalensis L.*).

Introduction:

Heavy metal pollution in aquatic ecosystem has been recognized as a serious environmental problem .In many cases heavy metals occurs in natural water bodies at levels bellow their toxic threshold, however due to their non degradable nature, such low concentrations may still pose risk of damage via uptake and subsequent bioaccumulation by organisms, which cannot effectively metabolized and excrete the absorbed metals (Wayker et al. 2013). Metal bioaccumulation can be of importance of public health point of view, especially when a human consumes the accumulators. Secondly, this phenomenon is now being exploited in assessment of environmental quality, in addition to chemical survey of water and sediments (Javanshir and Shapoori 2011).Heavy metals are persistent and non biodegradable and may pose high toxicity on the aquatic organisms. Mercury is considered as toxic metal that causes environmental problems and can be very harmful even at low concentration (Devagi Kanakraj et al. 2009).

As the concentration of metal increases, the accumulation of metal and its damage effect increases (Cain and Louma 1986; Buschiazzoa et al. 2004). Cumulative effects of metals or chronic poisoning may occur as a result of long term exposure.

The gastropod snail Bellamya bengalensis (L.) was chosen to determine the ability for the bioaccumulation of Mercuric chloride ($Hgcl_2$) in their soft parts and to show the extent of their tolerance towards these pollutants in the fresh water ecosystem.

Coriander is a well known herb for its antioxidant properties and contains compounds that are free radical scavengers .Coriander contains the active phenolic acid compounds like caffic acid, chlorogenic acid, vanillic acid, p-coumatic acid, ferulic acid (cis and trans forms) (Rajeshwari et al., 2010, Nambir *et al.*,2010). The flavonoids in coriander leaves have been identified as quercetin (an important free radical scavenger), kaemferol and acaetin (Rajeshwari et al., 2011, Nambir *et al.*, 2010, Deepa *et al.*, 2011). The research of Dr.Yashiki Omura showed that consumption of clientro lowered the level of Mercury in patients via chelation mechanism(Omura,1996).Coriander's antioxidant properties are seen as treatment with SOD, CAT, GPx levels in the tissue of liver and kidney (Sharma , 2011).

In the light of above mentioned medical properties of coriander, this study was carried out investigate the possible protective properties of coriander extract against heavy metal bioaccumulation and elimination from the whole body tissue of model animal Bellamya bengalensis during chronic toxicity treatment of Mercuric chloride.

Material and Methods:

Selection and collection of experimental animals:

The gastropod snail *Bellamya bengalensis* (Viviparus) were collected from the suki dam near Garbardi village Tal.Raver Dist.Jalgaon (M.S.). The gastropods were acclimatized to laboratory condition for 2 to 3 days, before setting the experiments. Water was changed after every twelve hours. Healthy and active animals of approximately same size (25 to 30 mm) and weight were chosen.

Preparation of aqueous leaves extract:

The fresh green leves of *Coriandrum sativium (L)* (1kg) were collected from a local market in Raver. The leaves were dried at atmospheric temperature .After complete drying the leaves were ground to a fine powder of which 100 gm powder was added to 500 ml distilled water After 24 hours maceration was done at room temperature , the mixture was then heated for 30 min. in the water bath at 65^{o}c. The extract was filtered, concentrated by heating over the water bath at (65^{o}c). The extract was stored at 4^{o}c and used to treat animals as needed.

Experimental design:

Healthy and active animals of approximately equal size (25 to 33mm) and weight were selected to avoid the experimental bias during the research work. The acclimatized active gastropods were divided in to three groups as A, B and C. The group 'A' gastropods was maintained as control. The group 'B' gastropods was exposed to chronic concentration of heavy metal salt Mercuric chloride 0.173ppm $HgCl_2$ up to 21 days treatment, The group 'C' gastropod was exposed to chronic concentrations of respective heavy metal and 5 ml/lit. of *coriandrum* extract up to 21 days.

After 21 day's exposure, the gastropod snails from group 'B' were divided in to two sub groups as group 'D' and group 'E'. The snails of group 'D' were allowed to self cure naturally in normal water. The snails of group 'E' were allowed to cure in 5 ml/lit extract of *Coriandrum sativium (L.)* up to 21 days. During experimentation the snails were fed on fresh water algae.

Collection and processing of tissue samples:

The tissue mass of whole body of the gastropod snail, *Bellamya bengalensis* (L.) were collected after every seven days and were dried at 80^{oc} in an oven till constant weight was obtained and stored in air tight specimen bottles by waxing the cork outside. The 50 mg sample was taken for digestion. The tissue was digested in 10 ml of acid mixture of Hcl: HNO_3 in (3:1) ratio on hot plate till dryness. The digested mixture was kept in water bath for 5-7 hour until the samples were cooled. Cool digested samples were filtered (Whatman grade 541). The samples were analyzed on the instrument atomic absorption spectrophotometer (A.S.).

Observation table:

Bioaccumulation of Mercury (Hg) in the whole body tissue mass of the gastropod snail, *Bellamya bengalensis* (L.) after chronic exposure to mercuric chloride 0.173ppm with and without coriander extract and recovery in normal water and in coriander extract has been summarized in table 1.1 and 1.2

Table 1.1. Mercury content (□gm /Kg dry weight) in whole body tissue of *Bellamya bengalensis (Lamark)* after chronic treatment .

Treatment			Hgcontent □gm/Kg dry weight		
			7 days	14 days	21 days
During 21 days exposer0.173ppm Hg Cl_2	A	Control	307	316	309
	B	0.173ppm Hg Cl_2	928 +66.918●	1794 +82.385●	2157 +85.674●
	C	0.173ppm Hg Cl_2+5 ml coriander extract	749 +59.012● -23.898 ®	1057 +70.104● -69.725 ®	1662 +81.295● -30.569 ®

Table 1.2. Mercury content (□gm /Kg dry weight) in whole body tissue of *Bellamya bengalensis (Lamark)* after chronic treatment during recovery.

Treatment			Hg content □gm/Kg dry weight		
			287days	35 days	42days
After21days exposer to 0.173ppm Hg Cl_2	D	Normal water(recovery)	210 +84.726● -7.313 #	1967 +83.934● -9.659 #	1948 +84.137● -10.728 #
	E	Normal water+5 ml/|lit coriander extract (recovery)	1751 +82.467● -23.186 #	1281 +75.331● -68.384 #	1176 +73.724● -83.418 #

●-Compaired with respect to A

Δ - Compaired with respect to B.

*-Compaired with respect to 21 days of B.

Result:

The bioaccumulation data from Table no. 1.1 and 1.2 indicates that the amount of mercury (Hg) accumulated in whole body tissue of animals on exposure to mercury chloride (0.173ppm $HgCl_2$), gets increased with increase in exposure period from 7, 14 and 21 days as compaired to control group ‘A’. The mercury (Hg) contents are expressed in µgm/kg dry weight. The control groups of animals showed minute quantity of mercury (Hg) as compaired to the experimental group ‘B’ and ‘C’.

The control group of animals ‘A’ showed 307.0 µgm/kg mercury in whole body tissue, while the amount of accumulation of mercury in presence of mercuric chloride (0.173 ppm) in the snails group ‘B’ for 7 days was 928.0µgm/kg. The concentration in the tissue was raised after 14 days which was 1794.0µgm/kg. While after 21 days the rate of accumulation was 2157.0µgm/kg. There was a minute change in the accumulation in control group animals. The rate of accumulation was lower in $Hgcl_2$ and coriandrum sativium extract (5 mg/lit) exposed snail groups ‘C’ as compaired to those exposed to only $Hgcl_2$ treated group ‘B’ in respective period of exposure and for 7 days it was 749.0 µgm/kg, after 14 days it was 1057.0 µgm/kg, while after 21 days it was 1652 .0 µgm/kg.

The gastropod snail, Bellamya bengalensis pre exposed to mercuric chloride (0.173 ppm), showed fast detoxification and recovery in presence of coriandrum sativium extract (5 mg/lit.) than those allowed to cure naturally in normal water. The accumulation as observed after 28 days was 1751.0µgm/kg., after 35 days was 1281.0µgm/kg., while after 42 days the amount of mercury was 1176.0µgm/kg. and those allowed to cure naturally in normal water , the rate of accumulation observed for 28 days was 2010.0 µgm/kg., after 35 days , it was 1967.0 µgm/kg. While after 42 days the concentration of accumulated Hg was 1948.0µgm/kg.

Discussion:

Many workers found that the accumulation patterns of heavy metals are dependent on both uptake and elimination rates (Hakman 1984, Goma *et.al.* 1995).The accumulation of metals in aquatic invertebrates can be divided in to three phases 1) Metal intake, 2) Metal transport, distribution , and sequestration (detoxification) with the organism and 3) Metal excretion (present/ absent).Accumulation strategies of invertebrates vary intra specifically between metals and inter specifically for the same metal in closely related organisms (Rainbow; 2002).

High cost modern medicines and many side effects of these medicines lead people to switch around from modern medicines to herbal medicines for the treatment of many infectiocious diseases (Ambuja s.k.s.; 2012). Mitra et.al (2012) reported that the coriander leaves are rich in photochemical such as poly phenol, carotinoids and essential oils like linalool which shows higher free radical scavenging activity.

In present study the accumulation of heavy metal mercury in the whole body tissue of *Bellamya bengalensis (L.)* was found to have similar pattern to that report previously for several gastropod species exposed to various concentrations of heavy metals. In response to increased concentrations of mercury chloride, high level of mercury was observed as compaired to control group of animals. The gastropod snail *Bellamya bengalensis (L.)* pre exposed to chronic concentration of mercury chloride along with 5 ml/lit *Coriandrum sativium (L.)* extract showed the poor bioaccumulation as compaired to exposure of chronic concentration of respective heavy metal only. *Bellamya bengalensis (L.)* pre exposed to mercury chloride showed fast detoxification recovery in presence of *Coriandrum sativium (L.)* than those allowed to cure naturally in normal water.

Significance of study:

The present proposed research work would be useful as, to provide protective and curative measures against heavy metal toxicosis, to provide the knowledge about interaction of coriander extract with heavy metals in to the body, to provide the knowledge about importance of coriander in preparation of food, to provide the safe remedy to the peoples living in heavy metals affected areas. In city’s automobile exhaust release lead and hence content in air is high. This study may give protective and curative use of coriander.

Conclusion:

The coriandrum sativium extract shows free radical scavenging and chelating activity against heavy metal bioaccumulation and removes the heavy metal bioaccumulated in the body.

Acknowledgement:

The authors are thankful to principal Dr.S.S.Patil, D.N.College Faizpur for providing the laboratory facilities.

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Impact of Manganese Ions on the Gel Grown Brushite Crystals

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Abstract:The impact of manganese on the growth of urinary brushite crystals was studied using the spectroscopic techniques, which included optical microscopy, SEM, FTIR and EDAX. It was found that, manganese ions transform the morphology of brushite crystals from rectangular plate shaped crystals to star shape, T shape dendratic crystals. In SEM, the layer by layer growth pattern, focus the influence of manganese ions on the growth of brushite crystals. In FT-IR spectroscopy, the intense reflection was only observed at lower frequencies, while very low intensity reflection peaks was in higher frequency region.The observed changes in the vibrations were due to the impact of manganese ions.EDAX revealed that the grown crystals was mixed composition.

***IndexTerms* – Urinary Crystals, Doped Brushite, Agar Gel, Single diffusion.**

1. INTRODUCTION

The urinary crystals are deposited in the urinary system, which belong the pair of kidney, ureters, a bladder, and urethra [1]. The function of kidney in the system is to filter the blood.After filtration, the wastes which is in the form of urine is then leave the kidney through the ureters and store in the urinary bladder. During urination, the urine leaves the bladder via the urethra to the outside of body. Such urine is more complex solution, and contains various crystalloids and colloids supersaturated crystals forming substances.

Calcium is an important structural and functional element of the body, and has been a part of normal diet. Those calcium not use by the body elements can be goes to kidney and flushed out by the urine. Excessive calcium in urine combines with the other waste products to form solid crystals in kidney. Approximately 70-80% of the kidney stones in industrialized countries are calcium oxalate and calcium phosphate [2]. Calcium hydrogen phosphate dihydrate (CHPD) also known as Brushite [3-4] is one of the form of calcium phosphate crystals.

During the investigation of urinary stones, it was reported that the large number of trace elements including Cd, Pb, Zn, Mg, Sr, Cr, Mn, Ni, Co, Au, Bi etc., are presented along with the main constituents [5]. Suresh et al reported that the increasing level of trace elements in the body fluid leads to crystal deposition which results in the development of kidney stones [6]. However the Lundager Madsen [7] investigated the influence of 14 different di- and trivalent metal ions on brushite formation and reported that some ions inhibit and some ions promote the formation of brushite. While the presence of magnesium reported to inhibit the formation of brushite crystals [8]. The investigators also grown the single crystals of pure and Sr^{2+} and $P_2O_7^{4-}$ doped brushite in silica gel and reported that the doping causes effects on the crystal habits [9]. K. Suguna examines the role of strontium, magnesium and other additives on the crystallization of brushite crystals grown in silica gel [10]. However, the impact of manganese on the growth of brushite was not yet reported. So in the present study, we examine the role of manganese ionson the crystallization of brushite in agar gel by single diffusion techniques at ambient temperature. Then the grown crystals were characterized by Optical Microscopy, Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Energy dispersive X-ray analysis (EDAX).

2. EXPERIMENTAL

The preceding paper [11], reported the optimized condition for the growth of Brushite crystals using agar gel by single diffusion technique. In the extension of such study, the effect of Zn^{2+} ions on the growth of Brushite was alsoreported [12]. However in the present study, we examine the impact of Mn^{2+} ions in the form of chloride solution was used in supernatant solution and observed the effect of crystallization on the growth of brushite crystals. Single glass tube of 25 mm in diameter and 20 mm in height were used as the crystallization vessels. Calcium chloride (Qualigens) of concentration (1.0M) and potassium dihydrogen phosphate (Merck) of concentration (1.0M) were used as reactants. Manganese chloride (Himedia) having in different concentrations were used as additive reactant. Agar gel (Himedia) solution was prepared by mixing 0.5 gm. agar powder in 100 ml double distilled water at boiling temperature. Then the prepared hot agar-agar solution was transferred in the test tube which contains an aqueous solution of calcium chloride (1M) in appropriate amount and was allowed to set for mixture. After setting the gel in different test tubes, 20 ml supernatant solution of 1.0 M potassium dihydrogen phosphate prepared with 0.25 M, 0.5 M and 1.0M manganese chloride solution in different volume was slowly poured. Closing the test tubes by cotton plugs, kept undisturbed for growth. Forty days of crystallization, manganese doped brushite crystals were found in different morphologies. The growth parameters of manganese doped brushite crystals was shows in Table 1.

Table 1 Growth parameters of brushite crystals grown in manganese chloride.

Set No.	Concentration of $CaCl_2.2H_2O$ (I Reactant) (M)	Concentration of KH_2PO_4 (II Reactant) (M)	Concentration of $MnCl_2$ (Additives) (M)	Volume of Additives (ml)	Percentage of Agar-agar gel (%)
1	1.0	1.0	0.25	1.0	0.5
2	1.0	1.0	0.25	2.0	0.5
3	1.0	1.0	0.5	1.0	0.5
4	1.0	1.0	0.5	2.0	0.5
5	1.0	1.0	1.0	1.0	0.5
6	1.0	1.0	1.0	2.0	0.5

3. RESULT AND DISCUSSION

Manganese chloride doped brushite crystals were grown in agar- agar gel. There have been significant changes in the growth pattern as compared to the similar crystals grown with zinc doped [12] and without manganese chloride solution. In case of manganese added experiment, the Mn^{2+} ions did not influence the selective nucleations, as that was found in zinc doped [12] but did have a pronounced effects on the growth habits of crystals. The spherulite crystals those found in zinc doped [12], were not observed in manganese doped experiment. The effect on pure sample due to the additive depends on impurity and concentration of additives. Also it was observed that the Mn^{2+} doped brushite crystals are relatively in different morphology such as twin crystals, T shape, star shape spherulite and plate shape crystals as seen in Fig.1. The shape and size of doped brushite crystal were affected by concentration and volume of the manganese impurity. When the concentration and volume of Mn^{2+} was increased, the sizes of grown crystals were found to be considerably reduced. For the further clearance in morphology and chemical composition of Mn^{2+} doped brushite crystals, they were characterized by Optical microscopy, SEM, FTIR and EDAX techniques.

4. CHARACTERIZATION

4.1Optical Microscopy

The optical microscopy is the oldest and simplest method to give clear picture of the surface of sample. It uses visible light and a system of lenses to magnify images of small sample [13]. The microscopic morphology of the grown crystals was studied using a "CZM4 LABOMED" stereo microscope with magnification of 4x, 8x and the pictures were recorded by the camera eyepiece. Fig.1 shows the morphology of Mn^{2+} doped brushite crystals. The different morphologies such as semitransparenttwins star shape, T shape dendratic as well as transulant rounded edge "rice" shape crystals were observed under the stereo microscope. When the images of Mn^{2+} doped brushite crystals was compared with undoped sample [11], it was found that the manganese ions affect the morphological growth of brushite crystals. This may be due to fact that the additives are active in relatively large concentration [14].

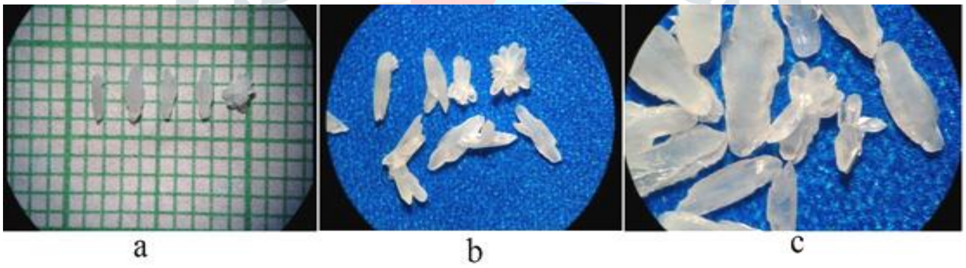

Fig.1 Harvested brushite crystals grown in manganese chloride

4.2 SEM Analysis

SEM images are the images of the sample surface by scanning it with electron beams in a raster scan pattern. The electrons interact with the sample atoms producing signals that contain information about the sample's surface topography, composition and other properties of the surface or the near-surface [15]. Fig.2 (a,b,c) shows the SEM images of the manganese doped brushite crystals. The morphologies seen in the SEM images were significantly affected due to manganese ions transforming from rectangular plate shaped [11] crystals to layer by layer growth pattern.

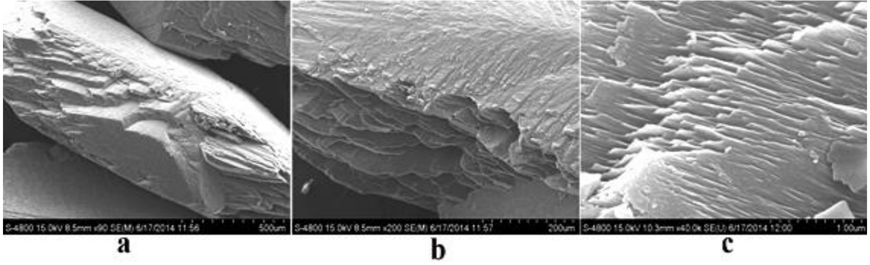

Fig.2 SEM images of brushite crystals grown in manganese chloride

As seen in Fig.2 (a), the step growth pattern was observed in the scale bar of 500.0 μm, however in Fig.2 (b) whose scale bar is 200.0 μm, the growth of crystals seems like layer by layer. The observed layers are very sharp in different size, while the top surface is rough. Fig.2(c) whose scale bar is 1.0 μm, the broken layer in different step growth morphology was observed. The former morphologies observed in SEM clearly indicate that the manganese ions did the pronounced effect on the growth of brushite crystals.

4.3 FTIR analysis:

Fourier transform infrared spectroscopy (FTIR) provides fundamental information on the molecular structure of organic and inorganic components, and is one of the most versatile analytical techniques for the non-destructive, chemical characterization of the samples [16]. In order to analyze the presence of functional groups in Mn doped brushite crystals, the FTIR spectrum was recorded in the range of 400-4000 cm^{-1}. The FTIR spectra of Mn^{2+} doped brushite crystals are depicted in Fig.3. As seen in Fig.3

the intense peaks were observed at lower wave number region. However in higher region, very low intensity transmittancepeaks were observed. This difference in transmittance may be arises due to difference in concentration or crystallanity of the grown crystals. In the spectrum of pure sample [11], four intense components at 3541.42 cm^{-1}, 3485.1 cm^{-1}, 3151.79 cm^{-1} and 2900.00 cm^{-1} due to O-H stretching of water [4,17-18] were found to be disappears at 3151.79 cm^{-1} and 2900.00 cm^{-1} in Mn^{2+} doped sample attributed due to doping effect. The presence of sharp band at 862.21 cm^{-1}in pure and around 834.24 cm^{-1}in manganese doped spectra confirms the presence of brushite phases [19]. The sharp peaks slightly change from 1649.19 cm^{-1}to around 1682.95 cm^{-1}in doped sample is also assigned to the bending of water molecules. The weak adsorption band at 2395.67 cm^{-1}in pure sample was shifted to 2370.5 cm^{-1} in doped sample is attributed to HPO_4^{2-} [20] , while the other weak absorption band at 1766.85 cm^{-1} observed in undoped was found to be absent in Mn^{2+} doped sample. The stretching vibrations associated with P=O were found to be shifted from undoped sample at 1278.85 cm^{-1},1115.86 cm^{-1}and 1030.02 cm^{-1} [21-22]. In case of pure sample, the strong absorption at 580.59 cm^{-1} and 520.80 cm^{-1}due to acid phosphate [10] was shifted to higher wave number side at 613.38 cm^{-1}in case of Mn^{2+} doped sample.The variation of intensity in undoped and mangnese doped brushite crystals shows that the two samples must have some difference. Thus the change observed in the vibrations was due to the dopants, while no additional peaks were obtained in the case of doped sample. The FTIR wave numbers and vibrations assignment of brushite crystals grown in pure and manganese doped are shown in Table 2.

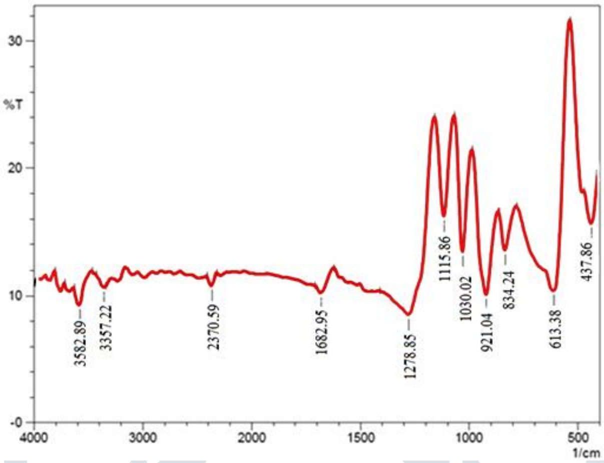

Fig.3 FTIR spectrum of Brusite crystals grown in manganese doped

Table 2 FTIR wave numbers and vibrations assignment of brushite crystals grown in undoped and manganese doped

Sr. No.	Bonds/Vibrational assignments	Observed wave number in cm^{-1}	
		Without manganese chloride[11]	With manganese chloride
1	O-H stretching of water	3541.42	3582.89
2	O-H stretching of water	3485.1	3357.22
3	O-H stretching of water	3151.79	--
4	O-H stretching of water	2900.00	--
5	Weak absorption HPO_4^{2-}	2395.67	2370.59
6	Weak absorption HPO_4^{2-}	1766.85	--
7	H-O-H symmetric bending vibrations	1649.19	1682.95
8	PO_4 P=O associated stretching vibrations	1215.19	1278.85
9	PO_4 bond, P=O stretching vibrations	1126.47	1115.86
10	PO_4 bond, P=O stretching vibrations	1062.81	1030.02
11	P-O-P asymmetric stretching bond	987.59	921.04
12	P-O-P asymmetric stretching bond	862.21	834.24
13	P-O-P asymmetric stretching bond	808.20	--
14	(H-O-) P=O bond acid phosphate	580.59	613.38
15	(H-O-) P=O bond acid phosphate	520.80	437.86

4.4 EDAX analysis:

EDAX is used to find the percentage composition of each elements present in the doped crystals [23]. Fig.4 is the EDAX spectra of Mn^{2+} doped brushite crystals.The highest peak of Ca, P, and O, revealed that the sample was of brushite, while the small peak of manganese in the spectrum indicates that the manganese elements are also presents in the sample. This was due to fact that, the ionic radii of manganese is less than calcium ions. Due to presence of such elements in sample, revealed that the sample was of a mixed composition. In undoped brushite [11], calcium to phosphorus (Ca/P) ratio was found to be 1.09, while in Mn^{2+} doped (Ca + Mn)/P ratio was 1.28. The change in molar ratio causes manganese ions to reacts with phosphorus than calcium.

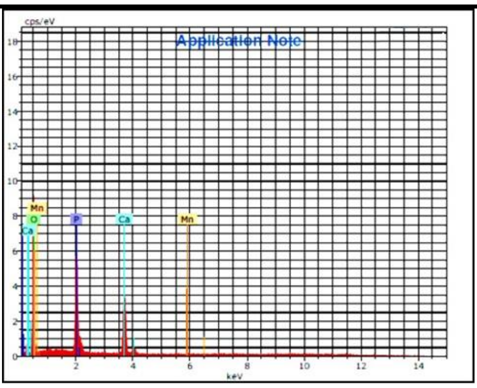

Fig.4 EDXA spectrum of brushite crystal grown in manganese chloride

5. CONCLUSIONS

The Brushite crystals were successfully grown by Mn^{2+} doped in agar gel by single diffusion techniques. The shape and size of doped brushite crystals were affected due to increasing the concentration and volume of the manganese ions. The different morphologies are observed in such manganese doping as compared to undoped brushite crystals. The SEM images confirms that the growth was significantly affected due to manganese ions transforming from rectangular plate shaped crystals to layer by layer growth pattern.The presence of various functional groups obtained in manganese doped sample was confirmed by FTIR. The disappearance of the components at 3151.79 cm^{-1} and 2900.00 cm^{-1} as well as slightly shifting of wave numbers in H-O-H symmetric bending vibrations , P=O stretching vibrations and acid phosphate was due to doping effect. The shifting of wave numbers of the vibrations signifies that some changes related to impurities.EDAX revealed that the change in molar ratio causes manganese ions to reacts with phosphorus than calcium.

Acknowledgements

The authors are thankful to The Principal Shri V S Naik Arts, Commerce & Science College Raver Dist.- Jalgaon for providing experimental facilities.

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“BIO-EFFICACY OF *SOMECARPOUSANACARDIUM SEED*EXTRACTS AGAINST *CALLOSOBRUCHUS CHINENSIS* L. (COLEOPTERA: BRUCHIDAE) ON *PHASELOUS ACONITIFOLIUS GRAINS*”.

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ABSTRACT

The study was carried out to determine potential biopesticidal effect of *Somecarpousanacardium* fruits extract against the store grain pest *C.chinensis* L. infestation in *Phaselousaconitifolius grains.* The dry fruits were used for extraction with Chloroform solvent. Result indicates that raw fruit oil was most effective grain protectant for controlling the attack of pest.

KEY WORDS: Efficacy, fruits extract, *Callosobruchuschinensis*, *Somecarpousanacardium.*

INTRODUCTION

Insect pests cause damage to stored grains and processed products by reducing their dry weight and nutritional value (Sinha 1985). The pulses beetle, *Callosobruchus chinensis (L)*is cosmopolitan post-harvest pestsof stored pulses. It causes quantitative and qualitative losses shown by seed perforation, reduction in weight, market value and reduced germination of seeds (Anonymous 1989).However, storage of grains is one of the most important because pest can infest grains all around the year under favorable atmospheric conditions like temperature, humidity etc.(Ahmed *et al*.(2003)Gujar and Yadav (1978) reported that pulses attacked by several insect pest including *Callosobruchuschinensis (L).* According to Aslam and Suleman (1999)*C.chinensis (L)* is a destructive pest under storage sincethe larvae bore into the pulse graincauses damage 55-60% loss in seed weight and 45.50-66.30% loss in protein content which becomes unsuitable for human consumption, viability for replanting or for the production of sprouts.Tripathy*et al*.(2001) tested effect of plant powder and extract against *C.chinensis*attacking black gram. Al-Lawati*et al*.(2002) also reported that potential effect of plant powder and extract against oviposition, adult emergence and mortality of *C.chinensis.*

At present insect pest control methods in storage condition the indiscriminate use of synthetic insecticides and fumigants led to number of problems including insect pest resistance, toxic residue in food grains(Fishwick,1988), environmental pollution (WMO 1995) and increasing cost of application.

The present studies were undertaken to evaluate the biopesticidal potency of plant *SomecarpusAnacardium*plant seed extract against the *C.chinensis (L).*,in stored grain*P.aconitifolius.*

MATERIALS AND METHODS

1. **Rearing of *Callosobruchuschinensis*-** adults were collected from naturally infested *Phaselousaconitifolius*grains from godowns and ware houses of city. The insect pests werereared on clean, uninfected and sterilized grains. 10 pairs of adult insect pest were released in 1 kg seeds in glass jar and covered with muslin cloth to ensure ventilation. The jar was maintained at room temperature 28±2 ^{o}C at relative humidity 70 ± 5^{o} after 48 hours adults were removed and the jar was left for 45 days to obtain adult beetles and subsequently these beetles were used for the experiment.

2. **Preparation of seeds extract-** the seeds of *Somecarpusanacardium*were purchased from the local marketand washed with distilled water and air dried and ground powder using domestic grinder. The powdered materials were separately subjected to chloroform extraction. Then crude extract were filtered and filtrate were used for respective concentration prepared by dilution. 25 gms of disinfected pulse grains were taken in each of the glass bottle and10 males and 10 females were released in bottle containing 25 gm of the grains and were allowed to grow the adult females laid the eggs on the grains. One bottle was maintained as a control and others were used for experiment. 0.4, 0.8, 1.2, 1.6 and 2.0 ml seed extract was dissolved in respective solvent diluted extract were added in each bottle containing 25 gm grains. Bottles were kept for 48 hrs. in well ventilated room to evaporate the chloroform. After 48 hrs freshly hatched male and female from stalk culture were released in each of control and experiment. The mortality of adults released was observed for 24 hrs and 96 hrs of the exposure in different concentration of plant fruit extract. After the death of all adults, the no of eggs laid in each of the control and experimental bottle counted. Then infected grains in each bottle were counted and record weight. of 100 infected grains from each bottle was taken and recorded. Where the number of infected eggs was less the available infected eggs from the respective set was weighted and converted to that of 100 eggs.

Similarly wt. of 100 noninfected grains was taken and recorded. 25 grm of seeds of *Phaselousaconitifolius*contained on average 1086 grains. The mortality, number of eggs laid , number of grain infected and number of adults emerged out in different concentrations of the extract were estimated. Protein contents of noninfected grains and hollow grains from different experimental sets were estimated by the method of Lowry's et al.,(1951).

OBSERVATIONS:

Table: Effect of chloroform extract of *Somecarpusanacardium*seed (Golambi)on the weight and protein loss in grains of *P.aconitifolius*bythe stored grain pest, *C.chinensis*

Dose in ml	Initial weight of grains	Total no of grains	No. of infected grains till adult death	Wt. Of 100 solid grains	Wt. of 100 hallow grains	%wt. loss in infected grains	% wt. loss in total grains	Protein content of solid grains	Protein content of hallow grains	Total protein loss %	% protein loss in total grains
(A)	**(B)**		**(C)**	**(D)**	**(E)**	**(F)**	**(G)**	**(H)**	**(I)**	**(J)**	**(K)**
Con -trol	25	1086±41	143	2.302±0.17	0.565±0.12	75.45	9.93	24.87±1.32	9.73±0.62	60.87	8.015
0.4	25	1086±41	13	2.302±0.17	1.32	42.65	0.51	24.87±1.32	18.13	27.10	0.324
0.8	25	1086±41	11	2.302±0.17	1.52	33.97	0.34	24.87±1.32	19.86	20.14	0.204
1.2	25	1086±41	1	2.302±0.17	-	-	-	24.87±1.32	-	-	0.000
1.6	25	1086±41	2	2.302±0.17	-	-	-	24.87±1.32	-	-	0.001
2.0	25	1086±41	Nil	2.302±0.17	-	-	-	24.87±1.32	-	-	

RESULTS AND DISCUSSION:

In the present investigation the bio-efficacy of*Somecarpusanacardium* seed extracts afford better protection to the infestation of *C.chinensis* the level of damage caused by *C.chinensis*in the control and treated grains of*Phaseolusaconitifolius* were calculated and are given in Table percent loss in the weight of the infected grains was 75.45 and the total grain loss 9.93 during the experimental period .present weight loss in infected and total grains was reduced in low concentrations of the chloroform extract of *Somecarpusanacardium* and was nill in above 1.2 ml per kg extract.

The whole grains of *Phaseolusaconitifolius*were found to have 24.87±1.32 percent protein while the infected hollow grains 18.13 and 19.86 % proteins on exposure to 0.4 and 0.8 ml chloroform extract of raw fruits of *Somecarpusanacardium* while present protein loss in total grains at the said concentrations was only 0.324 and 0.001.

Pradhan et al., 1963 reported that Neem seed kernul possess an extra ordinary repellent properties. Rouf etal., 1996 shows that mixing of Neem leaf powder with lentil seeds resulted in reduced oviposition and adult emergence of the pulses beetle*C.chinensis.*

CONCLUSIONS

The result ofour study reveals that chloroform diluted seed extract of *Somecarpusanacardium*as superior natural insecticides for controlling the store grain pest *Callosobruchuschinensis*at storage condition and it may play an important role to prevent loss of pulses and minimize the protein loss. It will also help to minimize the environmental pollution caused by the synthetic pesticides.

ACKNOWLEDGEMENTS

The authors are thankful to the Principal,Nanasaheb Y.N.Chavan Arts,Science and Commerce College,Chalisgaon,Dist.Jalgaon,for encouragement and laboratory facilities

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Studies on thermodynamic stability constant of amino acids with Yb(III) complexe.

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Abstract

The thermodynamic stability constant of the complexes were also calculated. The formation of complexes has been studied by Job's method. The results obtained of stability constant were good agreement. The metal-ligand and proton–ligand stability constant of Gd(III) with amino acids (L-GLutamic acid + serine) were determined at various ionic strength in 1% potassium chloride solution by pH metric titration. $NaClO_4$ was used to maintain ionic strength of solution.

Key word: Amino acid, Stability constant, ionic strength.

Introduction

Glutamic acid is considered as the essential amino acid for the protein synthesis. Glutamic acid offers the several health benefits and maintains the healthy functioning of body. It supports the good health of immune system, digestive system as also aids in the energy production in the body. Nehete et al have studied the effect of ionic strength on stability of complexes[1]The effect of ionic strength of medium on stability constant of cu (II) complex of 2-amino-5- Chloro benzene sulphonic acid at 301K[2]. The stability constant of Co (III) with 1-Amidino-0-methylurea as primary ligand at different ionic strength [3]. The influence of ionic strength of medium on complex equilibria [4]. Association and dissociation constant of Pr (III) complexes with 3-(2-hydroxy-3-Iodo-5-methyl phenyl) 1, 5 diphenyl pyrazoline at different ionic strength[5]. Stability constant of vanadium with glycene at various ionic strength by potentiometric titration technique [6] . The stability constant of Mo (IV) with Iminodiacetic acid at different ionic strength maintain by using sodium per chlorate was investigated [7]. Effect of ionic strength and solvent effect on thermodynamic parameters [8]. They have also studied the mechanism of protonation and complex formation of binary complexes of La (III), Ce (III), Pr (III) and Nd (III) with aminopyridines. The apparent metal-ligand stability constants and confirmation of complexes studied [9] .The composition of complexes were confirmed by Job's method as modified by Vasburgh and Gold [10].

In this work, we have determined the pK, metal-ligand stability constant at different ionic strength. We have studied in the 1% potassium chloride. We have thought of interest to study the effect of ionic strength on thermodynamic parameters of complexes of L-GLutamic acid with Gd(III) metals in 1% sodium benzoate by pH metrically and spectrophoto metrically.

Experimental

The pH measurements were carried out with equip-tronic EQ-610 pH meter (accuracy ± 0.01 units) using combine glass electrode at 208 K. Pure rare earth nitrate (99.9% Pure) was used. Metal nitrate available from Sigma Aldrich Chem. Co., U.S.A. Metal nitrate was prepared in triply distilled water and concentration was estimated by standard method. The solution of amino acid was prepared in 1% potassium chloride. The pH metric readings in 1% potassium chloride were converted to $[H^+]$ value by applying the correction proposed by Van Uitert Haas. The overall ionic strength of solution was constant maintains by adding $NaClO_4$. All the solutions were titrated with standard carbonate free NaOH (0.2N) solution at different ionic strength. The titration was carried out at ionic strength by adding $NaClO_4$ (0.02, 0.04, 0.06, 0.08 M)

The experimental procedure involved pH metric titrations of solutions of –

1) Free $HClO_4$ (A)
2) Free $HClO_4$ + Ligand (A+L)
3) Free $HClO_4$ + Ligand +Metal ion (A+L+M)

Data obtained from each titration is plotted as pH Vs volume of NaOH added and corresponding volume at successive pH for each set is determined and calculated. The metal–ligand stability constant of lanthanide metals complexes with amino acid were investigated spectrophoto metrically. The absorbances measured were carried out with Shimadzu UV-1800 ENG 240V, Japan spectrophotometer. $NaClO_4$ was used for maintaining the constant ionic strength. The different composition of metal ion ($1x10^{-4}$M) and ligand ion ($1x10^{-4}$M) were prepared in ten series. For determination of $\lambda_{max,}$ 50% metal ion solution at which maximum absorbance observed. The absorption of all composition was measured at constant wave length (λ_{max}) and at constant pH.

Result and discussion

In the present investigation the dependence of proton-ligand stability constant and metal-ligand stability constant on ionic strength of medium was examined by taking fix concentration of metal nitrate and ligand solution during pH metric titration. The system has been studied at 0.02, 0.04, 0.06, 0.08M ionic strength by varying the concentration of sodium per chlorate. The total ionic strength of medium is calculated by equation.

$$\mu = \Sigma\ 1/2\ \mathbf{C_i Z_i^2}$$

C_i , Z_i are the concentration and valences of i^{th} ion respectively.

The values of proton–ligand and metal-ligand constant of Gd(III) at different ionic strength 0.02,0.04,0.06 and 0.08M determined. These values were determined by using Irving-Rossotties method. From table-1, it was seen that the values of proton–ligand stability constant (P^K) decreases with increasing ionic strength of medium. The metal-ligand stability constant (logK) also decrease with increasing ionic strength.

The conditional stability constant of amino acid–lanthanide metal complexe were determined for all systems by using equation.

$$K= x / (a_1-x) (b_1-x) = x / (a_2-x) (b_2-x)$$

K= stability constant, x = Concentration of complex, a_1 and b_1 were concentration of metal ion and ligand before dilution. a_2 and b_2 were concentration of metal ion and ligand after dilution. The values of ‘x’ were calculated from graph optical density Vs % composition of metal ions in solution.

From table-2, it was seen that the good agreement among thermodynamic constant obtained from pH metry and spectrophotometrically.

Table1. Proton–ligand (pK) and metal-ligand stability constant (Log K) value for Yb(III) with amino acids at various ionic strength(μ)

μ	$\sqrt{\mu}$	$\sqrt{\mu}/1+\sqrt{\mu}$	$[\sqrt{\mu}/1+\sqrt{\mu}] -0.3\sqrt{\mu}$	pK	$LogK_1$	$LogK_2$
L-GLutamic acid **+ Yb(III)**						
0.02	0.1414	0.1239	0.0815	7.6167	6.15	3.50
0.04	0.2000	0.1667	0.1067	7.6458	5.50	3.25
0.06	0.2450	0.1968	0.1233	6.8842	5.35	2.75
0.08	0.2828	0.2205	0.1356	5.6448	4.70	2.60

Table 2. Metal-ligand stability constants (Log K) values obtained by pH-metry and Spectrophotometry technique (Ionic strength = 0.08m)

System	pH metry	Spectrophotometry
Yb (III)+ L-GLutamic acid	4.55	4.5257

Conclusion

The calculated values of stability constant at various ionic strength are high. From data the conclusion is, the complexes of amino acid with Gd (III) metal ion were quite stable at over all range of ionic strength. The values of conditional metal-ligand stability constant shows good agreement with the values determined by pH metrically.

Acknowledgement

Authors are thankful to the Prin. Dr. R.T. Chaudhari for kindly cooperation.

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P^{H} – METRIC STUDY OF SUBSTITUTED HETEROCYCLICDRUGS WITHTRANSITION METALSIN MIXED SOLVENT.

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ABSTRACT

In the present work, the interaction of transition metal ions with substituted heterocyclic drug Clarithromycin in 70% ethanol-water mixture at 303.15Khas been studied by pH metric method. The interaction has been studied at 0.02M ionic strength by Bjerrum method as adopted by Calvin & Wilson. The data obtained is used to estimate the values of proton-ligand stability constant (pK) and metal-ligand stability constant (logK). The above study shows1:1 and 1:2 complex formations takes place with substituted heterocyclic drug.

Keyword: Stability constant, substituted heterocyclic drug.

INTRODUCTION

Stability constant of complex compound is very essential forMRI, Catalysis for RNA cleavage, kinetics of reaction,Radiopharmaceuticals, Molecular recognition, Macrocycliccomplexes, Host-guest interactions, Enthalpy determination,Cation and Anion selective complexation, Supramolecularcomplexes, Action of Drug, Environmental effects. The medicinal properties of any molecule are checked by various physical methodologies. For theinvestigation of stability constant various techniques are utilizing such as potentiometry etc. pH-metric study isone of the best widely used technique because it has several superiority such as, it is easy to understand andwork, cheap technique etc.A pH meter is using to find the stability constant which is useful for the formation ofa complex in solution**[1-6]**.The stability of metal complexes with medicinal drugs perform greater role in thebiological and chemical activity**[7]**. The studies of metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport of metal ion in the biological kingdom.The selected substituted heterocyclic drug Clarithromycin is an antibiotic and used to treat various bacterial infections**[8]**. Numerous researchers**[9-12]**have studied the formation and stability constant of metal complexes with transition metals.Mane et. al. have been investigated the pH metric study of synthesized heterocylic compounds isoxazoles with Cu (II), Fe (II) metal ions at 0.1 M ionic strength at 303K in 70% dioxane-water **[13]**. Pandhare**[14]** have been investigated the study of stability constant of transition metal complexes with 7-Hydroxy Flavonesat 30°C in 50 % (V/V) dioxane - water medium and 0.1 M ionic strength. Azharuddin**[15]** has been investigated the stability constants of binary complexes of some rare earth and nuclear metal ions with some peptides at 0.1 M ionic strength pH-metrically. It is observed that there is formation of 1:1 and 1:2 complexes between metal ions and ligand. Pawar**[16]** has been studied the determination of stability constants of the complexes of some peptides with d block metal ions in ethanol-water mixtures at 300 Kat 0.1 M constant ionic strength pH-metrically.EbruMavloglu et al. have studied the stability constant of Ni(II), Co(II) ,Cu(II) and Zn(II) complexes of hypoxynthine at physiological condition by potentiometric method**[17]**. Vyas et.al.have determined the stability constant of binary complexes of d_{10} metal ions Cu(II),Ni(II),Co(II) and Mn(II) with substituted derivatives of coumarin by using Irving –Rossoti method at constant temperature 303 K and 0.1M ionic strength**[18]**.Tayadeet. al. have been studied stability constant determination of substituted Imidazolinone drugs pH-metrically at 0.1 M ionic strength in 70% DMF-water mixture at 298K **[19]**.

After review of literature survey, the detail study of complex under identical set of experimental condition is still lacking. It was thought of interest to study the chelating properties of substituted heterocyclic drugs under suitable condition with transition metal ions by pH metrically.

EXPERIMENTAL

Determination of stability constants:

The pH measurements were carried out with equip-tronic EQ-610 pH meter (accuracy ± 0.01 units) using combine glass electrode at 303.15 K. Pure transition metal nitrates and sulphates (99.9% Pure) were used. All metal nitrates and sulphates available from Sigma Aldrich Chem. Co., U.S.A. Metal solution was prepared in triply distill water and concentration was estimated by standard method. The solution of drug was prepared in solvent .The pH metric reading in 70% ethanol-water mixture were converted to [H^+] value by applying the correction proposed by Van Uitert Haas**[20]**. The ethanol was purified by the method described by Vogel**[21]**.The overall ionic strength of solution was constant maintains by adding $NaClO_4$. All the solutions were titrated with standard carbonate free NaOH (0.2N) solution at constant ionic strength (0.02M). The titration was carried out in double wall glass jacketed titration cell connect to the constant temperature circulating bath. The temperature of reaction cell is constant by circulating water from Thermostat (0.1°C). The experimental procedure involved pH metric titrations of solutions of –

1. Free $HClO_4$ (A)
2. Free $HClO_4$ + Ligand (A+L)
3. Free $HClO_4$ + Ligand +Metal ion (A+L+M) against standard NaOH solution.

Data obtained from each titration is plotted as pH Vs volume of NaOH added and corresponding volume at successive pH for each set is determined and calculated.

RESULTS AND DISCUSSION

Proton-ligand stability constant (pK)

The substituted heterocyclic drugs may be ionized as acid having replaceable H^+ ion from ^-OH group. Therefore it is represented as HL,

$$HL \longrightarrow H^+ + L^-$$

The titration data used to construct the curves between volume of NaOH and P^H. They are called free acid and acid-ligand titration curves. It is observed from titration curves, the ligand titration curve start deviating from the free acid curves at P^H =3.5 and deviating continuously up to P^H =12.0. The deviation shows that dissociation of proton in substituted drugs.

The average number of proton associated with the ligand (n_A) was determined from free acid (A) and acid - ligand (A+L) titration curves employing the equation of Irving and Rossotti**[22]**.

$$\bar{n}_A = \gamma - \frac{(V_2 - V_1)(E^0 + N)}{(V_0 + V_1)\,T^0_L}$$

Where,

V_0 = Initial volume of solution

V_1 =Volume of alkali required during free acid titration.

V_2 = Volume of alkali required during free acid +ligand titration.

N = Normality of sodium hydroxide.

E^0 = Concentration of mineral acid ($HClO_4$)

γ = Number of replaceable hydrogen ion.

T^0_L = Concentration ofligand

The P^K values were determined from formation curves (n_A V/s P^H) by noting the P^H at which n_A=0.5 (half integral method). The accurate values of pK were calculated by point wise calculations which are presented in table-1.

Table-1: Determination of proton-ligand stability constant (pK) of substituted heterocyclicdrugs at 0.02M ionic strength.

System	pK Values	
Clarithromycin	Half integral	Point wise calculation
	9.97	9.58

Metal-ligand stability constant (Log k)

Metal-ligand stability constant of metal chelates with some substituted heterocyclic drug were determinedby employing Bjerrum Calvin P^H metric titration method as adopted by Irving and Rossotti.

The metal-ligand formation number $\bar{n}$ () was determined from Acid-Ligand (A+L)and Acid-Ligand-Metal(A+L+M) titration curves employing the equation of Irving and Rossotti.

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N)}{(V_0 + V_2)\,n_A T^0_M}$$

Where,
V_0 = Initial volume of solution
V_3=Volume of alkali required during free acid + ligand + metal titration.
V_2 = Volume of alkali required during free acid + ligand titration.
N = Normality of sodium hydroxide.
E^0 = Concentration of mineral acid ($HClO_4$)
T^0_M = Concentration of metal

The values of metal ligand stability constant (log K_1 and log K_2) were determined from formation curves ($\bar{N}$/s P^H) by using half integral method. The accurate values of log K_1 and log $K_2$are presented in table-2.

Table-2: Determination of metal-ligand stability constant (logK) metal ion withClarithromycin at0.02M ionic strength.

System	Logk_1	Logk_2	Logk_1–Logk_2	Logk_1 / Logk_2
Ni (II) –Ligand	7.90	4.85	3.05	1.6288
Cu (II) –Ligand	7.85	4.70	3.15	1.6702
Zn (II)-Ligand	7.25	4.40	2.85	1.6477
Mg (II) –Ligand	7.30	4.50	2.80	1.6222

CONCLUSION

The result shows the ratio of Logk_1 / Logk_2 is positive and greater than one in all cases. The higher value of ratio (Log k_1 / Log k_2) indicates more stablestepwise complex formation takes place. This implies thatthere is little or no steric hindrance to the addition of secondary ligand molecule. The difference betweenlogK_1 and logK_2 was sufficiently large indicates the stepwise formation of 1:1 and 1:2 complexes.

ACKNOWLEDGEMENTS

The Authors are thankful to Principal, D. D. N. Bhole College, Bhusawal for providing necessary facilities and for kindly cooperation.

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