Spiritus Scientiae

STUDENTS' JOURNAL

CHRISTIAN COLLEGE CHENGANNUR, KERALA
Vol. 2 Issue 1 Dece. 2018

www.christiancollege.in
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SPIRITUS SCIENTIAE

Place of Publication	:	Christian College Chengannur, Kerala
Periodicity of Publication	:	Anual
Chief Editor	:	Dr. Achamma Alex
Editor	:	Dr. John George Athyal & Dr. Hysen Thomas
ISSN No.	:	
Printed and Published by	:	Dr. Achamma Alex , Principal, Christian College Chengannur, Chengannur - 689 122, Kerala
Nationality	:	Indian
Address / Ownership	:	Christian College Chengannur Chengannur - 689 122, Kerala

I, Dr. Achamma Alex, do hereby declare that the particulars given above are true to the best of my knowledge and belief.

Sd/-

Dr. Achamma Alex,
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Contents

Editorial

It is with great pride, boundless joy and enthusiasm that I invite you to read the second issue of Spiritus Scientiae. An enormous amount of work goes into the completion of each issue of this journal that aims at providing a wonderful platform for budding researchers to announce before the academia how they are on a move to carve out their own space in the world of 're- search' where boundaries are fast receding. Earlier, we used to stick on to the discipline of our choice at the UG level, till the very end of our educational period. Now a days, however, inter disciplinary studies and researches replace the older practises, and we see how Arts, Fine Arts, Humanities and Science have an inter dependent existence. Every issue or situation taken up as research problem is analysed in a multidimensional manner that require the expertise of academic experts from numerous fields that make the study truly inter disciplinary. Our educational institutions have to encourage students to take up more and more of such research projects and come up with suggestions and solutions that could alleviate human problems and sufferings bearing in mind the oft quoted lines of Alexander Pope , the famous Victorian poet, who wrote:

A little learning is a dangerous thing;
Drink deep, or taste not the pierian spring:
The shallow droughts intoxicate the brain,
And drinking largely sobers us again.

Let our young researchers delve deeper into every problem and resurface with solutions to make like possible and viable on this planet!

Prof. Linchu Elizabeth Samuel

Evaluation of Kinetic triplets and the evolution of magnetic properties with micro-structural transformations in and Fe based metallic glass.

Hysen Thomas[1] and **M. R. Anantharaman**[2]
[1]Department of Physics, Christian College, Angadical, Chengannur - 689 122, Kerala, India
[2]Department of Physics, Cochin University of Science and Technology
, Cochin 682 022, Kerala, India
Corresponding author email: hysenthomas@gmail.com

Fe based magnetic metallic glasses are widely sough after due the thesuperior magnetic properties exhibited by these materials. The kinetics of crystal;lization of $Fe_{40}Ni_{38}B_{18}Mo_4$ alloy is investigated using isokinetic, isoconversion and model free isoconversion methods. The kinetic triplets estimated using the various models were compared and analysed.

Introduction

Recently there is renewed interest in metallic glasses due to their potential applications in soft magnetic devices[1]. The presence of short-range order combined with the absence of crystal defects such as grain boundaries and dislocations make them cheap alternatives for various applications. Metallic glasses are usually synthesized by rapid quenching techniques with cooling rates often exceeding 10^6K/s. They can also be synthesized by viz, melt quenching, splat cooling, laser glazing, electro-deposition, ion implantation, swift heavy ion irradiation, and vapour deposition[2].Synthesis of nano-crystalline materials, derived form amorphous metallic glasses through thermal treatments, have opened up new vistas for tailoring the properties of these classes of materials[3,4]. The extreme magnetic softness exhibited by many of these amorphous and nanocrystalline alloys can be attributed to the averaging of anisotropies over grains and the counterpoise between exchange correlation length and grain size. They exhibit ferromagnetism characterized by high saturation magnetization, vanishing macroscopic anisotropy, negligible magnetostriction and large magnetic permeability [3]. $Fe_{40}Ni_{38}B_{18}Mo_4$ is one such alloy that is widely used for sensor

and soft magnetic applications. Boron and molybdenum were added to Fe and Ni to improve the glass forming ability, increase thermal stability and to impede grain growth. The material is reported to have two-stage crystallization as is usually the case with most Fe based metallic glasses[5]. Its softness after nanocrystallization can be ascribed to its two phase nature consisting of an ultra-fine grained Fe-Ni phase embedded in the remaining boron rich amorphous matrix. The two phases has Curie temperatures of ≈ 760 K and ≈ 485 K respectively and their contributions to the total saturation magnetisations are ≈ 46 emu/g and ≈ 49 emu/g respectively. It has room temperature saturation magnetization of 8.8 kG. Its increased curie temperature of 626 K and low saturation magnetostriction of 12 x 10^{-6} accounts for the good soft magnetic properties exhibited by this material. The material can be tailored by annealing to induce nanocrystallization for inducing superior soft magnetic properties such as H_c= 7 mOe, M_r = 7.5 kG and a dc permeability of about 45000[3].

Activation energy of crystallization is aimportant parameter that decides the application potential of metallic glasses. Heat treatment of metallic glasses can induce crystallization in the material by supplying thermal energies to overcome the activation energy for crystallization. The material devitrifies into a supersaturated solid solution which consequently decays into a mixture of solid solution and crystalline phase or phases [6]. In any material, crystallization proceeds through nucleation, subsequent growth and Oswald ripening.Without losing generality one can combine the energy barriers for all these processes into a single activation energy E_c[7]. The approximation is warranted by the reasoning that for most of the materials these three stages has overlapping energy curves.

There are discrepancies between the activation energies E_c of different crystallization stages of $Fe_{40}Ni_{38}B_{18}Mo_4$ alloy reported by various investigators. Antonione et al[8]was the first to report the crystallization dynamics of the material. Using non-isothermal calorimetric studies he had reported two-stage crystallization with activation energies 3.07 eV/atom and 3.46 eV/atom respectively for the two phases. However Majumdar and Nigam [9]observed three stage crystallization in the material. Cubrera et al [10] had done a quantitative investigation on the crystallization kinetics and activation energies using both

non-isothermal (2.984 and 3.678 eV/atom) and isothermal methods (2.984 and 4.673 eV/atom) using Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA)and resistivity. Nicolai [11] has found five-step crystallization in the sample. Jen et. al.[12] reported the activation energy for α-Fe to be 2.92 eV/atom, and for (Fe, Ni) B to be 3.85 eV/atom. The above discussion suggests that reports on the crystallization dynamics of $Fe_{40}Ni_{38}B_{18}Mo_4$ are rather scanty and there exists diverse opinions about the activation energies for the nucleation and phase separation.

Metallic glasses are considered to exhibit structural and chemical disorder because of the high quenching rate involved in the fabrication process. In devitrification of metallic glasses, the nucleation rate sigmoidally increases from zero to an ultimate steady state value. Kolmogorow-Johnsen-Mehl-Avarami (KJMA) model replicate the nucleation rate with a sigmoidal curve and the model was widely used for evaluating Avarami exponentwhich signifiesthe dimensionality of crystal growth.

In the present work we report the crystallization dynamics of $Fe_{40}Ni_{38}B_{18}Mo_4$ employing DSC, X-Ray Diffraction (XRD) and different analysis methods like isokinetic and isoconversionalmethods. A precise knowledge about the kinetics of crystallization is extremely important to determine the activation energy of crystal growth from DSC data. The present study employs techniques like DSC to establish the mechanism of crystallization and to evaluate the activation energy of crystallization and Avarami exponents.

Experimental

High purity alloy ribbons with composition $Fe_{40}Ni_{38}B_{18}Mo_4$ prepared by melt quenching technique were subjected to X-ray diffraction to confirm their amorphous nature. The ribbons were 20 nm in thickness and 25 mm in width. They were subjected to non isothermal DSC studies for heating rates 5, 10, 20, 25 K/min. The activation energies were estimated employing the isokinetic and isoconversional techniques. Based on the results of DSC studies the samples were subjected to thermal annealing at a high vacuum of $\approx 10^{-6}$ Torr at temperatures 100, 200, 300, 400 and 700ºC. The sample is heated to the annealing temperature at a heating rate of 5 K/min and is maintained at that temperature for one hour and subsequently cooled with the same ramp rate. The XRD pattern of the METGLAS

samples, pristine as well as annealed were recorded with Rigaku D-max-C X-ray diffractometer using CuK_α radiation (λ=1.5405 Å). The average particle size is determined from the measured width of their respective diffraction curves using Scherer formula $D = \left(\frac{0.9\lambda}{\beta \cos\theta} \right)$, β is the full width at half maximum [FWHM]. The hysteresis loop parameters namely saturation magnetisation (Ms), coercivity (Hc) and retentivity (Mr) of the metglas samples were evaluated using a vibrating sample magnetometer (VSM) (model: EG & G PAR 4500) in the parallel and perpendicular fields (magnetic field parallel and perpendicular to the film plane) at room temperature for both pristine and annealed ribbons.

Results and Discussion

Theoretical Models

Kolmogorow Johnson MehlAvarami (KJMA) kinetic equation is formulated based on different assumptions and is assumed to be valid when the growth rate of new randomly distributed nuclei is controlled by temperature and independent of time and the growth rate is linear [13]Deviations from predictions of KJMA model can happen if one or more of these conditions are not satisfied.

Phase transformations in glassy materials are modeled using the KJMA transformation rate equation derived for isothermal heating experiments. The equation is

$$\frac{d\alpha}{dt} = nk(1-\alpha)[-\ln(1-\alpha)]^{\frac{n-1}{n}} \quad 1$$

Where α is the degree of crystallite volume fraction transformed at time t, n the avarami exponent and k the rate constant obeying an Arrhenius type relation

$$k = k_0 \exp(-\frac{E}{RT}) \quad 2$$

where k_0 the pre exponential factor , E the activation energy and R the universal gas constant.

The isoconversional techniques are based on the kinetic equation

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad 3$$

where k(T) is the rate constant given by equation 2 and f(α) is the model used to explain the reaction. The integral form of the above equatin can be obtained by substituting 2 in 3 and integrating by separation of variables $\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta}\int_0^{T_f} \exp(-\frac{E}{RT})\,dT = \frac{k_0 E}{\beta R}\int_{y_f}^{\infty} \frac{\exp(-y)}{y^2}\,dy$ where, $y_f = \frac{E}{RT_f}$ and T_f is the temperature at a particular equivalent stage of crystalline transformation fraction (α) for different constant heating rates β. The integral in the above equation is called the temperature integral or Arrhenius integral. The equation can be extended to non isothermal conditions by scaling't' with the equation $T = T_0 + \beta t$. However according to Henderson this is valid in certain special circumstances in which the growth proceeds from a system saturated with nuclei[14]. He also argued that the conversion factor α depends on the thermal history on the material. Model free isoconversional methods are widely used to give accurate values of activation energies. Isoconversionmetods are generally categorized into two. One set of methods springs by approximating the temperature integral[15] using various approximations. This methods includes the Kissinger-Akahira-Sunose method, Flyn-Wall Ozawa Method and Starink models[13,16–19]. The other set of models even though does not use any approximations but rely on the determination of reaction rate at an equivalent stage of the crystallization process for various heating rates. Friedman method falls into this category[13]. Starink has provided an in depth discussion about the various isoconversional methods and their accuracy in estimating the kinetic triplets ($(\alpha)k_0$ and E)[13]. The aim of this work is to estimate the kinetic parameters for the alloy $Fe_{40}Ni_{38}Mo_4B_{18}$ from nonisothermal DSC data using the various isoconversionalans isokinetic methods so as to have a comparative estimate of the values predicted by various models.

Discussion

The DSC of the as-prepared ribbon samples were conducted at constant heating rates of 5, 10, 20 & 25°K min^{-1} to investigate the inherent thermodynamics governing the crystallization process (figure 1.1.).

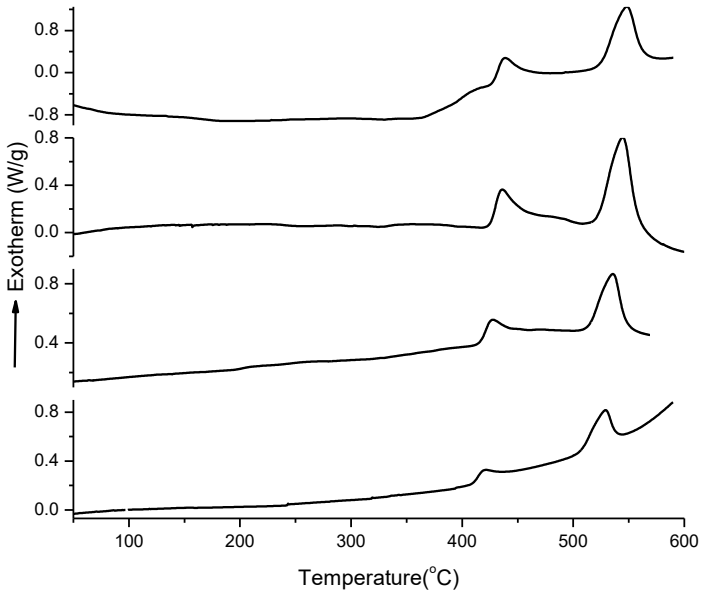

Figure 1.1 DSC thermograms of METGLAS ribbon at different heating rates

The first crystallization peak inception occurs at T_1 = 699 K while the second one is at T_2 = 809 K (heating rate15 K min^{-1}), and up to 900 K, on DSC trace, no other thermodynamic events were found which is the characteristic response showed by Fe rich amorphous alloy materials with low B content. However the small kink just before the first pertinent peak in the DSC trace at a heating rate 20 K min^{-1} can be ascribed to the structural relaxation, chemical ordering and glass transition in the material with thermal gradients. This type of thermal relaxation may be prominent near the glass transition temperature, which is revealed as an endothermic peak in the DSC spectrum due to change in specific heat. The total heat content for this thermodynamic event is 11.8 J/g.

Structural Studies Using XRD

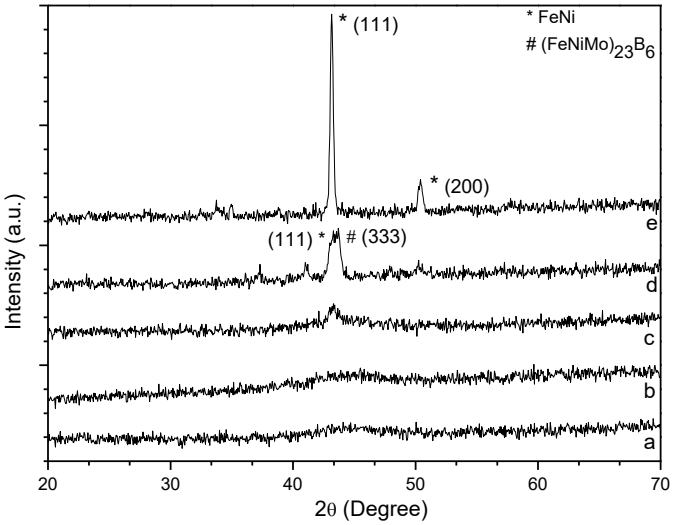

Figure 2: XRD of metglas ribbon a) Pristine b) annealed at 100^{o}C c) annealed at 300^{o}C d) annealed at 400^{o}C e) annealed at 700^{o}C.

The x-ray diffraction pattern of the unannealed metglas ribbons are shown in Fig 2 The pristine films show broad diffraction peaks, which indicate their amorphous nature and the fine dispersion of Fe and Ni in the sample. The crests in as quenched samples are in harmony with the earlier reports on crystallization of metglas[9]. The amorphous peak in pristine sample can be attributed to FeNi solid solution[5]. Evidence of the earlier assumption of the existence of a metastablestate of metastable equilibrium for the quenched alloy is found in the x-ray diffraction pattern of the pristine alloy. The basic argument to support this assumption emerges from the fact that after annealing the glass at 100 and 300 distinct Bragg peaks were noticeable at the position the braod peak appeared in the pristine sample. The ribbons annealed at 400^{o}C in vacuum possess heterogeneous microstructure consisting of FeNi and $FeNiMo_{23}B_6$. At temperatures above the crystallization temperatures of the first phases (FeNi at

420°C) crystallites tends to grow to micrometric dimensions. Fig shows the XRD spectrum of ribbons annealed at700 °C. There is progressive grain growth of FeNi phase with increase in annealing temperatures. Above 400 °C, $FeNiMo_{23}B_6$ phase starts to appear whose presence is reported to have been deleterious to the soft magnetic properties [20]. The intensity of boride phase increases with annealing temperature at the expense of the FeNiMo phase, while the FeNiMo crystallite size increases. At 400 anneal almost 55% of the crystalline volume fraction were FeNiMo particles of size~13.37 nm, substantiating the classification of $Fe_{40}Ni_{38}B_{18}Mo_4$ as a nano-crystalline soft magnetic alloy

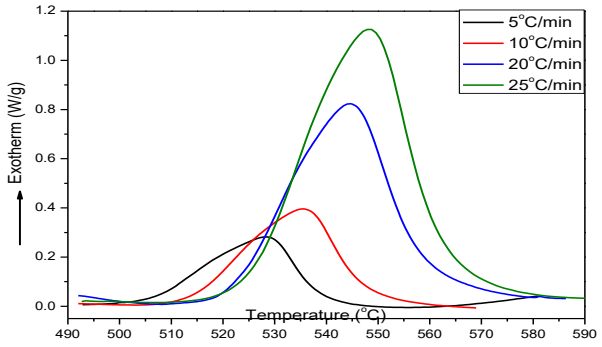

Figure 3:DSC Peak of FeNiMoB corresponding to the first crystallization at different heating rates. The shift in peak position towards high temperature with increase in heating rate is clearlyvisible.

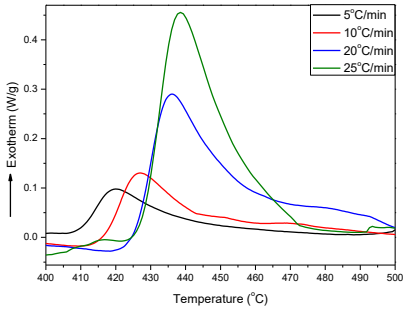

Figure 5: DSC Peak of FeNiMoB corresponding to the second crystallization at different heating rates. The shift in peak position towards high temperature with increase in heating rate is clearlyvisible.

Applicability of KJMA model

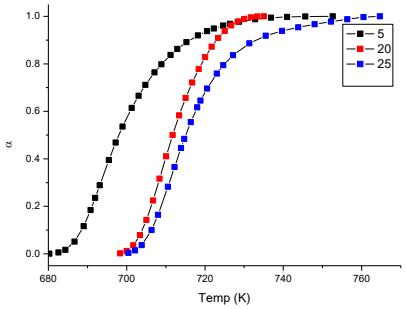

Figure 6: Crystalline volume fraction versus temperature for the first crystallization peak

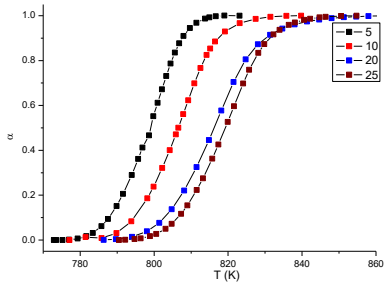

Figure 7: Crystalline volume fraction versus temperature for the second crystallization peak

The kinetics of phase transformations is usually modeled using the well-known KJMA equation [21]. The equation predicts an “S type sigmoidal curve” for the transformation with slow rate of transformation at the beginning which then accelerates and there after decelerates. The KJMA equation is erected on the basic assumption of random distribution of nuclei in the material. Figure 5 and 6 corresponding to the first and second crystallization steps show a sigmoid curve. However that doesn’t mean the KJMA model can readily simulate the

crystallization event. Applicabilty of the KJMA equation to a transformation can be verified by the linearity of the plot of $\ln[-\ln(1-\alpha)]$ verus $\frac{1}{T}$. However this method is widely accepted to be unreliable. Another validity check given by Malek invloles plot of the function $z(\alpha) = \frac{d\alpha}{dT}T^2$ verus α[22]. For the KJMA equation to be valid the maximum of this plot should fall within $0.62<\alpha_p(z_{max})<0.64$. The plot of $z(\alpha)$ verus α for both crystallization peaks are shown in figure below. Another validity check for KJMA is to plot $y(\alpha) = \left(\frac{d\alpha}{dT}\right)\exp(\frac{E_c}{RT})$ verus α. The maximum of y(α) plot depends on the value of n and it is equal to zero if n< 1 and greater than 0 if n>1 [23].

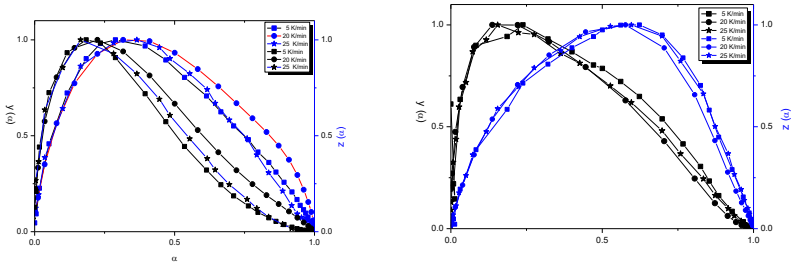

Figure 8: Plot of y(α) and z(α) versus a for the a) first crystallization step and b) second crystallization step.

The above plot clearly shows that the first peak of crystallization does not follow the KJMA model. The maximum of y(α)=0.21 and z(α)=0.32 which is clearly different from the value for KJMA model However the second peak have y(α)=0.132 and z(α)=0.624 suggesting the applicability of KJMA model. Hence for evaluating the kinetic triplets for the first crystallization step it is required to apply other models.

Table II: Local activation energies for the first and second crystallization peak corresponding to different conversion factors estimated using the KAS, Friedman and OFW methods.

	Activation Energy (kJ/mol)					
	Peak 1			Peak II		
α	KAS	FRIEDMAN	OFW	KAS	FRIEDMAN	OFW
0.1	371	373	344	-	402	463
0.2	379	389	351	-	396	448
0.3	404	407	359	-	394	437
0.4	412	421	364	450	391	430
0.5	-	-	-	435	390	430
0.6	419	468	395	424	373	413
0.7	351	471	403	416	354	407
0.8	358	467	416	416	342	388
0.9	-	-	-	399	337	363

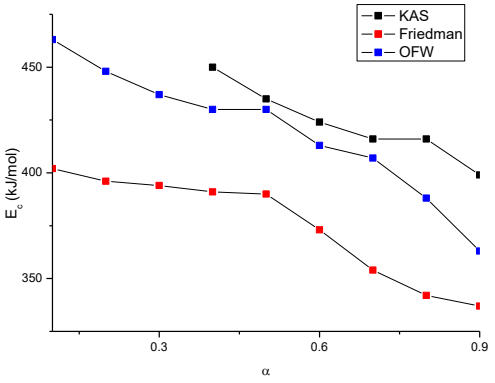

Figure 9: Graphical representation of the variation of local activation energy with conversion factor estimated using different models

Linear Integral Iso-conversional Techniques

Kissinger-Akahira-Sunose Method

This technique suggested by Kissinger, Akahira and Sunose use an approximation put forward by Coats and Redfern tomodify the temperature integral. According to this method $ln\frac{\beta}{T^2} = \ln\left(\frac{k_0R}{Eg(\alpha)}\right) - \frac{E}{RT}$ where T is the temperature corresponding to a particular conversion factor . From the slope of the plot of $ln\frac{\beta}{T^2}$ versus 1000/T gives $-\frac{E}{1000R}$ from which E value can be estimated. Special cases of this general model were also reported in literature based on choosing specific values of temperature based on certain conditions.

(i) Kissinger Model

This model assumes maximum reaction rate as well as constant conversion factor at the peak crystallization temperature. $ln\frac{\beta}{T_p^2} = \ln\left(\frac{k_0R}{E}\right) - \frac{E}{RT_p}$. A slope of the plot of $ln\frac{\beta}{T_p^2}$versus $1000/T_p$gives $-\frac{E}{1000R}$ from which E can be evaluated. From the intercept the preexponential factor k can also be evaluated. The analysis gives an activation energy of 331 and 429 kJ/mol. The frequency factor is evaluated as $6.79x10^{22}$$6.40x10^{25}$ for the first and second crystallization event respectively.

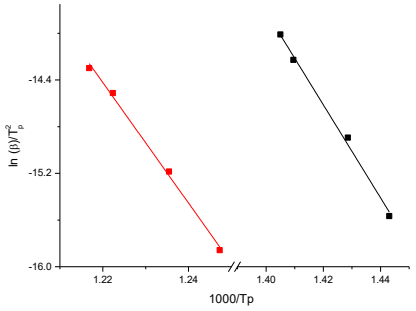

Figure 10: Kissinger Plot corresponding to the first and second crystallization events.

(ii) Augis and Bennet Method

This method is a variant of Kissinger method and incorporates the onset temperature of crystallization also for the calculation of activation energy. This method is reported to be one of the most accurate method for evaluating E. $ln\frac{\beta}{T_{p-T_0}} = \ln(k_0) - \frac{E}{RT_p}$. The values of E and ko can be estimated from the slope and intercept of the straight line fit to the plots of $ln\frac{\beta}{T_{p-T_0}}$ versus 1000/Tp. Further $n = 2.5\frac{T_p^2}{\Delta T\, {}^{E}/_{R}}$ where ΔT is the FWHM of the DSC peak. The kinetic triplets are [349 (E), 1.56 (n) and 7.75x10^{24} (k0)] and [498, 1.28 and 5.1x10^{30}] for the first and secod crystallization step respectively.

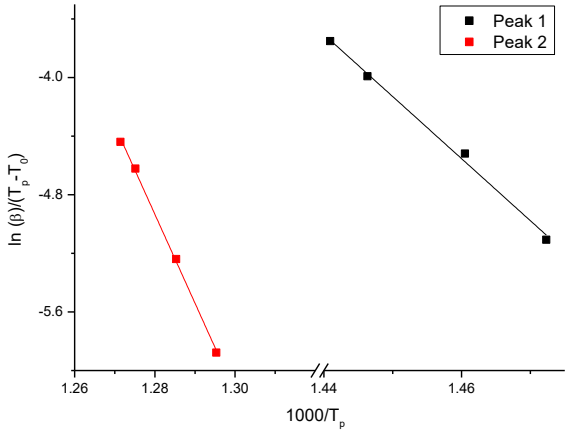

Figure 11: Augis and Bennet plot for the two crystallization steps

. Avarami's analysis of nucleation and growth process leads to a value n = 1.5 if all the nuclei are present at time t = 0 and the subsequent growth of particles is parabolic. Heating the first crystallization step favors parabolic growth of crystallites. According to Christian [19], the Avarami exponent for the first phase with n = 3.5 signifies nucleation with constant nucleation rate, while the secondary phase with n = 1.2 signifies growth by diffusion without nucleation.

This fact also agrees partially with investigation by other techniques that α-FeNiMo crystallites first grow in size and number, but then nucleation stops at the later stage of crystallization. However the assignment of n = 3.5 with the first stage of crystallization is fraught with error**.** This higher value for nucleation and growth in the alloy ribbon may be due to overlooking the presence of initial islands of compositional fluctuations in the alloy that can serve as nuclei for heterogeneous nucleation and growth during heating. During rapid quenching, some compositional fluctuation or even nuclei may be quenched in and a high quenching rate will reduce the size and number of such quenched-in nuclei reflecting in the Avarami exponent of the alloy [20]. The values of the Avrami exponent, n = 1, are consistent with diffusion-controlled growth with a nucleation rate close to 0. We have observed the second stage to have only one n value corresponding to n~1.28. This can be ascribed to the one dimensional growth of $FeNiMo_{23}B_6$ crystallites in the amorphous matrix.

(iii) Boswell method

Boswell method suggests an expression of the form $ln\frac{\beta}{T_p} = -\frac{E}{RT_p} + const.$ Plots of $ln\frac{\beta}{T_p}$ versus 1000/Tp can be used to estimate the activation energy. The activation energy calculated from the linear plots are 337 and 437 kJ/molrespectivelt for the first and second crystallization processes.

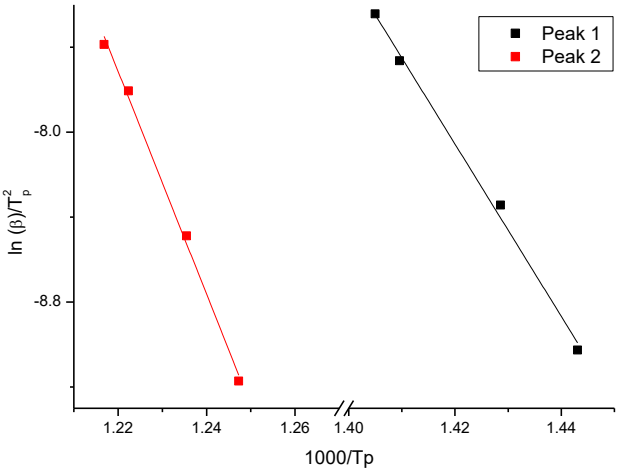

Figure 12: Boswell plot for the two crystallization steps.

Ozawa-Flynn-Wall method. In this method the temperature integral is modified using the Doyles Approximation ans assumes the form $ln\beta = -1.0516\frac{E(\alpha)}{RT_p(\alpha)} + const.$ The plots of $ln\beta$ versus 1000/T for various crystallization rate fractions can be used to evaluate the local activation energies. At T(a) =T(p) the equation is called the Ozawa equation which is a special case of the Ozawa Flynn Wall equation.

Transformation rate isoconversion methods

These methods do not make any mathematical approximations but rather needs the value of rate of transformation at $T_f(\beta)$. This method is also called liner rate isoconversion method.

Inserting equation in equation and taking the logarithm yields $\ln\left(\frac{d\alpha}{dt}\right)_f = -\frac{E}{RT_f} - ln\, f(\alpha)$. If in nonisothermal DSC measurements at different heating rates b the times at which the particular fraction of fraction transformed can be identified, then $f(\alpha)$ wll be a constant. For a particular transformed volume fraction, the

straight line fir to the plot of $\ln\left(\frac{d\alpha}{dt}\right)_f$ versus 1000/Tf can be used to evaluate the activation energy of crystallization. However since it is easier to evaluate $\frac{d\alpha}{dT}$ than $\frac{d\alpha}{dt}$, the denominator of the RHS of the equation can be changed using the relation $T = T_0 + \beta t$ yielding $\ln\left(\beta\frac{d\alpha}{dT}\right)_f = -\frac{E}{RT_f} - ln\, f(\alpha)$. Hence a plot of $\ln\left(\beta\frac{d\alpha}{dT}\right)_f$ versus 1000/Tf can be used to evaluate E. Since thie method do not assumes any functional form or approximation for $f(\alpha)$ it is called a model free method and is considered to be an accurate method for the estimation of activation energy. Special cases of this model are also reported in the literature

(i) Gao and Wang model.

When $T_f = T_p$ the Friedman model reduces to the Gao and Want model and suggest an expression of the form $\ln\left(\beta\frac{d\alpha}{dT}\right)_p = -\frac{E}{RT_p} - ln\, f(\alpha)$. The model suggests a very low activation energy of 275 and 382 kJ/mol respectively for the two pahses .

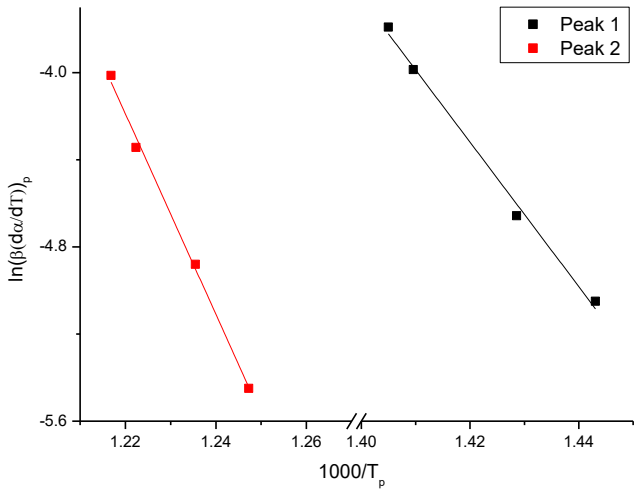

Figure 13:Gao and Wang plot for the two crystallization steps.

Isokinetic Methods

Matusita and Saka Method

When a glass is heated to ahigher temperature from room temperatre the crystal nucleation rate will be highest at a temperature above the glass transition temperature and will not be the the same as the temperature where the transformation rate is the maximum. During heating the nuclei are formed at a lower temperature and thereafter increase in size. Based on these assumptions Matusita and Saka dervived and expression $\ln[-\ln(1-\alpha)] = -n\ln(\beta) - 1.052\frac{mE}{RT}$

Hwere n is the Avarami exponent and m is a parameter that is connected to the dimensionality of crystal growth. From the slope of the straight line fit to the plot of $\ln[-\ln(1-\alpha)]$ verus $\ln(\beta)$ at any particular temperature gives the value of n. Aplot of of $\ln[-\ln(1-\alpha)]$ versus 1000/t gives a straight line and the m value can be extracted from the slope.

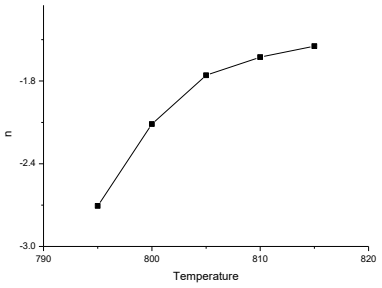

Figure 14: Variation of avarami exponent with transformation temperature estimated using Matusita and Sakamethod.

Conclusions

The analysis of DSC data to evaluate kinetic triplets employing the various analytical techniques, leads to the pertinent question ‘which is the best model for evaluating these paramaters?’

The isokinetic methods are widely used for the evaluation of activation energy of crystallization. This method gives a single activation energy for the entire crystallization process. Also the choice of a suitable model for simulating the reaction process is also cumbersome in isokinetic analysis. On the other handisoconversional models give activation energies as a function of conversion factor a. considering the fact that crystallization is a thermodymaic process and also the process of crystallization depends on the thermal history of the sample the assignment of different activation energies for the different stages of crystallization can be justified. Thusisoconversional methods are superior as far as the evaluation of activation energies are concerned.

In metallic glasses heat treatments produce profound changes in the microstructure of the materials and often results in a nanocrystalline material from an amorphous precursor. Also the nature of growth, size, dimension of growth and crystal structure affects the magnetocrystalline anisotropy, exchange interaction and their by the magnetic properties of the material. Hence from the application point of view in addition to estimating activation energy it is very important to probe the crystal growth mechanism. KJMA equation is widely used for modeling the crystallization dynamics in metallic glasses. Using this modelthe three kinetic parameters could be successfully estimated.However this is possible only if the system satisfies the fundamental assumptions made by the theory. If the system does not follow the KJMA kinetics then one should find a satisfactory model to describe the crystallization dynamics of the system.

Hence it can be concluded that isoconversional methods are superior in estimating the local activation energies, where as isokinetic methods are superior in estimating the crystallization dynamics of the system.

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Pragmatic quantification of optical band gap in CuO thin films

R. Jayakrishnan and Varun G Nair
Photovoltaic Research Centre, Department of Physics, Christian College, Chengannur-689122
Email: rjayakrishnan2002@yahoo.co.in

Abstract:

Most semiconductor devices operate by the creation of charge carriers in excess of thermal equilibrium. When the excess carriers arise, they can dominate the conduction process in the semiconductor material. This paper presents an alternative method to the widely used first order extrapolation of the optical absorption data. The results indicate that the explored alternate method yield values comparable to the widely used Tauc plot for optical band gap determination.

Keywords: Thin films; Optical Absorption; Tauc Plot; Inflection point;

1. Introduction:

Opto-electronics deals with interaction of electronic processes with light. Such a process is accompanied by an energy conversion (either electrical to optical or vice-versa). Devices which can interact in this way are made with semiconductors and the present work aims at understanding these properties in some of the binary and ternary compound semiconductors. Semiconductors are materials having electrical resistivity in the range 10^{-2} to 10^{9} ohm-cm, intermediate between good conductors (10^{-6} ohm-cm) and insulators (10^{14} to 10^{22} ohm-cm).[1] The characteristic feature that distinguishes semiconductors from metals and insulators is their band gap. The electrons in semiconductors can have energies only within certain *bands* lying between a ground state, [corresponding to electrons tightly bound to the atomic nuclei of the material] and the free electron energy, [corresponding to the energy needed by an electron to escape from the interactions inside the atoms]. Each 'energy band' corresponds to a large number of discrete and closely packed quantum states of valence electrons. In most semiconductors, the bands are filled up to a particular one called valence band (VB), above which the bands are almost empty at low energy conditions. The band lying just above the VB is called the conduction band (CB). Energy difference between the two

bands is referred to as the band gap of the material. If energy greater than the band gap of the material is supplied to electrons, the electrons in the VB can cross the band gap and reach the CB.[2]

Optical absorption is described qualitatively through the absorption coefficient α. In the simplest case, neglecting reflection or interference effects, if light of intensity I_o is incident on a material of thickness d with absorption coefficient α, the intensity of the transmitted light I is given approximately by Beer's law as [3]

$$I = I_o \exp(-\alpha d) \qquad (1)$$

The phenomenon of optical absorption in semiconductors can be divided into two: 1) Intrinsic and 2) Extrinsic optical absorptions.

Intrinsic optical absorption corresponds to photo-excitation of an electron from the VB to the CB. If the minimum of the CB is at the same position as the maximum of the VB in the k-*space*, a vertical transition takes place, involving the absorption of a photon only. Such a transition is called 'direct optical transition'. The minimum photon energy for absorption is given by $\hbar\omega = E_{GD}$, where E_{GD} represents the direct band gap of the material and the change in k upon making the transition, is given as $\Delta k = 0$.This is because the momentum associated with the photon is very small compared to the width of the Brillouin zone and can effectively be neglected.

According to quantum mechanical calculation, during direct absorption, the effect of light is treated as a first order perturbation. For a direct absorption, the transition probability depends on the square of the matrix element involving only the interaction of light with electrons and hence it is a first order process. The variation of the absorption coefficient α is given by [3]

$$\alpha^2 = (\hbar\omega - E_{GD}) \qquad (2)$$

A plot of α^2 versus $\hbar\omega$ gives a straight line whose intercepts with the $\hbar\omega$ axis corresponds to E_{GD}. Direct optical transitions are characterized by a rapid increase in the value of α when incident energy becomes greater than the band gap. If the minimum of the conduction band is at a different k-value compared with the highest point in the VB, the process should involve the absorption of a photon and simultaneous emission or absorption of a phonon. In this case, $E_{GI} = \hbar\omega_{\min} \pm E_{phonon}$ where E_{GI} is the indirect band gap of the material and E_{phonon} is the energy of the phonon involved in the process. Here a positive sign corresponds to phonon absorption while negative sign corresponds to phonon emission. The change in 'k' upon an indirect optical transition is given by $\Delta k = k_{phonon}$. In this case, the matrix element depends on

the interaction of photons and phonons with electrons and hence is a second order process. The magnitude of α is smaller than that obtained in direct optical absorption.

From a typical plot of α^2 vs. $\hbar\omega$ for a direct band gap material, the point of intersection of the straight line with the $\hbar\omega$ axis corresponds to the band gap of the material above which the optical absorption increases many folds. A typical plot of $\alpha^{1/2}$ vs. $\hbar\omega$ for an indirect band gap material gives two straight lines. If these two straight lines intersect the $\hbar\omega$ axis at $\hbar\omega_1$ and $\hbar\omega_2$ with $\hbar\omega_1 < \hbar\omega_2$, then[4]

$$E_{GI} = (\hbar\omega_1 + \hbar\omega_2)/2 \text{ and}$$

$$E_{phonon} = (\hbar\omega_1 - \hbar\omega_2)/2 \quad (3)$$

In semiconductors, imperfections in the crystal may introduce in the forbidden energy gap, discrete energy levels with localized wave functions. Absorption involving such imperfection levels are called 'extrinsic optical absorption'. The optical absorption can raise the electrons from the valence band to these localized states or from these states into the conduction band. The absorption constant is proportional to the density of absorbing centers, N by relation [3]

$$\alpha = S_0 N \quad (4)$$

where S_o is called the optical cross section for the absorption process. Optical absorption coefficient reaches appreciable value at energies corresponding to the transitions taking place between the levels or imperfections situated within the band gap. The magnitude and dependence on photon energy on S_o have been calculated by a variety of quantum mechanical approximation.

2. Materials and Methods

An inflection point is a point on a curve at which the sign of the curvature changes. In other words the point of inflexion is the point where the gradient of the curve stops falling and starts rising, or vice versa. Some authors also use the term the concavity in association with the inflection point as at this point a curve changes from being concave upward to concave downward or vice versa. Inflection points may be stationary points, but are not local maxima or local minima.[5] Another way of thinking about points of inflexion is that they are points where the gradient attains a maximum or a minimum. Therefore they may be located by finding those places where the second derivative is zero. The first derivative test sometimes distinguishes inflection points from points of extrema for differentiable functions. A necessary condition for a variable x to be an

inflection point is its second derivative should be equal to zero at *x*.[6] A sufficient condition requires that f(x+ε) and f(x-ε) should have opposite signs in the neighborhood of *x*.[7]

3. Results & Discussion:

Figure 1 represents the plot of absorbance versus wavelength for thin film samples carried out at room temperature. One of the films correspond to a CuO thin film prepared using sequential ionic layer adsorption reaction with the reaction bath maintained at 60 ^{0}C. The second film is obtained by annealing in air the as prepared sample at 200 ^{0}C. It is clearly observed that the slope of the absorbance curve for the as prepared sample is larger than that for the annealed samples. The point of inflexion for the two curves are distinctly separated which demonstrates that the threshold for optical absorbance to increase manifold is separated widely for the two samples.

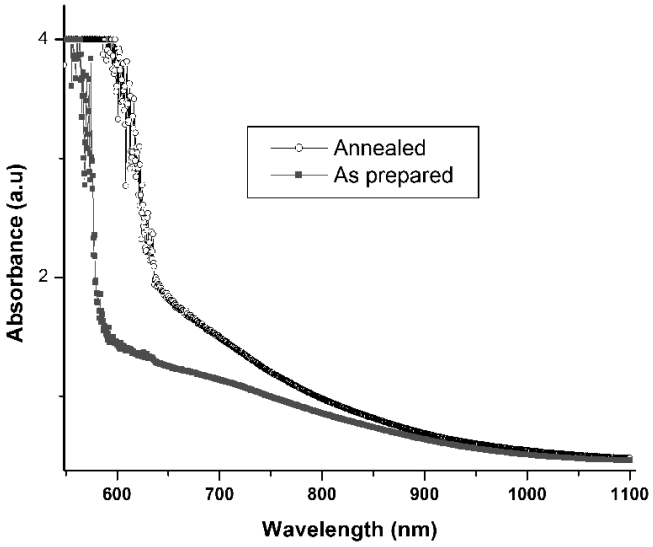


Fig 1: Optical absorption spectrum for as prepared and annealed sample.

The most commonly used method to determine the optical band gap of the thin films is the Tauc plot where, "$(\alpha h\nu)^2$ versus $h\nu$" is plotted in figure 2. The intercepts of this plot on the energy axis gives the energy band gap of the material. It is to be noted that this procedure is valid only for first order optical transitions which satisfy relation 2. Since most of the films are born with inherent defects the shape of the curve is different to the theoretical expectation. The point of intersection of the tangent drawn to the rising edge

of the plot to the energy axis is used as the optical band gap. [8-10] This method is inherent with the problem that, when it comes to investigating the graph of a function, the tangent line fails to say anything about how the graph of a function "bends" at a point. While the tangent line is a very useful tool, it fails to be exact in this case.

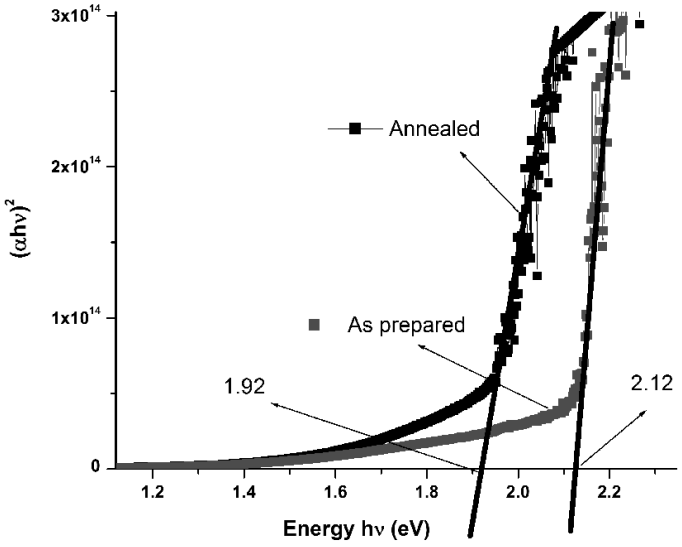
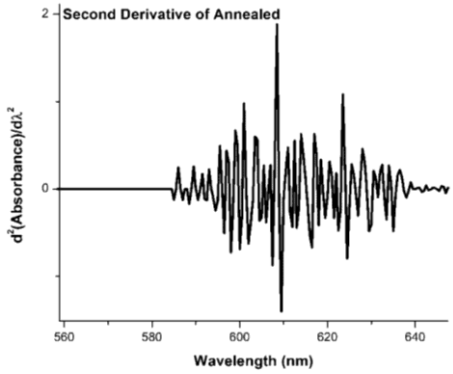
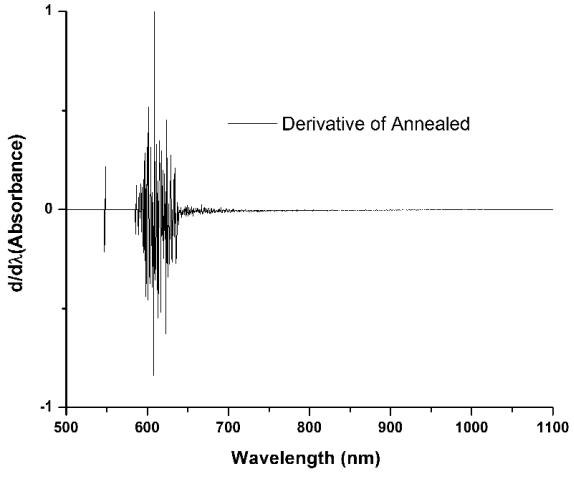


Fig 2: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for the samples.

An alternative approach as suggested earlier is to use the first derivative of the absorption spectrum to identify the point of inflection. As shown in figure 3 it leads to a spectrum filled with noise in the vicinity of the optical band gap energy. One of the more distinguishing feature in the spectra is that the shift observed in the optical absorption spectra are clearly reproduced in this graph and shows that for the annealed sample the point of inflection is centered around ~ 600 nm for the annealed sample whereas for the as prepared sample it is centered ~570 nm.


Second Derivative of Annealed
d²(Absorbance)/dλ²
2
0
560
580
600
620
640
Wavelength (nm)


Derivative of Annealed
d/dλ(Absorbance)
1
0
-1
500
600
700
800
900
1000
1100
Wavelength (nm)

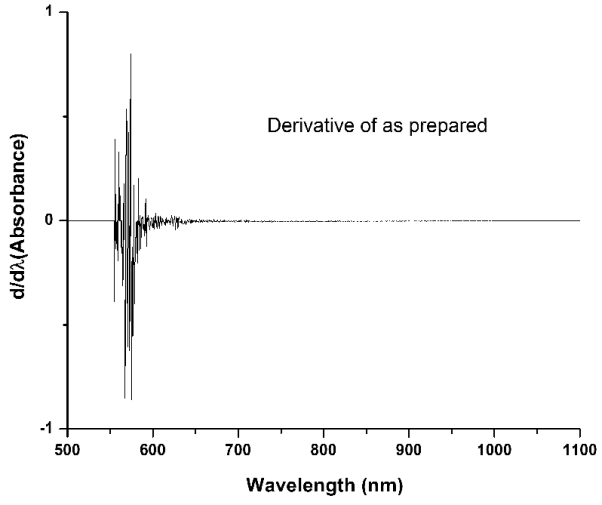

Derivative of as prepared
d/dλ(Absorbance)
1
0
-1
500
600
700
800
900
1000
1100
Wavelength (nm)

Fig 3: Derivative of the absorbance plotted as a function of wavelength for the two samples.

Figure 4 shows the plot of the second derivative of the absorbance with respect to the wavelength for the two samples. There are a number of points that satisfy the necessary condition and condition for sufficiency for being a point of inflection as seen in the figure. Taking the point of inflection with the largest magnitude swing from positive to negative leads to identification of the point of inflection as ~574 nm 2.16 (eV) for the as prepared sample and 604 nm (2.04 eV) for the annealed sample.

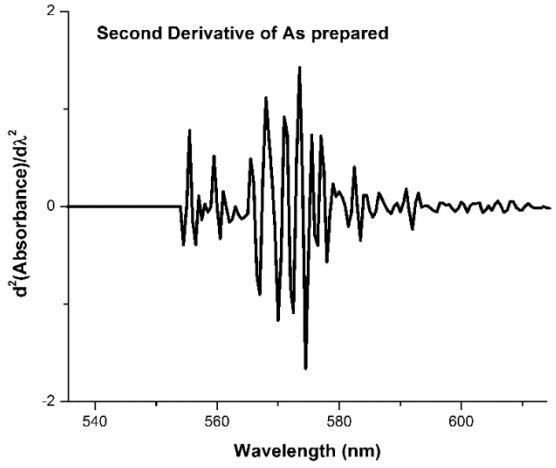


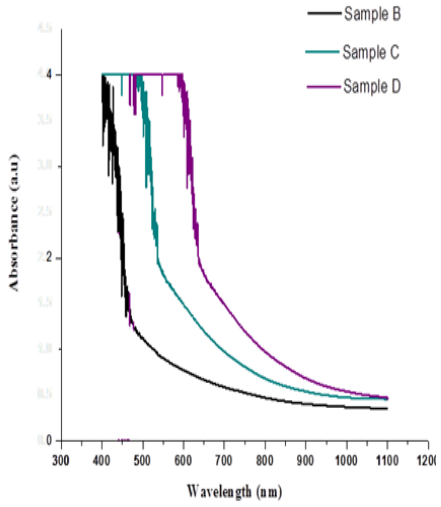
Fig 4: Second derivative of the absorbance plotted as a function of wavelength for the two samples.

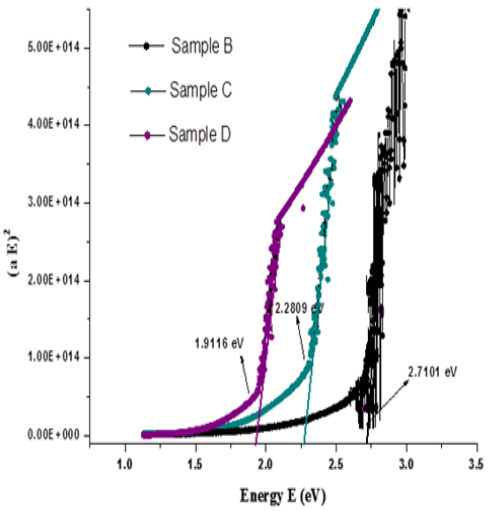
Table 1 provides a comparison between the band gap values estimated from the Tauc plot and from the calculus method.

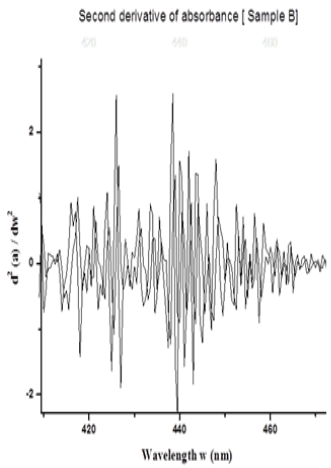
Sample	Band gap from plot E_g (eV)	Band gap from second derivative(eV)	RMS Error (%)
As prepared Sample (	2.12 ± 0.12	2.16 ± 0.18	+1.88
Annealed Sample (5)	1.92± 0.08	2.04 ± 0.12	+6.25

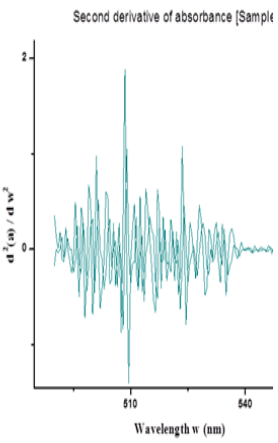
Table 1: Comparison between optical band gap obtained using Tauc plot and calculus method

The same methodology was tested on another set of samples. Figure 5 shows the optical absorption spectrum, the Tauc plot and the second derivative of the optical absorption of for each of the samples. The results conclusively prove that the procedure yields reliable information on the band gap of the thin film samples studied.









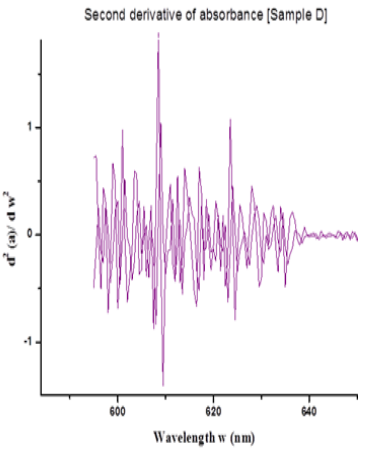


Fig 5: Results of optical absorption, Tauc plot and calculus on a set of thin film

Sample	Band gap from Γ plot E_g (eV)	Band gap from second derivative (eV)	RMS Error (%)
Sample B (5)	2.71± 0.13	2.83 ± 0.15	+4.42
Sample C (5)	2.28± 0.10	2.44 ± 0.13	+7.01
Sample D (5)	1.91± 0.15	2.04 ± 0.11	+6.81

samples.

Table 2: Comparison between optical band gap obtained using Tauc plot and calculus method.

Table 2 provides a comparison between the band gap values estimated from the Tauc plot and from the calculus method for the second set of samples.

4. Conclusions:

The method presented may be used as a first hand tool to comprehend change in optical band gap of thin film samples. It remains to develop an ideal mathematical calculation which can be used to identify the exact optical band gap within the experimental limitations of the technique. The calculations compliment the most preferred technique of optical band gap calculations currently followed by researchers' world over.

Acknowledgement:

RJ would like to extend this gratitude to UGC and SERB for financial support provided to carry out this work vide UGC MRP scheme **F. No.41-966/2012 (SR)** and **SERB SB/FTP/PS-013/2013.**

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Study on Extraction, Purification, Quantification and Control of Aflatoxins in Different Food Grains

Anjana Mohan*, **Roshni Thomas****
Department of Chemistry, Christian College, Chengannur.
**M.Sc.student,email id. Anjanamohankni13@gmail.com.*
***Asst.Professor, email id. rayxak@gmail.com.*

Abstract

Aflatoxins are toxic carcinogenic secondary metabolites produced by the fungal species Aspergillus flavus and Aspergillus parasiticus. The molds may grow under suitable climatic conditions on several agricultural commodities including cereals, pulses, spices etc. These mycotoxins are mainly hepato-carcinogenic and causes a wide range of health problems including internal hemorrhage. In the present study, aflatoxin content in rice, wheat, green gram, black gram and ground nuts were quantified using HPLC and it was found that all the samples contain aflatoxins within an allowed limit of30µg/kg for cereals, pulses and ground nuts.

Introduction

Aflatoxins are difuranocoumarin molecules produced through a polyketide pathway in the respective fungal molds. Out of the 18 different types of aflatoxins were identified sofarAflatoxin B1(AFB1), Aflatoxin B2(AFB2), Aflatoxin G1(AFG1), Aflatoxin G2(AFG2) are significant contaminants in our daily using food stuffs[(1)].

Aflatoxins are the most important mycotoxins which were classified under group 1 carcinogen by the International Agency for Research on Cancer[(2)]. Since these mycotoxins have serious effect on human health, their presence in food stuffs is to be identified and controlled.

In India, a tolerance limit of 30µg/kg for cereals, pulses and ground nuts has been prescribed under the Food Safety and Standards Regulations 2011, for human consumption while European Union permits only 5µg / kg[(3)].

Experimental

Aflatoxins in different local market available samples were extracted using ASE (Accelerated Solvent Extraction) technique, purified using IAC (Immuno Affinity Column) and quantified using HPLC (High Performance Liquid Chromatography)

ASE technique accelerates the extraction process and reduces the total amount of solvent used at elevated temperature and pressure.IAC contain antibodies that were attached to an inert support material and specifically used to bind the aflatoxins while the impurities pass through it. Then the bounded aflatoxins were extracted using HPLC grade methanol.

Quantification of aflatoxins were done using HPLC with fluorescence detection and post column derivatization. The instrument was standardized using various concentrations of aflatoxin standards under specific conditions - injection volume of 50µl, temperature of 30ºC, flow rate of 0.8 ml/min etc.Then the concentration of aflatoxins in the injected sample were obtained instrumentally under the same conditions and by using equations the amount of aflatoxin in the whole of the given sample was calculated.

$$\textbf{Concentration(ppb)} = (c \times V_1 \times V_2 \times V_3)/(g \times V_4 \times V_5)$$

C = Concentration obtained from post run analysis

V_1 = Volume of extraction solvent

V_2=Volume diluted with PB

V_3=Volume after elution

V_4=Volume of extract aliquot

V_5=Volume applied to immuno affinity column

Results and Discussion

The representative HPLC profiles of different aflatoxin standards (AFG2, AFG1 and AFB2) were presented in Figure 1. The concentrations of aflatoxins present in rice samples were given in Table 1. From the results, it is apparent that, only rice sample 04 contained aflatoxin. In all other samples, it is below the limit of quantification. The limit of quantification of the HPLC instrument used in the current study is 0.3 ppb. The

HPLC profile of aflatoxin present in rice sample 04 is presented in Figure 2.

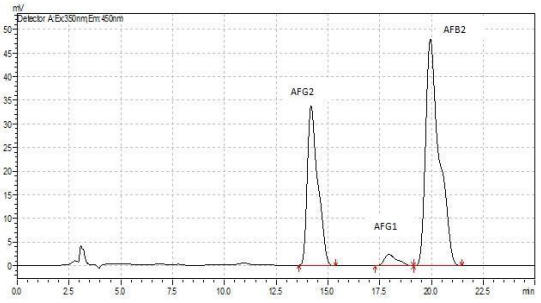

Fig. 1: HPLC Profiles of Aflatoxin Standards G1, G2 and B2 detected within 360-450 nm

Table 1: Quantification of Aflatoxins present in rice samples

Samples	Concentration of AFG1 (ppb)	Concentration of AFG2 (ppb)	Concentration of AFB2 (ppb)	Total concentration (ppb)
Rice 01	BLQ	BLQ	BLQ	BLQ
Rice 02	BLQ	BLQ	BLQ	BLQ
Rice 03	BLQ	BLQ	BLQ	BLQ
Rice 04	BLQ	0.35±0.014*	BLQ	0.35±0.014*
Rice 05	BLQ	BLQ	BLQ	BLQ

*Values are expressed as mean±SD of triplicate determinations.

BLQ - Below Limit of Quantification. The limit of quantification is 0.3 ppb.

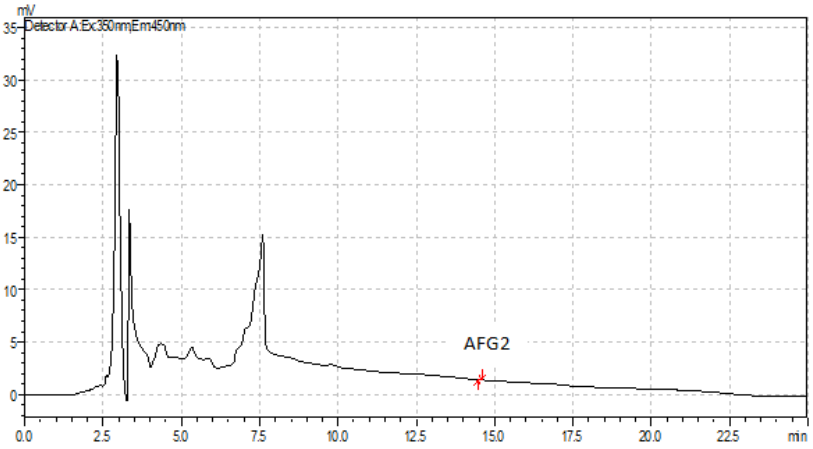

Fig. 2: HPLC Profile of Aflatoxin present in Rice 04 detected within 360-450 nm

The concentration of aflatoxins present in wheat samples weredepicted in Table 2. From the results, wheat sample 02 and 05 contains aflatoxins. In all other samples, it is present below the limit of quantification. The limit of quantification of the HPLC instrument used in the present study is 0.3 ppb. The HPLC profiles of aflatoxins present in wheat samples 02 and 05 are presented in Figure 3a and 3b respectively.

Table 2: Quantification of Aflatoxins present in wheat samples

Samples	Concentration of AFG1 (ppb)	Concentration of AFG2 (ppb)	Concentration of AFB2 (ppb)	Total concentration (ppb)
Wheat 01	BLQ	BLQ	BLQ	BLQ
Wheat 02	BLQ	0.36±0.014*	BLQ	0.36±0.014*
Wheat 03	BLQ	BLQ	BLQ	BLQ
Wheat 04	BLQ	BLQ	BLQ	BLQ

Wheat 05	BLQ	0.61±0.024*	BLQ	0.61±0.024*

*Values are expressed as mean±SD of triplicate determinations.

BLQ - Below Limit of Quantification. The limit of quantification is 0.3 ppb

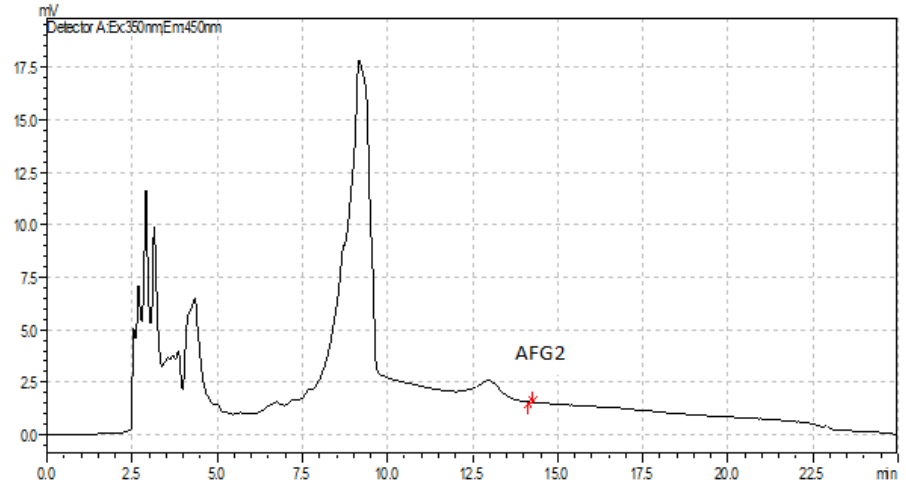

Fig. 3a: HPLC Profile of Aflatoxin present in Wheat 02 detected within 360-450 nm

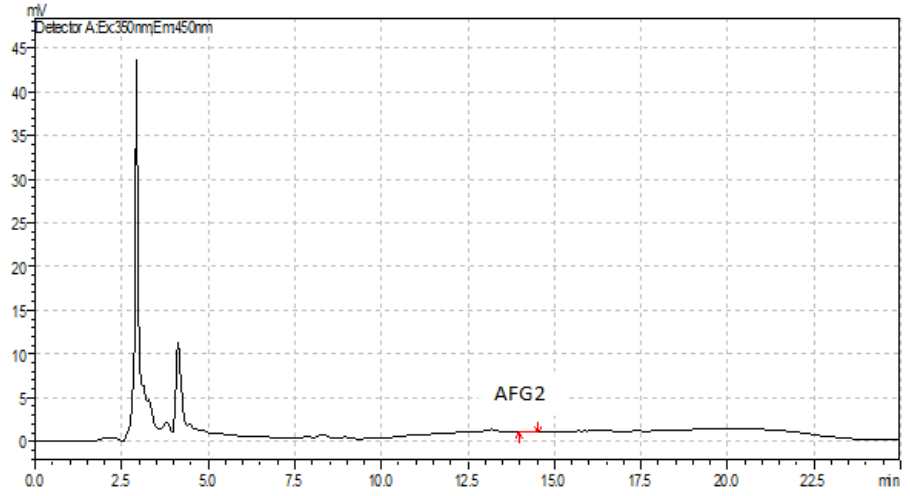

Fig. 3b: HPLC Profile of Aflatoxin present in Wheat 05 detected within 360-450 nm

Aflatoxin presence were identified in three out of the five analyzed green gram samples. (02, 03 and 05) (Table 3). In green gram sample 01 and 04, it is below the limit of quantification. Sample 03 contained two types of aflatoxins; that is AFG1 and AFG2 and the total aflatoxin concentration is 12.55 ppb, which is the highest among the

five samples. The HPLC profiles of aflatoxins present in green gram samples 02, 03 and 05 are presented in Figure 4a to 4c respectively.

Table 3: Quantification of Aflatoxin G1, G2 and B2 in Green Gram Samples

Samples	Concentration of AFG1 (ppb)	Concentration of AFG2 (ppb)	Concentration of AFB2 (ppb)	Total concentration (ppb)
Green gram 01	BLQ	BLQ	BLQ	BLQ
Green gram 02	8.83±0.360*	BLQ	BLQ	8.83±0.360*
Green gram 03	12.20±0.498*	0.35±0.014*	BLQ	12.55±0.256*
Green gram 04	BLQ	BLQ	BLQ	BLQ
Green gram 05	BLQ	BLQ	3.33±0.135*	3.33±0.135*

*Values are expressed as mean±SD of triplicate determinations.

BLQ - Below Limit of Quantification. The limit of quantification is 0.3 ppb.

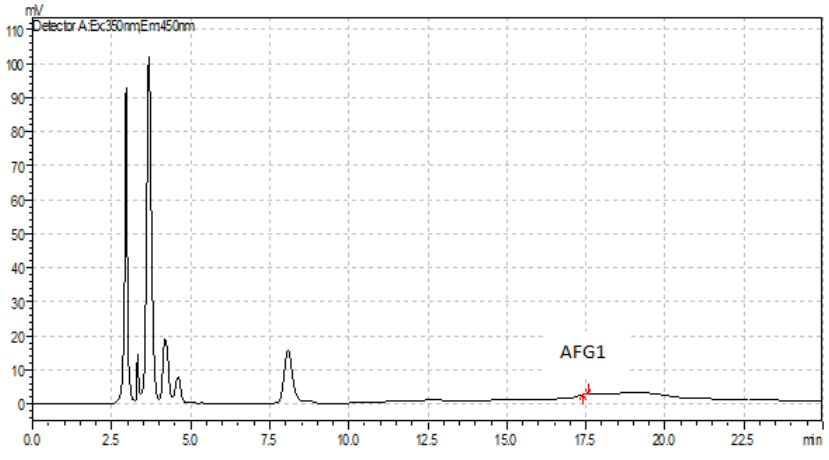

Fig. 4a: HPLC Profile of Aflatoxin present in Green Gram 02 detected within 360-450 nm

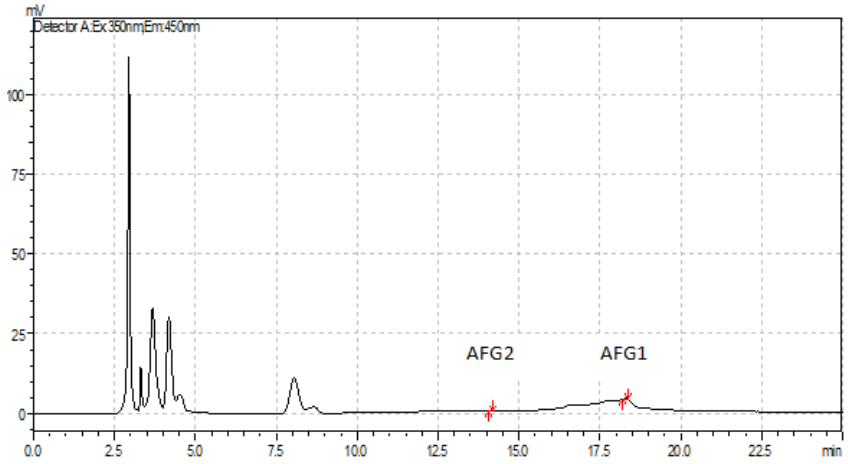

Fig. 4b: HPLC Profile of Aflatoxin present in Green Gram 03 detected within 360-450 nm

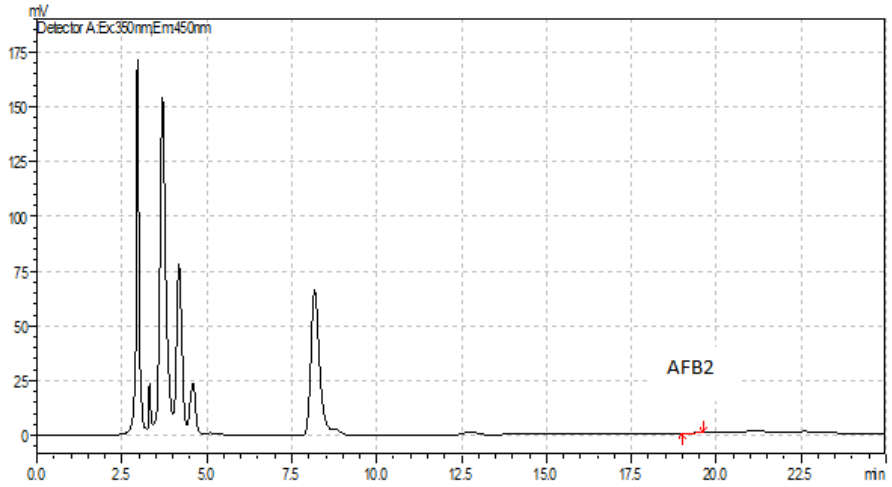

Fig. 4c: HPLC Profile of Aflatoxin present in Green Gram 05 detected within 360-450 nm

Table 4 presents the results on black gram samples. In black gram sample 01 and 03, it is below the limit of quantification. Sample 02 contained three types of aflatoxins; viz. AFG1, AFG2 and AFB2 and the total aflatoxin concentration is 6.23 ppb, which is the highest among the five samples studied. The HPLC profiles of aflatoxins present in black gram samples 02, 04 and 05 are presented in Figure 5a to 5c respectively as shown below.

Table 4: Quantification of Aflatoxin G1, G2 and B2 in Black Gram Samples

Samples	Concentration of AFG1 (ppb)	Concentration of AFG2 (ppb)	Concentration of AFB2 (ppb)	Total concentration (ppb)
Black gram 01	BLQ	BLQ	BLQ	BLQ
Black gram 02	4.57±0.186*	1.66±0.067*	3.67±0.149*	6.23±0.134*
Black gram	BLQ	BLQ	BLQ	BLQ

03				
Black gram 04	BLQ	0.60±0.024*	BLQ	0.60±0.024*
Black gram 05	BLQ	0.39±0.014*	0.34±0.011*	0.73±0.012*

*Values are expressed as mean±SD of triplicate determinations.

BLQ - Below Limit of Quantification. The limit of quantification is 0.3 ppb.

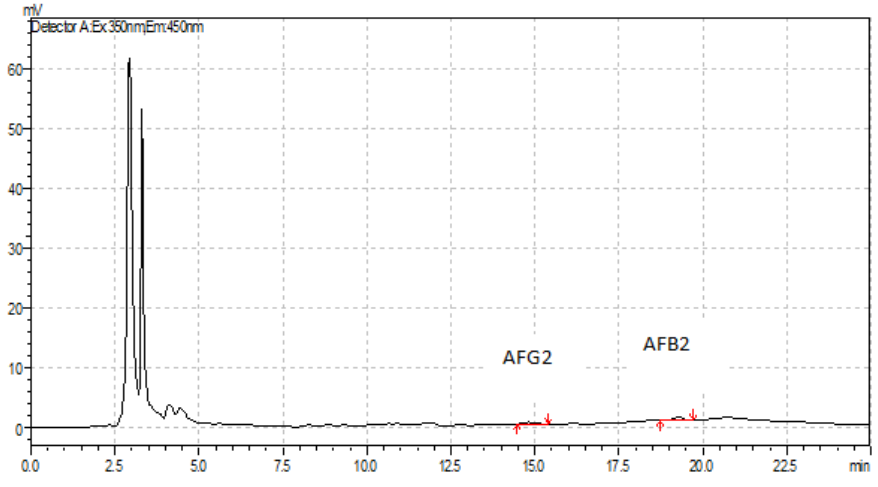

Fig. 5a: HPLC Profile of Aflatoxin present in Black Gram 02 detected within 360-450 nm

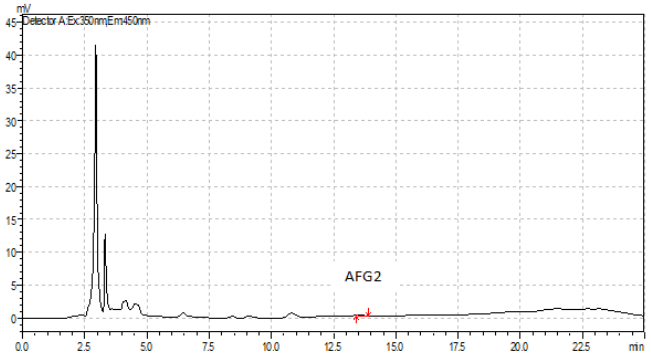

Fig. 5b: HPLC Profile of Aflatoxin present in Black Gram 04 detected within 360-450 nm

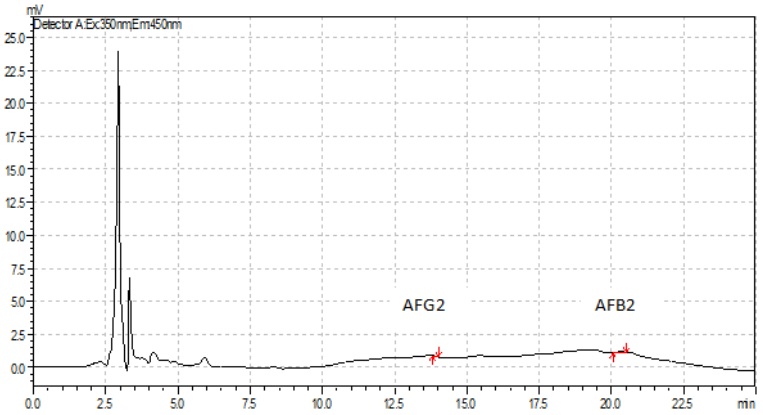

Fig. 5c: HPLC Profile of Aflatoxin present in Black Gram 05 detected within 360-450 nm

The concentration of aflatoxins present in ground nut samples were given in Table 5. From the results, it is clear that, ground nut sample 02 and 04 contained aflatoxins and aflatoxin G1 alone present in both these samples. In ground nut sample 01, 03 and 05, the levels were below the limit of quantification. The limit of quantification of the HPLC used in this study is 0.3 ppb. Sample 02 contained the highest concentration of aflatoxin G1 (19.88 ppb) followed by sample 04 (9.07 ppb). The HPLC profiles of aflatoxins present in ground nut samples 02 and 04 were presented in figure 6a and 6b respectively

Table 5: Quantification of Aflatoxin G1, G2 and B2 in Ground nut Samples

Samples	Concentration of AFG1 (ppb)	Concentration of AFG2 (ppb)	Concentration of AFB2 (ppb)	Total concentration (ppb)
Ground nut 01	BLQ	BLQ	BLQ	BLQ
Ground nut 02	19.88±0.811*	BLQ	BLQ	19.88±0.811*
Ground nut	BLQ	BLQ	BLQ	BLQ

03				
Ground nut 04	9.07±0.370*	BLQ	BLQ	9.07±0.370*
Ground nut 05	BLQ	BLQ	BLQ	BLQ

*Values are expressed as mean±SD of triplicate determinations.

BLQ - Below Limit of Quantification. The limit of quantification is 0.3 ppb.

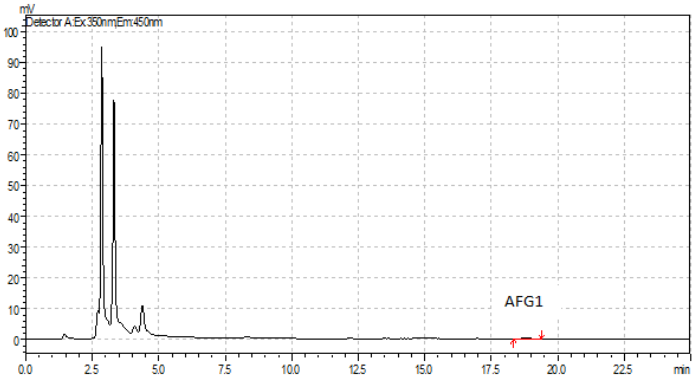

Fig. 6a: HPLC Profile of Aflatoxin present in Ground nut 02 detected within 360-450 nm

Irrespective of the type of food grains, the Food Safety and Standards Authority of India (FSSAI) prescribes the maximum limit of total aflatoxin content up to 30 µg/kg (30 ppb) and there is no limit specified for individual aflatoxins. All the five classes of food grains analyzed in the present study had aflatoxin levels falls within the prescribed limits. So in terms of the quantity of mycotoxins (aflatoxins), these food grains are safe for human consumption.

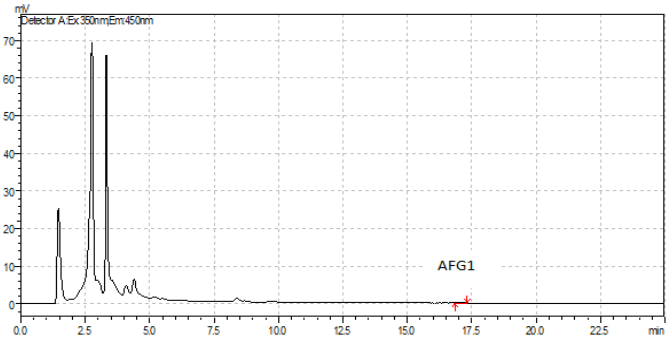

Fig. 6b: HPLC Profile of Aflatoxin present in Ground nut 04 detected within 360-450 nm

Conclusion

The quantities of aflatoxins obtained in this study are within the limits; consumption of these aflatoxin contaminated food grains for a long time will cause the exposure of these mycotoxins and will result in serious biological effects such as cytotoxicity and even hepatic cancer. So there should be proper management of storage and handling of food grains to control the levels of aflatoxins to a minimum. Good agricultural practices, plant disease management and adequate storage conditions can reduce aflatoxin levels in the food grains. Food processing can further reduce aflatoxin level in food grains by physical removal and decontamination by chemical or enzymatic treatment of aflatoxin into less toxic products. Biological control has also been developed as the most innovative potential technology of controlling aflatoxin contamination in food grains, which uses competitive exclusion of toxigenic strains by non-toxigenic strains.

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Acknowledgement

Sincere thanks to CFRD, Konni,and Pathanamthitta for providing instrumental support.

The 'cAAC wonder' in low coordination chemistry

Prinson P Samuel*

Dedicated to Prof. Dr. Dr. hc. mult. Herbert W. Roesky

Abstract: The last five years witnessed tremendous progress in developing low coordination complexes based on cyclic alkyl amino carbenes (cAAC). Several reactive species of both main group and transition metal elements were trapped in the low coordination environment of cAACs and such compounds were seen to exhibit unusual electronic and magnetic properties in addition to their exceptional reactivity.

For many decades it remained as a challenging task for chemists to stabilize metal atoms in their lower oxidation states and with lower coordination numbers. After the first report of a singlet N-heterocyclic carbene (NHCs) by Arduengo,[1] it was employed to stabilize some metal atoms in different oxidation states.[2] Very soon it had been realized that a closed-shell configuration is not always necessary for a complex to become stable, since NHC can very strongly donate its lone pair to the metal centre. However, complexes containing NHC centred radicals bound to a metal were not stable.[3] After cyclic alkyl(amino) carbene (cAAC) was prepared by Bertrand,[4] it was identified as a wise choice to stabilize the otherwise unstable compositions. In cAACs, one of the N atoms of NHC is replaced by one σ-donating quaternary C atom. (Fig. 1) Since the HOMO−LUMO energy gap is smaller in cAAC when compared with that of NHC, the former has been proven to be much more effective in stabilizing electron rich species.[5] Further evidence suggests that the carbene carbon atom of cAAC can use the lone pair of electrons present on the adjacent nitrogen in a more controlled way depending on the accumulation of electron density on the

[*] Dr. Prinson P. Samuel
Department of Chemistry
Christian College
Chengannur
E-mail: prinsonpsam@gmail.com

bound metal. As a consequence, cAAC can
be utilized as an excellent ligand for the stabilization of low coordinate complexes. The low coordination chemistry based on cAAC was triggered after Roesky and co-workers identified for the first time in 2013 that a Si(0) can be stabilized between two cAAC molecules.[6,7] This finding was soon led to the exploitation of similar chemistry in transition metal elements too. Such a motive was based on the presumption that such transition metal complexes will

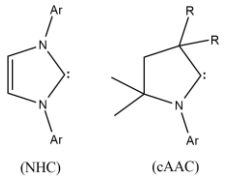
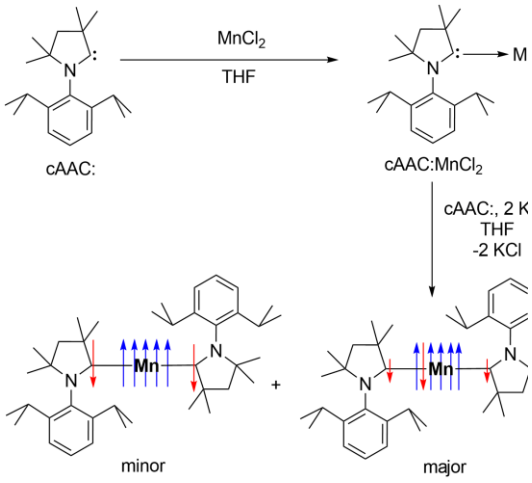


Figure 1. Core structure of NHC (left) and cAAC (right). Ar represents the aromatic substituent at the nitrogen atom. Usually bulky aromatic systems are employed in low coordination chemistry.

have remarkable electronic, magnetic and catalytic properties. This perspective will look into the most important low coordinate compounds synthesized using transition metals and cAAC. A complete review of the main group cAAC compounds can be seen elsewhere.[8]

The application of cAAC to obtain two coordinate first row transition elements got the attention of the chemists after synthesis of $(cAAC)_2M$ (M= Zn, Mn) complexes by Samuel et al. and Singh et al. in 2013.[9,10] Both complexes were prepared by the two electron reduction of the adducts $(cAAC)MCl_2$ using potassium graphite (KC_8) as the reducing agent. The resulting zinc complex was blue whereas the manganese counterpart was purple in color. However both compounds were electronically different. in the case of $(cAAC)_2Zn$, the carbene carbon atoms were converted into radical centers with the electron sharing bond formed between Zn and the carbon atoms. The spins of the electrons in the radical centers in both sides of Zn were found to have opposite directions. This make the molecule EPR silent. However, the electronic structure of $(cAAC)_2Mn$ was much more complex. From the ab initio calculations it was revealed that $(cAAC)_2Mn$ has a quartet (S = 3/2) spin ground state having two spin conformers. The minor conformer is represented as $(cAAC\cdot)_2Mn$ which has one unpaired electron each in both carbon atoms bound to the metal.

These two electrons have spins in same direction but antiferromagnetically coupled with the electronic spins in Mn atom. (cAAC)Mn(cAAC·) is the major conformer which features a more sophisticated situation than in the minor spin conformer. This molecule can be understood by considering that one of the electrons in the carbon radical centres of the minor spin conformer lands in the manganese centre and undergoes spin pairing with one of the metal electrons. The remaining radical electron will be delocalized between the two carbon atoms. In simplest terms, an electron spends half its time in one carbene carbon atom and the other



Scheme 1. Synthesis of $(cAAC)_2Mn$ and different spin arrangements in two conformers.

half time in the second carbene carbon atom. This consideration leads to overall spin of 3/2 in both cases which was experimentally confirmed (Scheme 1)

In order to obtain (cAAC)2Cu, a similar synthetic strategy is not applicable as cAAC ws found to reduce CuCl2 to CuCl. However the ionic compound (cAAC)2Cu+I- can be synthesized by the direct reaction of CuI with two equivalents of cAAC. Further one elecetron reduction of this compound with sodium yields $(cAAC)_2Cu$.[11] The EPR spectrum of this compound suggested a copper (I) centre with a delocalized electron between the two carbene carbon atoms. Similar to this, $(cAAC)_2Au^+Cl^-$ was prepared by simply reacting $AuCl(SMe_2)$ with two equivalents of cAAC. Further reduction of this compound with potassium metal yielded $(cAAC)_2Au$. The gold atom was seen to have an oxidation state of +1 in this compound.[12]

In a different synthetic strategy, $(cAAC)_2Ni$ was synthesized by reacting $(cAAC)_2NiCl_2$ with the base $LiNiPr_2$.[13] The compound was analogous to its NHC counterpart with Ni atom in the zero oxidation state.[14] $(cAAC)_2Pt$ and $(cAAC)_2Pd$ were obtained by a reaction in which four

triphenyl phosphine ligands of $M(PPh_3)_4$ were replaced by two cAACs.[15] The replacement is spontaneous because of the fact that cAAC is a stronger σ donor than PPh_3. Reaction of cAAC with $CoCl_2$ yields $(cAAC)_2Co_2Cl_4$, a dimer of $(cAAC)CoCl_2$. This dimer on reaction with two equivalents of KC_8 produces three coordinate $(cAAC)_2CoCl$. Further one electron reduction leads to the formation of $(cAAC)_2Co$ which was isolated as dark blue crystals.[16-18]

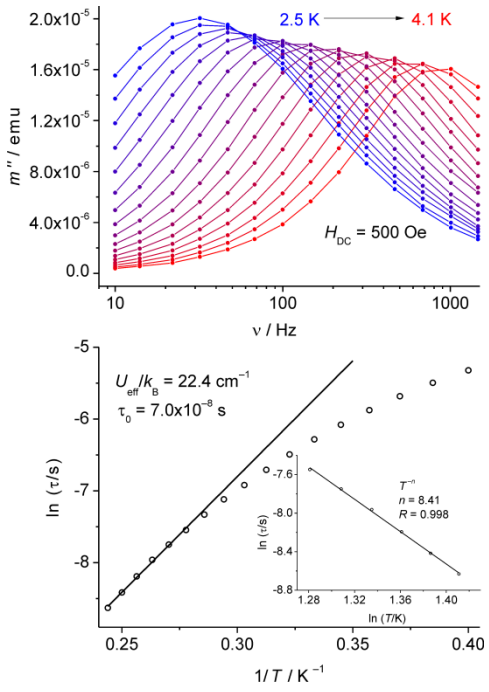


Figure 2. Top: frequency dependence of the imaginary part of the AC susceptibility under a DC field of 500 Oe for $(cAAC)_2FeCl$. Bottom: Arrhenius plot of the temperature dependence of the relaxation time τ. The black line describes a thermally activated relaxation. Inset: power law analysis in the form ln(τ) vs. ln(T).

One among many notable outcomes of the cAAC chemistry of transition metal elements was the synthesis of $(cAAC)_2FeCl$ and $[(cAAC)_2Fe]^+$.[19] The former was obtained by the one electron reduction of $(cAAC)_2FeCl_2$ adduct using KC_8. The compound was isolated as red crystals which was extensively studied for their magnetic properties. Reaction of this compound with $LiB(C_6F_5)_4$ gives the two coordinate cationic complex $[(cAAC)_2Fe]^+[B(C_6F_5)_4]^-$. $(cAAC)_2FeCl$ shows a distorted trigonal planar geometry while $[(cAAC)_2Fe][B(C_6F_5)_4]$ is linear. SQUID, Mössbauer, HF-EPR and theoretical studies reveal that both compounds have iron atoms in the +1 oxidation state with a spin ground state of $S = {}^3/_2$. The chemical structure of $[(cAAC)_2Fe]^+$ shows the first example of a cationic two-coordinate Fe(I) complex. The magnetic studies revealed the slow magnetic relaxation of both compounds under an applied DC magnetic field typical for SMM behavior. (Figure 2) An easy plane

anisotropy for $(cAAC)_2FeCl$ was understood from high frequency EPR measurements**.** Further reduction of $(cAAC)_2FeCl$ yields $(cAAC)_2Fe$.[20]

This perspective shows that entry of cAAC ligand into coordination chemistry has opened up a new era in which many low coordinate complexes has been materialized which were illusive till the time. The single molecule magnetic behaviour of some of these complexes opens up a new possibility. cAAC based low coordination complexes have also found application in homogeneous catalysis. More elements from different groups are to be screened for the possibility of low coordination using cAAC and their physical and chemical characteristics are to be analysed.

Acknowledgements
The author thanks University of Göttingen, Germany for the post doctoral position during 2011-2017 and thereby becoming a part of the above described research. Funding from German Research Foundation is greatly acknowledged.

Keywords: *cAAC • low-valent • • low-coordinate • single molecule magnet*

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EVALUATION OF PHYSICO-CHEMICAL PARAMETERS OF FOUR DIFFERENT PONDS IN VETTIYAR REGION OF THAZHAKKARA PANCHAYAT

DEEPA RAMACHANDRAN [1],DIVYA.S.RAJAN[2*]

1.Deepa Ramachandran : P.G. Student, P.G Department of Zoology,Christian College, Chengannur
2. Divya.S.Rajan* : Guest lecturer , P.G Department of Zoology, Christian College, Chengannur .
***Corresponding author: Divya.S.Rajan**, **divyashyju2010@gmail.com,**Guest Lecturer,
PG Department of Zoology, Christian College,Chengannur, India

ABSTRACT

The world's pond ecosystems are being threatened by many factors. These include a variety of anthropogenic activities, which entail urgent need of research and education programs to create awareness in the society for their protection and conservation. In the present study physico-chemical parameters of four different ponds in Vettiyar region of Thazhakkara panchayat, Alappuzha district,Kerala,India was determined.Vettiyar is located in Mavelikkara tehsil of Alappuzha district in Kerala, India. It is situated 8km away from sub-district headquarter Mavelikkara and situated in Thazhakkara grama panchayat.More than 8 ponds are situated in Vettiyar village. The present study was conducted over the selected four ponds in Vettiyar village namely, Ramanalloor pond, Kandakalankavu pond, Valiyaveetil pond and Panchayath pond. The objectives of the study was to investigate the seasonal variations of physico-chemical parameters such as temperature, pH, transparency, turbidity, hardness, salinity, ammonia, carbon dioxide, dissolved oxygen, Biological Oxygen Demand and Chemical Oxygen Demand. Water samples were collected during the year 2017-2018 from the study area and the physico-chemical parameters were analysed with respect to the seasons following standard methods. The study indicates that there is a pronounced variation of most of the water quality parameters with variations in season. The alteration of these water quality parameters may provide an early warning signal about the degradation of these precious ecosystems.The pond water quality is degraded mainly due to discharge of wastes from residential area, sewage outlets, solid wastes, detergents and automobile oil waste. The findings of the present study also provide a better understanding of this damaged ecosystems and remind the need for the restoration of these natural precious ecosystems.

KEY WORDS: Physico-chemical,BOD,COD,DO

INTRODUCTION

Water is one of the most important and abundant compounds of the ecosystem. Freshwater is one of the basic needs of mankind and it is essential for the existence of all forms of life. It exists in lentic and lotic habitats. All the lentic habitats, such as ponds and lakes are extremely important as they are enriched with other natural resources too. Less than 1% of water is present in ponds, lakes, rivers, dams,etc.,which is used by man for domestic, agricultural and industrial purposes. Due to the increased human population, industrialization, use of fertilizers in the agricultural and anthropogenic activities water is highly polluted with different harmful contaminants. Out of many freshwater sources, ponds are useful in many ways and it is one of the methods of artificial infiltration of underground water.

Ponds are important hotspots of biodiversity. Collectively they support more species, and more scarce species, than any other freshwater habitat. (Cereghino *et al.,* 2008).They are more abundant than almost any other freshwater habitat. They often contribute more to regional biodiversity than rivers or other habitats. Ponds are easily disrupted by human activity. The pond water is polluted mainly due to discharge of wastes from residential area, sewage outlets, solid wastes, detergents and automobile oil waste. (Bhuiyan and Gupta, 2007).Physico-chemical parameter analysis of any aquatic ecosystem is necessary because their hydrochemistry affects its biota to a great extent. Water quality influences the existence of aquatic organisms.(Jyotsna *et al.,* 2014).

The physico-chemical characteristics of pond water have a direct impact on prevailing organisms as well as human being using such water. The study of different water quality parameters help in understanding the metabolic events of the aquatic system. Certain parameters such as Temperature, pH, Transparency, Turbidity, Hardness, Salinity, Ammonia, Carbon dioxide, Dissolved oxygen, Biological oxygen demand and Chemical oxygen demand are necessary for the proper understanding of flora and fauna and their abundance and distribution with time. The changes in these parameters provide valuable information on the quality

of water, the sources of the variations and their impacts on the functions and biodiversity of the pond. The present study deals with the assessment of fluctuations in the physico-chemical characteristics of four ponds in Vettiyar region that would form a reminder to conserve these precious ecosystems. These ponds were facing high threat due to high anthropogenic activities. The ponds selected for the study were:

1. Ramanalloor pond.
2. Kandakalankavu pond.
3. Valiyaveetil pond.
4. Panchayat pond.

MATERIALS AND METHODS

Water samples were collected during the year 2017-2018 from the study area and the physico-chemical parameters were analysed following APHA(2005). Vettiyar is located in Mavelikkara tehsil of Alappuzha district in Kerala, India. It is situated 8km away from sub-district headquarters Mavelikkara and 50km away from district headquarters Alappuzha. Thazhakkara is the grama panchayat of Vettiyar village.The selected ponds were:

Site 1 (Ramanalloor pond)

Ramanalloor is a place in Vettiyar geographical area of Vettiyar ie of 1217 hectares. Agriculture is the main professional livelihood of people of this village. More than 8 ponds are situated in Vettiyar Village. Of which four ponds were selected for the analysis of physico-chemical factors.and have the name because of the presence of Ramanalloor Mahavishnu temple. Ramanalloor pond is situated near the temple and the place is very calm and cool. Many plants and trees are located around the pond.

Site 2 (Kandakalankavu pond)

Kandakalankavu pond is located in Kalithattu region of Vettiyar. It is associated with Kandakalankavu Mahadeva temple. It is a small pond with clear water.Komma puncha is situated near this pond.

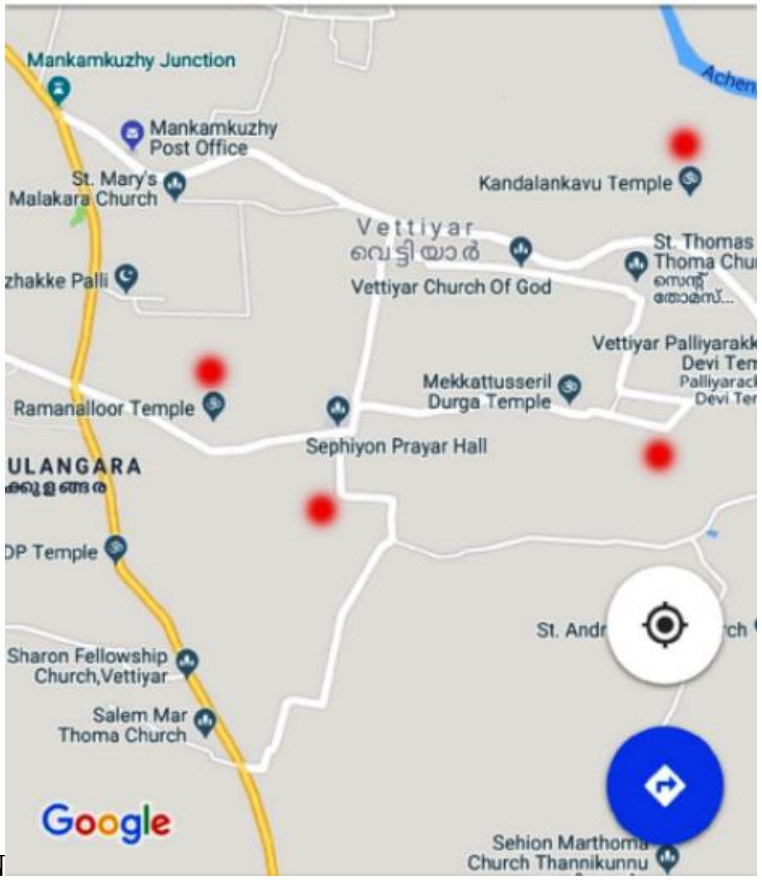
Site 3 (Valiyaveetil pond)

Valiyaveetil pond is located in Valyayyathu region of Vettiyar. It is situated in the side of Palliyarakavu-Nalumukku road. Domestic waste and plastics are deposited on it. Pistia species is abundantly found in this pond.

Site 4 (Panchayat pond)

Panchayath pond is located in Kochikkal region of Vettiyar. It is a pond found in residential area. Many people use this pond for washing purposes. Plastic wastes are also dumped in this pond. Pistia species are abundantly found in this pond.

MAP SHOWING THE STUDY SITES IN VETTIYAR REGION



PHOTOGRAPHS SHOWING THE SELECTED PONDS IN VETTIYAR REGION

SITE 1(Ramanalloor Pond)

SITE 2 (Kandakalankavu Pond)

SITE 3 (Valiyaveetil Pond)

SITE 4 (Panchayat Pond)

RESULTS

The study of physico-chemical parameters of selected four ponds in Vettiyar region of Thazhakkara panchayat, site 1(Ramanalloor pond), site 2(Kandakalankavu pond), site 3 (Valiyaveetil pond), site 4 (Panchayat pond) of three seasons were analysed and compared. The physico-chemical parameters of each sites exhibited variations in each period.

Temperature

The temperature showed a minimum range of 26^0C and exhibited a maximum range of 32^0C.All these sites showed an average temperature range from 27^0C -30.25^0C. In pre monsoon period, the temperature ranges from 28^0C to 31^0C.A high range of temperature was observed in site 3 (31^0C) and a lowest temperature was observed in site 1 (28^0C). In monsoon period, the temperature ranges from 26^0C to 28^0C . A high range of temperature was observed in site 3(28^0C) and low range was exhibited in site 1 (26^0C). The temperature of water samples in the post monsoon period ranges from 29^0C to 32^0C. A higher temperature was shown in the site 4 (32^0C) and lower range was noticed in the site 1 and site 3(29^0C). (Table 1 and Fig 1).The mean ± standard deviation ranges from 27 ± 0.82 to 30.25 ± 1.5.

pH

From the study, in pre monsoon season the pH ranged from 6.7 to 9.1. A higher level of pH was observed in site 4 (9.1) and lower pH was observed in site 3 (6.7). In monsoon season the pH ranges from 6.5 to 7.2. A higher level of pH was observed in site 4 (7.2) and lower pH in site 3 (6.5).The pH of water sample in post monsoon season ranges from 4.6 to 6.6. A higher level of pH was observed in site 1 (6.6) and lower pH in site 3 (4.6).First three sites exhibited almost acidic pH in all seasons and only the site 4 shows the alkaline pH in two seasons. (Table 1 and Fig 2).The mean ± standard deviation ranges from 5.7 ± 0.96 to 7.36 ± 1.52.

Transparency

Transparency range showed variations in all the seasons .A higher transparency value was noticed about 34.5 c.m in site 2 of post monsoon season.A lower range of was 5 c.m in site 1 of pre monsoon season. In pre monsoon season the transparency of water ranges from 5 to 29 c.m.Transparency of water in

monsoon season ranges from 8.5 to 32.5 c.m. In post monsoon season the transparency value ranges from 15.5 to 34.5 c.m. A high range of transparency observed in site 2 in all seasons and a lower range was observed in site 1 in all seasons. (Table 1 and Fig 3).The mean ± standard deviation ranges from 17.13 ± 9.82 to 8.67.

Turbidity

In the pre monsoon season the turbidity of water samples ranges from 11.2 to 101.2 NTU.A high range of turbidity was shown in site 1(101.2 NTU) and lowest was found in site 3(11.2 NTU).Turbidity of water in monsoon season ranges from 6.3 to 104.5 NTU.A high range was observed in site 3 (104.5 NTU) and lowest was showed in site 2 (6.3 NTU).Turbidity of water in post monsoon season ranges from 9.6 to 76.1 NTU. A high range of turbidity was observed in site 3 (76.1 NTU) and lower range was shown in site 2 (9.6 NTU). (Table 1 and Fig 4). The mean ± standard deviation was about 39.75 ± 42 2 to 53.43 ± 49.3.

Hardness

Hardness of the water samples in the pre monsoon season ranges from 22 to 40 mg/l. Highest range was observed in site 4 (40 mg/l) and lowest range was shown in site 2 (22 mg/l). In monsoon season, hardness ranges from 26 to 44 mg/l. In post monsoon season maximum hardness was shown in site 1 (34 mg/l) and minimum hardness exhibited in site 3 (14 mg/l). A high range of hardness was observed in site 4 in monsoon season. (Table 1 and Fig 5). The mean ± standard deviation was about 27 ± 8.87 to 34.5 ± 7.55.

Salinity

Salinity of water sample in the pre monsoon season ranges from 3.2 to 9.7 mg/l. A highest range was obtained in site 3 (9.7 mg/l) and lowest range was observed in site 1 (3.2 mg/l). In monsoon season salinity ranges from 3.2 to 9.6 mg/l. Maximum range was observed in site 4 (9.6 mg/l) and minimum range was shown in site 1 (3.2 mg/l).Salinity of water sample in the post monsoon season ranges from 3.1 to 9.4 mg/l.The site 1 shows comparatively minimum range of

salinity in all seasons. (Table 1 and Fig 6). The mean ± standard deviation ranges from 5.53 ± 3.01 to 7.23 ± 3.09.

Ammonia

Ammonia of water sample in the pre monsoon season ranges from 17 to 42.5 mg/l.Maximum range was observed in site 4 (42.5 mg/l) and minimum range was observed in site 2 (17 mg/l).In monsoon season ammonia of water sample ranges from 17 to 25.5 mg/l.The maximum range was obtained in site 3 and site 4 (25.5 mg/l) and minimum range was observed in site 1 and site 3 (17 mg/l). Ammonia of water sample in the post monsoon season ranges from 17 to 51 mg/l. A higher range was observed in site 4 (51 mg/l) and lowest range was observed in site 3 (17 mg/l).The site 4 showed comparatively highest range of ammonia in all seasons.(Table 1 and Fig 7). The mean ± standard deviation ranges from 21.25 ± 4.9 to 34 ± 15.52.

Carbon dioxide

Carbon dioxide in water sample in pre monsoon season ranges from 10.5 to 33.4 mg/l.The maximum range was observed in site 3 (33.4 mg/l) and minimum range was observed in site 2 (10.5 mg/l). In monsoon season, carbon dioxide of water samples ranges from 16.7 to 51 mg/l.The maximum range of carbon dioxide obtained in site 3 (51 m g/l) and minimum range was obtained in site 2(16.7 mg/l).Carbon dioxide of water sample in post monsoon season ranges from 21.1 to 33.5 mg/l.Maximum range was observed in site 3(33.5 mg/l) and minimum range was observed in site 1 (21.1 mg/l). (Table 1 and Fig 8).The mean ± standard deviation ranges from 18.9 ± 10.09 to 30.8 ± 14.97.

Dissolved oxygen

Dissolved oxygen of water sample in the pre monsoon season ranges from 2.2 to 5.1 mg/l. The maximum range was obtained in site 2 (5.1 mg/l) and minimum range was obtained in site 4 (2.2mg/l). Dissolved oxygen of water sample in monsoon season ranges from 0.8 to 5.2 mg/l. Maximum range was

observed in site 2 (5.2 mg/l) and minimum range was observed in site 3(0.8 mg/l).Dissolved oxygen of water samples in post monsoon season ranges from 1.4 to 6.8 mg/l.The maximum range was showed in site 3 (6.8 mg/l) and minimum range was showed in site 4 (1.4 mg/l). (Table 1 and Fig 9). The mean ± standard deviation ranges from 2.88 ± 1.84 to 4.15 ± 2.38.

Biological Oxygen Demand

Biological Oxygen Demand of water sample in the pre monsoon season ranges from 1.4 to 3.5 mg/l.Highest range was observed in site 3 (3.5 mg/l) and minimum range was showed in site 2 (1.4 mg/l). In monsoon season, Biological Oxygen Demand ranges from 0.6 to 1.8 mg/l.Maximum range was observed in site 4 (1.8 mg/l) and minimum range was observed in site 2 (0.6 mg/l). Biological Oxygen Demand of water sample in the post monsoon season ranges from 1 to 1.9 mg/l. A highest range was observed in site 3 (1.9 mg/l) and lowest range was observed in site 2 (1 mg/l). Site 2 shows a comparatively minimum range of BOD value in all seasons. (Table 1 and Fig 10). The mean ± standard deviation was about 1.2 ± 0.59 to 2.33 ± 0.87.

Chemical Oxygen Demand

Chemical Oxygen Demand of water sample in pre monsoon ranges from 1.6 to 6.3 mg/l.Maximum range was observed in site 1(6.3 mg/l)and minimum range was observed in site 2 and site 3 (1.6 mg/l). In monsoon season Chemical Oxygen Demand ranges from 4.8 to 8 mg/l.The maximum range was observed in site 2 and site 4 (8 mg/l) and minimum range was observed in site 3 (4.8 mg/l). Chemical Oxygen Demand of water sample in post monsoon season ranges from 1.6 to 8 mg/l.The maximum range was observed in site 3 (8 mg/l) and minimum range was observed in site 2 (1.6 mg/l).(Table 1 and Fig 11). The mean ± standard deviation ranges from 3.58 ± 2.36 to 6.8 ± 1.53.

TABLE- 1

SEASONAL VARIATIONS OF PHYSICO-CHEMICAL PARAMETERS

PARAMETS	SEASONS	SITE 1	SITE 2	SITE 3	SITE 4	MEAN±SD
Temperature (^{0}C)	Pre monsoon	28	30	31	30	29.75± 1.26
	Monsoon	26	27	28	27	27 ± 082
	Post monsoon	29	31	29	32	30.25 ± 1.5
pH	Pre monsoon	6.9	6.8	6.7	9.1	7.36 ± 1.52
	Monsoon	6.7	6.6	6.5	7.2	6.75 ± 0.31
	Post monsoon	6.6	6.4	4.6	5.2	5.7 ± 0.96
Transparency (cm)	Pre monsoon	5	29	18	16.5	17.13 ± 9.82
	Monsoon	8.5	32.5	19	18	19.5 ± 9.87
	Post monsoon	15.5	34.5	20.5	17	21.87 ± 8.67
Turbidity (NTU)	Pre monsoon	101.2	13	11.2	33.6	39.75 ± 42.2
	Monsoon	86.5	6.3	104.5	16.4	53.43 ± 49.3
	Post monsoon	63.3	9.6	76.1	22.7	42.93 ± 31.8
	Pre monsoon	30	22	26	40	29.5 ± 7.72

Hardness (mg/l)	Monsoon	32	26	36	44	34.5 ± 7.55
	Post monsoon	34	17	35	42.5	27 ± 8.87
Salinity (mg/l)	Pre monsoon	3.2	9.6	9.7	6.4	7.23 ± 3.09
	Monsoon	3.2	6.2	9.5	9.6	7.13 ± 3.05
	Post monsoon	3.1	6.4	3.2	9.4	5.53 ± 3.01
Ammonia (mg/l)	Pre monsoon	34	17	34	42.5	31.86 ± 10.69
	Monsoon	17	25.5	17	25.5	21.25 ± 4.9
	Post monsoon	42.5	25.5	17	51	34 ± 15.52
CO_2 (mg/l)	Pre monsoon	14.1	10.5	33.4	17.6	18.9 ± 10.09
	Monsoon	22.9	16.7	51	32.6	30.8 ± 14.97
	Post monsoon	21.1	22	33.5	22.9	24.86 ± 5.79
Dissolved oxygen (mg/l)	Pre monsoon	4.4	5.1	3.5	2.2	3.8 ± 1.25
	Monsoon	3.2	5.2	0.8	2.3	2.88 ± 1.84
	Post monsoon	3.1	5.3	6.8	1.4	4.15 ± 2.38
BOD (mg/l)	Pre monsoon	2.2	1.4	3.5	2.2	2.33 ± 0.87
	Monsoon	1.6	0.6	0.8	1.8	1.2 ±0.59
	Post monsoon	1.4	1	1.9	1.4	1.43 ± 0.37
COD (mg/l)	Pre monsoon	6.3	1.6	1.6	4.8	3.58 ± 2.36
	Monsoon	6.4	8	4.8	8	6.8 ± 1.53
	Post monsoon	4.8	1.6	8	3.2	4.4 ± 2.73

FIGURES

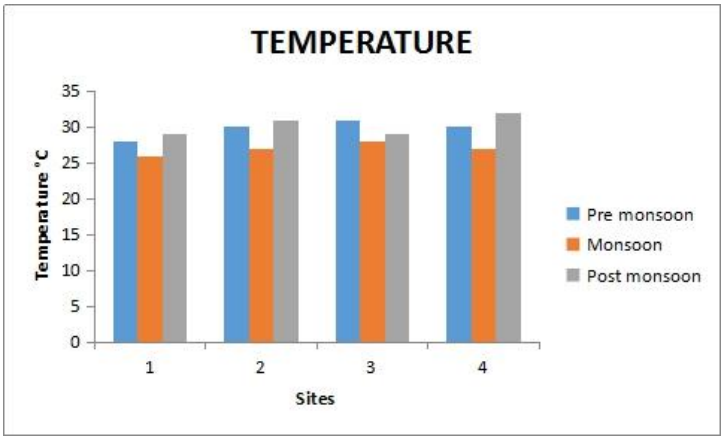


Fig 1: Graph showing seasonal variations of temperature

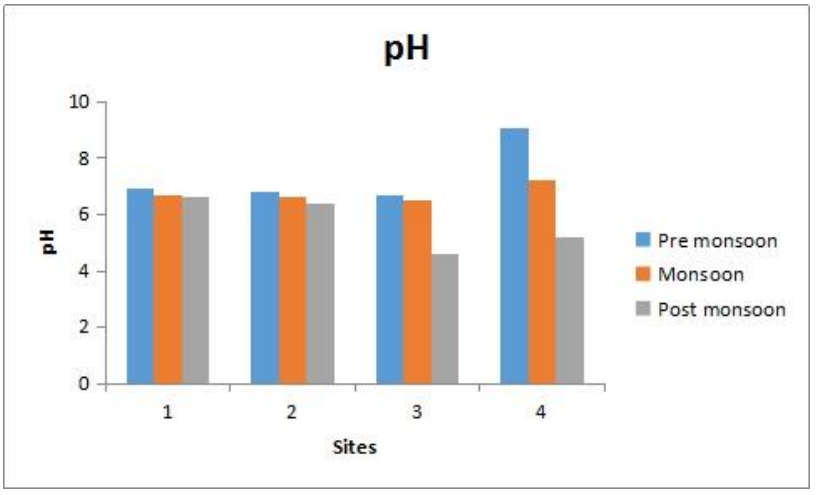


Fig 2: Graph showing seasonal variations of pH

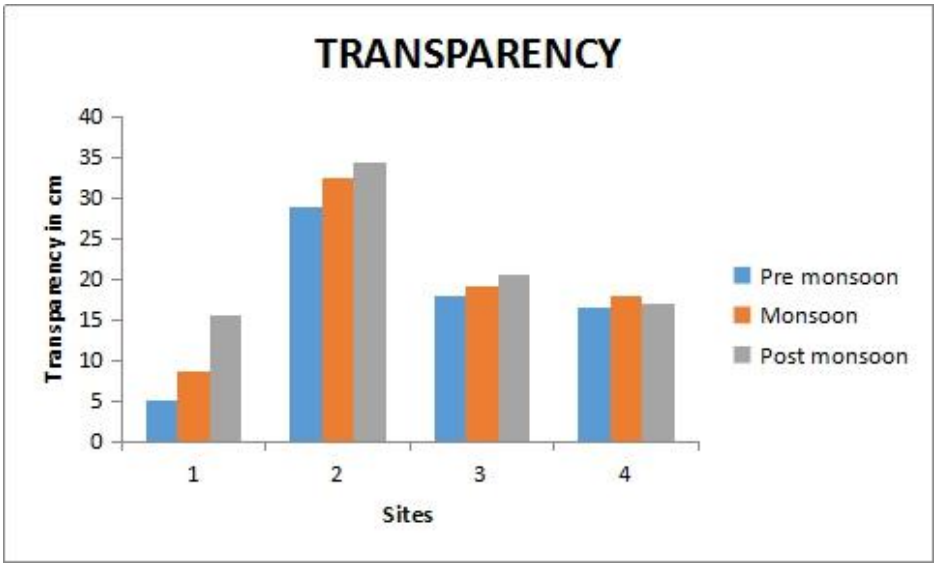


Fig 3: Graph showing seasonal variations of transparency

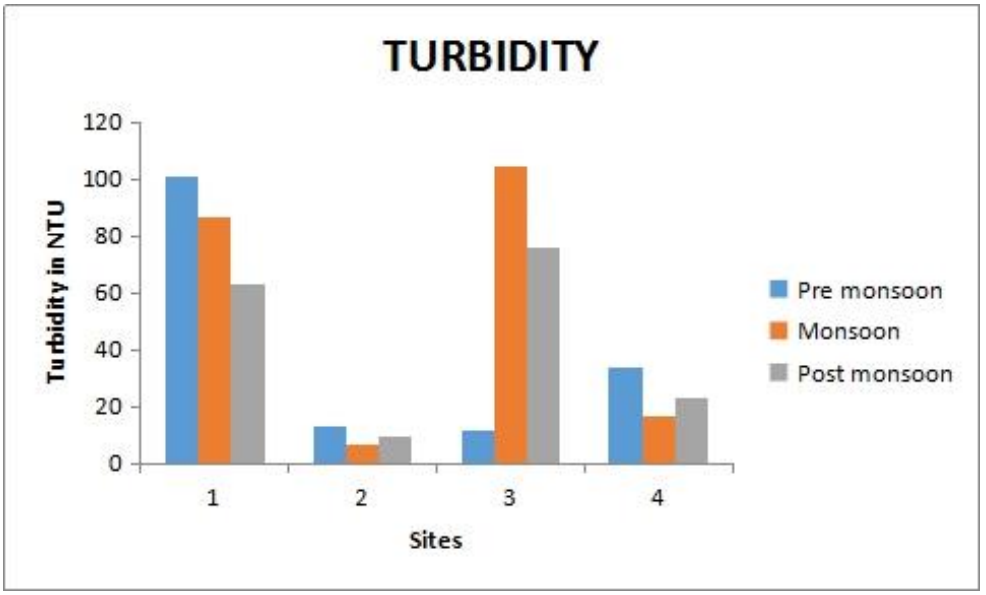


Fig 4: Graph showing seasonal variations of turbidity

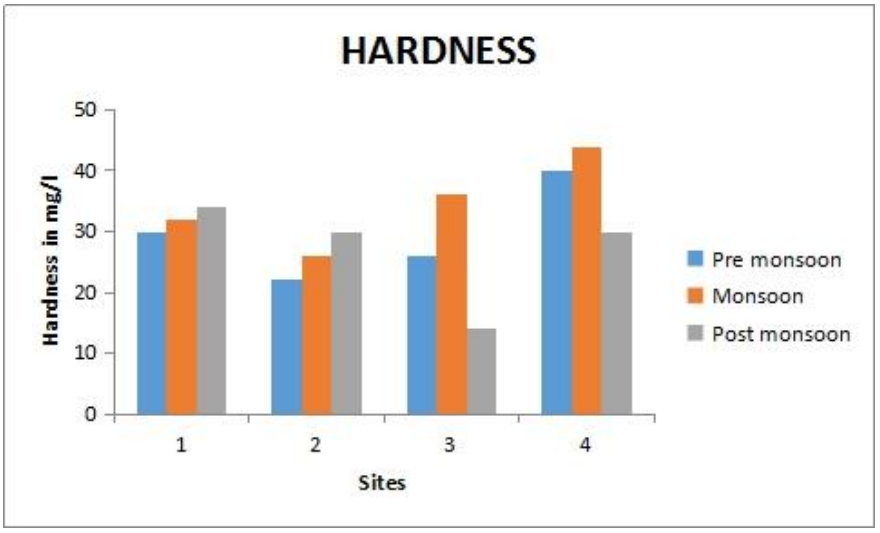


Fig 5: Graph showing seasonal variations of hardness

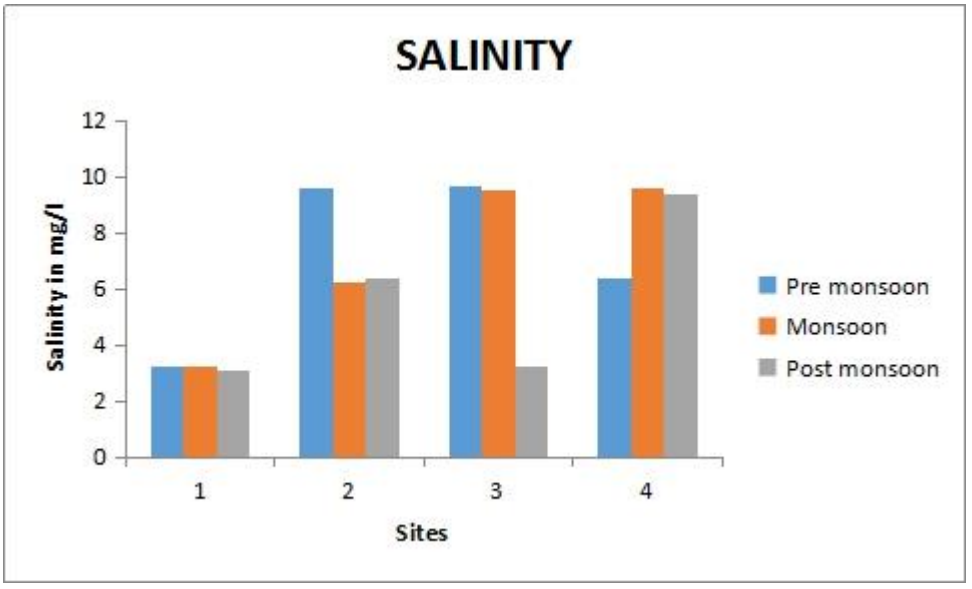


Fig 6: Graph showing seasonal variations of salinity

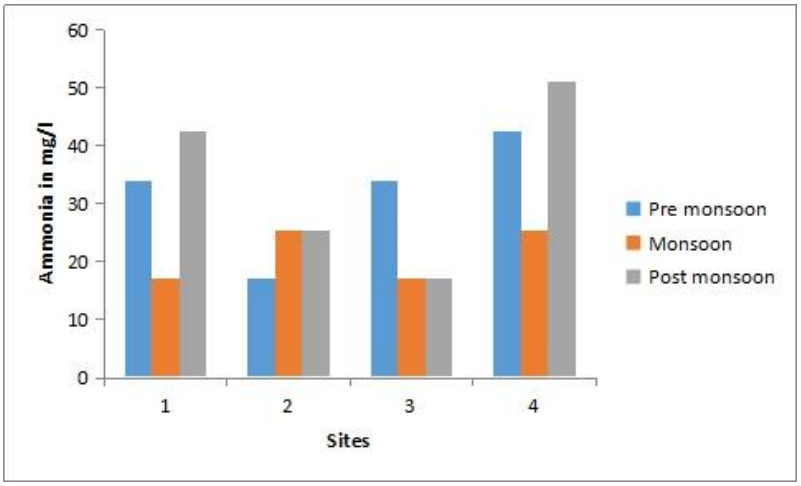


Fig 7: Graph showing seasonal variations of ammonia

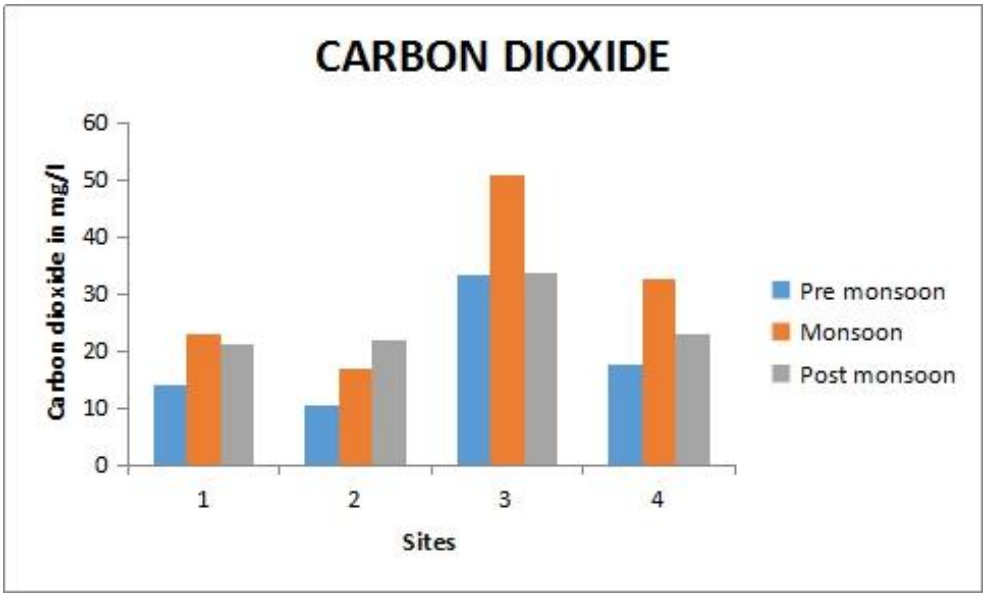


Fig 8: Graph showing seasonal variations of carbon dioxide

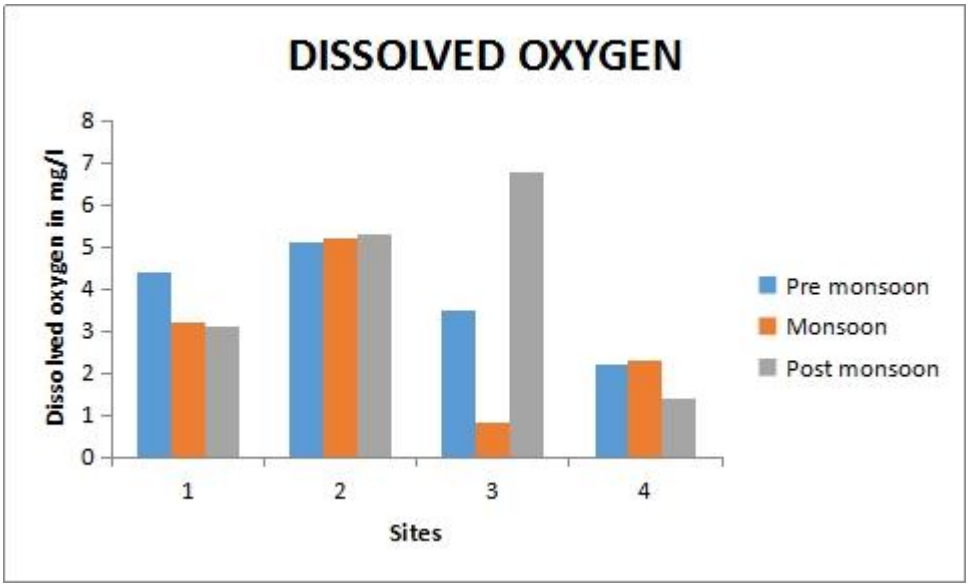


Fig 9: Graph showing seasonal variations of dissolved oxygen

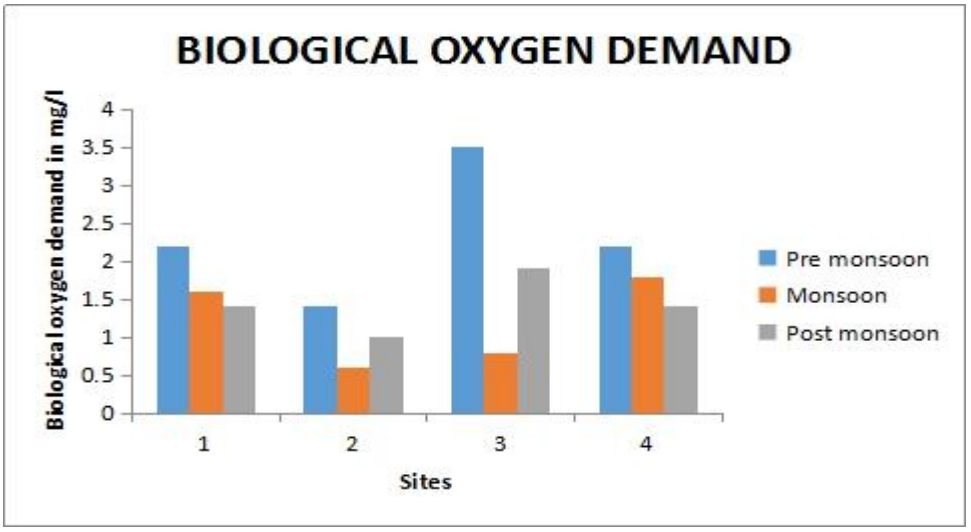


Fig 10: Graph showing seasonal variations of Biological Oxygen Demand

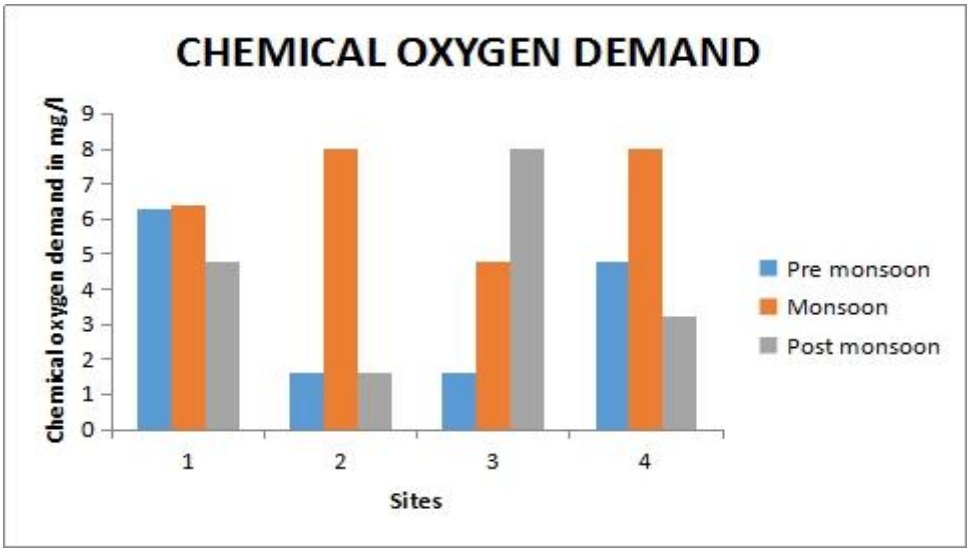


Fig 11: Graph showing seasonal variations of Chemical Oxygen Demand

DISCUSSION

Physico-chemical characteristics of water are highly influenced by the richness of biota, its exploitation and distribution (Unanam and Apkan,2006). Ponds are important hotspots for biodiversity. They support more species than any other fresh water habitat. They are more abundant than any other fresh water habitats and are found in virtually all environments.The pond water temperature is highly influenced by local climatic conditions. Temperature has an important role in physical, chemical and biological properties of water. Water temperature values ranged from 26^0C to 32^0C. The minimum value was recorded in monsoon period and maximum in post monsoon period. The temperature difference might be either due to the geographical differences in the location or due to difference between the collection times (Madhuri and Meenakshi, 2008). Considering the four sites, high temperature was recorded in site 4 (32^0C) during the post monsoon period. According to Desai (1995) water temperature varies depending on the season. This is reflected by lower water temperature at site 1 in monsoon due to cloudy weather and rainfall.The pH of pond water is considered as an index of

environmental conditions. It affects the biochemical reactions and controls the activities and distribution of aquatic fauna and flora. A slight variation in the pH can change the acidity or alkalinity of water. In the present study, the pH value was maximum in pre monsoon period (7.36 ± 1.52) and minimum in post monsoon period (5.7 ± 0.96). A high value of pH 9.1 observed in station 4 during pre monsoon period. The amount of calcium increases during pre monsoon period due to rapid oxidation or decomposition of organic matter and pH become alkaline state . Site 3 showed a low pH value of 4.6 during post monsoon season. Slight deviation towards acidity can be attributed to the anthropogenic activities like improper irrigation and weathering process (Sajitha *et al*., 2016).

Transparency is the measurement of light penetration in the water body. The secchi disc transparency correlates closely with the percentage of transmission of light. The average range of transparency was 17.13 c.m to 21.87 c.m. High transparency of 34.5 c.m was observed in site 2 during post monsoon season. Transparency of water is generally influenced by factors like wind action, suspended silt particles, plankton concentration and decomposition of organic matter at the bottom .Turbidity is a measure of the degree to which the water loses its transparency. The value of turbidity ranged from 6.3 NTU to 104.5 NTU. Higher value of turbidity, 104.5 NTU was recorded in site 3 during monsoon season. The colloidal material which exerts turbidity provides adsorption site for chemicals that may causes undesirable taste and may be harmful for biological organisms.

Water hardness is mainly caused by the presence of iron, magnesium and calcium ions and also because of Al, Zn, Ni and some other heavy metals in water. In the present study hardness varied from 14 to 44 mg/l in different seasons. Maximum hardness is recorded in site 4 (44 mg/l) during the monsoon season and minimum hardness is recorded in site 3 (14 mg/l) during the post monsoon period. According to APHA (2005) the desirable limit for hardness is 300 mg/l. Compared to the desirable limit, the values of the sample is found to be lie within the limit. Hardness is an important parameter in the detection of water pollution and causes various diseases.Salinity is the saltiness or dissolved salt content of a body of water. In the present study it has been observed that salinity ranged from

3.1 to 9.7 mg/l. Maximum salinity is recorded in site 3 (9.7 mg/l) during the pre monsoon period and minimum is recorded in site 1 (3.1 mg/l) during the post monsoon period.Ammonia is lethal to aquatic life even if present in small concentration. In the present study, the amount of ammonia ranged from 17 to 51 mg/l. The maximum range of ammonia was observed in station 4 (51 mg/l) during post monsoon period. Higher values of ammonia was observed in all sites during the post monsoon season. When algae and other suspended micro organisms die and settle down to the bottom and release their nitrogen content during decomposition. Ammonia in natural waters can be traced to percolating nitrates from sources such as decaying plant and animal material, agricultural fertilizers and domestic sewage (Adeyeye and Abulude, 2004). Drinking water contains more than 500 mg/l ammonia can cause methamoglobinemia in infants (Uba *et al*., 2001). High amount of ammonia in water bodies cause over growth of algae and other organisms and produce foul smell.Carbon dioxide is the end product of organic carbon degradation in almost all aquatic environments and its variation is often a measure of net ecosystem metabolism (Hopkinson, 1985). In the present study the maximum carbon dioxide range was recorded in site 3 (51 mg/l) during the monsoon period and minimum range was recorded in site 2 (10.5 mg/l) during the pre monsoon period. Gurumayum *et al*., (2002) also reported higher values of free CO_2 during monsoon months. According to Joshi *et al*.,(1995), the increase in carbon dioxide may be due to decay and decomposition of organic matter.

Dissolved oxygen is one of the most important parameters of the water quality and fundamental requirement of plant and animal life in water. Dissolved oxygen demonstrating the level of water quality and organic production in the water. In the present study, the dissolved oxygen is varied from 2.88 ± 1.84 to 4.15 ± 2.38 mg/l. According to Chaurasia and Pandey (2007), the quantity of dissolved oxygen in water is directly or indirectly depends on water temperature, partial pressure of air, etc. Rodgi and Nimbergi (1978) found that disposal of domestic sewage and other oxygen demanding wastes reduced the dissolved oxygen of the receiving water body. The maximum range of DO was recorded in site 3 (6.8 mg/l) during the post monsoon season .Biological Oxygen Demand is a measure of organic material contamination in water. It is the measure of degradable organic matter present in water. The BOD and other microbial activities are

generally increased by the introduction of sewage (Hynes, 1971). BOD varied significantly among the ponds.BOD values ranged from 0.64 to 3.52 mg/l.The maximum value of BOD was noticed in site 3 (3.52 mg/l) during the pre monsoon season. The minimum value of BOD was observed in the site 2 (0.64 mg/l) during the monsoon season. Higher values of BOD indicate the higher consumption of oxygen and higher microbial population load in the pond water .Chemical Oxygen Demand is an important parameter assessing the carbonaceous fraction of organic matter.Sayeshwara *et al*;(2010). COD of water sample ranged from 1.6 to 8 mg/l.Highest range of COD was observed in monsoon season (6.8 ± 1.53 mg/l) and lowest range was observed in pre monsoon season (3.58 ± 2.36 mg/l).

CONCLUSION

The present study indicates the seasonal variations of physico- chemical parameters of four different ponds in Vettiyar region of Thazhakkara panchayath namely Ramanalloor pond (site 1),Kandakalankavu pond (site 2),Valiyaveetil pond (site 3) and Panchayat pond (site 4). The study indicates that there is a pronounced variation of most of the water quality parameters with variation in season.The temperature range was maximum in the post monsoon period and minimum value was recorded in monsoon period. pH value was maximum in pre monsoon period and minimum in post monsoon period. First three sites exhibited almost acidic pH in all seasons and only site 4 shows the alkaline pH in two seasons. Moderately high levels of transparency were observed in post monsoon period. Moderately high levels of turbidity and hardness are recorded in the monsoon season. Salinity is maximum in the pre monsoon period. Ammonia is maximum in the post monsoon period. Higher values of ammonia were observed in all sites during the post monsoon season. Carbon dioxide availability was maximum in the monsoon period. Increased carbon dioxide affects the pH which affects the biota of that region. Dissolved oxygen and Biological Oxygen Demand are dependant on each other. The maximum value of BOD is noticed in the pre monsoon season. Highest range of COD was observed in the monsoon season. Ponds have been used a source as a traditional source of water supply from time immemorial in India. These water bodies are now polluted mainly due to discharge waste water, water from residential areas, sewage outlets etc. The study

indicates that the physico-chemical factors investigated exhibited well marked variations with distinct minima and maxima. The investigation reveals the necessity for rejuvenation of these ponds for preventing the dark future of these ponds if no effective measures are undertaken.

ACKNOWLEDGEMENT

The authors are extremely grateful to the PG Department of Zoology of Christian College, Chengannur for the facility rendered during the tenure work.

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A PRELIMINARY STUDY OF SPIDER DIVERSITY IN SAROVARAM BIOPARK KOZHIKODE

ASWANI SREEDHARAN O K[1], NISHI BABU[2*]

1. **Aswani Sreedharan** O K : P.G. Student, P.G Department of Zoology**,** Christian College, Chengannur
2. **Nishi Babu**[*] : Guest lecturer , P.G Department of Zoology**,** Christian College, Chengannur

***Corresponding author: Nishi Babu**, **nishibabu510@gmail.com,**Guest Lecturer, PG Department of Zoology, Christian College,Chengannur, India.

ABSTRACT:

Insects are the largest taxonomic group in the animal kingdom and their significant role in ecology needs no description. Spiders are exclusively predatory, hence can play a very important role in regulation of insect population in any ecosystem. Spiders are abundant and wide spread in almost all ecosystems and constitute one of the most important components of the global biodiversity. Best known for its predatory potential, social behavior, parental care, camouflage, mimicry, defensive technique and using different modes of communication. Due to their diverse predatory potential they act as potential bio control agent in agro ecosystem, which entail urgent need of research and education programs to create awareness in the society for their protection and conservation. The present study was done in Sarovaram Biopark Kozhikode Sarovaram (also known as Sarovaram Bio Park) is an eco-friendly development near Kottooly in Kozhikode city in India. The park is situated adjacent to Canoly Canal. The project has been developed with an eco-friendly theme and is located in an ecosystem consisting of wetlands and mangrove forests containing bird habitats. The present study revealed that the Sarovaram Biopark is qualitatively rich in spiders with 27 species of spiders coming under 10 families. A total of 72 spiders revealed 7 feeding guilds. The objective of the study was to analyze the spider diversity.

The period of study extended for two months from the first week of April 2018 to the last week of May 2018. Spiders also functions as ecological indicators signalling the health of natural ecosystem. Present study will yield valuable information of spider availability in the region.

***Key words*:** spiders, predatory potential, bio-control agent, arovaram Biopark

INTRODUCTION:

Spiders were among the earliest animals to live on land, probably evolving about 400 million years ago. About 40,000 spider species are currently known throughout the world.14447 species from 59 spider families has so far been reported in India (Zoological Survey of India). Spiders are abundant in most terrestrial ecosystems and are affected by change in vegetation structure (Utez, 1991). The current diversity of spider over 42,751 described species placed in 3,859 genera and 110 families. According to their web building ability, generally the spiders are considered as weavers or non-weavers. The weavers make the snares to trap insect for food, while the non-weavers hunt the prey by chasing or by stalking. The Araneids or typical orb-weaving spiders are seen all over the world. They prefer to live in moist places and very rarely found in the arid regions. Almost all species are construct orb-webs on foliage, either trees or shrubs and herbs or grass. And but they are not ground dwellers. The orb-webs are construct for predation and for protection for eggs. Spiders like the jumping spider, the lynx spider, the crab spider, and many others do not use webs to catch prey. They use their eyes and speed to catch insects.

Spider webs are made of continuous strands of silk produced from the six silk glands, beneath the abdomen. The webs are different in structure among different spiders. Mainly six different types of webs are seen in spiders. That is Orb webs, Irregular webs or nets, Sheet webs, Funnel webs, Triangular webs, and Single line snare. The principal characteristic feature of an orb web is that the central portion, the part lying within the supporting framework, consist of a series of radiating lines of dry and in elastic silk that support a thread of viscid and elastic silk. In Irregular webs or nets, the maze of threads extends in all

directions. In sheet webs the principal part of the web consists of a more or less closely woven sheet extend in a single plane and consisting of threads extending in all directions in that plane with no apparent regularity of arrangement. The principal part of funnel web is sheet like in structure, but webs of this type differ from the true sheet webs in having a tube extending from one edge. The triangular web, shaped like a triangle. And the single line snare is a single horizontal line, attached at both ends to branches, that stretches about four feet across open space in the forest. The spiders play most important role in the maintaining biological balance of nature. And they can play an important role in regulating and stabilizing the insect population in agriculture as well as in forest ecosystem. The spiders are used as a Biological control organism. Which emphasize the concept of integrated pest management in modern agriculture. Recently, there has been a realization by the ecologists that the components of agro ecosystem are tactable to manipulate and that spiders are convenient model organisms. They feed exclusively on insect and are of economic value to man because of its ability to suppress the pest abundance in agro ecosystem. It is a best method to reduce the use of chemical pesticides in agricultural field. So it reduces the many harmful effects in the agricultural field. They eat grasshoppers and locusts which destroy crops. Spiders also eat flies and mosquitoes which carry diseases. Spiders feed mostly on insects but some capture and eat tadpoles, small frogs, small fish and mice. Many researchers are study the spider as a Biological control organism. (vungs, labutr,1988; Sahu et al.1996; Patal,2003;Mathirajan and Raghubathy,2003; Vanitha et al.,2009; Bhatkar,2011; Phalgumchetia and Dilip Kumar kalita,2012 and Mohsin Bukhariet al., (2012). Many threats to spider diversity have been documented. The primary threat is habitat loss and degradation. Some spiders have become threatened due to urban development, land use management technique, air and ground water pollution by pesticides and fertilizers. Some spiders are venom producing poisons and some are not poisons. The poison contains proteins, amines, and polypeptides. Spiders have many enemies including snakes, frogs, toads, lizards, birds, fish and other animals.

The abundance of the spider can be summarized in the following few sentences of Gertsch (1949) “spiders are among the dominant predators of any terrestrial community”. When the fauna of a soil and its plants cover is

analyzed, they come to light in vast numbers, in convincing abundance that it is evident that they play a significant part in the life of every habitat. And this is the first work of sider diversity in Sarovaram Bio park, Kozhikode.

MATERIALS AND METHODS:

The collections were taken from Sarovaram BioPark of Kozhikode district. The period of study extended for two months from the first week of April 2018 to the last week of May 2018. Spiders were collected during morning or evening time because of most of them were active during that time. The collection was carried out three days in a week. Sarovaram Biro park is an ecofriendly development, near Kotooli in Kozhikode city in Kerala.

Required materials includes a note book, pen, collection bottle with 70% alcohol etc. Collection of most web building and surface dwelling spiders was made by DIRECT HAND PICKING METHOD with the help of bottle. INVERTED UMBRELLA METHOD, an inverted umbrella was placed below the flowering shoots and bushes and when the tree or branch was thoroughly shaken, spiders along with insects fallen to the inverted umbrella. Then spiders were transferred into collecting bottles.

The collected spiders were preserved in bottles of 70% alcohol. The identified, collected data was transferred into Excel spreadsheets, from which graphs were generated to assist in analysis. Diversity indeces like Shannon – Wiener index, Richness index, Dominance index, and Evennes index were used to assess the diversity of spiders in Sarovaram Biopark using PAST software.

RESULT:

The objective of the given work was to study the diversity of spiders. The study was carried out in Sarovaram Biopark Kozhikode, Kerala. The area selected for study was mainly endowed with different types of habitat.

In the present study, 27 species of spider were recorded from the SarovaramBiopark, Kozhikode, during the period, first week of April 2018 to last week of May 2018. A total of 97 spiders, which belonging to 27 species

(Table 1), under 10 families (Table 2), were collected from the study area. These 27 species of spiders belongs to families Salticidae, Hersiliidae, Thomisidae, Tetragnathidae, Sparassidae, Lycosidae, Eutichuridae, Araneidae, Oxyopidae, and Theridiidae (Table 1). The family Salticidae is the most group divers family. A total of 27 species of spiders revealed 7 feeding guilds, Stalker, Sensing web, Ambusher, Orb web weaver, Foliage hunter, Ground runner and Space web builder.

Biodiversity of collected spiders in the SarovaramBiopark, Kozhikode was assessed by species richness index by Mergaef, dominance index by Simpson's index, the species diversity index by the Shannon – Weinerr index and Evennes index by Pielou. Shannon – Weinerr diversity index of spider recorded a value of 2.734 and the Margalef species richness was 5.683. The value of Evennes index is 0.5715 and the dominance index recorded was 0.8928.

TABLE 1: List of spider species collected from the site during the study

FAMILY	SPECIES	NO.OF SPECIES	GUILD
Salticidae	*Hyllus semicupreus*	18	Stalker
	Plexippuspetersi	9	Stalker
	Plexippuspaykulli	7	Stalker
	Baviainsularis	2	Stalker
	Carrhotusviduus	9	Stalker
	Stenaelurillus sp.1	4	Stalker
	Menemerusbivittatus	1	Stalker
	Telamoniadimidiata	4	Stalker
	Asemoneatenuipes	6	Stalker

	Phintellavitata	7	Stalker
	Thianiabhamoensis	4	Stalker
	Bianos sp.1	1	Stalker
Hersiliidae	*Hersiliasavignyii*	2	Sensing web
Thomisidae	*Xysticus sp.1*	2	Ambusher
	Camaricusformosus	1	Ambusher
	Thomisusprojectus	1	Stalker
Tetragnathidae	*Guizygiellamelanocrania*	3	Orb web weaver
	Tetrgnathamandibulata	1	Orb web weaver
	Tyloridaventralis	1	Orb web weaver
Sparassidae	*Heteropodavenatoria*	2	Foliage hunter
	Olios sp.1	1	Foliage hunter
Lycosidae	*Lycosamackenziei*	1	Ground hunter
Eutichuridae	*Cheiracanthiummelanostomum*	4	Foliage hunter
	Araneua sp.1	1	Orb web weaver
Araneidae	*Argiopeanasuja*	1	Orb web weaver
Oxyopidae	*Oxyopesbirmanicus*	2	Stalker
Theridiidae	*Euryopisepisinoides*	2	Space web builder

TABLE 2: Family wise distribution of spiders in the study area

SL.NO	FAMILY	NO.SPECIES		TOTAL
		MALE	FEMALE	
1	Salticidae	19	53	72
2	Hersiliidae	1	1	2
3	Thomisidae	1	3	4
4	Tetragnathidae	2	3	5
5	Sparassidae	0	3	3
6	Lycosidae	0	1	1

7	Eutichuridae	0	4	4
8	Araneidae	0	2	2
9	Oxyopidae	0	2	2
10	Theridiidae	1	1	2

TABLE 3 : The species with most number of specimen collected

SL NO	SCIENTIFIC NAME	NO: SPECIES COLLECTED
1	*Hyllus semicupreus*	18
2	*Plexippus petersi*	9
3	*Plexippus paykuli*	7
4	*Carrhotus viduus*	9
5	*Asemonea tenuipes*	6
6	*Phintella vittata*	7

FIGURE
Chart showing most number of specimens collect

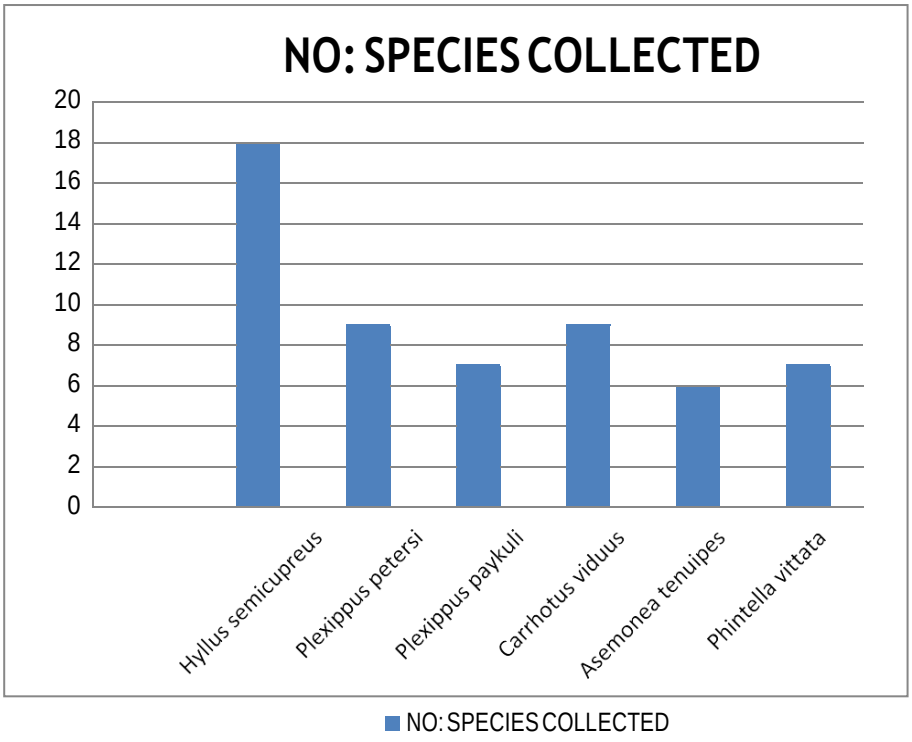


TABLE 4: List of species with least number of specimens collected

SL.NO	SCIENTIFIC NAME	NO.OF SPECIMENCE COLLECTED
1	*Baviainsularis*	2
2	*Hersiliasavignyi*	2
3	*Stenaelurillus sp.1*	4

4	*Telamoniadimidiata*	4
5	*Menemerusbivittatus*	1
6	*Thianiabhamoensis*	4
7	*Xysticus sp.1*	2
8	*Guizygiellamelanocrania*	3
9	*Tetragnathamandibulata*	1
10	*Heteropodavenatoria*	2
11	*Tyloridaventralis*	1
12	*Lycosamackenziei*	1
13	*Cheiracanthiummelanostomum*	4
14	*Araneus sp.1*	1
15	*Camaricusformosus*	1
16	*Argiopeanasuja*	1
17	*Olios sp.1*	1
18	*Oxyopesbirmanica*	2
19	*Bianos sp.1*	1
20	*Euryopisepisinoides*	2
21	*Thomisusprojectes*	1

FIGURE 2

Chart showing least number of specimens collected

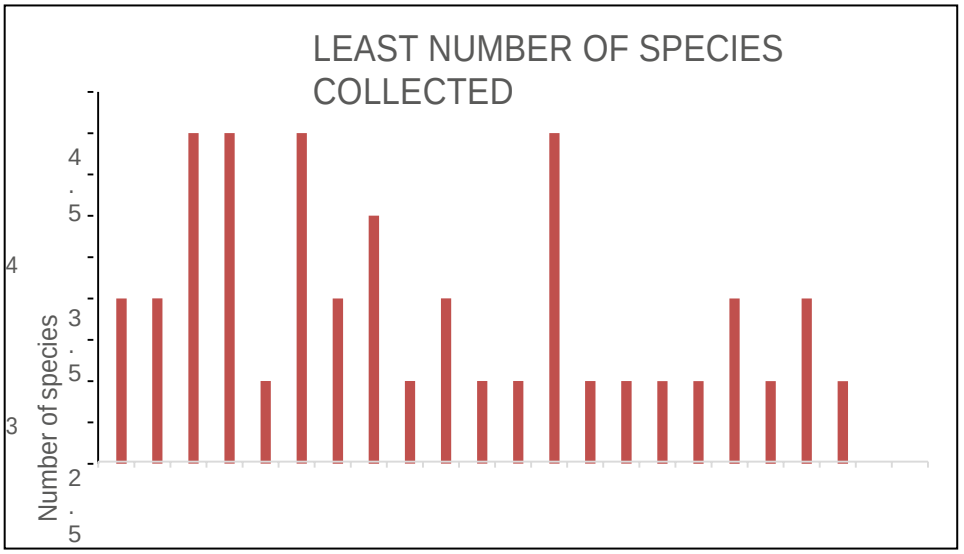
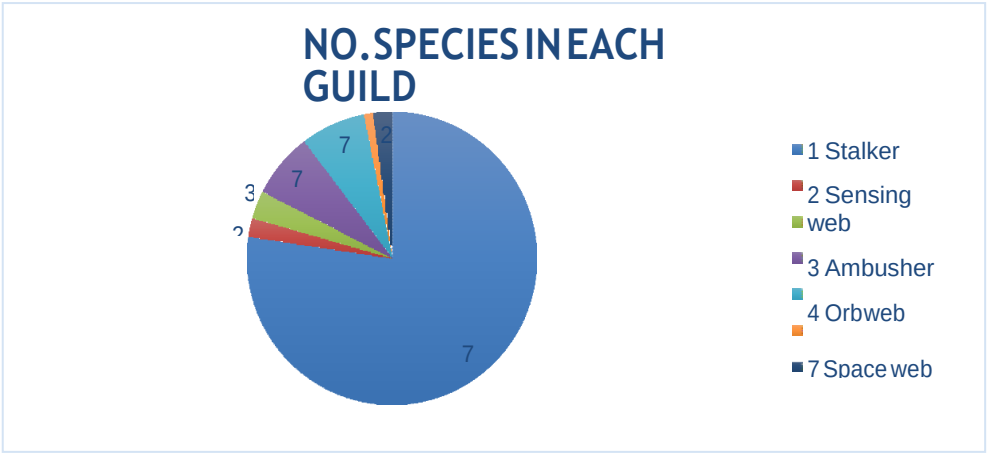


TABLE 5 : Number of species in each guild

SL.NO	GUILD	NO.SPECIES
1	Stalker	75
2	Sensing web	2
3	Ambusher	3
4	Orb web weaver	7
5	Foliage hunter	7
6	Ground runner	1
7	Space web builder	2

FIGURE 3

Showing number of species in each guild



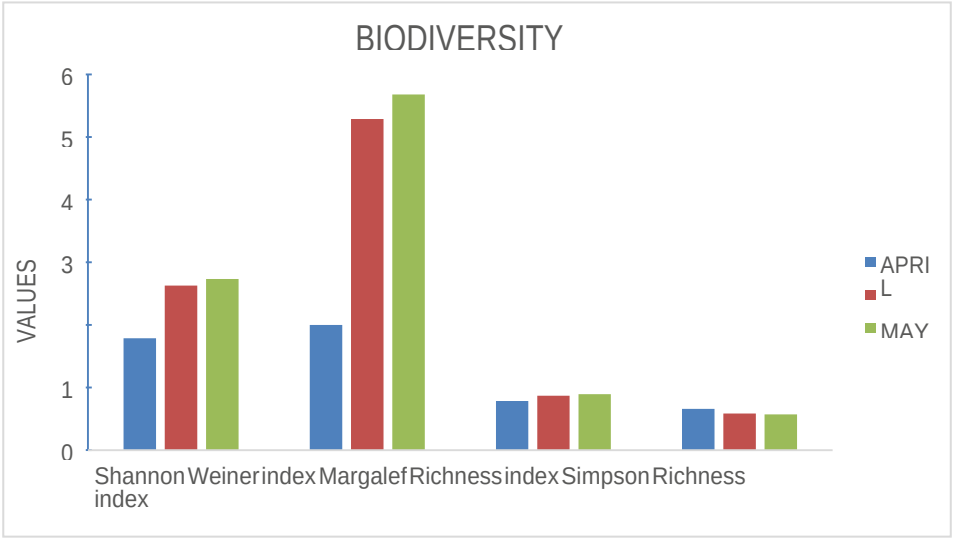


FIGURE 4: Chart showing biodiversity indices of collected spiders

PHOTOGRAPHS OF COLLECTED SPIDERS

Hyllus semicupreus petersi

Plexippus

Plexippus paykuli

Bavia insularis

PHOTOGRAPHS OF COLLECTED SPIDERS

Carrhotus viduus

Hersilia savigniyi

Telamonia dimidiate projectus

Thomisus

PHOTOGRAPHS OF COLLEECTED SPIDERS

Euryopis episinoides

Oxyopes birmanicus

Camaricus formosus

Cheiracanthium melanostomum

PHOTOGRAPHS OF COLLECTED SPIDERS

Tylorida ventralis

Tetragnatha mandibulata

Phintella vittata

Thiania bhamoensis

PHOTOGRAPHS OF COLLECTED SPIDERS

Heteropoda venatoria

Argiope anasuja

DISCUSSION:

The present study revealed that the Sarovaram Biopark at Kozhikode is qualitatively rich in spiders with 27 species of spiders coming under 10 families. A total of 72 spiders revealed 7 feeding guilds.

A total of 72 spiders were collected from Family Salticidae (Table 1). The

12 different species were *Hyllus semicupreus, Plexippus petersi, Plexippus paykuli, Bavia insularis, Carrhotus viduus, Stenaelurillus sp.1, Menemerus bivittatus, Telmonia dimidiata, Asemonea tenuipes,Phintella vitata, Thiania bhamoensis and Bianos sp.1* (Table 1). The species *Hyllus semicupreus* is heavy bodied jumper and also known as the "Semi coppered heavy jumper". They construct oval, thick silken webs webs on the underside of leaves. The species *Plexippus petersi* also known as known as "Small zebra jumper". It is common in around households on compound walls and tree trunks. The species *Plexippus peykuli* is a jumping spider. This spider doesnot spin a web but builds a silken retreat in an elevated position such as the edge of the ceiling from which it makes hunting forays. The species *Bavia insularis*, the genus of Bavia is the first record of jumping spider. The species *Carrhotus viduus* commonly called "Double striped Carrhotus". It is usually around low vegitations and flowering plants close to water source. The genera of Stenaelurillus, have two white longitudinal stripes on the carapace, both sexes show strong bristles around the eyes. The species *Menemerus bivittata* is commonly known as "Gray wall jumper" and usually found on the walls of buildings or on trees trunks where it Stalks its prey. The species *Telamonia dimidiata* is commonly called "two striped jumper" and found in leaves of bushes and trees. The species *Asemonea tenuipes* also known as "Tailed spider" and they are mainly oriental in distribution. The species *Phintella*

vitata is commonly called “Banded Phintella”. It found in bushes and medium sized plants. The species *Thiania bhamoensis,* build a siliken retrays by binding of a pair of green leaves.

The family Hersilidae represented total of 2 spiders (Table 2), of different species (Table 1). The species *Hersilia savignyi* also known as “Two tailed spider”. It found in tree trunks. It is a very common spider in our tree barks and exhibits colour variation according to the substrate on which it is found.

A total of 4 spiders were reported from family Thomisidae (Table 2), of 3 different species. The 3 different species were *Xysticus sp.1, Camaricus formosus, and Thomisusprojectus.* The species of genera Xysticus is distributed almost worldwide, but has not been recorded from South America. The species *Camaricus formosus* commonly seen in to reside on flowers or seen to rest within leaf folds. And the species *Thomisus projectus* commonly called “Cream crab spider”. It is an endemic species to India, commonly found inside the flowers and generally hide behind sepals and petals.

The family Tetragnathidae represent totals of 4 spiders (Table 2), of 3 different species. The represented species were *Guizygiella melanocrania, Tetrgnatha mandibulata* and *Tyloridaventralis.* The species of Tetragnathidae are called “Armoured spiders”. The species of *Tetragnatha* construct orb web usually in vegetation near or above streams and ponds.

A total of 3 spiders were reported from the family Sparassidae (Table 2) which of 2 species. The species represented were *Heteropoda venatoria, Olios sp.1*. The family Sparassidae is commonly known as “Giant crab spiders”. The *Heteropoda venatoria* is the common house spider inhabit in the houses and Tree trunks in gardens.

The family Lycosidae represent 1 spider (Table 2), of 1 species. The species represented were *Lycosa mackenziei*. The *Lycosa makenziei* is also a ground dweller spider commonly known as "Soil tycosid spider" that construct burrows in loose sand.

A total of 4 spiders were reported from family Eutichuridae (Table 2) which of 1 species. The species represented were *Cheiracanthiumm melanostomum*. The species of Cheiracanthum commonly known as the "Yellow sac spider".

The family Araneidae represent total of 2 spiders (Table 2), of 2 different species. The represented species where *Araneus sp.1* and *Argiope anasuja*. The species of family Araneidae are Orb web spiders. They use the "spin-wrap-attack" method to subdue this prey. The species *Argiope anasuja* found in gardens.

A Total of 2 spiders were reported from family Oxyopidae (Table 2), of 1 species. The species represented were *Oxyopes birmanicus*. The species *Oxyopes birmanicus* commonly encountered in foliage. They build no webs but are active solitary hunters.

The family Theridiidae represent total 2 spiders (Table 2) of 1 species. The represented species is *Euryopis episinoides*. The family Theridiidae constitutes "comb-footed spiders" or "Cobweb spider".

The family Salticidae is the most diverse family with 72 spiders of 12 different species (Table1).

The guild structure of collected spiders revealed 7 feeding guilds.viz., Stalker (Plant dwelling spider, commonly inhibit on grass, shrubs and trees), Sensing web (Habitat on tree barks), Ambusher (Habitat on leaves, hide flower or

leaves and capture insect that visit them), Orb web weaver (Inhabit in lower stratum of grass lands and construct perfect orb webs in the ground layer vegetation), Foliage hunter (Free living, inhabit in sac like retreals made up of green leaves), Ground runner (Free living ground dwellers, inhabit in woody debris, litter or humus on the forest floor in shaded areas).

The comparative study of guild structure of species from the collected spiders shows Stalker is the most abundant guild.

The biodiversity of collected spiders in the Sarovaram Biopark was assessed by species richness indeces by Mergalef index, dominance index by Simpson's index and the species diversity indeces by Shannon – Weiner index and Evenness index by Pielou. The Shannon – Weiner index value showed the high diversity of spider in the collected area. The Margalef richness index and Simpson dominance index showed the high richness and dominance of species. The Evenness index value showed, it is not evenly distributed.

Spiders make up a considerable portion of the animal life of the vast and diversified land. Spiders also functions as ecological indicators signaling the health of natural ecosystem. Present study will yield valuable information of spider availability in the region.

CONCLUSION:

The 27 species of spiders belonging to 10 families reported from the study indicate diversity of spiders in the area. The ecological as well as taxonomic information of Indian spiders are lacking up to a great extent and studies of spiders on these regards are completely untouched in this area. However spiders can be considered as the most efficient one, among the few bio-indicator species in ecological studies. (Kapoor, 2008; Noss, 1990). This study shows information related to the species distribution in the particular habitat. Detailed study on spider

fauna of this area and inclusion of spiders in conservational strategies are recommended.

ACKNOWLEDGEMENT

The authors are extremely grateful to the PG Department of Zoology of Christian College, Chengannur for the facility rendered during the tenure work. Also thankful to Mr. Pradeep M.S,Research scholar, Department of Arachnology, S. H College Thevara, Ernakulam for his valuable guidance during the project work.

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ECONOMICS OF TRAIN TRAVEL A CASE STUDY OF KOLLAM – CHENGANNUR ROUTE

Noeline Everest
MA Economics
Christian College, Chengannur
Email: noyalineverest32@gmail.com
Phone: 8089505201

Intoduction

Indian Railways (IR) is India's national railway system operated by the Ministry of Railways. It manages the fourth-largest railway network in the world by size, with 121,407 kilometers of total track over a 67,368-kilometre route. Forty nine percent of the routes are electrified with 25 KV AC electric traction while thirty three percent of them are double or multi-tracked.

IR runs more than 13,000 passenger trains daily, on both long-distance and suburban routes, from 7,349 stations across India. The trains have a five-digit numbering system. Mail or express trains, the most common types, run at an average speed of 50.6 kilometers per hour (31.4 mph).In the freight segment, IR runs more than 9,200 trains daily. The average speed of freight trains is around 24 kilometers per hour (15 mph).

As of March 2017, IR's rolling stock consisted of 277,987 freight wagons, 70,937 passenger coaches and 11,452 locomotives. IR owns locomotive and coach-production facilities at several locations in India. The world's eighth-largest employer, it had 1.308 million employees as of March 2017.

In the year ending March 2018, IR is projected to carry 8.26 billion passengers and transport 1.16 billion tons of freight. In the fiscal year 2017-18, IR is projected to have earnings of ₹1.874 trillion (US$28 billion), consisting of ₹1.175 trillion (US$18 billion) in freight revenue and ₹501.25 billion (US$7.5 billion) in passenger revenue, with an operating ratio of 96.0 percent.

By providing means of mobility to a large number of people and huge quantities of materials across the country, Indian Railways contribute substantially to the growth of the economy.

Review of Literature

Geethika, ShefaliNandan (2006)identifies components of service quality of IR on platforms through an empirical exploratory study and a survey of passengers. The important service components identified are refreshment and behavioural factors.

Durga Prasad Vijay V. (2007) evaluates the amenities offered by railways to its passengers, and points out the need for improvements in the railways to provide better services to their customers. The study is based on Hyderabad Division of Indian Railways.

Anuradha,(2014), "Study on Passenger's Satisfaction towards Railway Services in Erode Junction" concluded that majority of the sample passengers are having low level of awareness and dissatisfied with the services offered by the Indian Railways.

Rajeshwari and Tamilchelvi (2014)stated in their article entitled "factors influencing the passengers to prefer rail transport: A study in Coimbatore region "in this concept, railways as energy efficient transport mode ideally suited for long distance travel as well as prefect suited for bulk mode of transport Indian railways offer many services; the preferences and needs of the passengers are dynamic.

Indian Railways is the major mode of transport in the country for passengers as well as freight due to its large network, number of trains, and affordability. In India most of the people are preferring railway transportation due to low cost and convenience. On the industry front, it is the only player; hence, a monopoly has been created (which is legal). On the market front, the majority of its customers are illiterate/semi educated and low/middle income with no/low consciousness for quality aspects of service. The monopoly structure has created a typical situation where the service provider (Indian Railways) has no competition and can afford to ignore aspects such as quality of service, customer satisfaction, and product promotion.

Objectives

- To analyse the socio-economic conditions of railway passengers of Kollam- Chengannur route.
- To analyse the factors that influences the passenger's choice of railway as a mode of transportation.
- To analyse the passengers satisfaction of various services provided by the Indian Railway
- To study the problems faced by passengers while travelling in the train.

Data Source and Methodology

The present study is an empirical research based on survey method. The present study is confined to Kollam- Chengannur railway route. Random sampling technique is used to draw samples from both the railway junctions. The sample passengers are floating population and they remain busy in reaching their platforms, listening to announcement, making enquiry and looking at display charts. Hence, the sample size is chosen as 100 and it is considered to be adequate and representative.

The present study is largely based on primary data. Primary and secondary data are used in the present study. The required primary data are collected using well-structured questionnaire. The needed secondary data were collected from books, journals, newspapers, periodicals, reports, internet and the like.

After the collection of data, the filled up interview schedules were edited properly. A master table was prepared to sum up all the information. With the help of the master table, classification tables were prepared and they were taken directly for analysis. The data was analyzed using Simple percentage method, Likert scale, Multiple response analysis, Chi-square test, Bar diagrams and Pie charts

Limitations of the Study

The universe in this study is the entire population of the country but due to time constraint sample size is restricted to 100. Kollam and Chengannur Railway Junctions has been selected as the study area. Most of the respondents remained busy in reaching their platforms, listening to announcement, making enquiry and looking at display charts and they might have registered their remarks without proper application of mind.

Dataanalysis

The universe in this study is the entire population of the country; hence a definite statistically sound sample was not feasible. To evaluate the passenger satisfaction towards Indian Railways, a sample survey is conducted in the two stations of Southern zone of Indian Railways through a random sample of 100 respondents. The study was conducted during the period May 2018 to July 2018. The data is collected through structured schedule.

- **Socio-Economic Conditions of Railway Passengers**

The data was analysed using simple percentage method. It can be interpreted that a large percentage is graduates and salaried class belonging to middle class section of the society. Salaried class who operate daily or weekly between place

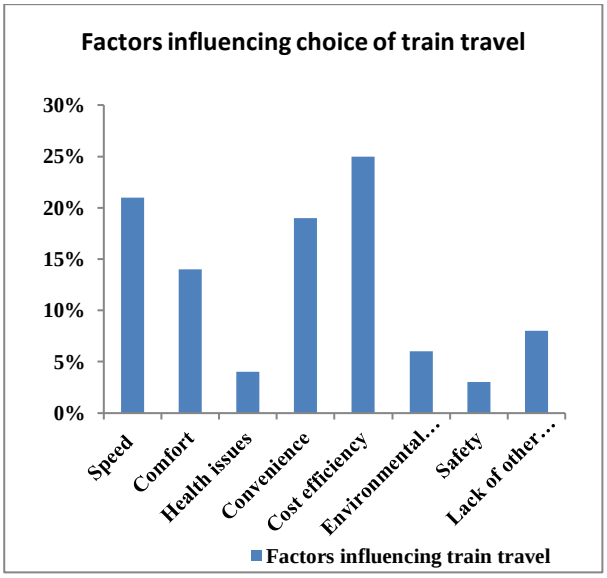
of work and their homes constitute a large part of rail travelers. Middle income groups find railway as a cheap and convenient mode of transit.

- **The Factors that influences the passengers choice of railways**

There could be a number of reasons for passengers to choose train travel. Major reasons that are attributed for this preference were listed out after careful thought and interaction. The respondents were asked to rank the first preference for their choice. The frequency of the first preference of respondents is computed and is analyzed using percentage. The result is checked using one way chi- square test. Following table presents the important reasons for preferring trains as the mode of transport.

Factors influencing choice of railways

SlNo	Factors	No of respondents	Chi-square value	Percentage of respondents
1.	**Speed**	21	39.84	21%
2.	**Comfort**	14		14%
3.	**Health issues**	4		4%
4.	**Convenience**	19		19%
5.	**Cost efficiency**	25		25%
6.	**Environmental problems caused by other means of transport**	6		6%
7.	**Safety**	3		3%
8.	**Lack of other cheap public transport**	8		8%



The data collected clearly shows that cost efficiency is the major reason for most of the respondents for choosing railways. 25 per cent of the total respondents choose train because they find it cost efficient.

The result is counter checked and confirmed using a One Way Chi Square test.Chi Square value,

$$\chi^2 = \sum \frac{(o-e)^2}{e}$$

Where o is the observed frequency and e isexpected frequency.

Here the null hypothesis is that there is no significant relationship between cost efficiency and choice of rail transport.

We get the chi square value as 39.84 and the critical value is14.067. Since calculated value is greater than critical value, the null hypothesis is rejected i.e. there is a significant relationship between cost efficiency and choice of rail transport.

- **Level of satisfaction**

The questionnaire is analyzed using statistical index and variables are graded into different levels of passenger satisfaction as highly satisfied,satisfied, good, dissatisfied, and highly dissatisfied.The schedule has been constructed on five point Likert scale with satisfaction levels from the highest to the lowest. Likert

scale enables to quantify opinion based items. The maximum score of 5 was given to the best, followed by4, 3, 2, and 1 to the lower level of satisfaction. Then the mean is calculated using the formula

Mean score = [(number of people who selected response 1)*(weighting of response 1)+(number of people who selected response 2)*(weighting of response 2)……+(number of people who selected response n)*(weighting of response n)] /(total number of respondents)

Passenger satisfaction is high for variables with mean scores ranging from 3.5-5, moderate for mean scores ranging from 2.5-3.5 and low mean scores ranging from 0-2.5

The study identifies the factors that determine passenger satisfaction with the quality and quantity of services provided by the Indian Railways in general and in the railways stations and on board.Analysis of level of satisfaction and the services offered by railways infer that the respondents are highly satisfied with the variables like fare & other charges,, provision of information about trains schedules/ platforms, display of reservation charts in the station, concession for senior citizens, provision of proper lighting and fan, ATM provision in the stationprovision for mobile charging and special compartment for ladies

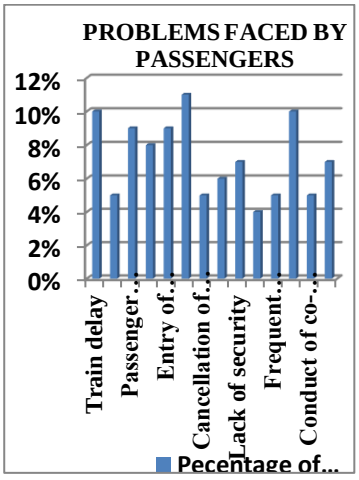
Passengers are highly dissatisfied with cleanliness of compartments and toilets and provision of first aid and medical facilities in train.

- **Problems faced by passengers**

  If the Indian Railways properly assess the problems and inconveniences of the passengers and deliver the service according to their expectation, it will be the most profitable public sector undertaking in India. Multiple Response Analysis is used to identify the problems faced at railway stations and travelling in train. Following table highlights the problems faced by respondents at railway stations and in trains during the time of train travelling.

Problems	**Frequency**	**Percent of responses**	**Percent of cases**
Train delay	90	10%	90%
Poor maintenance of platform	40	5%	40%

Passenger seating capacity	80	9%	80%
Poor pantry car service	65	8%	65%
Entry of unauthorized vendors and beggars	75	9%	75%
Poor maintenance of compartments	95	11%	95%
Cancellation of train	40	5%	40%
Conduct of personnel travel examiners and other officials	53	6%	53%
Lack of security	58	7%	58%
Less number of booking counters	35	4%	35%
Frequent failure of server and slow issue of tickets in the counters	44	5%	44%
Overcrowding in platforms	88	10%	88%
Conduct of co-passengers	39	5%	39%
Lack of general compartment	60	7%	60%
Total	862	100%	



Among the various factors considered, the problems faced by the majority of the passengers are bulk booking of tickets by agencies, heavy crowd in the platform and problems of theft. Railway Police Force could be strengthened to improve the security of the passengers. Better infrastructures can be introduced to avoid congestion in the stations and railway ticket reservation facilities can also be improved. If all the suggestions are considered by the railway authorities, then it is a hope that Indian railways will excel in the near future.

Findings and conclusion

The main findings of the study are the following:

- A vast majority of train travelling public are male which constitutes a 56 percent.
- Majority of the passengers fall in the age group 28-37 i.e.46 percent.
- 57 percent of the respondents have degree qualification whereas 8 percent of the respondents have only plus two qualification.
- Majority of the respondents are salaried. It is inferred from the data that salaried persons constitute 67 percent of respondents.
- From the data it can be drawn that it is low income and middle income group of passengers compute the majority. 47 percent of the respondents earn income less than
  20,000. 36 percent of the respondents earn income between 20,000-30,000.
- The unmarried passengers account for 34 per cent and the married account for 66 per cent. In the present study, most of the respondents are married.
- Majority of the respondents travel frequently. 90 per cent of the respondents travelled daily, whereas respondents 4 per cent travelled rarely.
- A large number of travelers preferred train journey for work, which constitute 75 per cent of total respondents.
- Middle income groups find railway as a cheap and convenient mode of transit.
- On analyzing the factors influencing the choice of rail transport using 8 variables, cost efficiency stands first preference to 25 percent of respondents. Speed stands the first preference to 21 percent of the respondents. These two factors are the most influencing ones. There is a significant relationship between the cost of travel and choice of railways

which is found using one way chi-square test. The chi-square value is 39.84

- Analysis of level of satisfaction and the services offered by railways infer that the respondents are highly satisfied with the variables like fare & other charges, number of ticket counters, provision of information about trains schedules/ platforms, display of reservation charts in the station, concession for senior citizens, provision of proper lighting and fan, ATM provision in the station, connection to other mode of public transport, provision for mobile charging, efficiency of chain pulling system and special compartment for ladies.
- Passengers are moderately satisfied with convenience of e-ticketing, ease of buying tickets, ticketing conversion facility with respect to class/ date, sign boards display in platforms, clarity of electronic information, clarity of announcement, provision of ramps and wheel chairs for disabled passengers, attitude of ticketing staff, information provided by ticketing staff, provision of seating arrangement in the platform, availability of waiting rooms, cleanliness and maintenance of station facilities, availability of quality food and refreshment, availability of prepaid taxi and auto services, comfort in seating, provision of lighting and fans, comfortable and convenient birth facilities and availability of quality food in trains.
- Passengers are highly dissatisfied with mechanical ticketing devices like automatic vending machine, refunding system in ticketing, ladies quota in ticket booking, display of porter charges in the station, assistance & information for disabled or elderly people, availability of cloak room facilities, provision of drinking water, availability of clean toilets, availability of first aid and medicine in station, sufficiency and affordability of protected parking facilities, punctuality and reliability of trains, sufficient seating capacity for passengers, cleanliness of compartments and provision of first aid and medical facilities in train.
- The main problems faced by railway passengers are train delay, poor maintenance of platform, passenger seating capacity, poor pantry car service, entry of unauthorized vendors and beggars, poor maintenance of compartments, cancellation of train, conduct of personnel travel examiners and other officials, lack of security, less number of booking counters, frequent failure of server and slow issue of tickets in the counters, overcrowding in platforms, conduct of co-passengers and lack of general compartment
- From the results obtained it can be inferred that poor maintenance of compartments is the problem that majority of the respondents finds severe

constituting 11 per cent of the total problems. Following problems like train delay and overcrowding in platforms computing 10 per cent each.

Suggestions

- Porter charges need to be displayed prominently in all railway stations to prevent overcharging of the passengers by the porters.
- Adequate ramps, wheel chairs and facilities for inter platform transfer for free movement of the aged and the disable should be improved.
- Maintenance of cleanliness in platforms and compartments should be regularly monitored.
- Provision of clean toilets in railway stations and compartments should be ensured.
- Medical facilities or emergency medicine should be enhanced and changed frequently.
- Availability of pre-paid taxi, auto services and connectivity to other public transport should be improved.

Conclusion

The study presents the socio-economic conditions of railway passengers. The level of satisfaction versus various services offered by Indian Railways is also analyzed. From the analysis we get that the highly satisfied variables are fare and other charges and the highly dissatisfied variable is availability of first aid and medicine. From the study it can also been inferred that cost efficiency is the main factor that influence the choice of railways by majority of the passengers.

From the study it is also clear that the services offered by the Indian Railways to its passengers need to be improved and modernized to satisfy the passengers. Among the various factors considered, the problems faced by the majority of the passengers arepoor maintenance of compartments, train delay and overcrowding in platforms. Railway Police Force could be strengthened to improve the security of the passengers. Better infrastructures can be introduced to avoid congestion in the stations and railway ticket reservation facilities can also be improved. If all the suggestions are considered by the railway authorities, then it is a hope that Indian railways will excel in the near future.

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Saint or Thief: A study of cultural analysis and perspectives based on Anand Neelakantan's *Asura, Tale of the vanquished*.

Anish T Babu
I^st^ year MA English
Christian College, Chengannur

The very ink with which the history is written is merely fluid prejudice.

-Mark Twain

Abstract:

The social relationship between man, society and culture within the grid indicated the creation of several didactic tale, different narratives and versions. These narratives indirectly aid us to expand or broaden our grid of perspectives resulting in overcoming the detrimental bigoted mindset. It allows the voices from the peripheries to unite with the mainstream guiding to a robust cultural pluralism. But we live in a culture where we are bombarded with other people trying to define us on their conception and stereotypes and tagging us with titles of 'Hero or villain'. This is an attempt to analyze the voices of the vanquished Ravana and his people who became the victims of cultural hegemony.

Social psychology has always emphasized the crucial role of social perception—that the reality or factual status of a social act depends often critically on "**the eye of the beholder**"—on specifically who is interpreting or imposing meaning on the event. The stories within the fluid and heterogeneous Ramayana tradition lend themselves to varied transformations in accord with people's changing concerns and perspectives. Truly, Ramayana is not a story but a tradition of storytelling, within whose capacious limits many different stories are contained.

As Paula Richman in his book *Many Ramayanas* states that out of many Ramayanas, Valimiki's text is one among many. Therefore we can firmly state that there is hundred of telling of a story in different culture, language and religious traditions to each other. Many of the time they are influenced by the prevailing or predominant tendencies of social, political and cultural atmospheres. In contemporary literature, many writers have ventured to recreate the epic and the fact is that to a very extent mythology has pervaded deep into our lives especially in this decade. As in the tone of publishers 'there is a good market for mythology'. Many authors with solid research and vivid imagination are dipping into the vast pool of Indian mythology to come up with powerful tales that retell our social and historical origins. They treat the epic in innovative ways, sometimes completely subverting the entire epic framework. The purpose of all good speculative fiction is to make the reader think by questioning prevailing ideas about reality

One of them is Anand Neelkantan's *novel Asura: Tale of the Vanquished* which is a retelling of Ramayana epics. The book is based on the alternative Ramayanas especially recited in the southern part of India. This adaptation involved the task of depicting a quintessential antagonist as a protagonist. It's an epic tale of the unsung hero Ravana and Asura people '**Ravanayana**', not the version told by the victors but by the losers who may have been misjudged by cultural stereotypes and whose voices were lost in silence.

As Paula Richman in his book "Ramayana Stories in Modern South India" says:

Valmiki's Ramayana is the most authoritative telling of Ramkatha in India. The phrase "authoritative tellings of Ramkatha" refers to texts that share three characteristics. First, they espouse normative ideologies of ranked social hierarchy. Second, they are influential beyond the temporal and geographical context in which they were written, continuing to be respected, studied, and transmitted centuries after their composition. Third, they have gained recognition as privileged texts.

Chimamanda Ngozi Adichie, a Nigerian writer in her famous Ted talk speaks about the threat of a single story.

"So that is how to create a single story, show a people as one thing as only one thing over and over again and that is what it become."

Neelakantan through his book gives voice to the muted community, the Asuras and presents the perspective of an unsung hero, Ravana who is vilified in this society. He unveils the misjudged notions about his ten headed and twenty armed figure of Ravana which actually symbolizes the ten base emotions like anger, pride, selflishness, intellect etc. As per Indian wisdom one need to shun the other nine emotions and outshine only his intellect inorder to be 'Supreme'. But Ravana prefers to be a man than to be a God, by withstanding with other base emotions.

In festival of Dussehra we burn the effigies of Ravana with these bad things which are as his ten head, but actually according to Ravana we need to follow this in order to be complete man. Ravana lived a life not based on calculative dharma or adharma standards but on his own thinking. At one instance Ravana states in Asura:

"I had been born to fulfill someone else's destiny. To allow someone else to become God (15)."

Neelakantan doesn't sanctify Ravana in his book but tells his perspectives in which he had his own rights and wrongs.

This adaptation runs parallel with the Ramakien version(the Ramayana as known in Thailand) according to which Sita is Ravana's daughter who is abandoned because of an astrological prediction that she will bring destruction on her father. It construct a narrative where Sita was abducted by Ravana in order to save her, from the masculinity rampant in the Deva kingdoms, because she was his daughter. Even if we think the other way around discarding this version, shouldn't Ravana avenge against Rama and Lakshmana for mutilating his sister. Before we stereotype Ravana, everybody should give the answer of these questions. Is it wrong, being a father to think about his daughter, to stand for his

sister or wrong to fight for his identity? The answer to these questions decide Ravana as a Villain or hero.

And on the other side, we praise a God for mighty deeds in the shade of dharma who frequently questions the chastity of his wife. Neelakantan uses Ravana as a mouthpiece and questions the basic principles of belief. He says:

'That is a good piece of propaganda, I must admit. Claim that God is with you, or better, you are God, then anything you do, any adharma you commit, becomes divine play'"

Cultural hegemony, caste, educations social and economic background may be distinguished as attributes of power that grey shaded this story. Adichie's states about the ability of power to not just tell the story of other person, but to make it the definite story of that person. Suppressing one based on others culture can be tempting catalyst to on-going harmony. The predominant culture in a society harnesses the other in order to maintain long held hegemony.

Ravana is far more than just a '*nazar battu*' to Ram, even which is not tolerated in our society.

Diverse instances like this are prevailing in our society like under the pressure of various groups; Delhi University has deleted essays written by scholar A K Ramanujan on Ramayana from its BA History syllabus. On October, 2011 the executive council passed a resolution to the academic council to remove the essay titled 'Three Hundred Ramayanas'. The inclusion of the 30-page essay, which offers a number of tellings of the epic story of Lord Rama, including the Jain, Buddhist and Kannada narratives was opposed by Hindu hardliners terming it as "blasphemous".

On 2016 members of the Thanthai Periyar Dravidar Kahagam were taken into preventive custody of police after organizing "Ravan Leela" while burning the effigy of Lord Rama near Mylapore, Chennai inorder to demonstrate their opposition to the Ram Leela celebration. They believe that Ramayana, though a mythological story was an Aryan- Dravidan conflict where Ram won against Ravana, who is considered as a Dravidian is vilified as a monster. The Ravana

Leela of 2016 in Chennai might be low profile one but the Ravana leela of 1974 was a much talked about event, a year after Periyar's death, Tamil Nadu witnessed its first Ravana Leela evoking responses from the masses as then the Prime Minister Indira Gandhi.

And I find it very evident to have contrary picture about the recent Deepawali celebrations in Ayodhya. The Chief Minister of Uttar Pradesh stated that 'we are attempting to revive history in Ayodhya', partially I think they succeeded in that to a degree. As the present government have re-started the shows after sanctioning a handsome budget for the Ram Leela. The budget had a special mention of Ayodhya, Varanasi and Mathura, earmarking Rs 1,240 crore for the Ramayan, Buddhist and Krishna circuits in these cities. The three-day "Deepotsav" celebrations were launched on a mega scale, with the Chief Minister welcoming actors playing the Lord Ram, Sita and Lakshman who arrived on a chopper decked up to resemble the mythological Pushpak Viman, amid a record 1.75 lakh "*diya*" or lamps along the banks of Saryu river. The government under his leadership has even planned a 100m long Lord Ram's statue at Sarayu bank as a part of Navya Ayodhya. The budgeted amount is 195.89 CR and in which three-forth amount is already sanctioned and approved.

I quote from Adichie's Ted talk:

"The single story creates stereotypes, and the problem with stereotypes is not that they are untrue but they are uncomplete. They make the one story the only story".

It's high time for us to understand and realize that there is never a single story because a single story builds wall of differences within our cultural pluralism. Until the doors of perception are cleaned, nothing would appear clear as it is in real and we need to realize the existence of other side.

Baijnath, an ancient pilgrimage town in Himachal Pradesh, is believed to be the place where Ravana made his austere penances to Lord Shiva, residents here believe that burning Ravana's effigies will bring the wrath of Lord Shiva upon them. Another example that contradicts the popular culture of Ravana as evil is

the Ravana temple in Kanpur, a city in the northern state of Uttar Pradesh, where Ravana is worshipped as God. The foundation stone of the temple was laid in 1868 and a few years later, an idol of Ravana was consecrated here an those who view him as a highly learned individual, who had knowledge of all Hindu scriptures, visit the temple to pay their homage. Ravana may be the arch villain in the epic Ramayana, but for some people of the Jain community he is an ardent follower of Lord Aadinath (or Rishabhadeva), their first religious teacher or Tirthankara, and a pious temple-goer in Himalayas. On Dussehra, when effigies of the demon king are burnt, many Jains honour him by creating rangoli or his image in their houses and perform a pooja seeking forgiveness for all their mistakes. In Gond, a village in Maharashtra the ten-headed king is worshipped as God. According to their version, Ravan was a Gond king who was slain by Aryan invaders. He was the tenth dharmaguru of the tribe, who believe in animism, consider Lingo and Ravan to be naturally just and environment-friendly deities. In fact, their narration of Ravan's story turns upside down the one in the Ramayan. This includes a contention over the geographical location of Lanka, which Gonds believe is Madhya Pradesh's Amarkantak mountain. Though the character of Ravana may seem like a closed book there is sufficient plurality in Indian traditions that make even Ravana capable of respect and veneration.

Ravana is considered as the demon of darkness but do we realize what actually drifted him to this shadow of darkness nothing else but the so-called impeccable cultural perspective. We proclaim the victory of good over evil but let's think for a second who are the evil? Ravana is stereotyped as a villain in minds of thousands of people based on ethnocentrism or the concept of otherness. We battle the identity or existence of others based on the standards of "us" and "them".

The otherness of the other becomes most rigid or dramatic when we have deep ties – to family, religion, nation, caste or ethnic group. They act like magicians who control others perceptions and make them see what they want them to see. We are distancing self from others in our life, we need to think beyond this dichotomies. The popular perceptions of the evil in Ravana have not really existed in the text as much as they have been utilized for the maintenance of certain primordial values which have been polarized in society and very often politicized

by communities to meet their own ends. And the funny part is inorder to burn the effigy of Ravana we actually make it first and that the point, the society creates a scapegoat for his own benefits. Because we are moving to a point where a monument which was considered as an epitome of pride and glory of our country is withdrew from the standard tourism handbook of the state for some unfit agendas. It's like we can't force each drop to meet the ocean. Instead we need to change our mentality of prejudging others based on our grid. We need to build a world where our coming generation must be taught how to think, not what to think.

As at the very same time this presentation on a critical view can be acknowledged as a suppression of my ideas and thoughts over yours, but I believe not on imposing my ideology or perspective but presenting the other side. It's your call to rethink, revaluate or let it go. For me, I don't believing in burning effigies of anyone, I don't believe in Dravidians or Aryans, I believe in men whom Almighty God created in his own image therefore it is our duty to respect each other. The true enrichment of our culture and tradition elevates when we think beyond the standards of "us" and "them" and break those big dividing walls. The world is a big game of perceptions and the perfect blend of duality is the basic requirement to play his candidly.

And I will conclude with a quote from *Friends with Voltaire* by Evelyn Beatrice Hall, an English writer known for her biography of Voltaire.

I disapprove of what you say but I will defend to the death your right to say it…

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A Retelling of the Resurrected Feminity in Augmented Reality: The Awakening by Kate Chopin

Literature is a reflection of culture and that culture can be affected by literature.

Change is the only true constant. And the impact these changes can create in our society is inextinguishable to a certain extent. Its sparks may remain dormant in the deep abyss but might spread like a bonafide fire engulfing the whole chasm. The cultural theories developed by Karl Marx and Friedrich Engels rests upon the principle that the history of humanity and the societal institutions is hell bent on the changes in economic organization. They assert to overlook the reasons behind political and social behavior of an individual who is being repressed by the capitalist ideology. Therefore the appraisal of the novel highlights the class system existed within the classes during the time when this novel was written; as a result, the protagonist realizes not only her class consciousness, but also herself as a woman and as an individual. She explores her identity which was suppressed due to the restrictions of Victorian norms and ideologies that had always kept her in dark.

The plot depicts the protagonist Edna Pontellier desperately trying to fit herself in the social and cultural practices of her husband's class. Leonce Pontellier represents the Creoles as he is an established person, rich and successful, and according to Victorian norms, he can marry any woman of his choice and recast her life. On the contrary is his wife Edna Pontellier, who has been raised in a middle class family and lived her own small life all within herself. Edna, could not fully adapt herself into becoming rich. The man that she falls in love with, Robert Lebrun, is a young, twenty-six-year old single man, who has the passion to adapt and fit himself into the higher social class. These are the motives that create socioeconomic demarcation amongst the group members within a society.

The reason why Kate gives different social and economic status for her character is to point out the construct of capitalist society which inflicted the protagonists mind to cast her away from its shackles and digress away from it. That is, the passion to excel and succeed socially as well as economically, causes Mr. Pontellier to take his wife for granted, and to see her merely as a valuable piece of his personal property. When Edna couldn't take her husband's attitude anymore she turns into an absolutely dissatisfied wife, a mother and a woman. When she became aware of the fact that she is being repressed by the Capitalist Ideology and forced into a relationship she can't bear, she rises above the impact of exploitation and alienation that the capitalist society has gifted her. She recognizes her potential, explores her sexuality, her identity, achieves awareness, control, and turns herself into a "woman" being. However, the story gets complicated or raher the life of Edna gets entangled as she dares to take control of the situation s/he was repressed for so long, and tries to act upon the oppression; it further isolates her from the society. The same happened with Edna. She describes herself as having declined in the social scale. She is overcome by enormous guilt for having committed an unpardonable mistake which may categorize and judge her as a bad subject in the society. She realizes that she wouldn't be considered as a good wife in the eyes of the conformist society and hence ends her life. Now the question arises who tags one as good and bad subject? What provokes her to put an end to her life and dreams? Althusser brings the term interpellation to define the subjection of an individual as subjects in a society. A subjected being who submits to a higher authority is therefore stripped of all freedom except that of freely accepting his/her submission. So to say the individual in question behaves in such and such ways adopts such and such attitudes. Throughout this scheme we observe that the ideological representation in itself is forced to recognize that every subject endowed with a consciousness believes that his ideas inspire him to freely accept 'how he must act according to his 'ideas'' if he does not do so, he is wicked. These 'ideas' are already inscribed in him as an individual and hence the individual including you and I are already subjects, and as such constantly practicing the rituals of ideological recognition which concretes the fact that we are indeed irreplaceable subjects. Though Edna could break free from the clutches of normative culture she could not really unclip herself from her own innate

consciousness of how a woman is coded to behave if she wants to have a place in the class conscious society.

'Dramatic!' is the one word which is apt for the irony that comes into play with the fact that she dislikes being ill-treated, without realizing the subjugation she afflicts upon her servants. Since she felt alienated, and subjugated by the upper societal demarcation, she inflicts the same upon her servants since she was trying hopelessly to fit in the upper class society. This viewpoint is contrasted with Edna's actual motive. These ideological battles present in the novella suggest significantly the Marxist melody throughout the work.

"'I hardly think we need new fixtures, Leonce. Don't let us get anything new; you are too extravagant. I don't believe you ever think of saving or putting by.'" "'The way to become rich is to make money, my dear Edna, not to save it,' he said" (Chopin 576).

The quote is excerpted from a conversation between Edna and her rich husband. Edna comes from a middle class family and that "her marriage to Leonce Pontellier was purely an accident," (Chopin 548) in which she is neither supposed nor expected to marry a Creole. In fact, she meets Robert and enjoys the moment with him in Grand Isle; she almost establishes a romantic relationship with Robert who is young, far less affluent as the Pontelliers and has a lower social status; yet his emergence makes Edna happier and raises the Marxism question – which social class does Edna literally connect to?

Edna finds it easier to get along with Robert because she is not used to a bourgeoisie life style. Robert is not used to Creoles life style as well. He saves cigars rather than consuming it which literally sounds like Edna is connected to Robert and every step she took forward gave her a sense of relief from the obligations and perhaps added to her strength and augmentation as an individual. Edna's capability to put at stake her social comfort so as to grow as an individual, and explore herself is worth the praise. Kate Chopin's underlying intentions, here, serve a two-fold purpose. On the one hand, she is letting her character Edna isolate herself and break the stereotypes from the structure of such a classist

society; and on the other hand, she wants Edna to grow as a person, as a woman, as an individual and create her own identity and not depend on any materialistic relationships and society.

Another aspect in the novel is the depiction of women's bodies (and women in general) as property belonging to the representatives of patriarchal culture: men. The bodies of women and female sexuality are depicted and perceived as property belonging to the male representatives of patriarchal culture. In the property system indirectly presented in *The Awakening*, Edna exists only as a sign of value. Léonce's ownership of Edna (and her body in particular) is well established from the beginning of the novel.

"The gulf looked far away, melting hazily into the blue of the horizon. The sunshade continued to approach slowly. Beneath its pink-lined shelter were his wife, Mrs. Pontellier, and young Robert Lebrun. 'You are burnt beyond recognition'".

Pontellier says looking at his wife as one looks at a valuable piece of personal property which has suffered some damage. Moreover, even Edna considers herself an item of property and wishes to own herself. Conditions would some way adjust themselves, she felt; but whatever came, she had resolved never again to belong to another than herself.

In the second half of the nineteenth century, the term 'self-ownership' was used to refer to a wife's right to refuse marital sex, and this seemed to be the key to female autonomy. The concept was first popularized by Lucinda Chandler in the 1840's and promoted by feminists who followed her and took up the practice of self-ownership. The term refers to a set of rights by means of which a woman can gain control over her own person and can, subsequently, become independent of the will and desires of her spouse. By the end of the novel the author digresses from the usual tone of calling the protagonist from 'Mrs Pontellier' to 'Edna' to point out that she has untangled herself from the class conscious conformist society. Thereby, Chopin makes it clear that individual discharge is more significant than societal out-turns, irrespective of Edna's depression and the end

of the novella. But Edna's despair resembles the frustration of the industrial worker. Edna desires a material selfhood, but the men in her life only allow her to have roles and personas ('wife', 'mother' and 'lover'). However, through the suicide act, Edna actually rejects the roles provided for her by the system ('wife', 'mother' and 'lover') and rebels against the speculative economy that seeks to exploit her body. According to Charlotte Perkins Gilman, in the civilized world, the woman/mother becomes a sexual commodity by means of her self-sacrificing love for the children and the husband. Feminists evoke the sacrificial figure of the mother to highlight the limited sexual independence of women. They argue that a woman's autonomous selfhood is relinquished through the self-giving role as a 'mother'. They can either refuse or willingly accept motherhood or sexual relations with their husbands. In *The Awakening*, Edna borrows not only the rhetoric of 'voluntary motherhood', but also that of 'self-ownership' with all the possible rights and freedoms that it entails. She does so especially when she vows that she will never again belong to another than herself. In terms of Marxian labour philosophy, Edna's life and death can only be read as the result of exhaustion leading to alienation of her labour and physical body as well as to the impossibility of ever achieving 'self-ownership'.

Throughout the novel it not only challenges the social class difference but it also challenges moral as well as literary standards in the sense that it violated some social mores. Whenever and wherever these changes bloom in our society against a predominant culture it creates a counter in the periphery which takes the main floor causing a hullaballoo just like the Shabarimala issue in Kerala. Perhaps the women who oppose the law of supreme court represents the thought process of Edna. They are the victims of the authoritarian culture whose identities were subjugated from bygone days. Hence they bent the realities and believe in norms which were imposed on them. All in all, Edna's problem is also that of Chopin herself. And as a farfetched imagery Chopin's voice is the voice of the captive. As Helen Cixous says in her seminal work *The Laugh of the Medusa* that women must write about themselves which again serves a twofold purpose: on a personal and historic level. On the personal level the woman will return to her body to feel comfortable in it. As mentioned earlier the consciousness that 'I am my own property' is what they indirectly throw light upon. Writing according to Cixous will give the woman back her assets and pleasures which strangled her and will

set her free from guilt. On the historic level a woman's writing marks her active entrance into history as an agent with initiative. Edna struggles with how to make the body 'other' without losing it, whereas Chopin also did not know how to make her novel 'other' without losing it. Some critics criticize the novella as if it was encouraging open marriage, which was absolutely unacceptable in the conformist society; and hence the story was restricted for decades. Nevertheless, nowadays, the message of this novel is well received by readers from different parts of the world, even though it was particularly relevant at the time when the novel was written. Chopin attempted to convince her late nineteenth-century readers and still inspires the contemporary visionaries to envision a new history and economy in which the New Woman (and the New Man) might share in the coordinated labor of social production where one does not get coded as subjects of any ideological norms.

Now It's our call. Either we resurrect like Edna or ever be caged in our own shackled minds.

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Printed by Rachel P. Chacko Published by Achamma Alex on behalf of Manager, Christian College, Chengannur and Printed at Shyamaly Press, Tiruvalla and published from Christian College, Chengannur, 689122, Alappuzha District, Kerala. Editors. John George Athyal and Hysen Thomas