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SYNTHESIS, GROWTH AND CHARACTERIZATION OF NEW OPTICAL, STRUCTURAL, THERMAL, Di-ELECTRIC, AND NON-LINEAR STUDIES OF L-HISTIDINE, L-VALINE, L-ARGININE DOPED KDP CRYSTALS FOR TUNED LASER APPLICATIONS

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ABSTRACT

The potassium Di hydrogen phosphate (KDP) is a well known nonlinear optical (NLO) material in the field of photonics and optoel ectronics. Since most of the amino acids exhibit NLO property, it is of interest to dope them in KDP. In the present study optically good quality crystal of pure KDP, L histidine L- valine and L- Arginine doped KDP have been grown from low temperature solution growth by slow evaporation technique using triple time deionized water as a solvent. The crystalline nature of the grown crystal was characterized by powder X-ray diffraction. The single crystal X-ray diffraction analysis reveals that the crystal belongs to tetragonal system. The presence of various functional groups of pure KDP, L histidine L- valine and L Arginine doped KDP crystals were identified by (FTIR) spectrum recorded in the wave number range 400 - 4000 cm1. The UV-visible spectra were recorded to find cut off wavelength and transmittance the results show an improvement in the optical transmittance compared to pure KDP crystals. The nonlinear optical (NLO) property of the grown crystal has been confirmed by Kurtz powder technique, the second harmonic generation (SHG) efficiency of L- histidine L- valine and L- Arginine doped KDP crystals were found to be more than pure KDP.

Keywords: Solution growth, FT-IR, Single crystal XRD, powder XRD, UV-visible, Thermal, Dielectric and SHG.

1.Introduction

Crystals are the unacknowledged pillars of modern technology, since the discovery of second harmonic generation of ruby laser radiation in a quartz crystal by Franken in 1961. In the recent years, the search for new crystals with good frequency conversion properties continues even today. For various device applications has lead to discovery of many organic, inorganic and semi-organic nonlinear optical (NLO) materials. Potassium Dihydrogen Phosphate (KDP, KH2PO4) single crystals attract much attention due to their wide applications in different fields of nonlinear optics, optoelectronics and photonics.

KDP group crystals possess high structure perfection ,mechanical strength, wide range of spectral transparency as well as relatively high values of laser damage threshold. Moreover, the growth technology makes it possible to obtain KDP crystals with well- developed growth sectors containing practically no defects. Crystals are widely used in the field of electronic industry, photonic industry, semi conductors, super conductors, sensors and non linear optics. Crystal using in the material science, chemical engineering, metallurgy, crystallography, mineralogy, which have potential applications in optoelectronics, second harmonic generation (SHG).

The numerous applications of the nonlinear optical (NLO) crystals in the vast field of science and technology made to process of search of the known crystal is a never stopping process. The optical crystals with a high degree of perfection find applications in critical technology areas such as high power laser technology, amplitude and phase modulation, higher harmonic generation, and the fast growing development of optical communication system and optical information storage devices, switching and other signal processing.

One of the most important applications of NLO materials is their use for fast data transfer, combined with a very high Signal-to-Noise ratio, even over long distances. In recent years, different applications of NLO and photorefractive materials have been developed, for example, optical frequency conversion, electro-optical modulation, dynamic holography, optical writing and optical guiding of laser beams It is seen that L-proline and (4R)- hydroxy-L-proline derivatives, containing donor groups are chiral carriers [98]. The introduction of chirality by means of an asymmetrically substituted carbon should in addition respect the molecular features leading to a high nonlinear behaviour. Proline and its derivatives are often used as asymmetric catalysts in organic reactions. Only noncentrosymmetric alignment of the chromophores in the crystal lattice leads to an observable bulk second-order NLO response . In order to obtain the adjustment of the nonlinear efficiency/transparency, based on the molecular engineering and crystal engineering approach, it is tried to develop a new method to design organic non-linear optical second-harmonic generation materials such as organic inclusion complex .

The NLO crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for numerous device applications major role in the field of photonics and optoelectronics technologies. KDP crystal is studied from various aspects and widely used NLO crystals. The non linear optical phenomena, frequency mixing and electro-optic are important in the field of optical image storage and optical communication. This chapter address the crystal growth technique, in particular the slow evaporation solution growth technique. This technique is used to grow a crystal in a simple manner and provide improvements in purity. Additionally, this technique can produce organic, inorganic and semi organic NLO crystal at ambient temperature in different solvents. Hence we chose this technique in growth our crystals, to analyze of amino acid based dopants on the non linear optical property of KDP crystals, efforts were made to dope KDP with the amino acids L-histidine, L-valine and L-arginine.

The effects of impurity atoms on the quality and performance of material are analyzed. In particular, amino acids family crystals possess high NLO efficiency because they have a proton donor carboxyl acid (-COO) group and the proton acceptor amino (-NH2) groups. In the present investigation, we studied the influence of the growth aspects of KDP crystals grown from the solution by using the low temperature solution growth technique and amino acids like namely L-histidine, Lvaline and L-arginine doped KDP crystals has been studied. also the characterization such Single crystals XRD, Powder XRD, FTIR, UV-Vis Spectra, thermal, dielectric and SHG efficiency studies were carried out and the results are presented and discussed in detail.

2 EXPERIMENTAL DETAILS

2.1 CRYSTAL GROWTH

The commercially available of the Potassium Di hydrogen orthophosphate, KH2PO4 (KDP) (Merck), L-histidine L-valine and L-arginine have been used for synthesizing the L-histidine doped KDP (LHKDP), L-valaine doped KDP (LVKDP) and L-arginine doped KDP (LAKDP) crystals.

a) LHKDP crystal

The LHKDP crystal were thus prepared by taking the Potassium Di hydrogen orthophosphate, KH2PO4 (KDP) and L- histidine weight of 0.2 gram salt were taken and dissolved in 100 ml triple time distilled water and under saturated solution of KDP was prepared. The solution continuously stirred for 6 hour with a magnetic stirrer to ensure homogeneity of the solution. After preparation of under saturated solution of pure KDP is doped with L-histidine continuously stirred for one hour then the solution was filtered in the Whatman 20-25 *u*m filter paper and transferred to a Petridish. The Petridish is covered with a pourous paper tied on top with a rubber band to facilitate and kept in a closed room where the slow evaporation gradually done, at room temperature. After a period of two weeks, optically highly transparent crystals of pure and L-histidine doped KDP crystals were formed. The figure 3.1 shows as grown pure KDP crystal and LH: KDP crystals shown in the figure 3.2.

$$KH_2PO_4 + C_6H_9N_3O_2 \longrightarrow KH_2PO_4\,(C_6H_9N_3O_2)$$

KDP+L-histidine **L-histidine doped KDP crystal**

b) LVKDP crystal

The LVKDP crystal were thus prepared by taking the Potassium Di hydrogen orthophosphate, KH2PO4 (KDP) and L-valine weight of 0.2 gram salt were taken and dissolved in 100 ml triple time distilled water and saturated solution of KDP was prepared. The solution continuously stirred for 6 hour with a magnetic stirrer to ensure homogeneity of the solution. After preparation of saturated solution of pure KDP is doped with L-valaine continuously stirred for one hour then the solution was filtered in the whatman20-25 *u*m filter paper and transferred to a Petridish. The Petridish is covered with a porous paper tied on top with a rubber band to facilitate and kept in a closed room where the slow evaporation gradually done, at room temperature. After a period of two weeks, optically highly transparent crystals of pure and L-valaine doped KDP crystals were formed. The figure 33 shows as grown LV: KDP crystal.

$$KH_2PO_4 + C_5H_{11}NO_2 \longrightarrow KH_2PO_4\,(C_5H_{11}NO_2)$$

KDP+L-valine **L-valine doped KDP**

c) LA KDP crystal

The LA:KDP crystal were thus prepared by taking the Potassium Di hydrogen orthophosphate, KH2PO4 (KDP) and – arginine weight of 0.2 gram salt were taken and dissolved in 100 ml triple distilled water and under saturated solution of KDP was prepared. The solution continuously stirred for 6 hour with a magnetic stirrer to ensure homogeneity of the solution. After preparation of saturated solution of pure KDP is doped with L-arginine continuously stirred for one hour then the solution was filtered in the whatman 20-25 m filter paper and transferred to a Petridish. The Petridish is covered with a porous paper tied on top with a rubber band to facilitate and kept in a closed room where the slow evaporation gradually done, at room temperature. After a period of two weeks, optically highly transparent crystals of pure and L-arginine doped KDP crystals were formed. The figure 34 shows as grown LA: KDP crystal.

$KH_2PO_4 + C_6H_{14}N_4O_2 \longrightarrow KH_2PO_4 (C_6H_{14}N_4O_2)$

KDP+L-arginine L-arginine doped KDP crystal

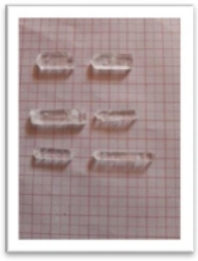


Figure 1 As grown pure KDP Crystal

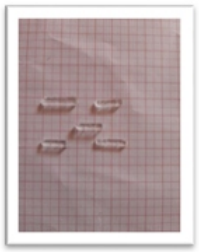


Figure 2 As grown LH KDP Crystal

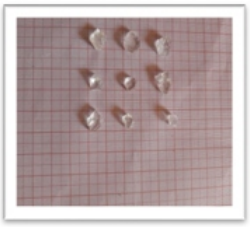


Figure 3 As grown LVKDP Crystal

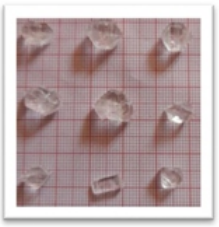


Figure 4 As grown LAKDP Crystal

3 Results and Analysis

The grown pure KDP and LHKDP, LVKDP and LAKDP crystal were characterized by different analytical methods and outcome is discussed.

3.1 Powder X-ray diffraction and single crystal analysis

The grown crystals where subjected to powder X-ray diffraction analysis using β Rigaku Minifix II-C, CuKα radiation of wavelength (1.5406Å) The powder X-Ray diffraction pattern of as grown KDP and doped L-histidine ,L-valine and L-arginine were shown in the figure 5 to 8. The Powder XRD shows the grown crystals are having good crystalline quality. The doped KDP powder XRD shows some shift in the peaks confirms the incorporation of dopants in the pure KDP crystals.

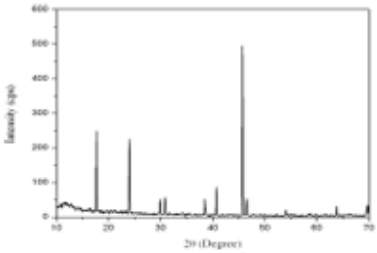


Figure 5 XRD Pattern of as grown pure KDP crystal

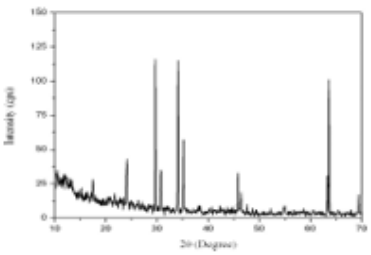


Figure 6 XRD Pattern of as grown L-histidine with doped KDP Crystal

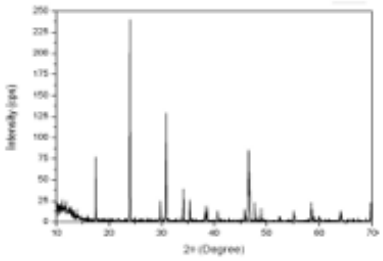


Figure 7 XRD Pattern of as grown L-valine with doped KDP Crystal

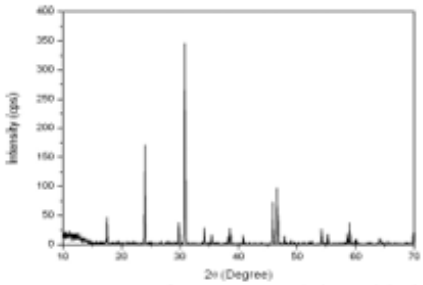


Figure 8 XRD Pattern of grown L-arginine with doped KDP Crystal

3.2 Single crystal X- ray diffraction of study of pure and amino acids doped KDP crystal

The cell parameter values of the pure KDP crystals and LHKDP, LVKDP and LAKDP crystals were studied by Single crystal X-ray single crystal diffractrometer CAD4/MACH3 and the data was collected using graphite mono chromate MOKα (λ=0.717Å) radiation of wavelength at room temperature 293K. Comparison of unit cell parameters of pure and amino acid doped KDP crystal suggests that a slight distortion has occurred as a result of amino acid doped KDP crystal. The XRD data of the present work is very well agreement the reported value.

Table 3.1 Cell parameter of pure and LAKDP, LVKDP and LHKDP crystals

crystal	Lattice Parameter a = b (Å)	Lattice Parameter (Å) c	Interfacial angles (°) α=β =γ	Cell Volume (A^3)
Pure KDP Crystal	7.448	6.977	90°	389
KDP +L–arginine	7.47	6.99	90°	390
KDP +L-valine	7.48	6.95	90°	392
KDP +L-histidine	7.47	6.98	90°	394
KDP +L-arginine	7.54	7.03	90°	400

3.3 Optical Transmission Spectrum

The optical transmission spectra of the grown the pure KDP, LH KDP, LVKDP and LA KDP crystals were recorded in the wavelength range of 190-900 nm using LABINDIA UV 3092. UV- Visible

spectrometer with a grown crystal of thickness the optical spectra are very important for any NLO material due to the fact that the material can be practical use only if it has optical transparency window and the UV-vis–NIR spectrum gives information about the structure of molecule because the promotion of the electron in the σ and Π orbital from the ground state to higher energy states. The UV-Visible NIR spectrum for growth Pure KDP, LHKDP, LV: KDP and LAKDP crystal of the transmittance spectrum are shown in Figure. 9 to 12 this spectrum shows good transparent nature of the sample L-ariginine and L-histidine doped crystal had more transmittance than pure KDP Crystals. It is interesting to more that the crystals are essential requirements for better optical quality and suitable for frequency doubling. The band gap energy Eg is calculated in eV using the planks equation as follows.

$$E_g = hc/\lambda$$

Where h is the Plancks constant c is the velosity of the light and λ is the lower cut- off wavelength. The calculated energy gap value of grown pure KDP, LHKDP, LVKDP and LAKDP crystal has 6.5 ev and cut- off wave length of each crystals has 190nm.from the energy gap values of pure KDP, LHKDP, LVKDP and LAKDP crystals belongs to the category of insulating materials. The LHKDP, LVKDP and LAKDP crystals will be very useful for nonlinear optical application.

Growth periods of pure KDP, LHKDP, LVKDP and LAKDP doped crystals are tabulated in table 3.2

Table3. 2 Growth period of Pure LHKDP, LVKDP and LAKDP doped KDP Crystals

Sl.No.	Crystals	Growth Period
1.	Pure KDP Crystal	10-12 days
2.	L-Histidine with doped KDP Crystal	12-15 days
3.	L-Valine with doped KDP Crystal	15-20 days
4.	L-Arginine acid with doped KDP Crystal	20-25 days

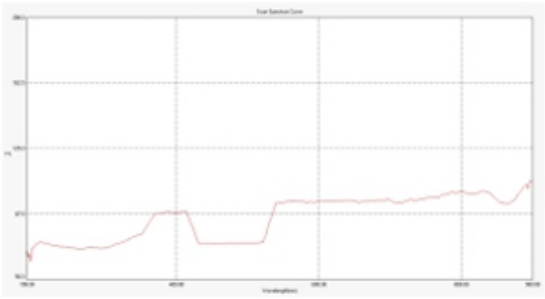


Figure 9 UV Transmittance spectrums of Pure KDP crystal

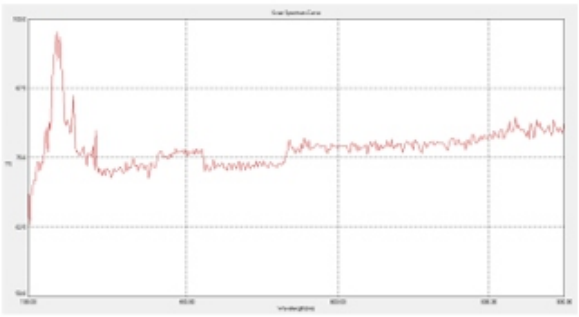


Figure 10 UV Transmittance spectrum of L-Arginine KDP crystal

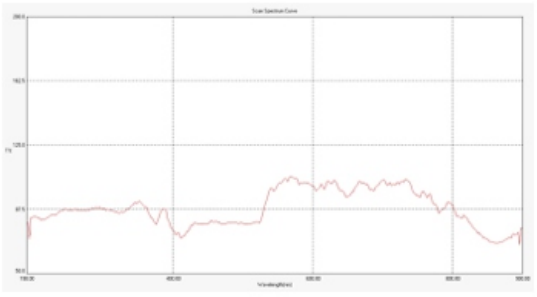


Figure 11 **UV Transmittance spectrum of L-Histidine KDP crystal**

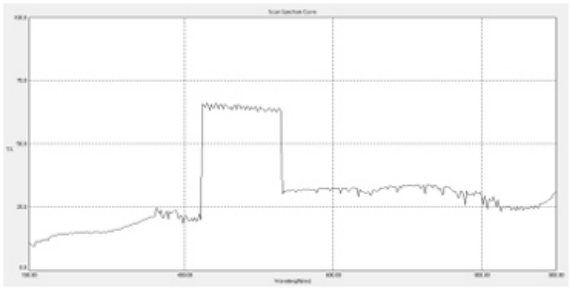


Figure 12 UV Transmittance spectrum of L-Valine KDP crystal

3.4 FT-IR ANALYSIS

The FTIR spectrum of pure KDP and L-histidine L-valine and L-arginine doped KDP crystals have been recorded on Perkin Elmer FTIR spectrometer within the wave number range 400 cm-1 to 4000 cm-1. Pellets of the mixture of each sample with KBr have been prepared and used in the experiment. In the FT-IR spectra of pure KDP crystal, the observed absorption peaks correspond to the P-OH stretching, P-OH is bending. In the FT-IR spectra of amino acid L-histidine L-valine and L-arginine doped KDP crystals, the same peaks have been observed with additional peaks. These additional peaks correspond to the functional groups of L-histidine L-valine and Larginine which confirm the doping of the L-histidine L-valine and L-arginine in the spectra of amino acids doped L-histidine L-valine and L-arginine crystals, some bands of H2PO4 overlap with amino acid vibration. Hence few a bands of Di hydrogen phosphate ion become broader and some of the frequencies are slightly shifted. The asymmetric stretching vibrations of Nh3 + of amino acid appear in the region 31003450 cm-1.

Some of them overlap with the OH stretching vibrations of Di hydrogen phosphate ion. The symmetric deformation of Nh3 + ion appears at around 1500cm-1 in the spectra of all doped crystals with medium intensity. The CH3 bending vibrations of amino acids appear around 1450 cm-1. These vibrations of amino acids present in the spectra of doped crystals reveals the incorporation of impurities in the crystals. The Figure 3.13 to 3.16 show .that FTIR spectrum of pure KDP and Lhistidine L-valine and L-arginine doped KDP crystals and Table No.3.3 shows that FTIR Wave number assignments for the L-histidine, L-Valine and L-arginine doped KDP grown crystals

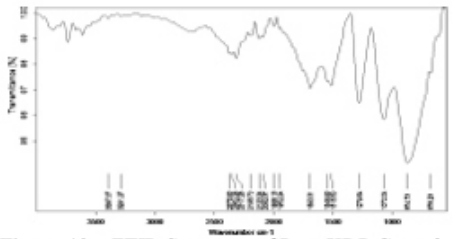


Figure 13 FTIR Spectrum of Pure KDP Crystal

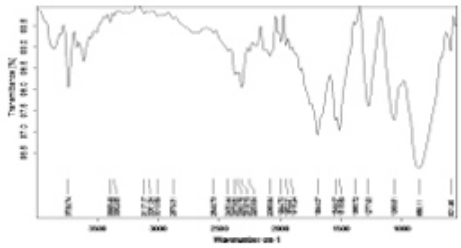


Figure 14 FTIR Spectrum of L-histidine doped KDP Crystal

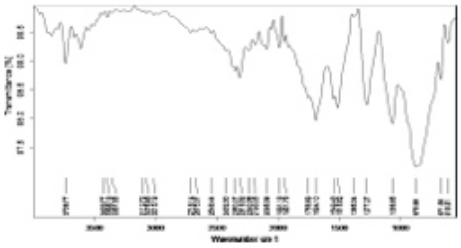


Figure 15 FTIR Spectrum of L-valine doped KDP Crystal

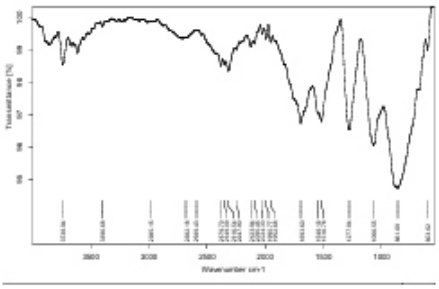


Figure 16 FTIR Spectrum of L-arginine doped KDP Crystal

Table. 3 FTIR Wave number assignments for the L-histidine, L-Valine and L-argnine doped KDP grown crystals

Pure KDP Peak values ($c\ m^{-1}$)	L-histidine doped KDP ($c\ m^{-1}$)	L-valine doped KDP ($c\ m^{-1}$)	L-argnine doped KDP ($c\ m^{-1}$)	Assignment
3739.74	3738.77	3397.07	3738.94	P-OH stretching of
3395.49	3433.77	3291.27		H_2PO_4 , O-H
3362.85	3396.19	2375.93	3396.68	stretching of COOH and water of crystallization, N-H
	3357.55	2350.26	2985.15	stretching of NH_3, C-H
3117.17	3112.72	2317.26		stretching of CH_2 and
3081.34	3076.83	2198.70		CH vibration
3010.89	3015.19	2123.24		
2879.31	2716.14	2092.37		
2549.73	2675.37	1998.13		
2430.44	2548.44	1952.24	2682.18	
2373.50	2432.30		2589.43	
2350.76	2350.07		2379.70	
2316.73	2316.32		2349.09	
2253.64	2240.38		2316.54	
2085.64	2193.05		2247.90	C=O stretching
1994.70	2095.39		2123.94	vibration, P-O-H
1952.21	1991.19		2090.45	bending and –C= NH_4 stretching
1916.24			2024.33	
	1951.76		1990.77	
			1952.68	
	1756.69			
1694.07	1694.10	1693.31	1693.60	Asymmetrical NH_3^+ bending vibration
1549.07	1549.43	1548.93	1548.16	COO^- asymmetric
1515.89	1515.52	1515.50	1516.78	stretching
1385.72	1385.34			CH_2 bending. P=O stretching of KDP, Asymmetric vibration
1277.90	1277.27	1279.64	1277.84	C-COO^- stretching
1066.61	1066.65	1070.04	1066.55	P-OH and C-H stretching Symmetric stretching of NO_3
856.11	876.88	874.73	861.69	P-OH deformation , C- CN scissoring of
601.96	671.56 615.51	678.23	603.62	-COO bend

3.5 Thermal Analysis

TGA /DTA/DSC are powerful tool to investigate the melting behaviour, of the pure KDP, LHKDP, LVKDP and LAKDP crystals were carried out as follows. In order to study the thermal stability of the grown crystals, Thermo gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) have been carried out using SDT Q600 model thermal analyzer. Differential scanning clorimetry is a thermoanalytical in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function temperature. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to the sample than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. The amount of sample taken for the analysis is about 15 mg and the temperature range is about30- 8000C with the heating rate of about 200C/minute. The TGA and DSC pattern of LHKDP crystal is shown in Figure 17. The DSC curve of LH: KDP shows that there is no phase transition up to 223.8ºC and there found two endothermic curves at 237.37 ºC and 338.73 ºC

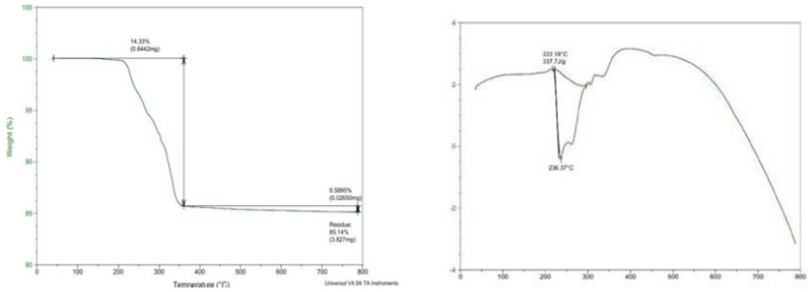


Figure 17 TGA and DSC curves of LHKDP Crystal

DTA and TGA of KDP were carried out with the help of an instrument (STA 409C) using KDP crystals as sample and alumina as reference. LV doped KDP sample was decomposed at 272.20 ºC. The graphs show the peaks at 435.85ºC and 520ºC reveal exothermic reaction due to escape of oxygen atoms from the KDP crystal. TGA curve sharply decrease at temperature at 214ºC and 350ºC is most probable melting point of KDP crystal. TGA curve shows that crystals are thermally stable below 220ºC. This shows that the presence of l-valine appears to increase the decomposition temperature of KDP. Fig. 18 and 19 shows TGA and DTA curves for LV doped KDP crystal. The DTA curve shows an endothermic peak at 272.20ºC, 435.85ºC, 520.5ºC. Enthalpy changes in the endothermic reaction are 241.44 J/gm, 63.75 J/gm.

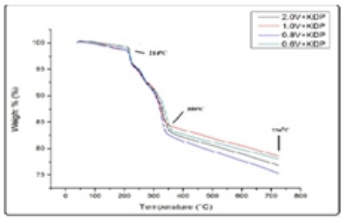


Figure 18 TGA curves of LV doped KDP

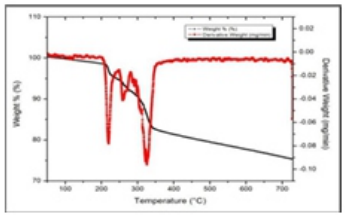
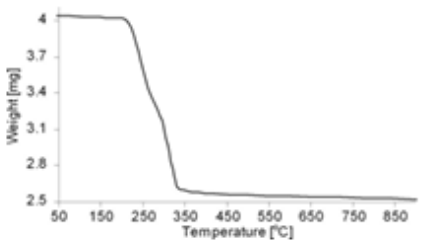


Figure 19 DTA curves of LV doped KDP

The TGA curve of L-arginine doped and pure KDP crystals have been recorded on Perkin Elmer Dimmer TGDTA at a heating rate of 20 ◦ C/min under argon atmosphere. For pure KDP crystal, after temperature about 230 ◦ C the weight loss starts due to the liberation of volatile substances, probably water molecule of decomposed KDP (Fig.20) The TGA curve for 0.6 mol% L-arginine doped KDP crystal has been shown in Fig. 21. The experimental results show that the initial weight loss starts at about,



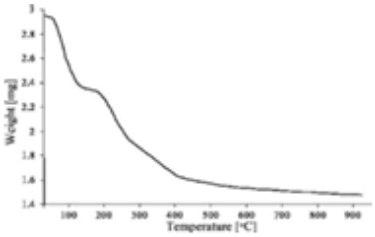


Figure 20 TGA curve of pure KDP crystal. **Figure 21.** TGA curve of LAKDP crystal.

67 ◦ C and ends at 120 ◦ C with about 18% weight loss, liberation of ammonia and wa which corresponds to the ter molecule. Second weight loss starts at about Rapid weight loss occurs up to 262 ◦ C and continues slowly up to 400 possibly due to the decomposition of the KDP and remaining L-arginine.

3.6 Dielectric Studies

The single crystals of pure KDP and amino acid L-histidine L-valine and Larginine doped KDP were used for dielectric studies. The dielectric constant was calculated by relation εr= Cd/ εoA, where, C = capacitance of sample, d = thickness of sample, A = area of sample and o = absolute permittivity. The dielectric loss is a measure of the energy absorbed by dielectric. It is known that in a capacitor, the dielectric usually has a resistance R and reactance 1/ C. Which are related to the phase angle tanδ = 1/ CR. Here tan is referred to as the dielectric loss. The dielectric constant and dielectric loss depend on frequency of applied field.

The dielectric analysis is an important characteristic feature that can be used to fetch knowledge based on the electrical properties of a material medium as a function of temperature and frequency. Based on this analysis, the capability of storing electric charges by the material and capability of transferring the electric charge can be assessed. (N.kangathara and G.Anbalagan). The dielectric constant is one of the basic properties of the solids.

The dielectric constant of the materials is due to the contribution of electronic, ionic, dipolar and space charge polarizations which depends on the frequencies.[S.M.dharmaprakash] Figure No.22 represents the dielectric constant and dielectric loss against log f for LHKDP crystals. From the figures, it is inferred that the value of dielectric constant is high at lower frequencies and it is lower at high frequencies. The low value of the dielectric loss at high frequency for these samples suggests that the samples possess enhanced optical quality and this parameter is very important for NLO materials in their applications [Balarew 1984].

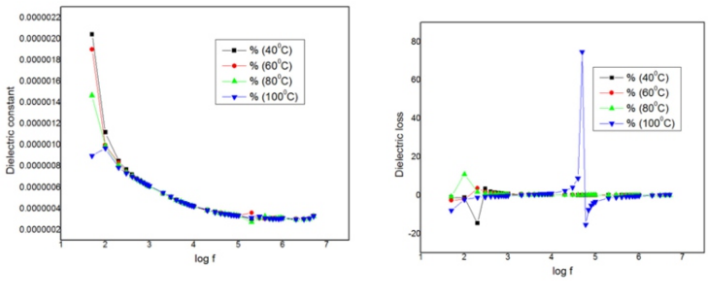


Figure 22 Dielectric constant and dielectric loss graph of LHKDP crystal.

The dielectric measurements of pure KDP and LVKDP crystals (2.5 mm) have been carried out in the temperature range of 40–120 °C at a frequency of 100 kHz using the HIOKI-3532 LCR cube meter. In order to obtain accurate results the parallel faced quality single crystals were applied by the silver paste

and connected to the electrical probes. The external electric field and temperature majorly influence the dielectric constant of material as shown Fig21. It is evident that the increase in temperature leads to instability in polarization activity (ionic, electronic, dipolar and space charge) of the crystal as a consequence of which the dielectric constant of crystals increases with the increase in temperature.

The analysis confirms that the dielectric constant of KDP crystal has been reduced to a lower level after the addition of LV. The lower dielectric constant favours less power consumption and enhancement in SHG coefficient of material which are advantageous parameters for designing electrooptic modulators, photonics, and NLO and microelectronics devices. The measurement of dielectric loss enables to investigate the dissipation of electromagnetic energy through defects (solvent impurities, macro and micro cracked, grain boundaries, porosity and random crystallite orientation) in crystal medium. The variation of dielectric loss with temperature is shown in Figure .23 and it reveals that the dopants LV effectively reduce the dielectric loss of KDP crystal demonstrating the improved optical quality and minimized electrically active defects in doped KDP crystals. The lower dielectric constant and dielectric loss of doped KDP crystals is a significant and decisive parameter for optoelectronics and NLO applications.

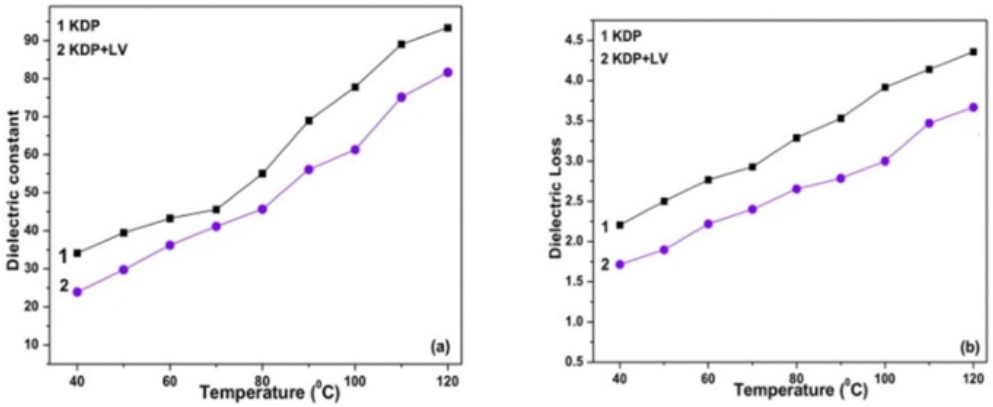


Figure 23 Di electric constant and dielectric loss graph of LVKDP crystal. Figure-24 shows the variation of r with frequency of applied field. The dielectric constant decreases rapidly as frequency increases. It is also observed that the doping concentration affects the values of dielectric constants. As the doping concentration increases the dielectric constant decreases. The rapid decreases in the values of the dielectric constant with increase in the frequency of the applied field suggest that the dipoles cannot comply with the changes in the frequency of the applied field after the certain value. More-or-less, the same type of nature is observed for the variation of dielectric loss (tanδ) with the frequency of applied field as shown in the Figure-25.

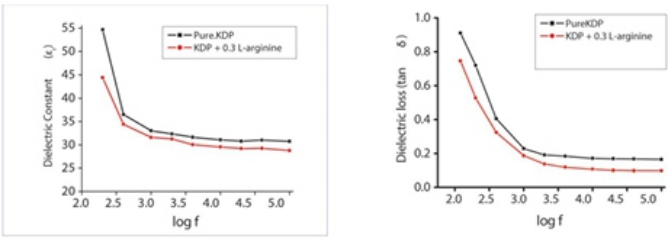


Figure 24 Plot of dielectric constant & Log f **Figure 325** Plot of dielectric loss & Log f

For pure and L-arginine doped KDP crystals for pure and L-arginine doped KDP crystals

3.7 Second Harmonic Generation efficiency analysis

To conform the NLO nature, the grown crystals of pure and doped grown pure KDP and LH KDP, LVKDP and LAKDP crystals were estimated by Kurtz and Perry powder technique. Second harmonic generation (SHG) efficiency was determined by the modified version of the powder technique developed by Kurtz and Perry using an ND ;YAG (QUANTA RAY Model LAB -170- 10) Q switched laser beam, 10ns laser with a pulse repetition rate of 10 Hz working at 1064 nm. The sample was grounded into powder and tightly packed in a micro- capillary tube. It was placed in the path of the laser beam of 0.69 joule of energy. The output light was passed through a monochromatic transmitting only the second harmonic green light was registered by a photomultiplier tube converted into an electrical signal. This was displayed on the oscilloscope screen.KDP ground into samples of identical size was used as reference material in SHG measurements.

The second harmonic signal of input energy (joule) and output energy mJ, respectively were obtained for pure and amino acid doped KDP, Thus the SHG efficiency of LVKDP and LAKDP crystals were found to 1.07 and 1.22 times greater than pure KDP crystals. Hence LHKDP, LVKDP and LAKDP are a potential material for the second order NLO applications.

Table 4 Comparison of frequency conversion efficiency for pure LHKDP, LVKDP and LAKDP crystal

Sl. No.	Crystal	Input nergy (J)	Output Energy (m.J)	η =(output / input) x 100%	SHG Efficiency
1.	L- arginine	0.69	12.4	1.80	0.92
2.	L-valine	0.69	14.3	2.07	1.07
3.	L-histidine	0.69	16.3	2.36	1.22
4.	KDP pure	0.69	13.34	1.9	

4 Summary and Conclusion

The transparent, colorless nonlinear optical single crystals of pure and amino acid doped LHKDP, LVKDP and LAKDP crystals have been successfully grown in a period of 10-12,12-15, 15-20 and 20-25 days at room temperature by using slow evaporation solution growth technique. The tetragonal crystal system, cell parameter values of the pure and LHKDP, LV KDP and LAKDP crystals were confirms by the single crystal X- ray diffraction studies. The powder X- ray diffraction test confirms the crystalline of the nature grown pure KDP crystal and LHKDP, LV KDP and LA: KDP crystal. The transmission spectra reveal that amino acid LH KDP, LVKDP and LAKDP additives were increased the optical transparency of the crystals and have sufficient transmission in the entire UV – Visible and IR regions. The presence of functional group in the grown pure KDP crystal, LHKDP, LVKDP and LAKDP crystal were identified by the FTIR spectroscopy analysis The thermal properties of the pure KDP and amino acids doped KDP crystals are studied by obtaining the TGA/DTA/DSC curves. The electrical properties were also studied by dielectric constant studies. The high dielectrisc constant in the doped crystal than pure crystal indicating that the doping is highly useful for NLO applications. The SHG efficiency studies is relatively confirm the nonlinearity of the grown pure KDP crystal, LHKDP, LVKDP and

LAKDP crystal by the emission of green light and the SHG efficiency of the grown LVKDP and LHKDP crystals relatively 1.07 and 1.22 times greater than pure KDP crystals, and the grown crystals confirms the suitability of the materials for the SHG application and LHKDP, LVKDP and LA KDP crystals are used in tuned laser applications and sensors.

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AN EXPERIMENTAL STUDY ON PARTIAL REPLACEMENT OF CEMENT WITH METAKAOLIN AND COARSE AGGREGATE WITH E-WASTE

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A B S T R A C T

An experimental study is made on the utilization of E-waste particles as coarse aggregates in concrete with a percentage replacement ranging from 0 %, to 20% i.e. (0%, 5% ,10%, 15%, and 20%) on the strength criteria of M25 Concrete. Compressive strength, Tensile strength and Flexural strength Concrete with and without E- waste plastic as aggregates was observed which exhibits a good strength. Also the study continuous by replacing metakaolin with cement in percentage of 10% and the mechanical properties are compared with e-waste and metakaolin and without metakaolin. The feasibility of utilizing E-waste plastic particles as partial replacement of coarse aggregate has been presented. In the present study, compressive strength was investigated for Optimum Cement Content and 15% E-plastic content in mix yielded stability and very good in compressive strength of 53 grade cement. Increase in split tensile strength is almost insignificant whereas gain in flexural tensile strength have occurred even up to 15 % replacements. E-waste seems to have a more pronounced effect on the flexural strength than the split tensile strength.

Keywords: E- waste, Concrete, Metakaolin, Compressive strength.

I. INTRODUCTION

The management and recycling of E plastic waste is rapidly growing as it is a valuable resource of IT industries and it is very hazardous substances and with low recycling rate. The Utilization of e plastic waste materials is a partial solution to environmental and ecological problems. As the use of E plastic waste will reduces the Aggregate cost and provides a good strength for the structures and roads. It will reduces the landfill cost and it is energy saving. The e plastic waste consists of discarded plastic waste from the old computers, TVs, refrigerators, radios; these plastics are non-biodegradable components of E plastic waste as a partial replacement of the coarse or fine aggregates. Electronic waste materials are one of the quick increasing waste materials in the planet. Every year approximately 50 million tons of E-Waste is formed. Unnecessary computers, mobile phones along with additional electrical and electronic wastes gives useless results. Therefore it's significant to exist alert of E-Waste here adding to the additional substantial wastes. Production of huge quantity of concrete is depleting natural raw material

sources. Here this project effort M mix up design be formed with understudy of normal coarse aggregate by E-waste material ranges like 0%, 5%, 10%, 15%, 20% and also cement is replaced by metakaolin with 0% and 10%.

The use of these materials in concrete come from the environmental constraints in the safe disposal of these products. Use of E-waste materials not only helps in getting them utilized in cement, concrete and other construction materials, it helps in reducing the cost of cement and concrete manufacturing, but also has numerous indirect benefits such as reduction in landfill cost, saving in energy, and protecting the environment from possible pollution effects.

OBJECTIVE OF WORK

The present work of partial replacement of cement with metakaolin and coarse aggregate with e-waste aims following objectives.

- To find the best suitable dosage of E-waste to incorporate in concrete.
- The influence of E-waste and metakaolin on fresh and hardened properties of SCC.
- To determine the percentage growth rate in hardened properties like compressive strength, split tensile strength.
- To study the durability characteristics of Ewaste Concrete using metakaoline as a mineral admixture.

II. LITERATURE REVIEW

Some research publications are pertaining to this thesis given as follows.

Ashwini Manjunath B T (2016)

This paper investigated, the use of Electronic plastic waste material like coarse aggregate in concrete with different ranges like 0%, 10%, 20% and 30% with M20 grade of concrete mix. By comparing the obtained consequences with conventional concrete at twenty eight days, it is reported to there is considerable reduction in compressive strength, split tensile strength and flexural strength of concrete due to E-Waste. This proves so as to the power of concrete get concentrated while coarse aggregate was replace with E-waste plastic particles.

Shoba Raj kumar, B Nithya (2016)

Here this paper, the research was achieved to find the replacement of coarse aggregate using Electronic waste in M25 grade concrete mix design. Polystyrene aggregate retained on 10mm sieve was used as E-waste material in different ranges like 10%, 15% and 20%. They conducted various tests in laboratory. The tests are; compression test, split tensile test and flexural test of concrete should be determined. Hence they recommended with the intention of Electronic waste aggregate be able to be used as understudy of natural coarse aggregate up to 10%.

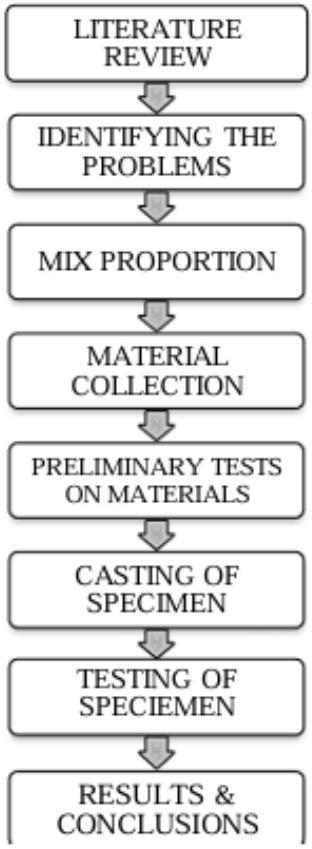
Megha Rani A, Dr.P.G. Bhaskaran Nair, Anisha G Krishnan(2017)

In this work, E-waste is used as partially replacement to the coarse aggregate. They conducted various tests in laboratory. The tests are; compression test, flexural test of concrete should be determined. Hence they finished with the intention of electronic waste aggregate be able to be used as understudy of natural coarse aggregate up to 10%.

P.K. Roy, Devanshjain, Vijay meshram (2019)

In this paper, it has been experimental that the coarse aggregate is replaced by E-waste and also cement is replaced by fly ash. They conducted compression test in laboratory, these test give poor strength of concrete. When fly ash content added to E-Waste concrete, workability increase is observed. It is reported that when fly ash is adding in the place of cement, the result is good.

III. METHODOLOGY



MATERIALS USED :

The Materials used for the study are :

I) Cement

ii) Fine Aggregate

iii) Coarse Aggregate

iv) E-waste

v) Admiexture

vii) Water

I) Cement

Ordinary Portland Cement (OPC) grade 53 as per IS:12269:1999 was used in this study. The physical properties of the cement conform to IS: 12269:1999 and have been tested at the Concrete Laboratory of Anamacharya Institute of Technology and Science, Kadapa.

ii) Fine Aggregate

Sand used in this experimental program was locally procured. It was tested for various physical properties in accordance with IS 2386 (Part 3) - 1963. Fine aggregate was natural sand conforming to zone III of IS 383-2016 passing through 4.75 mm size sieve. The specific gravity and fineness modulus are found to be 2.59 and 2.64.

iii) Coarse Aggregate

Aggregate is a granular material such as sand, gravel, crushed stone, crushed stone hydraulic cement concrete used with a hydraulic cementing agent to produce concrete or mortar. Aggregates are divided into many classifications based on their sizes. Crushed stone with 20 mm aggregate is used as coarse aggregate in the concrete mix.

iv) E-Waste

The E-Waste material of printed circuit boards are used. The printed circuit boards were crushed and considered as replacement of coarse aggregate substitute retaining the mix as the same. The divided particle size of E-Waste is 20mm. the specific gravity of E-waste is 1.81. The E-waste is collected from E-waste recycled shop, Hyderabad.

Fig 1. E-waste

v) Admixture

Metakaolin is also called as artificial mineral admixture. Metakaolin was collected from the area of Chennai. The specific gravity test was conducted in laboratory. The specific gravity of Metakaolin is 2.53.

vi) Water

The water used for mixing the concrete components, casting and curing the samples shall not contain impurities which, if present, may adversely affect the strength of the concrete as per IS:3025:1964 (Parts 22 and 23) and IS:456: 2000.

Detailed description of the materials used and their physical properties has been presented. The mix design for M25 grade of concrete according to IS: 10262-1982 has been designed.

Table 1 Mix design for M25 grade concrete

Cement	F.A	C.A	Water
524.31 kg	672.36 kg	928.08 kg	199.24
1	1.28	1.77	0.38

E-waste is replaced in percentages of 0, 5, 10,15 and 20 and the mix designs are as follows :

Conventional Concrete – 1 : 1.28: 1.77

Conventional Concrete with 5%replacement – 1 : 1.28 : 1.72

Conventional Concrete with 10%replacement – 1 : 1.28 : 1.67

Conventional Concrete with 15%replacement – 1 : 1.28 : 1.62

Conventional Concrete with 20%replacement – 1 : 1.28 : 1.57

Metakaolin is replaced 10% in cement and Ewaste is replaced in percentages of 0, 5, 10,15 and 20 and the mix designs are as follows :

Conventional Concrete – 1 : 1.28: 1.77

Conventional Concrete with 5%replacement – 0.9 : 1.28 : 1.72

Conventional Concrete with 10%replacement – 0.9 : 1.28 : 1.67

Conventional Concrete with 15%replacement –
0.9 : 1.28 : 1.62
Conventional Concrete with 20%replacement –
0.9 : 1.28 : 1.57

IV. EXPERIMENTAL INVESTIGATION

The following steps are performed in this phase.

1. Design of concrete mix
2. Mixing of concrete
3. Test Specimens
4. Preparation of Moulds
5. Harden properties of concrete
6. Observations and test Results

1. Design of concrete mix

The mix design for M25 mix is explained in the (Mix Design).

2. Mixing of concrete

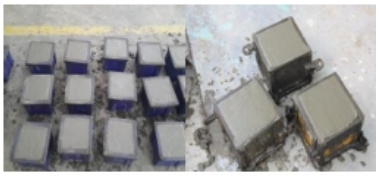


Fig 2. Mixing of concrete

3. Test specimens

4. Preparation of moulds

Fig 3. Preparation of moulds

5. Hardened properties of concrete

The compressive strength, tensile strength and flexural strengths of the used samples was measured with a compressive testing machine and flexure beam apparatus.

V. RESULTS & DISCUSSIONS

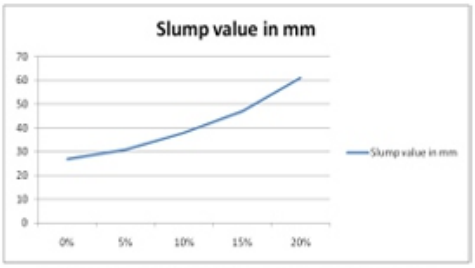
The results completed in the present investigation are reported in the form of tables and graphs for various fresh properties and harden properties of concrete for various percentage of E- waste as a partial

replacement to Coarse aggregate in concrete by 0%, 5%, 10%, 15% and 20 % are worked out and tabulated in the tables below and further more the procedure is repeated by replacing metakaolin in the place of cement with 10%.

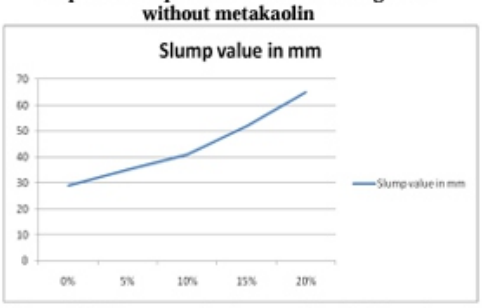
FRESH PROPERTIES

Slump cone results :

Following are the test result obtained from slump cone test for various grade and % replacement of E-waste for various grades of concrete.



Graph 1. Slump value in mm for M25 grade without metakaolin



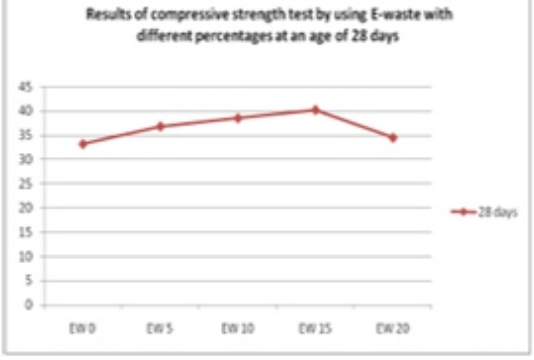
Graph 2. Slump value in mm for M25 grade with 10 % metakaolin

HARDENED PROPERTIES OF CONCRETE

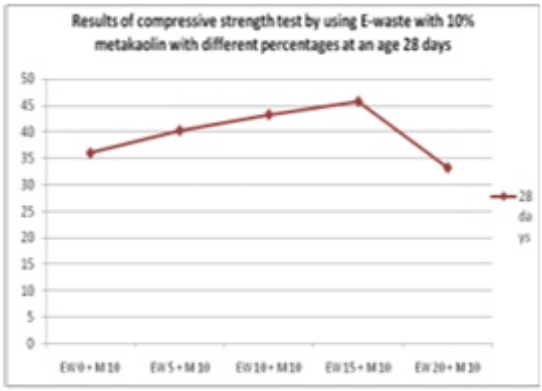
Compressive strength is the most important and useful property of concrete. In most structural applications, concretes are primarily used to resist compressive stresses. Concrete cube of size 150x150x150 mm were cast with various Ewaste percentages and with 0 and 10% of cement replacement by metakaolin. The cubes were cured for a period of 28 days. The compressive, split tensile and flexural strength results are tabulated.

COMPRESSIVE STRENGTH RESULTS

The Compressive strength results for various replacement levels of E-waste by (0-20%) at an increment of 5% for 28 days with and without metakaolin are presented below.



Grpah 3. Average compressive strength for 28 days without metakaolin

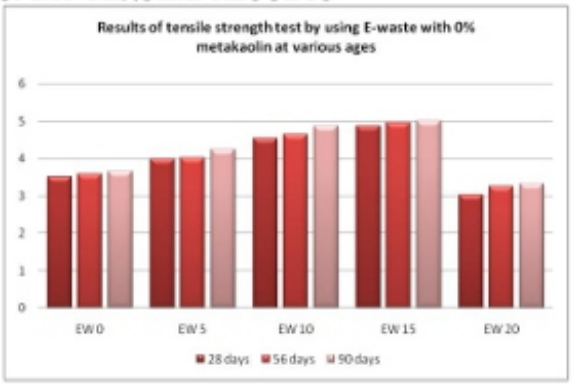


Grpah 4. Average compressive strength for 28 days with 10% metakaolin

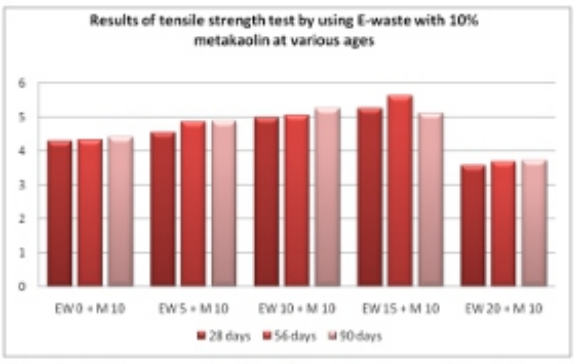
Combinations (%)	28 days (M 0%)	28 days (M 10%)
EW 0	33.25	36.03
EW 5	36.82	40.25
EW 10	38.51	43.22
EW 15	40.2	45.7
EW 20	34.52	33.26

Table 2. Results of compressive strength test by using E-waste with different percentages

SPLIT TENSILE RESULTS

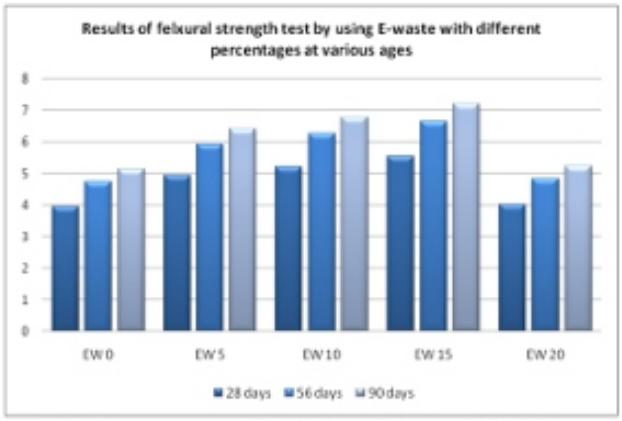


Graph 5. Average results of tensile strength test by using E-waste with 0% metakaolin at various ages

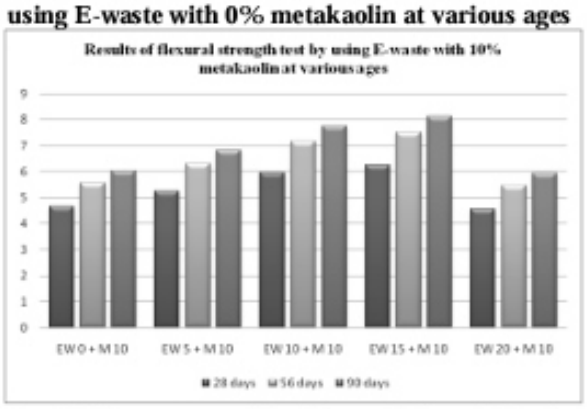


Graph 6. Average results of tensile strength test by using E-waste with 10% metakaolin at various ages

BEAM-FLEXURE RESULTS



Graph 7. Average results of flexural strength testby using E-waste with 0% metakaolin at various ages



Graph 8. Average results of flexural strength testby using E-waste with 10% metakaolin at various ages

VI. CONCLUSIONS

This study highlights the current situation of global e-waste generation and its effect on the environment. The scope of utilizing e-waste in the construction industry to prepare concrete is also reviewed. Moreover, techniques to produce e-waste aggregates and their effects on the properties of concrete are investigated in this study. The following conclusions and recommendations can be deduced from the above discussed topics :

- The disposal of toxic e-waste in landfill sites causes irreplaceable health and environmental hazards. Therefore, reusing raw materials obtained from e-waste recycling is the most viable solution to reduce the substantial growth in e-waste.
- The mechanical properties (e.g., compressive strength, flexural strength, and splitting tensile strength) of concrete containing e-waste aggregate decrease at higher e-waste aggregate replacement levels owing to the lower density of e-waste aggregates and increased porosity of the concrete matrix. Increasing the amount of ewaste plastic aggregates leads to high reduction in mechanical properties of concrete. However, using low w/c ratio to prepare concrete with e-waste aggregates can decrease the reduction in mechanical properties compressive (particularly strength).
- The fresh and dry properties of concrete with e-waste aggregates can be enhanced with admixtures (like metakaolin and steel slag), superplasticizer, and biomineralization. However, more data is necessary to estimate the long-term performance potential of e-waste incorporated concrete.
- The availability of limited data on the impact of e-waste on the engineering properties of concrete suggests in-depth analysis of e-waste modified concrete should be investigated comprehensively by

incorporating various factors, i.e., w/c ratio, concrete type, cement type, curing and environmental conditions. This will enable concrete technologists to conclude whether e-waste aggregates are suitable replacements for coarse aggregates in the preparation of concrete.

•E-waste modified concrete has the potential to decrease the thermal conductivity due to its lower density, which makes it a suitable material for energy conservation in buildings. However, limited literature is available on the mentioned topics, which makes it difficult to predict whether it would satisfy the conditions of designinglightweight or fireproof concrete.

•Manufactured e-waste modified concrete performs better than using unmanufactured e-waste aggregate. However, an evaluation of the cost and environmental impact of preparing manufactured aggregates is missing. Therefore, a life cycle assessment of e-waste modified concrete should be conducted to see how its manufacturing affects social, economic, and environmental
conditions. Such evaluation will enable concrete technologists to see if the environmental impact of e-waste may be diminished by using it as a supplement to coarse aggregates in concrete.

• Most of the studies suggest that e-waste aggregates can be used to prepare nonstructural members of a concrete structure. However, some researchers suggest that incorporation of e-waste increases durability and mechanical properties of concrete, which indicates that it has the potential to be used in preparing structural concrete. Moreover, a few studies also suggest that ewaste aggregate enhances the ductility of concrete as compared to conventional concrete, which indicates its ability to resist seismic loads. This should be studied more extensively to make the most of increasing e-waste worldwide.

• As mentioned earlier, e-waste causes environmental pollution both by disposing ewaste on landfill sites and via combustion. Although incorporation of aggregates gives a glimmer of hope to concrete technologist and environmental protection organizations to recycle and manage e-waste, processing of e-waste or/and enhancing the properties of e-waste modified concrete may increase the cost of the project. Therefore, LCA studies are recommended to better understand the potentials of e-waste modified concrete leading to acceptance of e-waste in the construction industry.

• Compressive strength of concrete decreases through increase in substitution of normal coarse aggregate with E-waste aggregate.

• The decrease in compressive strength is marginal up to 15% substitution of normal coarse aggregate by E-waste aggregate.

• Chloride ion permeability of concrete increases with increase in replacement of normal coarse aggregate by E-waste aggregate.

• Addition of 10% metakaolin has increased the compressive strength and decreased the chloride permeability.

• Hence, it is recommended that Printed Circuit Board E-waste aggregate be able to be use as partial substitution of normal coarse aggregate up to 15% by combining cement with 10% metakaolin.

• The addition of E-waste shows increase in compressive strength up to 15% replacement.

•Increase in split tensile strength is almost insignificant whereas gain in flexural tensile strength have occurred even up to 15 % replacements. E-waste seems to have a more pronounced effect on the flexural strength than the split tensile strength.

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Trace Element Geochemistry of the Ponnaiyar River Sediments, Tamil Nadu, India: Inferrences on Provenance.

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A B S T R A C T

The Ponnaiyar river sediments from nine sampling station between Thirukovilur and Cuddalore were subjected to geochemical studies to understand the trace elemental characteristics and their interrelation and to determine the source of trace elements present in the sediments. Chemical analysis was carried out on samples for P, Li, B, V, Cr, Co, Ni, Zn, Sr, Y, Nb, Mo, Sb, Ba, La, Ce, Pb and Zr. The granites, granitic-gneiss, charnockites, alkaline syenite-carbonatite, pyroxenites, garnetiferous-sillimanite gneiss, granite-pegmatites, mafic and ultra mafic litho-component and other granulitic rocks of the Ponnaiyar river basin form the source for all the trace elements studied. The migration of trace elements from source to river sediments could have taken place through particulate minerogenic phase as detrital heavy minerals and clay minerals. The average trace elemental content of the Ponnaiyar sediment exhibits an enhancement of P, V, Cr, Ni, Ba, La, Pb, Zr and a strong depletion of Zn relative to the upper continental crust (UCC) values. The study indicates that the Felsic rocks of the drainage basin contribute predominantly trace elements to the river sediments. The higher value of Cr, V, Ni, Pb, and P might have been derived from anthropogenic input to the river from industrial effluents and chemical contamination from agricultural lands, besides natural geochemical background contribution.

Key words: Sediment, trace elements, provenance, Ponnaiyar river.

1.0.0 Introduction:

The topography, climate, lithology, weathering processes of the source rock area determine the nature and composition of the river sediment. Trace element or trace metal are lithosphere component that are released into the environment during volcanism and rock weathering (Fergusson, 1990). The minerals present in the sediments exert control on the chemical composition of the sediments. The sandy and silty sediments are product of physical weathering whereas fine grained sediments are derived from chemical weathering process of the source rocks. Rivers play an important role in transporting the eroded sediment detritus from the continents to oceans. The eroded material would have been derived from various source rocks. The study of sediment geochemistry could give information about influence of provenance, weathering, tectonic and fluvial processes involved in making up the composition of sediments (Nesbitt and Young,1982; Taylor and McLennan,1985; Armstrong-Altrin et al. 2013; Nagarajan et al. 2017; Madhavaraju et al. 2020).

Sediment geochemistry of a few peninsular rivers of India have been studied by earlier workers; Singh and Rajamani, 2001; Rajamani et al, 2009; Sharma et al.2013; Silva, J. D. et al (2014): Madhavaraju et al. 2015; Saibabu et al. 2021; Shaik Saibabu et al. 2021. Though many studies have been carried out in the peninsular river, there still exists a gap in knowledge to understand the source and mode of transportation and dispersion of trace elements in the riverbed sediments. This present study attempts to investigate the source, correlation, and interrelationship among the trace elements of the lower

Ponnaiyar river sediments.

2.0.0 Study Area:

The Ponnaiyar river rises from Nandi hills in Karnataka and drains through Archaean rocks with Cretaceous formations (calcareous sandstone, claystone), Cuddalore sandstone and recent alluvium in the coastal region Tamil Nadu (Krishnan,1982 and Subramanian et.al, 2001), The riverbed comprises of medium and fine sand predominantly with occasional coarse sand occurrences. The constituent minerals are quartz, feldspars, amphiboles, ortho & clinopyroxenes, zircon, monazite, kyanite, epidote, tourmaline, ilmenite, magnetite, sphene, micas etc.

3.0.0 Materials and methods:

The Nine riverbed surface sediments were collected from channel bar, point bar along the course of the Ponnaiyar River 8 to10 km interval from Thirukoilur to Cuddalore (Fig-1). After proper cone and quartering representative samples from each location were taken for various laboratory analysis. Chemical analysis for trace elements was carried out on air dried samples for P, Li, B, V, Cr, Co, Ni, Zn, Sr, Y, Nb, Mo, Sb, Ba, La, Ce, Pb and Zr by ICP-AES techniques.

4.0.0 Bulk analytical data handling:

Chemical analysis carried out on nine bulk sediments for eighteen trace elements to understand their characteristic and relationship among various elements of the samples and to determine the source and mode of transportation, dispersion, and migration of elements in the river sediments. The abundance of trace elements in the Ponnaiyar river bed sediment is given in Table-1. The minimum, maximum and average elemental values obtained from the results of the analysis and the elements crustal value (UCC) are tabulated (Table-2). Pearson correlation coefficient for several trace elemental combination has been determined (Table-3). The correlation coefficient higher than 0.40 is considered significant at 98% confidence limit.

Study area Index map

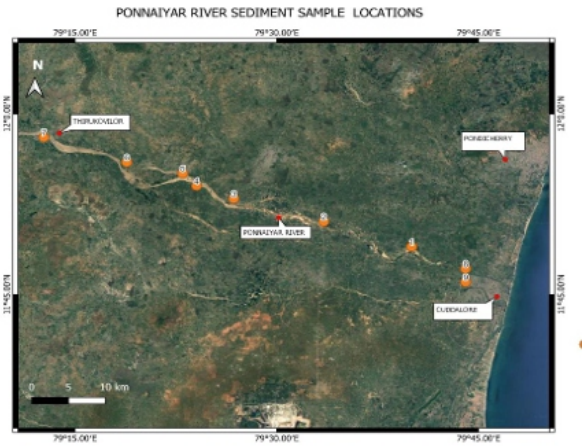

Fig. 2. Map showing Sediment sample locations in the Ponnaiyar River.

TABLE-1. ABUNDANCE OF TRACE ELEMENT CONTENT IN THE SEDIMENTS.

(Values in ppm)

Samp	P	Li	B	V	Cr	Co	Ni	Zn	Sr	Y	Nb	Mo	Sb	Ba	La	Ce	Pb	Zr
1	598	10	87	122	175	6	91	54	387	20	20	38	25	794	51	106	152	548
2	637	10	84	124	162	7	82	45	388	20	20	36	17	805	45	93	149	301
3	767	10	86	87	198	6	111	44	373	20	20	40	42	853	35	94	160	213
4	1312	11	89	276	241	19	108	64	368	27	41	34	15	733	189	389	175	826
5	1252	10	89	285	241	18	106	69	416	27	41	34	11	785	205	416	177	1017
6	830	11	87	135	219	11	116	44	386	20	20	39	39	860	67	164	168	277
7	903	10	87	212	215	14	101	52	362	21	26	34	14	747	100	218	161	579
8	778	10	86	129	188	8	98	45	389	20	20	38	41	850	57	138	166	450
9	363	13	89	0	261	9	137	49	103	20	28	55	91	567	42	137	173	962
MIN	363	10	84	0	162	6	82	44	103	20	20	34	11	567	35	93	149	213
MAX	1312	13	89	285	261	19	137	69	416	27	41	55	91	860	205	416	177	1017
Avg.	**827**	**11**	**87**	**152**	**211**	**11**	**106**	**52**	**352**	**22**	**26**	**39**	**33**	**777**	**88**	**195**	**165**	**575**

Table -2 TRACE ELEMENT CONTENT MINIIMUM. MAXIMUM. AVERAGE VALUES AND UPPER CRUSTAL VALUES (UCC).

Elements	MIN	MAX	AVG	UCC * Values
P	363	1312	**827**	610.00
Li	10	13	11	20.00
B	84	89	87	0.00
V	0	285	**152**	97.00
Cr	162	261	**211**	71.00
Co	6	19	11	17.30
Ni	82	137	**106**	44.00
Zn	44	69	52	71.00
Sr	103	416	352	350.00
Y	20	27	22	22.00
Nb	20	41	26	25.00
Mo	34	55	39	0.00
Sb	11	91	33	0.00
Ba	567	860	**777**	550.00
La	35	205	**88**	30.00
Ce	93	416	**195**	64.00
Pb	149	177	**165**	20.00
Zr	213	1017	**575**	190.00

UCC* from Taylor S R and McLennan, S. M. (1985).

TABLE -3 CORRELATION COEFFICIENT MATRIX OF TRACE ELEMENTS

Variabl	P	Li	B	V	Cr	Co	Ni	Zn	Sr	Y	Nb	Mo	Sb	Ba	La	Ce	Pb	Zr
P	**1.00**	-0.37	0.38	**0.95**	0.30	0.85	-0.15	**0.73**	**0.58**	**0.88**	**0.74**	-0.73	**-0.70**	0.27	**0.91**	**0.88**	**0.51**	0.29
Li		**1.00**	**0.54**	-0.47	**0.70**	**0.06**	**0.84**	-0.05	**-0.91**	-0.05	0.19	0.84	**0.80**	**-0.80**	-0.11	-0.01	0.49	0.46
B			**1.00**	0.31	**0.90**	**0.68**	**0.66**	**0.71**	-0.39	**0.64**	**0.78**	0.24	0.20	**-0.59**	**0.64**	**0.70**	**0.84**	**0.85**
V				**1.00**	0.17	0.84	-0.34	**0.77**	**0.64**	**0.84**	**0.70**	**-0.83**	**-0.84**	0.25	**0.90**	**0.86**	0.34	0.33
Cr					**1.00**	0.66	**0.84**	**0.49**	**-0.55**	**0.52**	**0.71**	0.39	0.37	**-0.65**	**0.52**	**0.62**	**0.90**	**0.75**
Co						**1.00**	**0.17**	**0.82**	**0.15**	**0.89**	**0.91**	-0.41	-0.43	**-0.21**	**0.95**	**0.97**	**0.72**	**0.65**
Ni							**1.00**	**0.00**	**-0.75**	0.04	0.25	**0.74**	**0.76**	**-0.59**	0.01	0.12	**0.69**	0.42
Zn								**1.00**	0.17	**0.93**	**0.92**	-0.37	-0.46	-0.26	**0.92**	**0.91**	**0.54**	**0.79**
Sr									1.00	0.24	-0.04	**-0.93**	-0.87	**0.88**	0.30	0.21	-0.28	-0.43
Y										1.00	**0.95**	-0.44	-0.48	-0.13	**0.98**	**0.97**	**0.65**	**0.67**
Nb											1.00	-0.20	-0.27	-0.41	**0.93**	**0.95**	**0.75**	**0.83**
Mo												1.00	**0.98**	**-0.66**	**-0.51**	-0.43	0.18	0.21
Sb													1.00	**-0.54**	**-0.55**	-0.46	0.22	0.11
Ba														1.00	-0.09	-0.16	-0.37	**-0.73**
La															1.00	**0.99**	**0.65**	**0.65**
Ce																1.00	**0.73**	**0.70**
Pb																	1.00	**0.69**
Zr																		1.00

TABLE-4 TRACE ELEMENTAL RATIOS of Cr/Ni, Cr/v, Y/Ni and Zr/Co.

SAMPLE	Cr/Ni	Cr/V	Y/Ni	Zr/ Co
1	1.92	1.43	0.22	91.33
2	1.98	1.31	0.24	43.00
3	1.78	2.28	0.18	35.50
4	2.23	0.87	0.25	43.47
5	2.27	0.85	0.25	56.50
6	1.89	1.62	0.17	25.18
7	2.13	1.01	0.21	41.36
8	1.92	1.46	0.2	56.25
9	1.91	2.61	0.15	106.89
Min	*1.78*	*0.85*	*0.15*	*25.18*
Max	*2.27*	*2.61*	*0.25*	*106.89*
avg	***2.00***	***1.49***	***0.21***	***55.50***

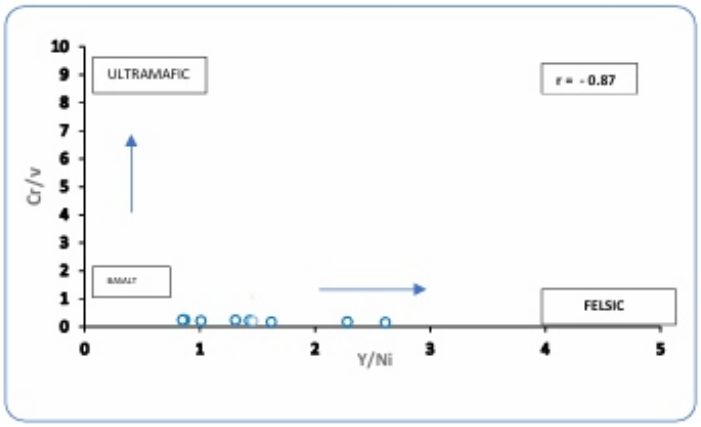

FIG. 3. Showing the ratio-ratio plot of Cr/V and Y/Ni of the Ponnaiyar River sediments.

(adopted from Mclennan et al. 1993 and Mongelli et al. 2006).

5.00 Results and discussion:

The Ponnaiyar river drainage basin experiences physical and chemical weathering due to dominant humid, tropical climate. The seasonal rainfall and temperature play important role in the weathering of rocks and in the liberation of the weathered mineral grains which later form the sediments of the riverbed, Chemical weathering influences the alkali and alkaline earth metal elements concentration of the sediments (Nesbitt and Young,1982).

The trace elemental content in the sediments (Table-1) of the study area varies from 98 to 7440.27 ppm with an average of 1869.22 ppm. The Pearson correlation coefficient among the elemental variables was calculated and presented in Table-3. The average trace element content (TE) of the Ponnaiyar river is 1869.22 ppm, which is higher than UCC and PAAS values of 1633.50 ppm (Rudnick et al.2003) and 1807.20 ppm (Pourmand et al.2012) respectively. The average elemental content of the Ponnaiyar sediment exhibits an enhancement of P, V Cr, Ni, Ba, La, Pb, Zr and a strong depletion of Co and Zn relative to the upper continental crust (UCC) values (Table-2). The correlation matrix (Table-3)

indicates positive correlations among a group of elements such as P, V, Co, Zn, Sr & Y, Nb, La, Ce, Pb, which could have been derived from the heavy mineral content of the source rocks. The Ba and Sr have negative correlation with other elements is inferred to be derived from the Cretaceous limestone occurring in the Ponnaiyar basin. The element Mo has strong positive correlation with Sb, Li and Ni. The element Sb has positive correlation with Li. Ni and Mo. Both Mo and Sb show strong negative correlation with P, V, and Sr. The Sb and Mo could have been derived from the gold bearing quartz veins and schitose rocks of the Ponnaiyar river basin. Positive correlation of P with Zn (+0.73) and Pb (+0.51) suggests that these elements are associated with phosphate mineral. High field strength elements such as Zr, Nb, Y reflect the provenance composition due to their immobile nature. The occurrence of the elements Zr, Nb and Y in the sediments indicates their derivation from heavy minerals such as zircon, rutile, and tourmaline. Tourmaline mineral can also contribute to La, Li and B. The heavy minerals, such as monazite and zircon, can contribute Ce, La, Nd, Y and P to the sediments.

The trace elemental ratios of Cr/V, Cr/Ni, Y/Ni and Zr/Co are presented in Table-4. The ratio of Cr/V shows 1.49 which is also higher than in UCC (0.95). Bhattacharya et al. (2012) reported Cr/V value 1.28 for granitic rock source. The ratio of Cr/Ni exhibits 2.00 which is higher than in UCC (1.95). If the Cr/Ni ratio value falls between 2 to 7, indicating the elements derivation from heavy minerals and cr minerals from the source (Garver et al.1996). The Y/Ni ratio is 0.21 which is lower than in UCC (0.44). Low Y/Ni <0.50 suggests a mixture of felsic and mafic source rocks.The plot of Y/Ni vs Cr/ V (Fig.3) shows that the samples analysed fall under felsic field indicating a granitic source for the trace elements (Mc Lennan et al. 1993; Mongelli et al. 2006). The ratio of Zr/Co is 55.50, which is much higher than in UCC (11.20). Borges et al. (2008) reported that Zr/Co ratio values on an average of 12 for mafic character for Lena river sediments; Zr/Co ratio value on an average 29, indicates felsic character in Salween river sediments. Accordingly, Zr/Co ratio value of 55.50 in the study area, suggests a felsic source rock for the Ponnaiyar river sediments.

The correlation coefficient value (Table-3) and elemental ratios (Table-4) discussed above suggest that the source for the trace elements are from felsic source rocks of the Ponnaiyar river drainage basin. The felsic rocks such as gold bearing quatz vein associated schists, granites, gneisse, alkaline syenite, carbonatites and Cretaceous limestones of the area played major role in the supply of trace elements to the sediments of the Ponnaiyar river. The higher value of Cr, Ni, Pb and P might have been derived from anthropogenic input from industrial effluents and chemical contamination from agricultural lands along the river course, besides natural geochemical background contribution. Overall, the study suggests that the mineral content of felsic rocks of the Ponnaiyar river basin form the major source for the trace elements present in the sediments. However, the mafic rocks might have played a subdued role in the supply of certain elements to the sediments in the study area.

6.0.0 Conclusions:

The mineralogy and trace element geochemistry of the sandy sediments of the lower reaches between Thirukoilur and Cuddalore part of the Ponnaiyar river indicate the following::

1. The chemical analysis of eighteen trace element content in the Ponnaiyar river sediments varies from 98 to 7440 ppm with an average value of 1869.22 ppm.
2. The correlation coefficient and elemental ratios of the trace elements suggest that felsic rocks of the Ponnaiyar river drainage basin form the source for these elements.
3. The felsic rocks such as gold bearing quatz vein associated schists, granites, gneisse, Pegmatites, alkaline syenite, carbonatites and Cretaceous limestones of the area played major role in the supply of trace elements to the sediments of the Ponnaiyar river.
4. The trace elements have been transported to the riverbed in particulate minerogenic phase as detrital

minerals.

5. High ΣTE in the river sediments of the study area is due to the enrichment of trace elements through anthropogenic input from industrial effluents and chemical contamination from agricultural lands along the river course, besides natural geochemical background contribution.

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DESIGN OF LUMBAR IVD IMPLANT BASED ON 3D PRINTING METHOD USING BIOCOMPATIBLE POLYMERS

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ABSTRACT

Spinal fusion surgery is a common procedure for treatment of degenerative disc disease, herniated discs, and spinal fractures. Intervertebral disc implants are commonly used to replace damaged or diseased discs and restore spinal stability. However, currently available implants have limitations such as limited range of motion, subsidence, and stress shielding. In this paper, we propose a new design for intervertebral disc implant that overcomes these limitations and improves clinical outcomes.

The proposed implant is designed to mimic the biomechanics of a healthy intervertebral disc, with a composite structure that allows for both flexibility and stability. The implant consists of an outer ring made of a durable polymer and an inner core made of a compressible material, allowing for shock absorption and load transfer. The implant provides a porous surface for bone ingrowth, promoting osseointegration and long-term stability.

Finite element analysis and was conducted to evaluate the performance of the proposed implant design. Results exhibited that the implant had superior load-bearing capacity and reduced stress concentration. In addition, the implant exhibited minimal subsidence and preserved range of motion, which may lead to improved patient outcomes and reduced revision rates. In conclusion, the proposed intervertebral disc implant design has the potential to improve clinical outcomes and provide a more effective treatment option for patients administered for spinal fusion surgery. Further studies are needed to validate the efficiency and safety of the proposed implant in clinical settings.

Keywords: Dynamic stabilization; Disc prosthesis; Motion preservation; Arthroplasty; Total disc replacement; Lumbar vertebrae.

I. INTRODUCTION

One of the vital parts of the human anatomy is the vertebral column which provides a pivotal role of being the structure of support and mobility for the torso region of the body, and a protective layer for the spinal cord preventing it from any damage or fatigue. This vertebral column is basically not a single structure but an array of many vertebrae of different size and morphology which is varied based on the position in the vertebral column.

The vertebral column of human body is categorized into 5 divisions namely: The Cervical spine, The Thoracic spine, The Lumbar spine, The Sacrum spine and The Coccyx. The categorization is made

possible by the anatomical structure of the vertebrae at each position. These vertebrae are nothing but bony structures, so to prevent any frictional abrasions between them Intervertebral Vertebral Disc (IVD) is present.

The intervertebral discs are found to be soft, structures located in the middle of two vertebrae (bones) of the spinal column. They function to absorb shock, distribute pressure evenly, and allow for movement and flexibility in the spine. Each disc is composed of annulus fibrosus which is a tough outer layer, and a soft, jelly-like center which is defined as the nucleus pulposus. The annulus fibrosus contains layers of fibrous tissue that surround and protect the nucleus pulposus. The nucleus pulposus is found to be a gel-like substance that provides cushioning and support to the spine. Together, they form the intervertebral disc.

At times these IVD get damaged which is stated as Degenerative Disc Disease, this is a condition of the discs between vertebrae with loss of cushioning, fragmentation and herniation related to ageing. There may be no symptoms. When the spine becomes less flexible, bone spurs may wrap a nerve root and cause pain or weakness. Spinal disc degeneration affects anywhere between 12% and 35% of the population today, making it a fairly common problem. When severe enough, it can result the intervertebral disc itself bulging and herniating. It typically affects the lumbar region of the spine.

Multiple treatment methods are currently available to address this issue, with spinal fusion surgery and total disc replacement (TDR) being two of the most popular. Although the majority of patients experience pain relief from these treatments, there are still a number of drawbacks. For instance, TDR can result in hypermobility in between the vertebrae and provide little to no shock absorption of loads, and spinal fusion surgery drastically restricts the mobility of its patients by joining two vertebrae together, prohibiting any individual movement. Therefore in order to ease patients' discomfort and retain shock absorption, motion, and load cushioning that are equivalent to the criteria of the healthy intervertebral disc while yet staying biocompatible, a better therapeutic alternative is required.

II.ANATOMY OF LUMBAR AND IVD

1.LUMBAR SPINE

The lumbar portion of the spine connects the thoracic spine to the pelvis and extends to the sacrum. It holds five vertebrae (L1-L5) and five discs between the vertebrae. The lumbar spine's principal roles include carrying high loads, protecting the spinal cord when there is a movement and when the trunk bends or twists, and providing utmost stability while preserving the trunk's essential mobility around the hips and pelvis.

The lumbar spine contains nerves which are much more similar to those of the spine in cervical , in that each nerve that comes out of the different levels of vertebrae have very unique functions, which if disturbed or damaged can hinder an individual's daily life and possibly leave them get paralyzed below the waist down .These nerves control mainly the anterior of the lower extremities, and include: L1 nerve that controls partial lower back, partial lower abdominal, and partial hip flexor muscles; L2 nerve that controls muscles that extend or flex the hip joint (hip flexors, outer gluteus/gluteus medial), and groin regions; L3 nerve that controls major quadriceps muscles to extend the lower limb leg and straighten the knee; L4 nerve that controls the ankle muscles that cause dorsi-flexion of the foot (drawing the toes upwards), great toe, and outer quadriceps muscle; L5 nerve that control outer muscles of the lower extremity (iliotibial tract, tibialis anterior), and major foot muscles .

The L1, L2, L3, and L4 nerves share sensations for the anterior and inner surfaces of the lower extremity; L4 and L5 nerves share sensations for the foot; L4 creates sensations in the medial side of great toe;

2.INTERVERTEBRAL DISC

Intervertebral discs, which are named after the two vertebrae they positioned between (e.g., C6-C7, T7-T8, and L4-L5, also known as L4/L5) for every set of vertebra all through out the vertebral column. About 20 to 30 percent of the spine is contributed by these discs, which perform a number of vital tasks like cushioning loads, absorbing shock from impacts, distributing weight, allowing individual vertebrae to move, and allowing nutrients along with other fluid to reach the spinal cord and spine.
The thickness of each disc varies across the spine along with a varied change in the cross-sectional areas of the discs. According to research, the cervical and the lumbar spines have substantially thicker discs than the thoracic spine, probably as an adaptation to the ROM (Range Of Motion) expected from these regions, including flexionextension and torsion.

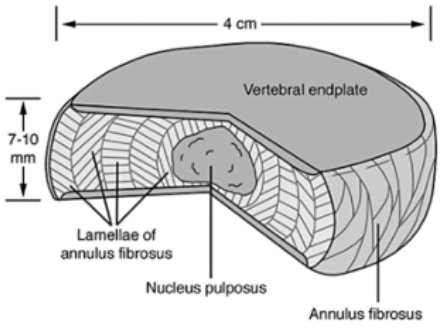

Figure 1: A Cutout Portion of IVD

3. LUMBAR DISC

There are five intervertebral discs in the lumbar spine, numbered L1/L2 through L5/S1. Out of all the spinal segments, the lumbar discs have the largest cross-sectional area, with L2/L3 - L5/S1 being nearly equal. This is necessary because these discs must withstand the most strain without becoming overly stressed and failing. The mean cross-sectional areas of the lumbar discs are as follows; L1/L2 having an area of 1400 mm2; L2/L3 having an area of 1640 mm2; L3/L4 having an area of 1690 mm2; L4/L5 having an area of 1660 mm2; L5/S1 having an area of 1680 mm2
The three major components of each intervertebral disc, which has a complex structure, are the nucleus pulposus, the cartilage vertebral endplates, and the annulus fibrosus. These components give certain necessary properties to the intervertebral discs' structural integrity and properties as a whole

4. ANNULUS FIBROSUS

The inner and outer annulus fibrosus are considered to be the two main portions of the annulus fibrosus, which is made up of concentric rings, or lamellae, enclosing the nucleus pulposus. Proteoglycans (11-20% inner and 5-8% outer dry weight), water, and fibrocartilage, and other factors involved in extracellular-matrix, however with increasing radial distance from the nucleus, the concentration of some of these components change, mainly collagen and proteoglycans. These tissues and cells contribute to the annulus fibrosus' more rigid structure, which is necessary for it to perform its essential functions in the intervertebral discs. The nucleus pulposus is housed in the annulus fibrosus, which also protects the spine by maintaining its pressure and prevents it from impinging on the disc by virtue of its inhomogeneous, anisotropic, and nonlinear mechanical characteristics. The structure of numerous lamella and alternate collagen fiber angles enables these key functions.

5. NUCLEUS PULPOSUS

The annulus fibrosus surrounds the nucleus pulposus, which prevents it from leaking into the spinal canal, and it is located in the centre of the disc. In order to perform its essential functions in the intervertebral disc of compressive load dispersion, compressive shock absorption, and maintaining the interior of the disc swelled for appropriate internal pressure, the nucleus, an incompressible structure, is composed of around 80–90% water.

6. VERTEBRAL ENDPLATES

The vertebral endplates are made of hyaline cartilage containing proteoglycans for swelling qualities, and they are located on the top and bottom of each intervertebral disc. Their main duty is to mechanically connect the vertebral nucleus and annulus to the dense, more durable cortical bone shell and prevent the nucleus from protruding into the trabecular bone's soft, spongy/cancellous middle. The strongest part of the intervertebral disc, the vertebral endplates, usually snaps after the vertebral body has already fractured. Additionally, the vertebral endplates play the unusual job of serving as the primary conduit for blood and nutritional flow into and out of the disc.. The mobile app initially displays the prescription to the pharmacist so that he or she may confirm that the meds are available before moving on to the next stage.

III. IVD ABNORMALITIES

1.DISC HERNIATION

Disc herniation, also known as a slipped disc or herniated disc, is a common IVD abnormality. It happens when a tear or other weakness in the out most layer of the intervertebral disc allows the soft interior material to emerge. Although it can happen anywhere in the spine, disc herniation frequently affects the neck and lower back (lumbar spine). Depending on where and how severe the herniation is, the symptoms of a disc herniation may vary.

2. DISC DEGENERATION

Disc degeneration is another common IVD abnormality, which can result in chronic pain in back bone and reduced mobility. It occurs when the intervertebral discs lose their ability of absorbing shock and provide support due to natural wear and tear over time. While disc degeneration is a normal segment of the aging process, certain factors can accelerate the degeneration, such as genetics, repetitive stress, poor posture, and injury. Preventive measures, such as maintaining good posture, engaging in regular exercise, and avoiding repetitive stress, can help reduce the risk of developing disc degeneration. A healthcare professional, such as a spine specialist or orthopedic surgeon, can provide guidance on appropriate treatment and preventive measures tailored to an individual's specific condition.

3.DISC BULGING

Disc bulging, also stated as a bulging disc or protruding disc, is a condition that occurs when the intervertebral disc extends beyond its normal boundaries. It is considered a common IVD abnormality and often occurs as a precursor to disc herniation or as part of the natural aging process. In disc bulging,

the outer most layer of the intervertebral disc weakens or sustains damage, causing it to bulge outward which exhibit effects like localised pain, radicular pain. However, unlike a herniated disc where the inner material ruptures through the outer layer, in disc bulging, the outer layer remains intact

4. DISC PROTRUSION

Disc protrusion is a type of intervertebral disc (IVD) abnormality in which a portion of the disc protrudes or bulges outside its normal boundary. It is often considered a mild form of disc herniation and can cause similar symptoms. In disc protrusion, the outermost layer of the disc may bulge outwards, but the inner material remains intact. This condition can occur anywhere in the spine but is most common in the lumbar (lower back) and cervical (neck) regions. Surgical intervention is typically not required for disc protrusion unless it progresses to a more severe condition or if conservative treatments fail to provide relief.

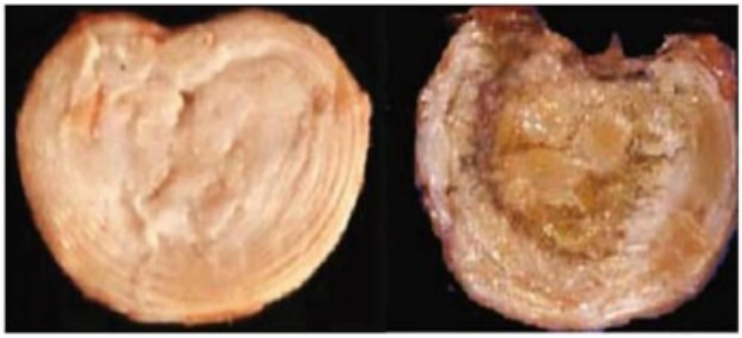

Figure 2: A comparison between a healthy and unhealthy disc

IV. EXISTING MODELS

Total disc replacement's original ideas first surfaced more than 30 years ago. Due to the intervertebral disc's intricate anatomical and functional makeup, an effective and trustworthy artificial disc is expected to both replicate motion and support loads. Total disc replacement (TDR), as opposed to spinal fusion, has produced outcomes that are comparable to or better than those of lumbar fusion. In lumbar TDR (0%-16.7%) and cervical TDR (0%-4.0%), a 5-year meta-analysis found that TDR had a reasonably low rate of problems

1.CHARITÉ

Unlike Charité I and II, which used stainless steel, Charité III and InMotion used CoCrMo with titanium calcium phosphate coating. The device had a highly mobile polyethylene core (Ultra High Molecular Weight Polyethlene [UHMWPe]) with convex surfaces that articulate with concave shaped metallic endplates. The Charité I implant's diminutive size contributed to its high subsidence frequency. This issue was addressed by the Charité II by adding thin lateral wings to increase the surface area. Sadly, these wings experienced early cracks.

2.PRODISC

The ProDisc II was created following the ProDisc I's original release. The upper metallic endplate and the upper surface of the polyethylene core act as a single movement interface in the contemporary

ProDisc implant, in contrast to the Charité. The polyethylene core (bearing surface) is fixed to the lower endplate but not to the upper endplate, making it possible to classify it as a semiconstrained device. A single sagittal keel and two little spikes, as opposed to the Charité III's six tiny teeth, are used to improve endplate fixation.

3.MAVERICK

The Maverick has a posterior centre of rotation to match that of the disc segment intended to unload the facet joint, two metallic CoCrMo endplates that directly create a balland-socket system with the goal of minimising wear, and hydroxyapatite (HA) coating on the bone-implant interface to maximise early fixation with bony ingrowth. The prosthesis has been used in clinical settings since 2002 after receiving its CE mark in 2001.

4.FLEXICORE

A two-piece, restricted metallic ball and socket joint, the FlexiCore disc has no room for endplate translation. Enrollment in the clinical IDE is finished. preliminary data for three years are being portrayed as positive, however complete study results are still necessary to verify these.

5.KINEFLEX

With its three-piece metal-on-metal construction and two CoCrMo endplates and one semi-constrained, fully articulating CoCrMo core, the Kineflex aims to provide of freedom movement (FOM) with translational stop. Outside of the United States, it has been utilised since 2002. With a comparison to the Charité TDR, an FDA IDE study started in 2005 and ended in 2006, with followup on the more than 500 patients lasting up to three years at this point.

6.MOBIDISC

The Mobidisc is a three-part design made up of two metallic endplates, a modular keel, and a polyethylene core. These geometries allow for regulated motion in all axes for an on-constraint prosthesis. In 2003, the device was made available. At the moment, it is unavailable in the USA.

7.XL TDR

Similar to Extreme Lateral Interbody Fusion (XLIF) cages, other implants, such the XL TDR, have a metallic design and are placed from the patient's side. An FDA trial began in 2009, and its primary completion date is anticipated to be in 2012.

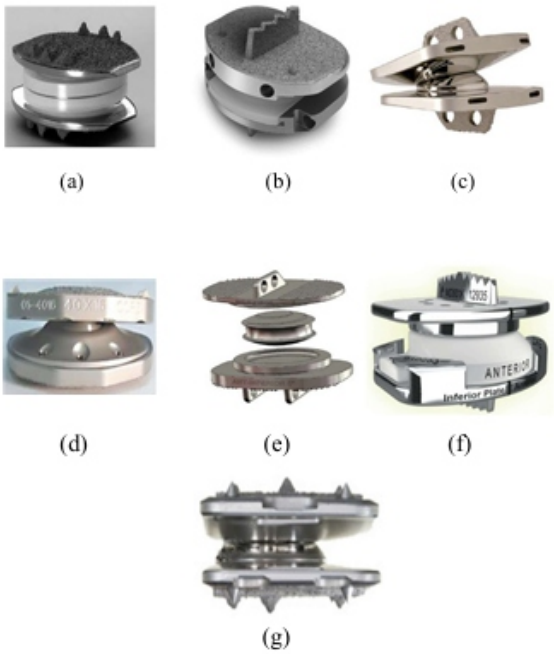

Figure 3: (a) Charité (b) ProDisc (c) Maverick
(d) FlexiCore (e) Kineflex (f) Mobidisc (g) XL TDR

V. METHODOLOGY

A CT scan of a human spine was used to isolate all the intervertebral discs between vertebrae T12 and L5, and measurements were gathered from all the 5 intervertebral discs. From the data gathered a disc was planned to be designed having a measurement which was the average of all the five discs. The finalised measurement was to have a height of 9 mm , anterior to posterior end had a distance of 32 mm and the widest length was 62 mm.

The overall implant design was highly inspired on the geometry of the intervertebral disc itself unlike other prevailing commercial implants which depended more on to the convex and concave surfaces. But we also used the idea of making two bodies attached to different but adjacent vertebrae but still bringing in the natural aspects of a intervertebral disc. So our proposed design has two bodies confining a superior endplate and inferior endplate

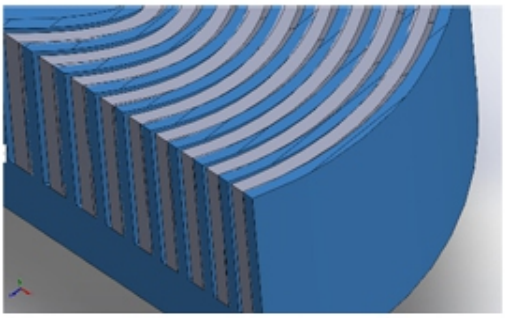

Figure 4 : An intersected view of the inside of implant

An average intervertebral disc was found to have 20-25 lamellae of annulus fibrosus, with this information our design was expected to have a number of 20 lamella at least and the number of lamella was divided into 2 and was shared between each endplate designs such a way that no two adjacent lamella were on the same endplate but the alternative ones were and all were designed such that each o f the lamella were concentric to each other.

There was a 0.5mm spacing between each of the lamella to facilitate the small range of displacement which could be observed under loading conditions which could disturb the true scale of the shape. The utmost specialty of the intervertebral disc was the 120degree orientation the muscle of each lamella from the other which facilitated in the cushioning effect and reduced torque. We also tried to induce the 120-degree changed orientation of lamella.

SolidWorks 2023 was used to produce the overall design of both the superior and inferior endplates and the annulus fibrosus lamellae. To determine the overall cross-sectional area, the outer circumference of the top view of the disc's SolidWorks 2023 design was set under evaluation. To calculate the core's area same feature from the SolidWorks 2023 was employed. After completion of the parts of the Intervertebral disc implant a keel on both the bodies was added at the centre of gravity. It was provided with sharp edges as to ease the procedure during surgery and also to increase the osseointegration. Each keel had two hole placed symmetrical to each other so as to get fixtured to the vertebrae of wish.

3D PRINTING AND MATERIAL CHOICE

The recent development in the additive manufacturing technology has brought us to achieving near to 100 percent of the originally designed model. However, limitations with preoperative modeling exist ranging from lack of surgically useful information such as joint instability and a sense of real-time

information as provided with imaging combined with a significant learning curve for the software and hardware required to create the models. The capacity of surgeons to construct implants uniquely for each patient using 3D printing is arguably the most interesting application of the technology. However, there is more research being done on 3D printing biodegradable scaffolds that replicate the suppleness of the intervertebral disc using a degradable polymer.

The material of choice for our 3d design was cut short and focused to polylactic acid (PLA), polyurethane, poly lactic-co-glycolic acid (PLGA), and polyether ether ketone. Out of which PEEK abbreviated as Polyether ether ketone was decided to be the choice of material has it had the best of the mechanical properties for any biocompatible material of standard values could be

IV. RESULTS

To understand the loading conditions of the design the two bodies are first made into an assembly in Solidworks 2023 and were perfectly made to fix with each other under fully defined condition. Now the behavior of the model under applied stresses is digitally simulated by finite element analysis. To simulate a vertebra providing support along the base of the disc, model was fixed to avoid movement during simulation using Altair inspire 2022. To imitate the load on a spinal disc experienced under normal walking condition, an axial 1000 N load was applied. This load was applied as a vertical downward 1000 N force on the center core component and along the outer ring of the superior endplates. The applied loads had to be made simpler for the programme to run the analysis because of the model's vast number of components.

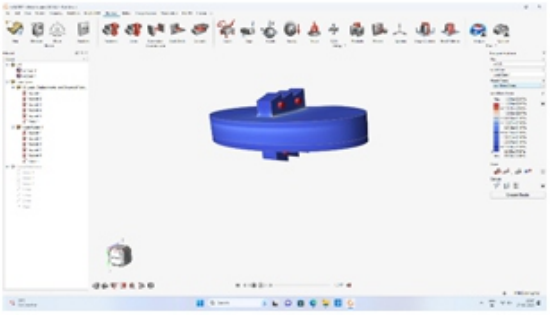

Figure 5: Output of von Mises stress simulation

Under the above stated load condition the von Mises stress was studied

V. CONCLUSION

The simulated study showed that the design was found to be functional at normal static conditions with minimal amount of work, with higher range of safety factor and limited stress load at anyone one defined point. According to finite element analysis, when supported by the keel at the endplates the load has its impact the the joining point of the keel to the surface of the superior endplate, however the load is found to be distributed across the area of the design and bares very minimum stress. The mechanical properties of the PEEK play a major role in this.

The finest qualities of both materials—rigidity to sustain loads and flexibility to resist fracture—are preserved by the alternating structure of the two materials with differing attributes.

Using understanding of biomechanics, the human spine, this research set out to 3D print a pattern found in nature and adapt it to a medical implant prototype. The proof of concept was confirmed, as in many other biomimicry situations, yet the artificial design did not perform as well as the design found in

nature. The greatest difference between the elastic modulus of any intervertebral disc to available biocompatible materials makes it difficult to full fill the utmost mimicking. Advanced future studies in the preparation of newer polymer materials may help in achieving it.

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PROBLEMS AND PROSPECTS OF CASH CROP PRODUCTION AND MARKETING IN BIHAR (A CASE STUDY OF SAMASTIPUR DISTRICT)

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A B S T R A C T

Vegetables are an item of daily consumption, they are essential in human diet but they are very perishable in nature. Therefore, the cultivation of vegetables is generally concentrated around towns and cities. The spread of vegetable cultivation in rural areas has created new problems, particularly of transport, handling, packing and storage which are still in their formative stage. There is also regional specialization in growing some vegetables. It is not enough just to produce a vegetable, it must be produced efficiently and marketed successfully. The system of vegetables marketing in Pusa Block of Samastipur has not proved to be adequate and efficient. Farmers are not getting surplus and they face widespread distress sales, particularly by marginal and small farm households. The vegetable markets is suffering certain structural weaknesses, like existence of unorganized small famers/producers weak storage capacity of the small producers, and the absence of good infrastructure, grading, cold storage and processing units.. More than 90 per cent of the vegetable growers sell their produce in daily mandis, weekly mandis and also take vegetables in bicycles to villages and from door to door, mainly to itinerant traders, at much lower prices than the procurement price of the respective agricultural commodities.

Key words: vegetable, cultivation, rural, areas, problems, and transport.,

INTRODUCTION

Vegetables have significant importance in providing vitamins and minerals in the diet, besides protein and energy. They play significant role in overcoming the common disorders like nutritional anemia, caused by the iron and folic acid deficiencies. Vegetables play a key role in neutralizing the acids produced during digestion of proteins and fatty foods and providing valuable roughages, which promotes digestion and help in preventing constipation. Other than these as we know that vegetables are short duration.All taken together, India's share of the world's vegetable market is 17 per cent. Presently, the horticultural crops cover 13.6 million hectares, i.e. roughly 7 per cent of the gross cropped area and contributes 18-20 per cent of the gross value of India's agricultural output. India is the second largest producer of fruits and Vegetables in the world next only to China and accounts for about 16% of the world's production of vegetables and 10% of world's fruits production. But we are still lagging behind in actual exports of these produce. For example, India produces 65 per cent and 11 per cent of world mango and banana respectively, ranking first in the production of both the crops.Our country is gifted with a wide range of agro-climatic conditions which enables the production of vegetables throughout the year in one part of the country or the other and then maintaining a continuous supply of fresh vegetables. These off season vegetables are in great demand in home market as well as in the neighboring Gulf countries. Bihar is considered destination for second Green Revolution in the country.

Bihar is a major fruit and vegetable growing state. Total vegetable production in Bihar is about 156.29 lakh tons. Potato, Onion, Tomato, Brinjal, Okra and 7 Cauliflower is the major vegetable crop of the state. Bihar is known all over India for its litchi and mango. The four most important fruit crops in Bihar

are mango, guava, litchi and banana. In 2013-14, their production levels were mango (12.74 lakh tones), guava (2.39 lakh tones), litchi (2.34 lakh tons) and banana (14.36 lakh tones). Flower production in Bihar has increased recently, providing immense opportunity of employment and income in rural areas of Bihar. In 2013- 14, about 99 tons of rose, 6799 tons of marigold, 317 tons of jasmine (Bela) and 536 tons of the tuberose were produced in Bihar. Fruits and vegetables play an important role in the economy of Bihar. Despite their utility, the cultivation, consumption and marketing aspects of fruits and vegetables are generally neglected. This is mainly due to severe handicaps associated with the production and marketing of fruits and vegetables. The cultivation of fruits and vegetables in the district is distorted by many factors like low yield and poor quality. The farmers get poor returns and a very little incentive to improve their farm management.

State agriculture faces multifaceted challenges that emanate both from within the system and also from outside. Low productivity across all the enterprises, crop, horticulture, milk, meat, egg and fishes has traditionally described the state agriculture. The low productivity has consequential effects on low income and high poverty of its population.

REVIW OF LITERATURE:

Dastagiri, M.B, Chand, Immanuelraj, R, Hanumanthaiah, T.K, Paramsivam , C.V, Sidhu and R.S (2013) Marketing of vegetable crops is quite complex and risky due to the perishable nature of the produce, seasonal production and bulkiness. The spectrum of prices from producer to consumer, which is an outcome of demand and supply of transactions between various intermediaries at different levels in the marketing system, is also unique for vegetables. Moreover, the marketing arrangements at different stages also play an important role in price levels at various stages viz. from farm gate to the ultimate user. Similar results found in [2].

Dhurvey, C.B, Choudhary ,V.K, Ravi, S.(2018) vegetable cultivation in India is still an unorganized sector with farmers following traditional practices. Besides, the vegetable growers are not as well served by the agriculture extension system as the farmers growing foodgrains; and due to this productivity and production efficiency remains low.

Dhurvey, C.B, Choudhary ,V.K, Ravi, S.(2018) Major vegetables grown in the state are potato, cauliflower, tomato, onion, brinjal, pea, cabbage and okra. Total area of vegetable production in Kumaon region is 17,609.25 Ha and 20842.42 Ha in Garhwal Region.

PROBLEMS FACED BY CASH CROP FARMERS:

Vegetables are an item of daily consumption, they are essential in human diet but they are very perishable in nature. Therefore, the cultivation of vegetables is generally concentrated around towns and cities, so that they can be harvested and transported to the market immediately and in fresh form. With the increase in transport and communication facilities, vegetable cultivation has spread in interior areas where irrigation facilities are available. This is because growing vegetable crops is more profitable than any other seasonal crop particularly the food grain crop. The spread of vegetable cultivation in rural areas has created new problems, particularly of transport, handling, packing and storage which are still in their formative stage. There is also regional specialization in growing some vegetables. It is not enough just to produce a vegetable, it must be produced efficiently and marketed successfully. It is necessary to improve the marketing systems to aid development for two reasons, firstly, additional produce does not fetch additional revenue in the market, it may work as a disincentive to increased production, secondary, if the market does not supply produce to consumer reasonable prices and at the time and place needed, then increased production has no meaning in welfare society. Vegetable marketing is a process which begins with the decision to produce a saleable commodity and involves all

aspects of market structure, functional and institutional, based on technical and economic consideration. It also includes pre and post-harvest operations assembling, grading, storage, transportation and distribution. They are grown in one area but marketed in other areas for creating wider market and also to fulfill the demand of some people, who have liking for them. This also involves long distance transport. For this purpose, good roads in the interior villages are necessary. Fortunately there are good state and national highways, but there are no good roads in rural areas and this stands as a major constraints in vegetable marketing for both farmers (producers) and vendors.

Production Constraints: The extent of production related constraints vary inversely with the farm size. Smaller farms face production related constraints more as compared to the larger ones. The most common production related constraints found to be long gestation period of the crop, followed by low profit margin of the producer, damage to crop due to diseases, wind, etc. As a result, the overall production level is not satisfactory. The production related constraints are discussed below:

Traditional Methods of Cultivation: The advanced agricultural practices like soil testing, seed testing, appropriate time of sowing, timely irrigation, proper time of harvesting, etc. are not adopted by the farmers because they are not aware of them. As a result, there is no significant improvement in the yield of fruit and vegetable crops.

Use of Traditional Varieties of Seeds: Good returns cannot be obtained from the poor quality of raw material. Almost 90 per cent of the farmers use traditional varieties of seeds that are responsible for low yield of fruits and vegetables. They are ignorant regarding the latest varieties of seeds such as hybrid, easy adaptability to climate, early ripening and disease resistant varieties.

Higher Input Costs: The other major constraint faced by the farmers at the production level is the lack of application of recommended fertilizers and plant protection chemicals during the development stage. Besides this, the fungicides/pesticides like Bavistin, Karathene, etc. used by the farmers are also duplicate. Because of substandard fertilizers and pesticides, these crops are prone to many diseases. Moreover, the charges paid to the labour for cleaning, plucking, loading and unloading are also found high. All these factors increase their cost of production. But, as compared to production, the prices received by them from the sale of their produce are quite less.

Lack of Technological Advancement: The production technology of fruits and vegetables is not adequate. The farmers do not adopt the advanced and protected production technologies like net house and poly-house technologies The net-house technology not only increases the productivity of vegetables but also helps in the improvement of their quality. But, the farmers of Bhagalpur district grow the crops on open fields and as a result due to temperature changes, heavy rains, etc. the yield of these crops is low. There are two agricultural universities, five agricultural colleges, one horticulture college, one agriculture engineering college, one dairy technology college and one veterinary college in the state. All the 38 districts have a functional Krishi Vigyan Kendra (KVK). ICAR has also a presence with eastern states regional headquarter at Patna. Besides, National Research Centre for Litchi and Makhana are established in state. However, State productivity remains low because of the slow adoption of modern technologies by the farmers. Dominance of cereals in cropping pattern reflects on the subsistence nature of state agriculture. Institutional extension system faces the challenge to take latest technologies to farmers field.

The Size of Farm Holdings: The size of farm holdings has a direct effect on the output of fruit and vegetable crops. Subdivisions and fragmentation of the farms lead to uneconomic holdings and result in lower output. So far as fruits and vegetables are concerned, it has been identified that 70 per cent of the farmers in Bihar have uneconomic holdings. They cannot efficiently use the farm management practices like planting the trees at an appropriate distance, spray of insecticides, etc. Therefore, the production is very less.

Marketing Constraints : An efficient marketing is an important means of raising the income level of farmers and the level of satisfaction of the consumer. In Bihar, the marketing system of fruits and vegetables is not efficient and lacks proper infrastructure. Fruit and vegetable growers are considered to be bad marketers not only because of their ignorance of modern methods of marketing but also due to the peculiar structure of marketing over which they have no control. The main problems faced by the producers and sellers during the marketing of fruits and vegetables in the study are as follows:

Transport Difficulties: Another major problem is the non-availability of adequate transport facility. Although the roads are pucca in the selected villages but the means of transport that growers and sellers hire are very much costly. The whole transportation is done through cantor, tempo and tractortrolley in Bihar. The rent of these hired means of transport is found to be high. Moreover, during rainy season, it becomes more difficult to transport the produce.

Faulty Method of Sale: The general method of sale is that produce of the farmer is sold by auction in the market. Auction is done under the supervision of market committee by the commission agents who act as wholesalers, No doubt, auction/bid is done under the supervision of market committee, but the market committee does not work honestly. It favours the commission agents/wholesalers who act as big traders. Further, because of the collusion of these commission agents with traders (retailers), the farmers do not get remunerative price of their produce. Generally, each producer sells the produce to the particular commission agent because of previous contacts or loan taken. Also, most of regular retailers have contacts with a particular commission agent. Sometimes the produce is not even accompanied by the producer and sent to the commission agent with whom the producer has a regular contact. The commission agents take advantage of this practice and after keeping their due share, they sell the produce to the retailers at low price.

Inadequate Marketing Intelligence: Price information helps the farmers to take decisions about when and where to sell the produce so that a better price may be obtained. But, they are not aware about the prices prevailing in the nearby markets. Moreover, the awareness about the prices of the distant markets through the government agencies is negligible. Only one or two large farmers observed to have knowledge about the prices in the distant markets and it is through their personal contacts. But, majority of the farmers do not have any source to get information about the market prices of fruits and vegetables in the nearby markets of the district as well as in the distant markets.

Therefore, they are compelled to sell the produce at throw away prices in the local market. Marketing and processing infrastructure are not adequate affecting farmer's income.

Lack of Infrastructure Facilities: Another problem faced by the fruit and vegetable growers in Bihar is related to infrastructural facilities for the quick disposal of the produce. The infrastructural facilities like cold stores, processing industries, cheap transportation charges, etc. are necessary in the case of fruits and vegetables as these are of perishable nature and cannot be store usual conditions. But in Bihar, the market system is deprived of infrastructure for post-harvest handling of fresh produce. Because of this, the small growers cannot afford to send their produce to distant markets for better returns. Road connectivity, storage godown and power availability to agriculture sector is inadequate to usher accelerated agriculture development in the state.

Financial Difficulties: There is no adequate credit facility to the farmers by the agencies in the study area. These people are usually dependent upon commission agents (money lenders) for finance. More than 95 per cent of the farmers take loan from these money lenders to fulfil the requirements related to the production of these crops. But, these people charge a very high rate of interest from producers and compel the farmers to sell their produce through them. Slow pace of implementation of kisan credit card leave large number of farmers dependant on high cost non institutional lending sources seriously impeding use of modern agri inputs and adoption of modern technology.

Lack of Cold Storage Facility: Because of seasonal and perishable nature of fruits and vegetables, these get spoiled easily. So, the farmers cannot retain them for longer periods to reap more benefits. Therefore, the cold storage facility to store the fresh produce at the time of low price offered in the market is necessary.

Lack of Processing Industry: The horticulture development is not possible without the establishment of processing industries. Fruits and vegetables are processed into very useful products such as jams, jellies, sauce, squash, syrup, etc. These industries play an important role in generating the income of the farmers. But in Bihar, there is no such processing industry, which uses fresh fruits and vegetables as raw materials to make the useful by-products.

No Grading and Standardization: The grading should be regularly practiced before the produce is marketed so that the producers can sell the produce at premium price. In Bihar, grading is not done on standardized basis. Moreover, there is a lack of grading facilities in the market. It has also been brought out that the grading is voluntary except for export in the case of few commodities like potato and peas. Traders for some commodities practice informal grading based on size, freshness and appearance of the produce at different levels of marketing. Most of the cultivators fear that if the produce is graded and sold, it may become difficult to dispose of the low graded produce. High Cost of Packaging Material: As regards packaging, the present method of packaging of horticulture produce has resulted in post-harvest losses. For packaging the produce, containers like wooden boxes, plastic crates and gunny bags are used by the farmers. The rent of empty plastic crate was found to be Rs.5 and gunny bags also cost Rs. 2-3 to the producer. Additionally, the farmers do not have much information regarding the comparative costs of present packing material used and improved ones like corrugated fibre board boxes. Moreover, the farmers are not aware of ethylene absorbent papers to prevent losses due to spoilage. Malpractices Adopted by the Middlemen: The malpractices adopted by the middlemen in the marketing of the produce. The malpractices adopted by the middlemen during the auction of the produce and in price fixation are under weightment, low prices through collusion, and refusal to purchase the low graded produce, etc. The cultivators face the risk of being cheated by the middlemen because of illegal deductions such as market fee.

Lack of Approach to Distant Market: The farmers cannot approach distant/desired markets to sell their produce at better prices. The reasons responsible for this are the low volume of the produce, high transportation cost and lack of awareness regarding desired distant markets. The other reasons being that the farmers are dependent upon commission agents for their financial requirements. The commission agents in turn compel them to sell their produce to them as the farmers have taken loan from them. The commission agents thus exploit the farmers by giving them low price for their produce.

Land Issues: More than 91 percent of all holdings fall in the category of marginal holdings with farm size less than 1 hectare. Each such holding is again fragmented in small parcels. Land records are obsolete, making any institutional investment virtually impossible. Small farm agriculture creates serious problems for economy of scale.

Rainfed agriculture: State agriculture still heavily depends on monsoon. In the last 5 years, there has been drought or drought like situation in four consecutive years. Kharif crops are almost a gamble leaving little prospect for investments in costly inputs. Canal Irrigation is scanty. Irrigation is majorly (70 percent) dependent on diesel based tube wells. High cost of diesel based irrigation makes it a very difficult input for even Rabi crops.

Flood & Drought: State agriculture is dependent on Monsoon. A heavy rainfall lead to flood and a deficient rainfall could lead to drought. The paradox of flood and drought occure simultaneously almost every year making agriculture highly vulnerable and unstable.

The agro-climatic environment of Bihar is favorable for about all types of Crops. The land holding

pattern in Bihar is scatter and more than 70% of farmer community belongs to marginal land holding segment. Bihar has established a milestone in the production of staple crops like Rice, Wheat, and Maize along with horticultural crops like Vegetables, Fruits (Like- Banana, Mango, Litchi, and Papaya), flowers and aromatic plants. This study aims to find out the major constraints faced by the farmers and cash crop marketing vendors of samastipur district of certain selected villages.

OBJECTIVE OF THE STUDY :

The main objective of the study :

- To examine the problems faced by the cash crop farmers, vendors and consumers.
- To evaluate the prospects of income and employment in this sector.

METHODOLOGY :

Data collection

The sample consisted of 120 farmers selected from three villages of Kalyanpur block. Namely Akbarpur, Bakhri and Balapur cash crop growing farmers were selected. Data was collected from the respondents with the help of well- structured interview schedule. The collected data were then classified and tabulated and subjected to statistical analysis to arrive at logical conclusions. The primary data for the study was collected.

RESULT AND DISCUSSION :

The study was conducted on 120 farmers, which include small, marginal and medium and were selected from three different villages of Pusa block . The analysis was done on a 3 point scale, the constraints has been marked according to the intensity of the problem faced by respondents of each village. The 3 point ranking was given as, mark -3to 2 for highly intensive issue, mark-2 to 1 for intensive issue and mark – for less intensive issue .

Table: 1.1
Area Wise Response of Constraints faced by Vegetables growers

Constraints	Akbarpur,	Bakhri	Balapur
Perishability of product	1.2	1	2
Seasonality of production	0.9	1.1	1
Bulkiness of products	0.7	0.8	0.5
Lack of cold storage place	2.1	2.3	2.4
Higher cost of stora	2.5	2.9	2.9
Lack of marketing channel	2.8	2.8	2
Lack of regulated market	2.8	2.8	2.2

Price gap between procurement and selling	1.0	2	1.2
lack of schemes for small land holding farmers	2.2	2.6	2.9
Large input cost	2.9	2.4	2.7
Larger cost of labor and un availability of labor	2.5	2.1	
Lack of irrigation facility	2.9	2.5	3
Higher cost of irrigation	3	2.8	3

The problem faced by the vegetable growers of all the three village are almost same, since the farmers are having a maximum of 5-10 katha of vegetable cultivation or some have nearly 1acre land under which the farmers cultivate vegetables and cereals crops along with pulses, Since all the farmers are small and marginal in type, they are not supported by any subsidies or schemes, the input cost and cost for irrigation is too high. Even though the farmers suffer all the pains by taking loans and from money lenders and banks, after harvest they are again disappointed because they don't receive good price for the produce, perishability of the produce, lack of cold storage and regulated market which provides to lack of cold storage facility. The farmers of Balapur responded that price gap between the procurement price and selling price is a main constraint faced by them due to lack of a good marketing channel.

Table 1.2

Area wise constraints faced by vendors

Constraints	Akbarpur	Bakhri	Balapur
Perishability of commodity	3	3	3
Seasonality of produce	2	2.3	2.1
Lack of infrastructure(storage/warehouse)	3	2.9	3
Lack of cold storage	0.8	0.9	0.6
Various players in market/intermediaries	1	1.1	1.4
Market fluctuation	2.3	2.6	2.7
Financial issues	0.4	0.9	0.5

local vegetable vendors in all the three villages had similar constraints, the highly intensive problem faced by the vendors in Akbarpur, Bakhri,, Balapur are perishability of commodity, lack of good storage and warehousing facility so that the produce can be stored and sold in the peak season, now they have to sell the commodities directly after the harvest and the next level of intensive constraints are seasonality of the vegetables, market fluctuations and various players or agents. The least intensive constraint as the vendors responded was that lack of cold storage facility and financial issues.

FININDINGS OF THE STUDY

• The highly intensive problems faced by vegetable growers are lack of irrigation facility, higher cost of irrigation, higher cost of storage, lack of marketing channel, lack of regulated market large input cost to small land holding farmers.
• There are very less supports available to small land holding farmers.
• Even though the Pusa block is surrounded by rivers and water bodies, during summer (starting o of March till July) the farmer suffer big problem of irrigation.
• The vegetables have to be irrigated from seedling to harvesting up to 8-10 times, the cost for irrigation ranges from Rs.100-150 for diesel motor for 1 hour for 1 katha and Rs.80-120 fir electric or solar pumps.
• The major constraints faced by the vegetable sellers are perishability of vegetables, lack of good infrastructural facility of storage of the vegetables, grading and sorting. The market price fluctuations are also big issues to vendors.
• The storage and transportation are the major constraints faced by the vendors. The vegetable due to the perishable nature have to be harvested at the right time and should be marketed, so the vendors need good transportation facility in which the produces will not be destroyed.

CONCLUSION

The other constrains include faced perishability of vegetables, lack of good infrastructural facility of storage of the vegetables, grading and sorting. The market price fluctuations are also big issues to vendors. Thus, the system of vegetables marketing in Pusa Block of Samastipur has not proved to be adequate and efficient. Farmers are not getting surplus and they face widespread distress sales, particularly by marginal and small farm households. The vegetable markets is suffering certain structural weaknesses, like existence of unorganized small famers/producers weak storage capacity of the small producers, and the absence of good infrastructure, grading, cold storage and processing units.. More than 90 per cent of the vegetable growers sell their produce in daily mandis, weekly mandis and also take vegetables in bicycles to villages and from door to door, mainly to itinerant traders, at much lower prices than the procurement price of the respective agricultural commodities.

RECOMMENDATIONS & SUGGESTIONS :

• Training on modern methods of production should be provided to the farmers before vegetable sowing/Propagation of appropriate practices suited to small & marginal farms.
• Timely supply of the quality inputs, irrigation facility especially seeds and fertilizer.
• Promotion of contract farming through vertical integration with large marketing and vegetable processing firms.
• Strengthening of the marketing infrastructure by increasing the number of market places, upgrading the facilities at the designated marketplaces, constructing rural god owns and cold storages.

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