Nanotechnology Perceptions
ISSN 1660-6795
www.nano-ntp.com

Synthesis of new Bio polymer Chitosan Double Schiff Basederivatives with Salicylaldoxime and 3-Chloro Aniline

P. Sivarajani[1], R. Ida Malarselvi[1], R. Pricilla[2], C. Ramachandra Raja[3]

[1] *Research centre, Department of Physics, D. G. Government Arts college for women (Affiliated to Bharathidasan University), India.*
[2] *Department of Physics, A.D.M College for Women (Autonomous), India.*
[3] *Research Centre, Department of Physics, Government Arts College (Autonomous), India.*

The Bio-composite (CS-3CA) material chitosan, salicylaldoxime and, 3-chloro aniline was synthesized at a temperature of 45°C. The functional groups were identified by FT-IR analysis. 3398cm- 1 band with (N-H) Stretching of imine in intermolecular bonding,3009cm- 1 (C-H) in vibrational bonding of Chitosan and, 1248cm- 1 (C-O-C) linkage of chitosan. The structure of this compound was confirmed by 1H NMR and 13C NMR spectroscopy analysis. The solution 1H-NMR (H-2 in 8.583 and H-6 in 4.881) and 13C-NMR (C-3 C=N-OH and C-6 C=N) is a confirmed structure of the Bio-composite. The purity of the bio-composite is 93% conformed to HPLC Analysis. The thermodynamical parameters Entropy = 2.431JK-1mol-1, Thermal stability = 160°C were calculated by TG/DSC. Chitosan derivatives will have a large impact show potential in biomedicine for the development of drugs in future.

Keywords: Bio-composite, FT-IR, 1H NMR and 13C NMR , Thermodynamical parameters.

1. Introduction

Chitosan is a natural Bio-Polymer derived from chitin which it is comes from the outer skeleton of shellfish, including crabs, lobster and shrimp. The Bio polymer of chitosan is used as medicine and in drug manufacturing [1] with the improvement of living standards, people have been paying more attention to the development of health and medical technology.

The recent year many polymer compounds have been widely used in Biology, Medicine, Beauty and other fields [2] Chitosan through the involvement of its amino, acetamido and hydroxy groups can give derivatives of enhanced solubility and remarkable anticancer activity [3]

Chitosan is insoluble in water and most organic solvents. Bio polymer chitosan derivatives can be Obtained by the chemical modification of chitosan-reactive functional groups. Here, the -OH and $-NH_2$ active groups on the chitosan molecule are prone to chemical reactions [4]

Fuctional groups on the chitosan molecules include C_3-OH,C_6-OH,C_2-NH_2 and acetyl amino and glycoside bonds [5].The chemical modeification of chitosan can improve its physical and chemical properties, as well as expand its applications and relevant fields [6]

Salicylaldoxime based compounds were obtained by interchanging the respective position of the OH (salicylaldehyde) and oxime groups. Salicylaldoxime is a Bio isosteric substitution of the phenol ring, a characteristic functional group of the majority of estrogen receptors (ER) ligands, the effects of estrogen receptor subtypes alpha and beta which are ligand-regulated transcription factors [7] Since carbonyl groups, chitosan Schiff base derivatives are regarded as one of the finest options for enhancing chitosan's antibacterial properties.

2. Experimental Section

2.1 Materials and methods:

The compound salicylaldoxime,chitosan and 3-Chloro aniline with an immaculateness of close to 100% were from Sigma-Aldrich. The Analytical Reagent is 99 percent pure when used as a solvent in the synthesis with acetic acid and DMSO. Without additional purification, they were utilized subsequent to being acquired from Sigma-Aldrich.

2.2 Synthesis

The purified chitosan (1.004 g mmol) was dissolved in 25 ml of acetic acid and stirred for two hours at 45°C. After that, salicylaldoxime (1.006 g mmol) dissolved in 20 milliliters of DMSO was added to the viscous solution and agitated for 12 hours. After adding 1.005 g mmol of 3-chloro aniline and stirring continuously for three hours at 45°C, an exact solution was obtained on the chitosan matrix, resulting in the formation of a Schiff base with a slight brownish hue. HPLC analysis, UV-Visible spectroscopy, FT-IR spectroscopy, NMR, analysis are used to control its purity. Thermogravimetric analysis (TG/DSC) was used to determine the effects of chitosan and aniline oxidation on the thermal durability of CS-3CA in order to evaluate the salicylaldoxime.

3. Result and Discussion

3.1 UV-VIS Spectroscopy

The UV-Vis spectroscopy analysis is one of the methods for determining that portion of the materials, optical transmittance, absorption[8], and various parameters the UV-VIS confirmed the degree of acetylation (DA).

Degree of acetylation

$$A = \varepsilon a.ca + \varepsilon g.cg$$

εa and εg are appropriate for GlcNAc and GlcN

$$DA = \frac{C_a}{C_a + C_g} ca$$

The degree of acetylation of the CS-3CA is 36.7%.

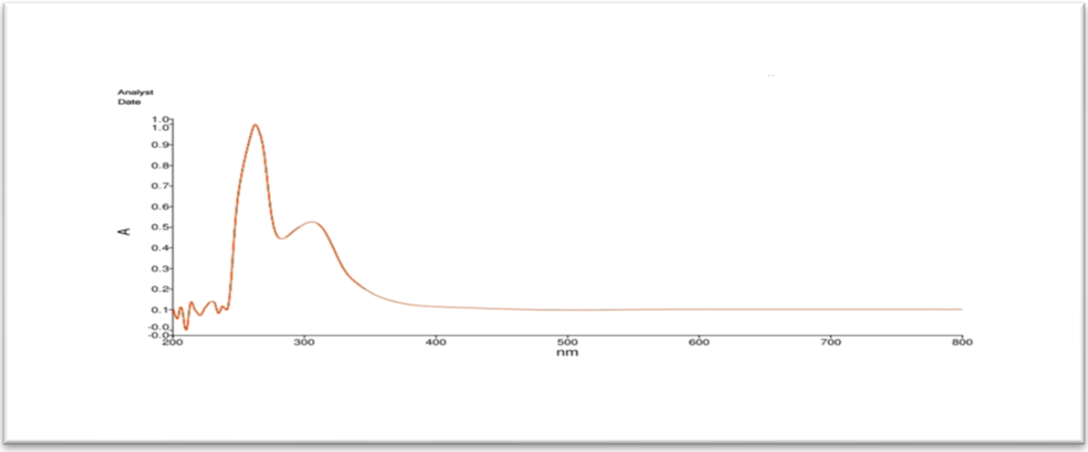


Figure 1. UV-vis spectroscopy of CS-3CA

3.2 High-performance liquid chromatography (HPLC)

HPLC is a method used in analytical chemistry to distinguish, pinpoint, and evaluate each element in a CS-3CA mixture [9]. HPLC analysis confirmed the purity of the compound CS-3CA

$$\% \text{ Purity} = \frac{\text{mass of pure product}}{\text{mass of impure product obtained}} \text{ X } 100\%$$

The percentage purity is 93%

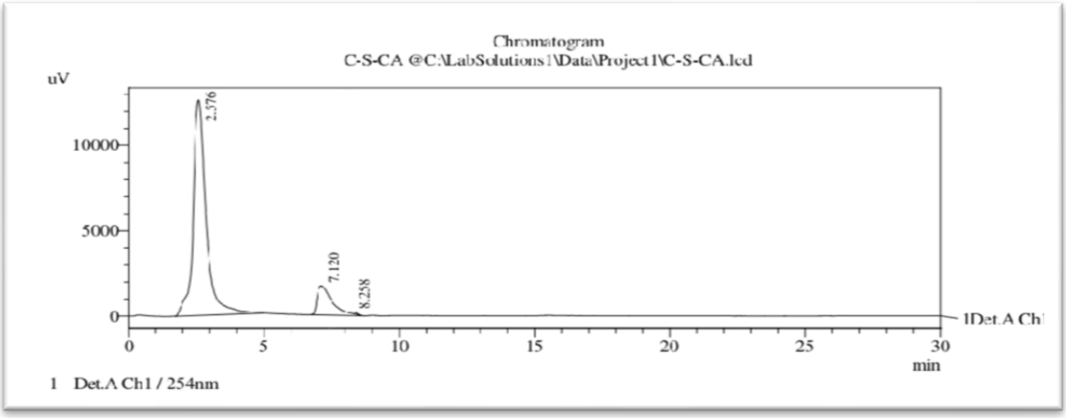


Figure 2: HPLC peaks of CS-3CA

3.3 FT-IR Structure confirmation

The functional group for this new compound has been confirmed by the FT-IR spectrum and it's shown that the occurrence of the vibration that stretches the imine linkage 3457.97 cm^{-1} (C=NH) at a C6 position of chitosan is a sharp band that replaced the broad amide band of chitosan. concomitantly an identifiable band of the amine groups 1489cm^{-1} diminished indicating its spectral-domain related to the high-frequency O-H stretching vibrations 3936 cm^{-1} and 3850 cm^{-1} is due to intra and intermolecular rearrangement of the hydrogen bonding network during the gelation process[10]. The formation of the azo (N=N) bond at a C3 OH-N position of chitosan and salicylaldoxime was confirmed by the sharp band 1729 cm^{-1}. C-N stretching of an Aniline band at 1272 cm^{-1} . The as-symmetric stretching of salicylaldoxime and Aniline[11]. The bond 2126 cm^{-1} is due to the CH=N stretching of chitosan and aniline.

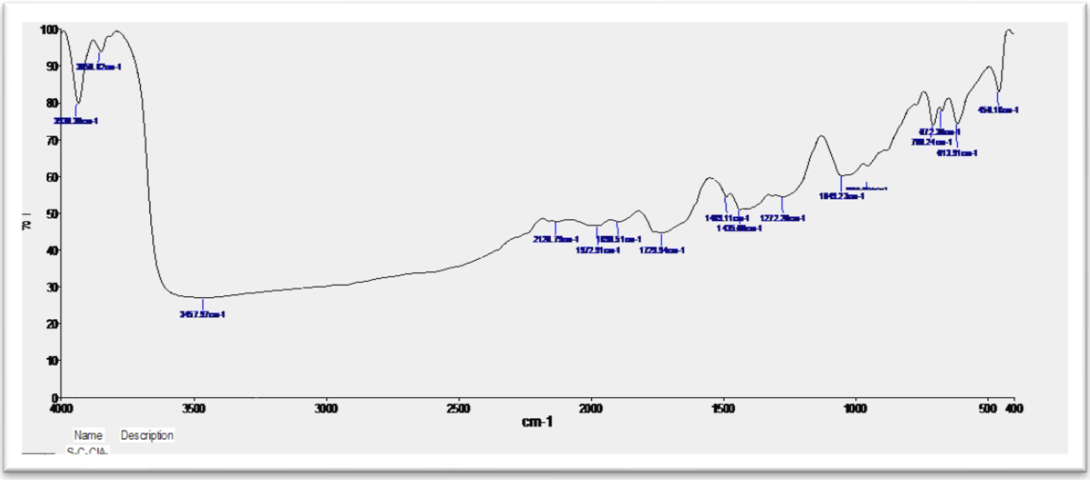


Fig 3: FI-IR in CS-3CA

3.4 NMR Spectroscopy

^{1}H-NMR and ^{13}C- NMR spectral studies

The structure of this compound was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy analysis. The solution ^{1}H-NMR (H-2 in 8.583 and H-6 in 4.881) and ^{13}C-NMR (C-3 C=N-OH and C-6 C=N) is a confirmed structure of the Bio-composite[15-18].

The signal from 153.38ppm to 154.72ppm confirmed the C=N-OH with H+ anions turned assays co-ordination of H+ anions turned assays co-ordination of H+ anion and NH_2 co-ordinates with chitosan in CS-3CA bio-composite. The multiplets from 111.79ppm to 152.17ppm due to the aromatic carbons in the new CS-3CA bio-composite of 3-Chloro aniline and salicylaldoxime. There are doublet, triplet, and quadruplets 21.45ppm to 40.35ppm due to amine NH_2 in the ring structure. The structure was confirmed by NMR spectrum[12].

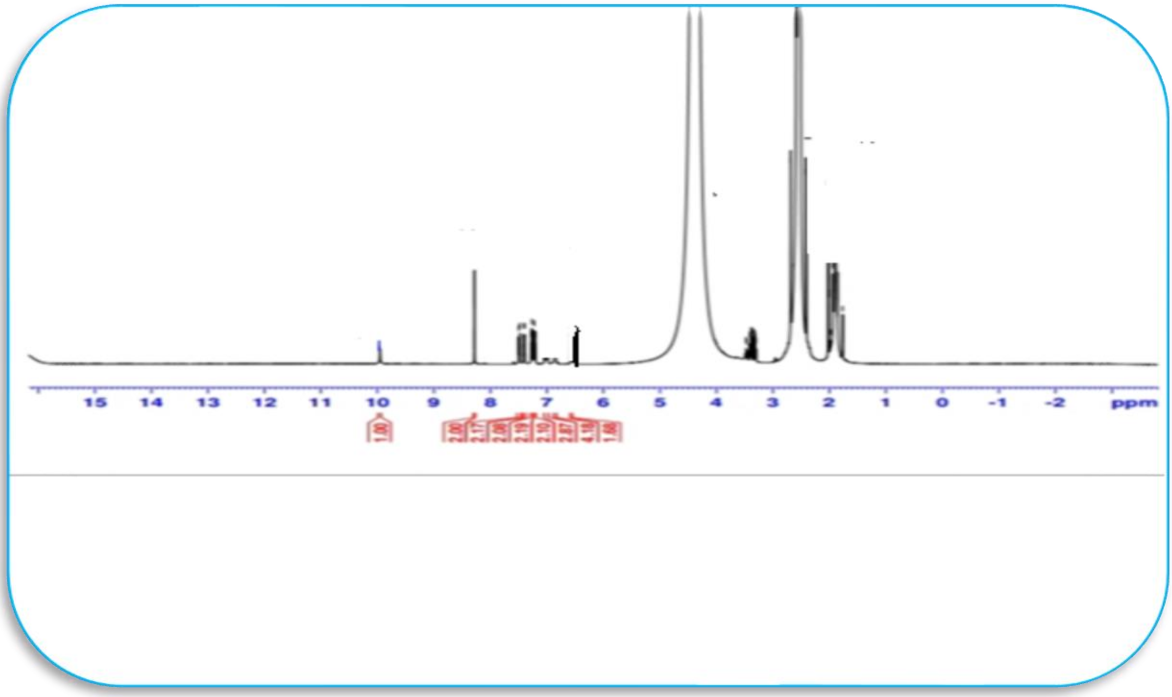


Fig 4: ^{1}H-NMR

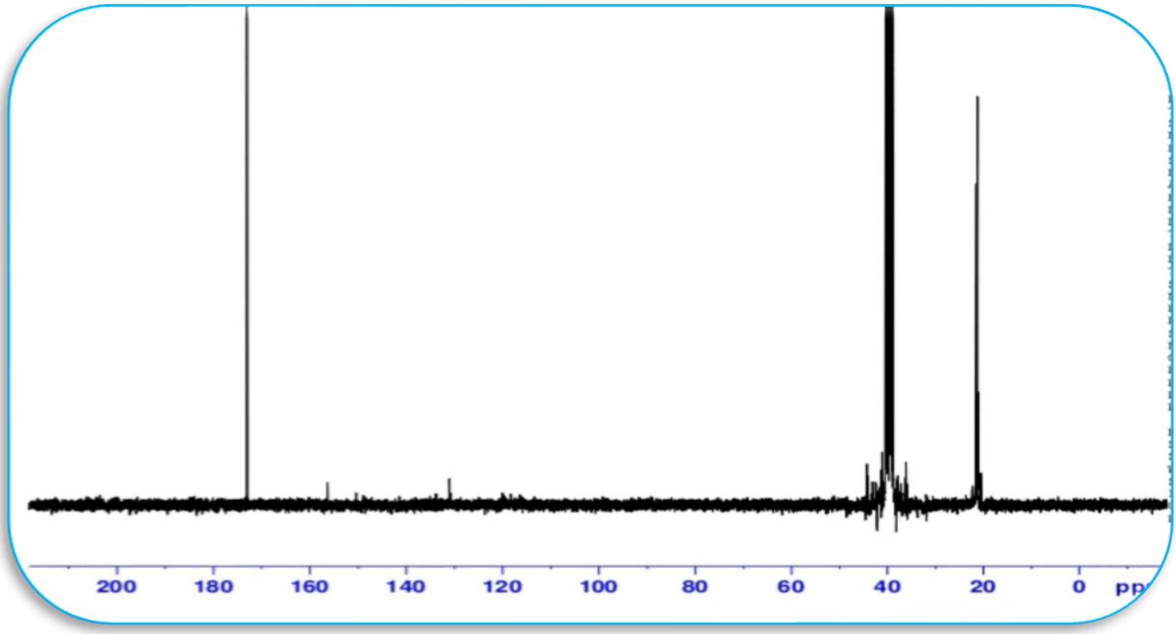
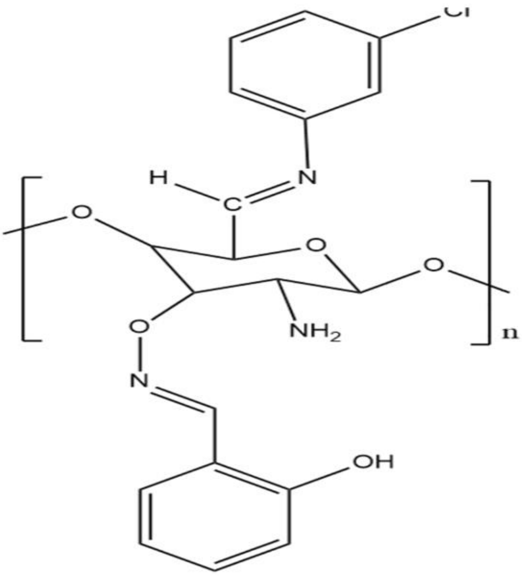


Fig 5: ^{13}C- NMR



(*E*)-2-hydroxybenzaldehyde *O*-((2*R*,3*R*,4*S*,6*R*)-3-amino-6-((*E*)-((3-chlorophenyl)imino)methyl)-2,5-dimethoxytetrahydro-2*H*-pyran-4-yl) oxime

Fig 6: Structure of CS-3CA

3.5 Thermal Analysis

The TG-DTA study provides reliable data about the melting-point, phase transition and mass changes of the sample. The TG/DTA curve of the CS-3CA Figure 7 and 8. Shows a 1st decomposition temperature 131.8°C with minimum (-51.46%) and decomposition temperature 188.6°C with minimum (-45.87%), mass loss indicating the loss of water molecules only [13-15]. To the title, CS-3CA the completed dissociation and its correlation with minimum weight loss well into the TG curve [16-17]. The sample measured for its real density, the resulting data are shown on the TG curve, and the sharp exothermic at 188.6°C represents a phase change is shown in Figure DSC curve exhibits partial two endothermic peaks observed on its heating curve, first endothermic peak is assigned as the heat capacity of enthalpy (137.7°C) and second endothermic peak as enthalpy of melting (191.5°C), which is shown in Table 1 and Figure 6.

Activation energy: The Arrhenius method has been used to measure the activation energy of the phase transition. The value obtained for the phase change in high-temperature is Ea = 179.9 kJ/mol. The value represents the adequate energy that stimulates both nucleation and development. This calculation represents the Activation energy

$$\mathrm{IN}\left[\mathrm{IN}\left(\frac{1}{y}\right)\right] = \left(-\frac{E_a}{R}\right)$$

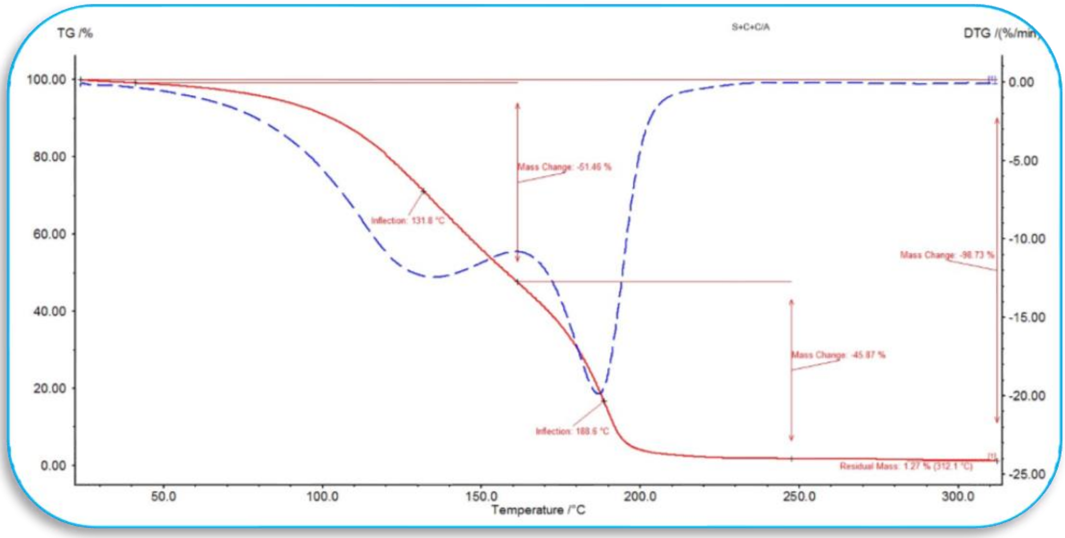


Fig 7: TG

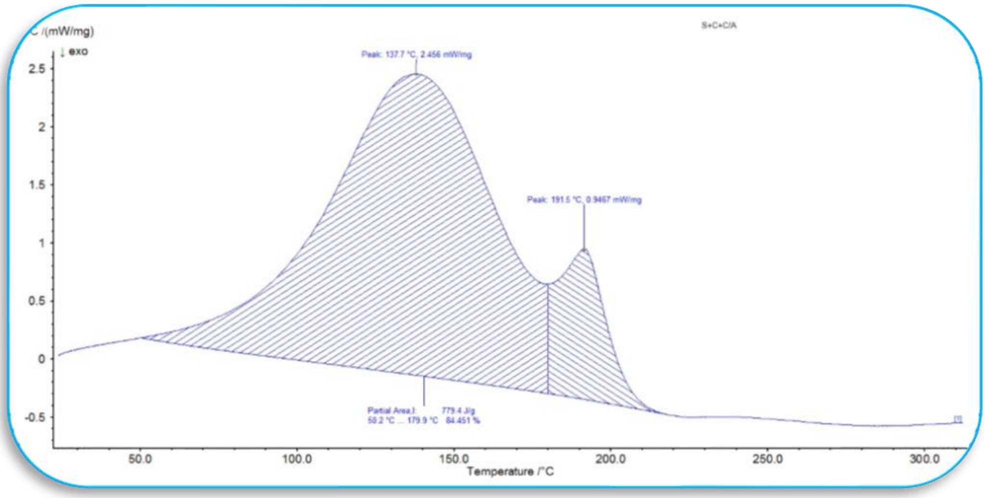


Fig 8: DSC

Table 1: Thermodynamical parameters

Melting Temperature T_m^a(ºC)	131.8ºC
Enthalpy of Fusion ΔH_f (J/g)	779.4
Entropy of Fusion ΔS_f (J $k^{-1}mol^{-1}$)	2.431$JK^{-1}mol^{-1}$,
Gibbs free energy ΔG_f ($Jk^{-1}mol^{-1}$)	0.9
Activation Energy Ea^c ($kJmol^{-1}$)	179.9.4
Phase transition	188.6°C
Thermal stability	160°C

4. Conclusion

In this work, the CS-3CA was confirmed by first time in C-3 and C-6 oxidation of chitosan. The Double Schiff bases HC=N and C=N on chitosan demonstrated. The results show the variation of the chemical structure on Anti-cancer activity in Bio composite CS-3CA. The FT-IR spectrum showed mass losses and the presence of double Schiff based Imine groups in the compound CS-3CA. ^{13}C-NMR (C-3 C=N-OH and C-6 C=N) is a confirmed structure of the Bio-composite. The double bonds of CS-3CA chains can be involved in a polymerization process.TG/DSC used to confirmed the thermal reactions has the potential to provide high level of Thermal stability, Activation energy confirmed.TG used on the effect of the endothermic polymerization reaction of the Bio polymer.

References

[1] Wenqiqn Wang,Qiuyu Meng et all.. International journal of Molecular Sciences MDPI 21,487-2020 DOI:10.3390/ijms21020487

[2] Razmi,F.A:Zhang,Y:Zhou, et all Inte.J.Clean.Prod 231,98-109 2019

[3]Ida Malarselvi Rajkumar,Deepika Asaithambi,Ramachandra Raja et all..Synthetic Communication https://doi.org/10.1080/00397911.2020.1780614-2020

[4] Khemnar Mnisha Dnyandev,Galave Vishal Babasaheb er all.. International Research journal of pure & Applied Chemistry ISSN:2231-3443-2021

[5] Muchtaridi Muchtaridi, Hasna Nur Syahidah, Anas Subarnas er all.. Pharmaceuticals MDPI doi:10.3390/ph10040081 – 2017

[6] Medeiros Borsagali,F.G.L; Carvalho et all..Int.J.Biol.Macromal 114,270-282-2018

[7] Zhang.Z;Jin,F.;Wu,ZJin,J.Wang et all.. Journal of Carbohydr.polymer 177,203-209-2017

[8] Fangyu.F.;Li.H.;Y.;Zheng et all… H. R Soc.Open Sci. 9.1-9-2018

[9]Dornish M., Aarnold M.,et all.. Journal of Pharmaceutical Sciences 4,153-1996

[10]Baran E. T.,Mano J.F et all.. Journal of materials Science- Materials in Medicine 15(7)-759-765,-2004

[11]Jayakumar,R.,Deepthy,M et all.. Carbohydrate Polymer 84,820-824-2011

[12] Belay Zeleke Sibuh,Sonia Khanna et all, Life scince 273(2021)119305-2021

[13] A .A Harold , W .O Gibbs Leonard , Garro Anthony, et all.. Thermochimica Acta Volume 374 Pp 137-143-2001.

[14]A .M .Silvana Critter , Claudio Airoldi , et all..J Braz Chem Soc, Volume 17 Pp 1250-1258-2006.

[15]Li KH, Olson DH, Seidel J, Emge TJ, et all... J. Am. Chem. Soc. 131, 10 368–10 369-2009. (doi:10.1021/ja9039983)

[16] Howarth AJ, Liu Y, Li P, Li Z, et all..Nat. Rev. Mater. 1, 15018-2016. (doi:10.1038/natrevmats.2015.18)

[17]Wee LHet et all.20171D-2D-3D J. Am. Chem. Soc. 139, 819–828-2017. (doi:10.1021/jacs.6b10768)