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Size Optimization And Thermal Studies On Calcium Alginate Nanoparticles

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ABSTRACT: *In the present study alginate nanoparticles were optimized through controlled gelification method and characterised for its formation and thermal behaviour. The prepared alginate nanoparticles were characterized using the analytical tools such as FTIR, TGA, DSC, XRD and DLS analysis. The effective crosslinking in the alginate nanoparticles was confirmed using FTIR studies. XRD results confirm that the less degree of crystalline phase and more in amorphous phase. The thermal stability of the alginate nanoparticles was determined from the TGA and DSC results. The DLS results confirm that the particle size was in nano size range.*

Keywords:*Biopolymers, Sodium alginate, Characterization*

I. INTRODUCTION

Biopolymers can be sustainable and are always renewable, because they are derived from plants and animals materials. The plant materials come from agricultural non-food crops and animal materials from marine wastes. Every biopolymer has its own material-specific properties which would create a sustainable industry. Biopolymers are the polymeric biomolecules composed of many monomeric units that are covalently bonded together [1, 2]. Among many biopolymers, by considering the availability and structural properties, in this present research work the most advantageous alginate polysaccharides was used.

Alginates are natural polysaccharides, which are isolated from brown seaweed (Phaeophyceae). The seaweed is extracted with a dilute alkaline solution which solubilizes the alginic acid preset. The alginic acid can then be converted to a salt of which sodium alginate is the major form currently used [3]. Alginic acid consists of the polymer chain in blocks that are separated by the random or alternating units of D-mannuronic acid and L-guluronic acid residues with different conformations and is highly dependent on pH and temperature modification. A flat ribbon-like chain conformation is followed by the diequatorial linkages which connects the mannuronic acid residues in M-blocks. In contrast, diaxially-linked guluronic acid residues lead to a more rigid structure for the G-blocks. MG-blocks (Figure 1) are characterized by alternating axial–equatorial and equatorial–axial glycosidic bonds connecting the residues [4]. It has been reported that the rigidity of the chain blocks was decreased along the series GG > MM >MG [5]. It is important to note that different alginate sources provide polymers with a range of chemical structures (e.g., bacterial alginate produced from *Azotobacter* has a high concentration of G-blocks and its gels have a relatively high stiffness [6].

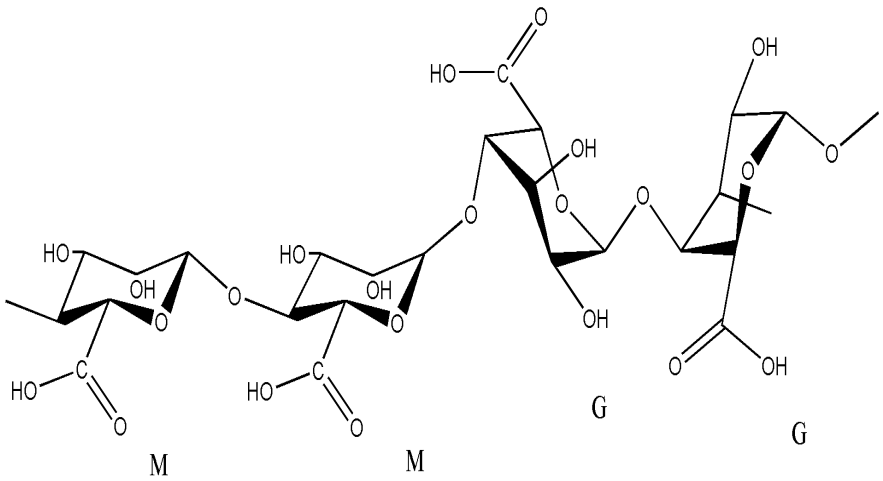

Figure 1: Structure of Alginate (Alginate block types: G=guluronic acid, M=mannuronic acid)

Alginates have been reported to undergo hydrolysis, which leads to the formation of a high-viscosity 'acid gel' due to intermolecular bonding. After gelation the water molecules are physically entrapped inside the alginate matrix , but are still free to migrate. This is of great importance in many applications like pharmaceutical, cosmetic and food industries. Bacterial alginates are useful for the production of micro- or nanostructures suitable for medical applications [2, 7].

The application of sodium alginate in foods industry as a flavour less gum is to increase viscosity. Alginic acid and its carboxylic salts are biopolymers which show interesting features such as biocompatibility, biodegradability, viscosifying and the ability of gelation with multivalent cations [8]. In pharmaceutical field, it is widely used in pharmaceutical preparation, tissue engineering, clinical treatment, cell culture and food processing fields because of its exclusive physicochemical property and favorable biocompatibility [9]. The first alginate applications in the cosmeceutical field date back to 1927 [10].

The property of crosslinking of alginate's salts such as sodium alginate by divalent calcium cations afforded that calcium alginate gels have been known as excellent carriers for a variety of drugs in drug delivery systems [11, 12]. A major application for sodium alginate is in reactive dye printing, as thickener for reactive dyestuffs in textile screen-printing and carpet jet-printing. The biological activities of alginates are closely linked to the molecular weight, sulfate content and anionic groups, which give it antioxidant activity [13]. Alginate bioactivity depends on the presence of molecular weights of sulfated content and anionic group that makes antioxidant activity. For example, it is applicable in skin grafting in plastic surgery. In addition, it has applications in wound healing, because of hydrogel formation and degradability and providing a moist environment for wound [14].

The present work is aimed to treat the heavy metal contaminated wastewater, which is the immediate requirement of the society. Since sodium alginate is soluble in water. This material cannot be used as it is. Thus sodium alginate is converted into the insoluble alginate nanoparticles using calcium chloride as a crosslinker. Calcium alginate, made from sodium alginate in which the sodium salt has been removed and replaced with calcium and has the chemical formula $C_{12}H_{14}CaO_{12}$. The concentrations of alginate and calcium chloride are responsible for the gelation [15] and the concentration of alginate is responsible for its pore size [16]. Calcium alginate is mainly used as a promising material in various applications especially as an efficient biosorbent for wastewater treatment. The mixture of calcium alginate nanoparticles with other biomaterials leads to its improved properties. Alginic acid and its sodium and calcium salts are regarded as generally non-toxic and biocompatible [8, 17]. These products are commercially available and over 200 different alginate grades, in addition to alginic acid and a number of corresponding salts are manufactured [18]. Many researchers reported that alginate derivatives could be effectively used as a biosorbent for the removal of cationic dyes [19].

The objective of the present investigation is to find out the alignate nano particles were synthesized and characterized using FTIR, TGA, DSC, XRD and DLS. The results were discussed.

II. MATERIALS AND METHODS

Materials

Sodium alginate, Polyethylene glycol, **C**alcium chloride dehydrate and Glutaraldehyde was purchased from Nice Chemical Pvt. Ltd, Kochi.

Preparation of calcium alginate nanoparticles (AL-NPs)

Alginate nanoparticles were prepared by the principle involving cation induced controlled gelification of alginate [20] with slight modification. 1.5 ml of calcium chloride (36 mM) was added to 28.5 ml of sodium alginate (0.06%) solution under constant stirring. Then the mixture is kept for stirring for about an hour. The supernant was decanted and kept for drying. The effect of alginate concentration on the particle size of AL-NPs was studied by varying alginate concentration as (0.03%, 0.09%, 0.12%, 0.15% and 0.18% w/v) with similar procedure.

Characterisation

Fourier transform infrared Spectra of AL-NPs measurements were performed with a Perkin Elmer 200 FT-IR spectrophotometer using KBr pellets. The FT-IR was obtained in the wave number range from 4000-350 cm^{-1} with a resolution of $4cm^{-1}$. Thermo gravimetric analysis of AL-NPs was done using Perkin Elmer thermal analysis instrument. The temperature range was aried from 35^oC - 850^oC with the heating rate of 100^oC/min. In this technique the change in mass of the substance was measured as a function of temperature. Differential scanning calorimetric analysis of the AL-NPs were carried out with the DSC Q200 V 24.4 Build 116 Perkin thermal analysis instrument, pierced lid in the nitrogen atmosphere at a heating range of 10^oC/min. X-ray diffraction patterns of AL-NPs were tested by an X-ray scattering Schimauz diffractometer using Ni filter Cu Kά radiation source (λ=0.15nm), set at a scan rate of 10 mins using a voltage of 40kv and a current of

30milliamperes. Dynamic light scattering analysis for AL-NPs the average particle size with was done measure Malvern Instruments Ltd.

Results and Discussion

Optimization of alginate nanoparticles

The optimization process was performed to get the expected size of alginate nanoparticles. The related dependent variable such as concentration was predicted. Though the particle size is influenced by many factors, the very important factor is concentration. The effect of concentration was studied by varying the concentration of sodium alginate keeping calcium chloride concentration as constant.

Table 1: Particle size of prepared alginate nanoparticles

Concentration of SA (%)	Alginate (ml)	$CaCl_2$ (36mM) (ml)	Particle size (d.nm)
0.03	28.5	1.5	342.0
0.06	28.5	1.5	124.7
0.09	28.5	1.5	295.3
0.12	28.5	1.5	255.0
0.15	28.5	1.5	295.3

The ability of alginate nanoparticles to gel rapidly upon contact with calcium chloride ($CaCl_2$) relied on the formation of inter molecular interaction. Through the continuous addition of calcium chloride to the alginate solution, it becomes more and more turbid due to the formation of aliginate nanoparticles. Since the creation of nanopaticles depends mainly on the evolved ionic interaction of alginate with cations, that eventually leads to the reduction of aqueous solubility of AL-NPs.

This improvement in mean particle size was related to the increase of alginate concentration and subsequent reduction in sodium alginate chains and number of the carboxylate, ether and hydroxyl groups that are jointed to the calcium cation. It has been reported that the main factor for creating nanoparticles is the tendency of functional groups of alginate chains especially carboxlate group to create complex structures with calcium ions. The increase of alginate concentration affording more functional groups can gather around calcium crosslinking agent and therefore further layers of alginate chains can join the calcium cations. In conclusion, the size of nanoparticles increases with increasing of alginate concentration. To compare different concentration calcium chloride (36 mm) into a SA solution (0.06% w/v) at high rates of mechanical nanoparticles.

FTIR studies

FTIR spectra of alginate nanoparticles (Figure 2) shows, the broad band (observed) at 3415 cm^{-1} corresponds to OH stretching, intermolecular hydrogen bond and polymeric association. The bands at 2924, 2854 and 1448 cm^{-1} are due to asymmetric CH stretching, symmetric CH stretching and CH bending vibrations respectively. The peaks at 1382 cm^{-1}, 1118 cm^{-1} and 1039 cm^{-1} correspond to secondary alcoholic group, C-O-C stretching vibration of pyranosyl ring and C-O stretching vibration. The peaks at 597 cm^{-1} and 489 cm^{-1} are due to C-H out of plane bending and C-C skeletal vibrations. Absorption region of stretching vibration of O-H bonds in calcium alginate appeared narrower than sodium alginate. This difference arises from the participation of hydroxylate group of alginate to the calcium ion in order to form chelating structure and consequent [21].

Asymmetric stretching vibration of carboxylate ion shifted to lower wave numbers because when calcium metal ions replaced sodium ions in the sodium alginate. The charge density, radius and atomic weight of the cation were changed and hence, this shifting should be expected. It is obvious that the bands concerning carboxylate groups can be used as useful bands to follow the changes in the structure of different polymers of the alginate [21].

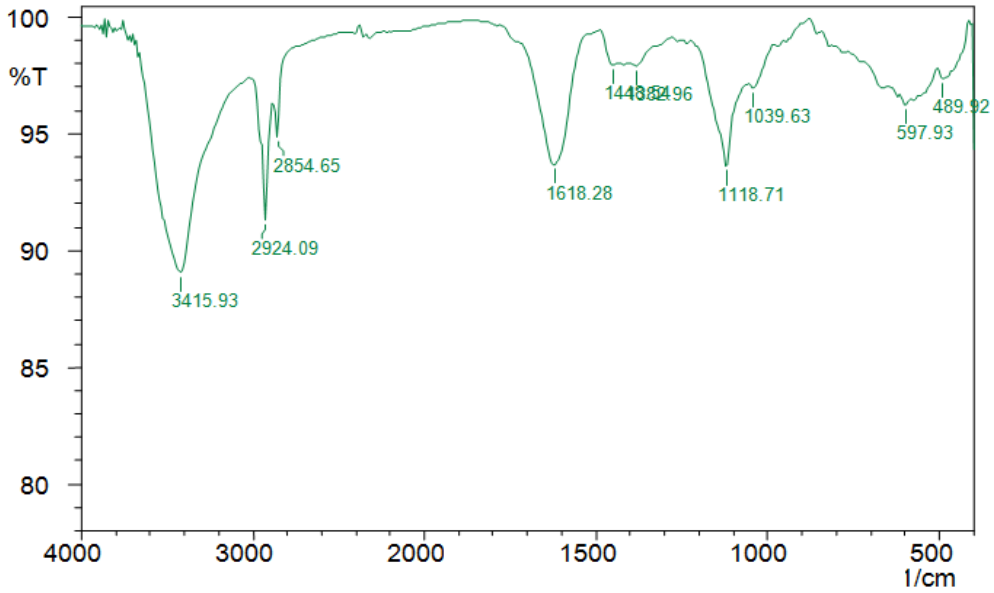

Figure 2: FTIR spectrum of Alginate nanoparticles

TGA studies

Thermogravimetric analysis is an experimental technique which can give some information about the thermal behavior of the AL-NPs (Figure 3). The first weight loss up to 450-550°C. It should be due to loss of residual water molecule/moisture present from the polymer matrix. The second stage observed within the temperature range of 600-700°C should be related to removal of dopant molecules from the polymer structure. The weight-loss observed after the removal of the dopant molecules should correspond to the complete degradation and decomposition of the polymer main chain [22, 23].

The thermogram of AL-NPs,55% of the sample had disintegrated in the temperature range of 700°C.Around 54.9% of the sample had disintegrated at the of experiment leaving behind 45.1%t of the sample as a residue Maximum weight occurs at 200 ºC to 400°C. Hence AL-NPs was found to be thermally more stable.

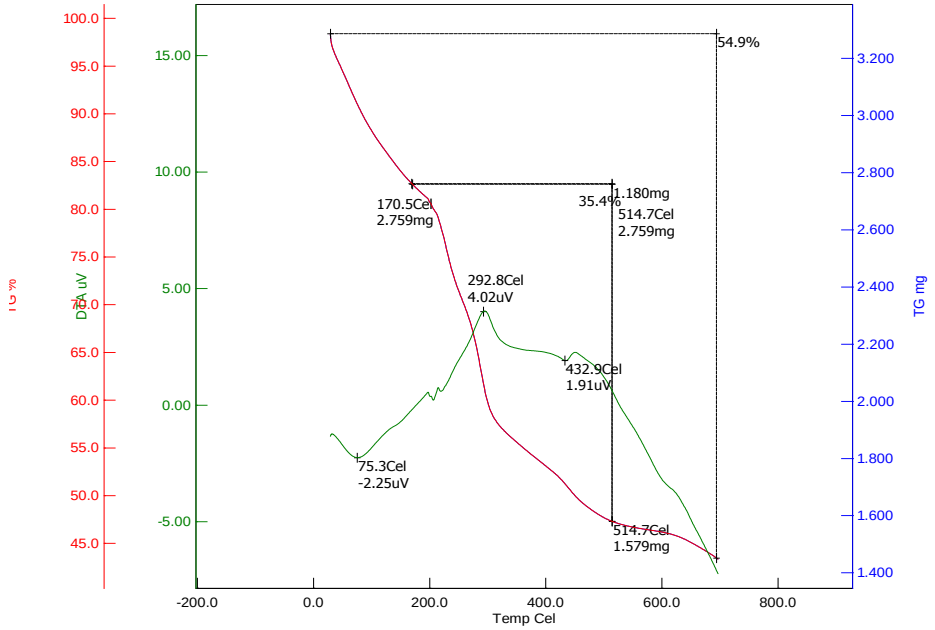

Figure 3: TGA thermogram of Alginate nanoparticles

Differential scanning calorimetry

DSC is an analytical tool, which helps to understand the thermal behaviors of polymers and polymer blends. The DSC curves shows the glass transition temperature of the AL-NPs is observed at 240ºC (Figure 4). A broad endothermic peak were observed at 96.8 and 222.0ºC indicating the crystallization of AL-NPs and sharp exothermic were observed at 291.1 and 442.1ºC shows the melting temperature of the prepared nanoparticles.

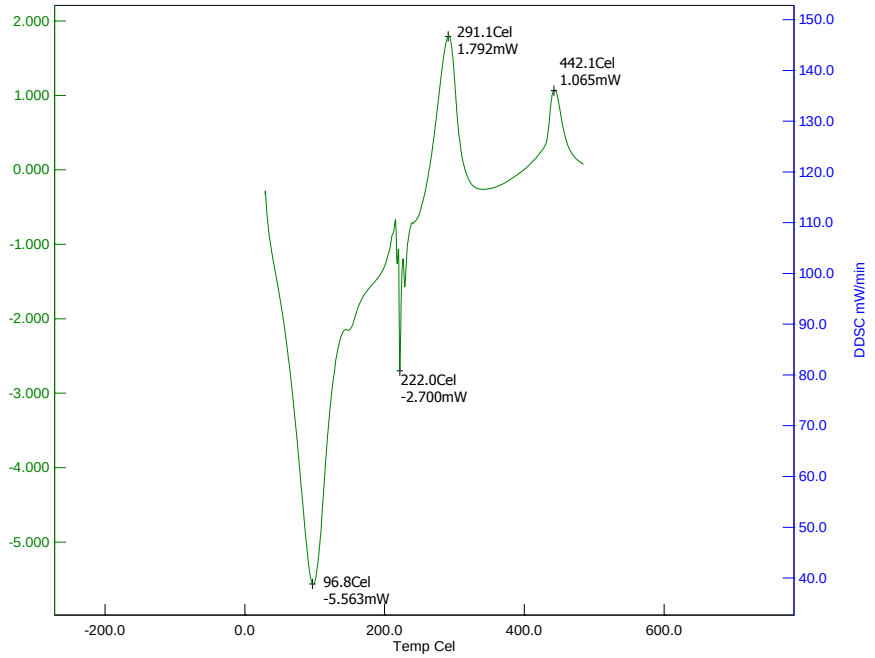

Figure 4: DSC thermogram of Alginate nanoparticles

X-ray diffraction analysis

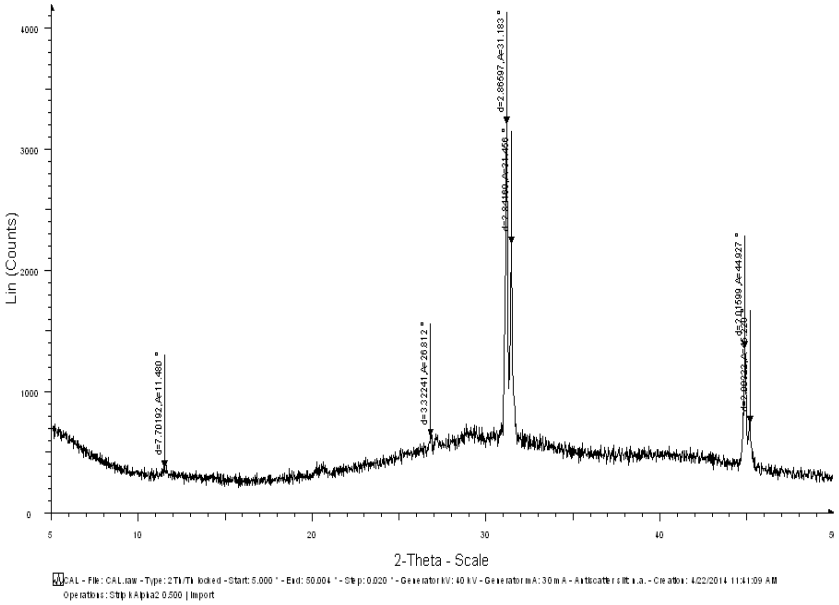

Figure 5: XRD pattern of Alginate nanoparticles

X- ray diffraction patterns of various samples were measured to Percentage of crystallinity. Xc% was measured as a ratio of crystalline area to total area of the peaks using the following formula [24]. Xc % =(*Ac/*

Aa+ Ac)*x* 100% Where, Ac = Area of crystalline phase, Aa = Area of amorphous phase, Xc = Percentage of crystallinity. The XRD pattern of AL-NPs (Figure 5)**,** The observed peak at 2θ=11.430, 28.81° shows the semi crystalline nature and broad amorphous nature. The calculated average crystallite size of the AL-NPs is 5.4054 nm. Hence less value crystallite phase and more amorphous phase.

III. CONCLUSION

The formation of alginate nanoparticles was confirmed by FTIR spectroscopy. The x-ray diffraction studies shows the semi crystalline nature of alginate nanoparticles. The prepared alginate nanoparticles were thermally more stable which was confirmed by TGA and DSC studies. In addition to this, the size of the nanoparticles increases with increasing the alginate concentration. Alginate nanoparticles can used as a promising material in various applications, it can also acts as an efficient biosorbent for wastewater treatment and when it is mixed with other biomaterial its efficiency increases with its improved properties.

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