Kinetic modelling of Okra and Gracilaria corticata hydrocolloid mucilage polysaccharides

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Abstract
The biopolymer has become essential component in the recent years to overcome the environmental issues raised from the synthetic polymer. In this aspect we attempt to make such valuable and economical important biopolymer from the natural sources such as Abelmoscus esculentus and Gracilaria corticata in an eco-friendly approach with thermally stable biopolymer. Thermal analysis of Okra and Gracilaria corticata mucilage polysaccharide has been carried out to ascertain their thermal degradation behavior and thermal stability. Thermal analysis of Okra and Gracilaria corticata mucilage polysaccharide weighed in the range of 5-10 mg was carried out with TGA (thermal gravimetric analyzer) and DSC (differential scanning calorimeter). Activation energy of the biopolymers for degradation studies was predicted and compared with Flynn-Wall-Ozawa (FWO) model. The activation energy obtained showed high R² value of 0.9999, 0.9951, 0.9997 for Okra and 0.9992, 0.9998, 0.9999 for Gracilaria corticata, respectively. The obtained results of this study established the thermal characteristics of Okra and Gracilaria corticata mucilage polysaccharide and suggest their potential application in the food, cosmetic and pharmaceutical sectors.

Keywords
Activation energy
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Thermogravimetry

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Introduction
A large number of plant polysaccharides with excellent water holding capacity are being used as natural hydrogels in functional foods, food additives and herbal products (Akbar et al., 2012). Some of them have been used as biomaterials for tissue engineering, pharmaceutical preparations as thickeners, stabilizer, emulsifier and drug carriers. Natural and biodegradable polymers have limited applications due to their inadequate thermal and mechanical properties. For instance, though polysaccharide is extensively used as gelling agents in the food industry, thermal treatment usually results in poor gelation due to weak structural interactions (Barbosa et al., 2020). The structure development rate (SDR) of the polymers during gelation could be measured under isothermal and non-isothermal conditions by measuring rheological properties. The SDR of protein system has been investigated using the non-isothermal kinetic models (Ben Slime et al., 2022). Temperature is one of the important thermodynamic parameters involved in most gelation processes at a given biopolymer concentration. Therefore, the gelation mechanism and structure development can be analyzed by interpreting the changes in thermal property of the biopolymers. Depending on the molecular configuration of the polymer network, temperature can have different effects on viscoelastic behavior of the gel (Cruz et al., 2018).

Okra polysaccharides contain a repeating unit of α-(1,2)-linked rhamnosyl and α-(1,4)-linked galacturonosyl residues and dimeric β-(1,4)-linked galactan side chains which are substituted to O-4 of half of the rhamnosyl residues (Distantina & Fahrurrozi, 2011). Okra pectin was found to form a gel at a relatively low concentration; however, a stable gel was formed after heating okra polysaccharides at 60 °C for 30 mins followed by a coolingat 4 °C for 24 h. Similarly, the main sugars present in Gracilaria corticata were galactose (65.4 mol %), 3,6-anhydrogalactose (25.1 mol %) and 6-O-methylgalactose (9.2 mol %), (Drechsler & Bornhorst, 2018). Gels formed...
with such polymers in given thermodynamic conditions, based on aggregation of double helices and the conformational transition occurs at a melting temperature (Tf) higher than the re conformational temperature corresponding to the gel formation; Agar has the ability to form gels upon cooling of a hot solution to 30-40 °C and to melt to sols upon heating to 90-95 °C. At temperatures above the melting point of the gel, thermal agitation overcomes the tendency to form helices and the polymer exists in solution as a random coil (Garre et al., 2020). On cooling, a three-dimensional network builds up in which double helices form the junction points of the polymer chains (Halabi et al., 2020). Increasing the heating rate results in a shift of the integral conversion curve towards higher temperatures, and hence, resulting in a shift of the differential curve. The size and shape of the particles influence the heat transfer into the particle and mass transfer from the particle. Therefore, it is very important to ensure the best possible contact between the particle and the heating area. Phenolic resins are known for their wide applications in various areas because of their thermal stability, easy availability, effectiveness and some of their excellent properties as reported by various studies. Recently the methods of thermogravimetry analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetric (DSC) provided reliable information on the physico-chemical parameters, characterizing the processes of transformation of solids or participation of solids in processes of isothermal or non-isothermal heating. Knowledge on degradation kinetics of enzyme inactivation and quality changes including the reaction order, the reaction constant and the energy of activation is essential to predict quality losses during thermal processes. In addition, FTIR investigations are necessary to confirm their chemical properties similar to those of other common ligno cellulosic fibers. The thermal analysis curves revealed that the okra fibers were stable until around 220 °C. This is in agreement with the values of many vegetables fibers reported in literature. The goal of this approach is to make a deeper insight into the reaction course of okra and Gracilaria corticata polysaccharide material; and an early detection of the stability/reactivity (Hansen et al., 2020). The aim of this work is to assess the thermal stability and to determine the thermal degradation pattern of Okra and Gracilaria polysaccharides by Flynn-Wall-Ozawa model in order.

Materials and methods
Sample collection and preparation
Seaweeds species (Gracilaria corticata) was collected from mandapam coast in Gulf of Mannar, Tamilnadu, Southeast coast of India at a latitude 9°45’N and longitude 79°0’ E on low tide, during December 2012. Collected samples were washed with tap water to remove epiphytes and other marine organisms. The samples were transported to the laboratory in sterile polythene bags. In the laboratory, samples were rinsed with tap water, shade dried and powdered in a mixer grinder. Similarly, Okra bio waste (upper crown head) collected from A. C. Tech canteen, Anna University, Chennai, was rinsed with tap water and was shade dried. The dried okra wastes were broken in to powder form in an electrical mixer. It was then sieved into particle sizes of 0.5-4 mm and stored in glass bottles for further use. All reagents used in the experiment were purchased from Sigma Aldrich with 99.9% purity (Hickman et al., 2019).

Extraction
The mucilage polysaccharide was extracted by the method followed in Distantina and Fahirarrozi (2011). 5 g of clean, dried seaweed and okra powder sample were soaked in distilled water for 15 min. After soaking, the water was separated from the seaweed by filtration. Firstly, a known amount of solvent (methanol, acetone; (1/50 g/mL)) was heated in a beaker as an extractor which emerged in a water bath equipped with a stirrer. If the temperature of solvent reached 85 °C, (Mohammed et al., 2020) then the samples were added into solvent, and the time of extraction started was counted. The speed of stirrer was set constant at 275 rpm. The constant ratio of seaweed weight to solvent volume (1/50 g/mL) was maintained by adding hot water. The extraction was stopped after 45 min (Jha et al., 2019). The filtrate was separated from residue using filter cloth and immediately poured into three volumes of cold (5 °C) acetone (90% w) which caused precipitation of polysaccharides. Precipitation was done for 30 min with stirring gently by hand. The precipitated polysaccharides were collected and oven dried at 50-60 °C to a constant weight. The experiments were carried out with different solvent such as acetone and thermal stability of the extracted polysaccharides was determined (Ji et al., 2019).

Thermal analysis
The powdered polymers were subjected to a simultaneous TGA and DSC analysis by thermal analyzer SDT, Q-600 (TA instruments, USA), (Kasperowicz et al., 2020). In nitrogen atmosphere (250 mL/min) in a programmed temperature range from 30 to 600 °C at a heating rate of 10 °C/min. Sample weights between 5 and 10 mg were placed in a platinum pan. The baseline correction was applied to DSC scans. The data were analyzed by the isoconversional Flynn-Wall-Ozawa (FWO) model (Li & Lin, 2021).

Results and discussion
DSC-TGA analysis
The isolated polysaccharides were white or light brown in colour and showed good swelling in water (Li et al., 2019). Typical DSC-TGA curves of okra and gracilaria polysaccharide were shown in Fig. (1) and (2). The melting occurred over a wide range of temperatures which might be due to amorphous nature or vaporization of the water which indicates the presence of hydrophilic groups in the crude samples (Liu et al., 2019). An exothermic transition has occurred in okra polysaccharide, beginning at ~200 °C and completed at ~400 °C as shown in the Fig. (1), through a peak of 225.48 °C (Madoumier et al., 2019; Merci et al., 2019). The Okra polysaccharide showed weight loss of
51.15% at 362 °C and completed decomposed at ~700 °C. In the case of *Gracilaria corticate* polysaccharide, the decomposition took place at three different phases. And corresponding weight loss was shown in the Fig. (2).

![Fig. 1. The combination curves of TGA-DSC curves of *Abelmoschus esculentus* polysaccharide powder.](image1)

**Fig. 1.** The combination curves of TGA-DSC curves of *Abelmoschus esculentus* polysaccharide powder.

**Fig. 2.** The combination curves of TGA-DSC curves of seaweed (*Gracilaria corticate*) polysaccharide powder.

### Thermal degradation kinetics

The data were analyzed by the isoconversional Flynn-Wall-Ozawa (FWO) method (Eq. 1).

\[ \ln \beta = \frac{\ln \alpha}{R T} - 5.331 - 1.052 \frac{E_a}{R T} \]  

(1)

Where \( g(\alpha) = \int_0^\alpha \frac{dx}{f(x)} \), \( g(\alpha) = \int_0^\alpha \frac{dx}{f(0)} \), \( g(\alpha) \) is the integral reaction model; \( f(\alpha) \)- reaction model; \( \beta \)-Heating rate; \( E_a \)-activation energy; \( A \)-pre-exponential factor; \( R \)-General gas constant and \( T \)-temperature (Nawaz et al., 2019).

The FWO method was the first isoconversional linear integral method developed by Flynn and Wall (1966) and Ozawa (1965), (Plazanet et al., 2018). This method is based on the assumption that for a fixed extent of conversion, the reaction rate depends upon temperature only as shown in Fig. (3). Thus, it eliminates the dependence of reaction kinetics on any model, which may be represented by an integral form \( g(\alpha) \). Therefore, this may be termed as a model-free approach and used at different heating rates, thus at fixedRate the plot of \( a, \log \frac{vs. 1/\text{T}}{\text{can}} \) be a straight line, the slope of which permits the calculation of \( E_a \). The \( \alpha \) is defined as \((w_i - w_f)/(w_o - w_f)\), where \( w_i \) is the weight of the sample at any temperature \( T \), \( w_o \) the initial weight and \( w_f \) is the final weight at the temperature at which the mass loss is approximately negligible. Thermal stabilities of the polysaccharides were determined by integral procedural decomposition temperature (IPDT) and comprehensive index of intrinsic thermal stability (ITS), (Schuldt et al., 2018). This method is considered to be most appropriate and reliable to determine these parameters because it takes into account the whole TGA curve by measuring area under it. The ITS and IPDT values were determined from TGA of all four heating rates and mean values are reported for each polysaccharide. The life-times of polysaccharides were also predicted by model-free approach based on Eq. (2). The model-free approach eliminates the limitations of other methods such as ASTM E1641 and E698 methods which assume that the \( E_a \) remains constant throughout the degradation step. Therefore, in cases where \( E_a \) is not constant in a step the model-free approach is more appropriate.

\[ t_\alpha = \frac{\int_{0}^{\alpha} \exp(-E/Rt)dt}{\beta \exp(-E/Rt_0)} \]  

(2)

Where, \( t_\alpha \) = time at any given degree of conversion; \( \beta \) = the heating rate; \( E \) = pre-exponential factor; \( R \) = gas constant; \( T \) = Temperature; \( T_\alpha \) = Temperature at any given degree of conversion and \( T_0 \) = Initial temperature.

This relationship exploits the variation of activation energy with a. The integral in the numerator has no analytical solution; however, it can be evaluated by different approximations. In this study we used the Senum-Yang fourth degree approximation. The integral in the numerator of this equation was solved by Senum-Yang fourth degree approximation (Shah et al., 2018).

![Fig. 3. Representative α-T curves for Okra and Gracilaria corticate at a fixed extent of conversion factor (α).](image3)

**Fig. 3.** Representative \( \alpha-T \) curves for Okra and *Gracilaria corticate* at a fixed extent of conversion factor (\( \alpha \)).

### Flynn-Wall-Ozawa analysis

The typical Flynn-Wall-Ozawa plots of *Okra* and *Gracilaria* polysaccharide showed similar trend for activation energy. The average \( E_a \)-value determined by Flynn–Wall–Ozawa method was found to be in the range of 41-998 kJ.mol\(^{-1}\) given
in as shown in Fig. (4) respectively. The $E_a$-$\alpha$ curves showed the dependence of $E_a$ on the degree of conversion $\alpha$ shown in Fig. (5). Both the materials Okra and Gracilaria corticata polysaccharide appeared to be as stable as some of the important commercial materials used as pharmaceutical ingredients (Simpson et al., 2020). Model-fitting analysis revealed that the major degradation step followed first order kinetics. The correlation coefficients are also close to unity. For okra the $E_a$ value was varied between 41.8-621.89 kJ.mol$^{-1}$, R value was 0.999, and for Gracilaria corticata the values were between 343-1025 kJ.mol$^{-1}$ and 0.999 for $E_a$ and R as shown in Fig. (5).

![FWO plot for Okra and Gracilaria corticata](image)

**Fig. 4.** FWO plot for Okra and Gracilaria corticata to calculate $E_a$.

![Dependence of activation energy ($E_a$) on $\alpha$.](image)

**Fig. 5.** Dependence of activation energy ($E_a$) on $\alpha$.

The $E_a$ for Okra and Gracilaria corticata varies with conversion $\alpha$, which suggested a multistep degradation of these materials. The multistep decomposition may be due to the diversity of sugar content of the polysaccharide materials. Based on the correlation coefficient and the closeness of the activation Energy, the FWO model was found to be best for these polysaccharides. All the polysaccharides so far investigated exhibited very high stability as predicted by the model-free analysis (Simpson et al., 2019). The $E_a$ values for both Okra and Gracilaria corticata polysaccharides increased with increasing heating temperature, which indicated the enhanced thermal stability of polymer materials. The mathematical model used in this study was able to describe the changes of mass loss with temperature; however, there are still some visible differences in the differential curve. The experimental data of sample residue from thermogravimetric analysis were compared with simulated data obtained by the optimization of kinetic parameters of Okra and Gracilaria polysaccharide. Experimental results showed that values of kinetic parameters from both method are in good agreement and can be used to understand the degradation mechanism of solid-state reaction and useful in the individual analysis of polymers in the blends (Vandenberghe et al., 2017). The increased thermal stability of these polysaccharides may help in the development of natural fiber composites, where the thermal stability of natural fiber material is of major concern (Vicent et al., 2019). Thus the establishment of kinetic parameters for these natural polymers over a wide range of temperature may be helpful in the modeling of polymer degradation during various industrial processes the established thermal decomposition kinetic parameters can help aid the development of polymer composites from heat treated Okra and Gracilaria corticata polysaccharides (Ren et al., 2021).

**Conclusion**

Temperature is the important thermodynamic parameter involved in most gelation processes at a given biopolymer concentration. Therefore, the gelation mechanism and structure development can be analyzed by interpreting thermal effects on rheological property changes. The weight loss of okra below 200 °C was minimal which may be due to increased inorganic materials or impurities in the crude sample. The okra polysaccharide showed good thermal stability. Gracilaria corticata polysaccharide had increased inorganic substances when compared with Okra. This may be due to methylation which releases inorganic materials like oxides and carbonaceous residues. Onset degradation of okra polysaccharide between the temperatures (220-310 °C) was associated to the thermal depolymerisation of hemicelluloses, pectin and the cleavage of glycoside linkages of cellulose above which the stability of Okra polysaccharide decreased gradually. An exothermic transition has occurred with Gracilaria corticata, running through a peak of 243.30 °C with a small enthalpy change of 31.06 J/g. These findings suggested that both Okra and seaweed polysaccharide are highly thermo stable and could be used in the development of biomaterials for various industrial purposes. The numerical algorithms in this work may be useful in modeling of polymer processing. The kinetic model showed nearly similar activation energies for both Okra and Gracilaria corticata that are suitable for the determination of the kinetic parameters of polysaccharide. We demonstrated that the approach was a powerful tool to estimate the activation energy of Okra and Gracilaria corticata polysaccharides for thermal decomposition.
References


