

Influence of Different Degradation Techniques on the Molecular Weight Distribution of κ -Carrageenan

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Abstract Carrageenan as an abundant natural carbohydrate could be used as a representative material instead of synthetic polymers. In this work, the degradation of κ -Carrageenan by means of ultrasound irradiation at a frequency of 24 kHz and its combination with heterogeneous Titanium dioxide, followed by a photocatalytic process was investigated. The scission of carrageenan chains induced by a high intensity field of ultrasonic irradiation; result in various molecular weights of carrageenan. The low molecular weight species of carrageenan have biological and pharmaceutical uses that only should be obtained from the degradation method. The ultrasound power not only led to enhanced turbulence and liquid streaming, but also increased the active surface area. Therefore, TiO_2 sonophotocatalysis was carried out faster than sonolysis and sonocatalysis processes. The influence of the basic operational parameters such as, ultrasound power and amount of TiO_2 on the degradation rate of carrageenan was also studied. The results revealed that the extent of sonolytic degradation was increased with increasing of ultrasound power (in the range 30–80 W) and at higher catalyst concentration, the degradation rate in the solution soared. The degraded carrageenans were characterized by gel permeation chromatography (GPC).

Keywords κ -Carrageenan, Sonolysis, Sonophotocatalysis, Molecular Weight, Viscosity, Degradation

1. Introduction

Carrageenans are linear polysaccharides of the Rhodophyceae family of red seaweed made up of galactans with alternating α (1/3) linkages and β (1/4) linkages and occasional 3, 6-anhydro-D-galactose units [1]. Three primary forms (κ -, λ -, ι -) of carrageenan are identified based upon the modification of the disaccharide repeating unit arisen from the occurrence of ester sulphate, or anhydride formation in the 4-linked residue [2].

κ -Carrageenan is a substantial gelling polysaccharide extracted from several species of red seaweed (Rhodophyceae). Structurally, it consists of repeating disaccharide units of alternating (1/3) - α -D-galactose-4 sulphate and (1/4)- β -3, 6-anhydro-D-galactose residues [3-5]. Fig. 1 shows the structural formula of the κ -Carrageenan.

Degraded carrageenan is used to induce ulcerative colitis in the colon in guinea-pigs as an experimental model to study the effects of pharmacological and therapeutic agents [6]. Low molecular weight fractions may be present in the raw material or may be created during production processes. Oligomers from carrageenans suggest promising anti-herpetic, anti-HIV (human immunodeficiency virus) activities and as anti-infectants [7-9].

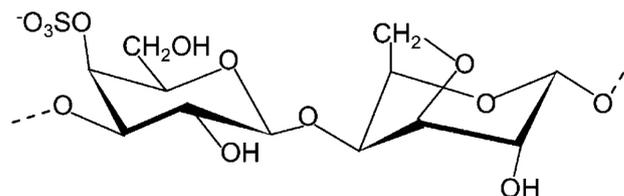


Figure 1. Chemical structure of κ -carrageenan.

Carrageenans of different molecular weights are generally prepared by different hydrolysis methods such as acid hydrolysis, oxidative degradation method, enzymatic hydrolysis, mechanical energy methods including shearing, ultrasonic, and also radiation degradation. High-intensity ultrasonic treatment can be applied to degrade polymers and to facilitate emulsifying and cleaning processes. The ultrasonic energy is dissipated in solution, leading to cavitations. Cavitation generates vibrational wave energy, shear stress at cavitation interphase, and local high pressure and temperature. These are the major factors causing the degradation of polymers [10-12]. Microbubbles collapse and produce intense shear and shocking waves on the polymer molecules near to the bubble. Because of this high shear, polymer molecules near the collapsing microbubbles move faster than the polymer molecules far from the cavitation. Due to this relative motion of polymer chains and the

generated mechanical stress, the polymer chain breaks almost at the mid-point. The molecular weight decreases continuously till it reaches a limiting molecular weight [13-16].

Nowadays, the simultaneous usage of ultrasound and photocatalysis, i.e. the so-called sonophotocatalysis has been studied either consideration of process efficiency to degrade various organics and dyes [17, 18]. Among semiconductor materials, TiO_2 powders have been widely implemented as the photocatalyst to treat pollutants because of their strong oxidizing power, non-toxicity, and low cost [19]. Many studies have been reported on combining ultrasonic with UV light irradiation in the presence of TiO_2 yielding to excellent removing ability [20-22]. This process provides a splendid opportunity for reducing of reaction time without any need for extreme physical conditions [23].

The scope of this work is to study the degradation of carrageenan by means of sonolysis, photocatalysis and their combined application, sonophotocatalysis, concerning the effect of catalyst presence on the kinetics of degradation process. In particular, the synergy effect of different degradation process was investigated and compared with individual effect of them.

2. Experimental

2.1. Materials

κ -Carrageenan powder (Gelcarin G-812 Carrageenan) was obtained from Duchefa Biochemie B.V. Degussa TiO_2 P-25 (anatase:rutile = 65:35, BET 50m²g⁻¹) was employed as photocatalyst in heterogeneous catalytic experiments and it was supplied by Degussa Huels. All other chemicals were of laboratory reagent grade and were purchased from Merck. All solutions were prepared using distilled and deionized water.

2.2. Methods

2.2.1. Experimental Setup and Procedure

Reactions were carried out in a cylindrical 100ml Pyrex glass vessel which is schematically shown in Fig. 2. An ultrasound generator (Dr. Hielscher Ultrasonic Processor UP200 H) operating at a fix frequency of 24 kHz and a variable power output up to 150W nominal value (power output for solution state is approximately 100w), in aqueous media was used for sonication experiments. A titanium-made H3 sonotrode ($\phi=3\text{mm}$) immersed in liquid from the open to the atmosphere top of the vessel was used to deliver the ultrasound energy in the reaction mixture. The bottom of the vessel was fitted with a glass cylindrical tube housing the light source; there were a pair of 8W UV lamps, emitting in the 200-300 nm wavelength range with a maximum emission at 254 nm. The incident photon flow of UV light, estimated under the same conditions as in the

photocatalytic experiments, was 1.8×10^{-4} Einstein.L⁻¹.min⁻¹. The vessel was fed with a 100ml carrageenan solution and the reaction temperature in all cases of sonolysis, sonocatalysis and sonophotocatalysis was kept constant at $25 \pm 1^\circ\text{C}$ by the use of cooling water circulating through the double-walled compartment, acting as cooling jacket. The reaction vessel was covered with a dark cloth to avoid unwanted photochemical reactions induced by natural light.

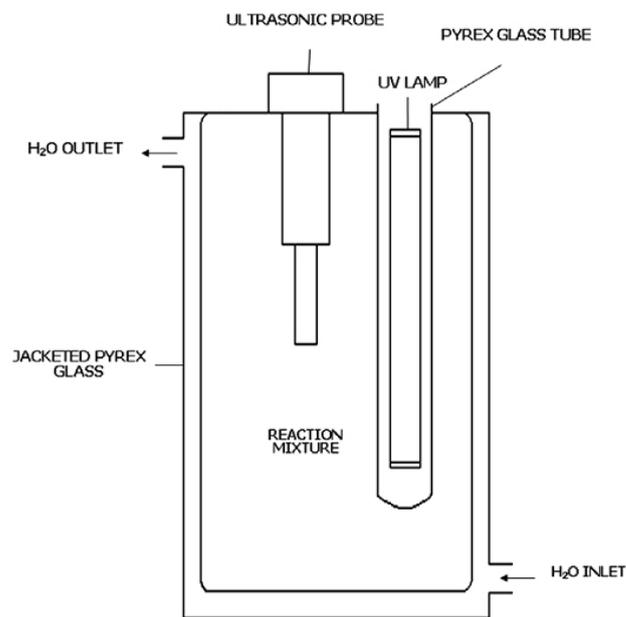


Figure 2. Schematic of the experimental setup.

2.3. Characterization

Carrageenan powder was sieved through a 200 mesh, then mixed with KBr (1:100) then pressed into a pellet. The absorbance of the hydroxyl band (3400cm^{-1}) was measured using a Shimadzu RF50 infrared spectrophotometer. The absorbance band of the hydroxyl group at 3400cm^{-1} was used as an internal standard to correct the disc thickness and for differences in the carrageenan concentration in the KBr disc making.

Gel permeation chromatography (GPC) (HLC6A, Shimadzu) was used to compare molecular weight and molecular weight distribution (polydispersity) of the original carrageenan and degraded samples at the end of 60 min and at different conditions of performed reactions. GPC analysis was performed by using aqueous column that calibrated according to calibration method based on ASTM D6579 (2006).

2.4. Viscosity Measurements

The intrinsic viscosities of the original carrageenan and its degraded solutions at 25°C were measured using the

capillary viscometer (Setavic Kinematic viscometer). The internal capillary diameter was 0.05mm. Efflux times were measured for carrageenan solutions (t_s) and for the solvent (t_0). Measurement of efflux times were repeated two times and average efflux time was then converted to the ratio of t_s/t_0 , being proportional to relative viscosity, η_r , of carrageenan solution:

$$\eta_r = \frac{t}{t_0} \quad (1)$$

$$\eta_{sp} = 1 - \eta_r \quad (2)$$

The intrinsic viscosity $[\eta]$ values can be related to the specific viscosity, η_{sp} , and relative viscosity, η_r , those in Huggins and Kramer equations [24]. The conditions used in this work ($\alpha = 0.95$ and $k = 0.00000311 \text{ g}^{-1}$) were adopted on the basis of previous findings in the literature [25, 26].

2.5. Kinetic Model

The rate of degradation is defined as the number of scission occurring in 1 L in time unit and a scission in a chain yields two pieces. Thus, the rate equation of the degradation is as follow:

$$R = \frac{dM}{dt} = kM^n \quad (3)$$

Where, M , is the total molar concentration of the polymer, k , is the rate constant and, n , is the order of reaction with respect to the total molar concentration of the polymer. Therefore, Eq. (3) leads to:

$$M^{1-n} - M_0^{1-n} = (1-n)kt \quad (4)$$

Where M_0 is the initial total molar concentration of polymer. The total molar concentration is related to the average number of molecular weight as followed [27]:

$$M = \frac{C}{M_n} \quad (5)$$

Moreover, average viscosity of molecular weight, M_v , is related to the average number of molecular weight, M_n , through [28]:

$$M_v = [(1+\alpha)\Gamma(1+\alpha)]^{\frac{1}{\alpha}} M_n \quad (6)$$

Where, $\Gamma(1+\alpha) = \int_0^{\infty} e^{-t} t^\alpha dt$

M_v is related to the intrinsic viscosity, $[\eta]$, through Mark-Houwink equation:

$$M_v = \left(\frac{[\eta]}{K} \right)^{\frac{1}{\alpha}} \quad (7)$$

Where α and k are the Mark-Houwink constants.

$[\eta]$ can be related to the specific viscosity, η_{sp} , and relative viscosity, η_r , by Huggins and Kramer equations:

$$\frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2 C \quad (8)$$

$$\frac{Ln\eta_r}{C} = [\eta] + (K' - 0.5)[\eta]^2 C \quad (9)$$

From Eq. (8) and (9), intrinsic viscosity is:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - Ln\eta_r)}}{C} \quad (10)$$

And finally fit our data at Eq. (11):

$$\Delta \eta^{1-n} - \Delta \eta_0^{1-n} = k't \quad (11)$$

3. Results and Discussion

3.1. Determination of Reaction Order of Degradation of Carrageenan

At the level of interatomic distances within the macromolecules, there is still some debate regarding the place where the bond breakage occurs. By analogy with the chemical degradation, it is expected to take place at the weakest links in the polymer backbone, however reports [29, 30] suggested that it significantly occurs at the midpoint of the polymer chains and the existence of a final limiting molecular weight is predicted; below which ultrasounds have no more effect. In general, polymer mechanochemistry stimulated by an acoustic field is a non-random process; for instance, the scission of polymer chains in solution occurs at a preferential position near the midpoint [31-33] Moore et al. approved this idea by an isotope labelling experiment in ultrasonic degradation of linear PEG. They demonstrated that when a single weak azo link was positioned at the center of a linear PEG chain, mechanically-induced cleavage was localized almost exclusively to the single weak site [34].

Several studies recommend a random chain breakage, though considering that some bonds are still more resistant [35]. Due to the polydisperse nature of most polymers, an accurate analysis of the degradation kinetics is almost impossible without having information about the location of chain scission and the dependence of rate coefficients on the molecular weight of the polymer. Two simplified models, based on different assumptions of the location of chain scission, have been proposed to quantitatively describe the degradation process of polymers [36].

Although a number of different rate models have been proposed for the degradation of polymers [37, 38]. Previous studies proved that with an increase in concentration, the rate constant, k , was decreased respectively [39, 40]. These observations are explained in terms of viscosity changes for different polymer concentrations. At higher concentrations,

the solution viscosity increases. An increase in viscosity raises the cavitation threshold. This increased threshold not only makes it more difficult for cavitating bubbles to shape, but also makes the velocity gradients around collapsing bubbles become smaller. Thus, the elongation of the polymer backbone is reduced [41-43].

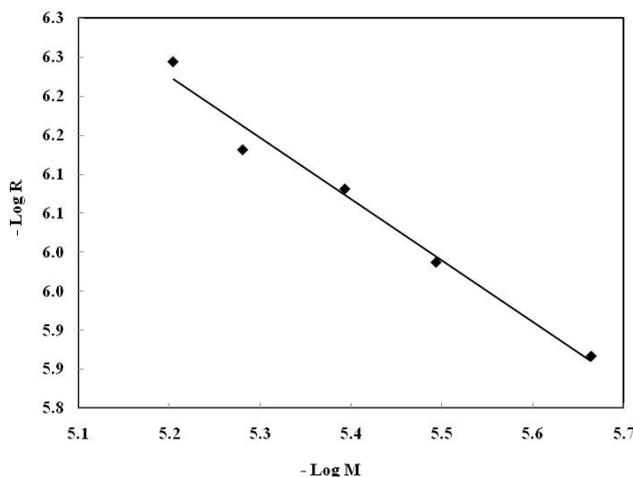


Figure 3. The plot of $\ln R$ versus $\ln M$ for degraded carrageenan at 25°C.

The slope of plots gives the initial rate of degradation by using Eq.11, the plot of $\ln R$ versus $\ln[M]$ is linear and is shown in Fig. 3. The slope of curve is -0.8, which suggests the order of reactions with respect to total molar concentration of polymer.

From substitution of the value of “ n ” in Eq.11, the following equation is obtained:

$$\Delta\eta^{1.8} - \Delta\eta_0^{1.8} = K't \quad (12)$$

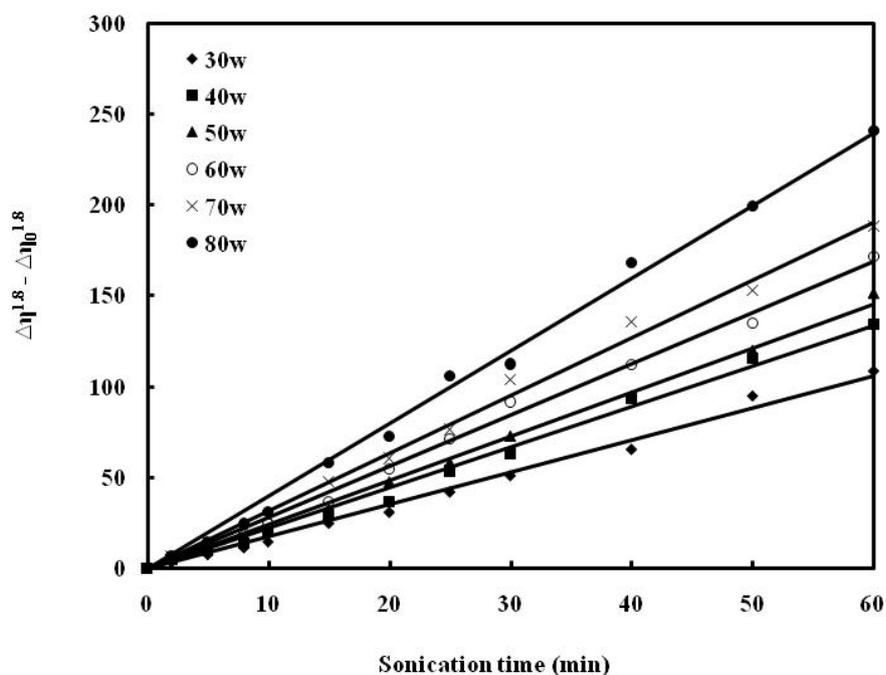
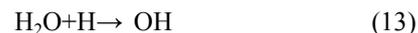


Figure 3. The plot of $\Delta\eta^{1.8} - \Delta\eta_0^{1.8}$ versus the sonication time in sonolytic process, for different power of ultrasound at 25°C.

3.2. Sonolytic (US) and Sonocatalytic (US+TiO₂) Degradation of Carrageenan

Relative viscosity decreases with increasing the nominal applied power from 30 to 80 W. In aqueous phase sonolysis, there are three potential sites for sonochemical activity: (i) the gaseous region of the cavitation bubble, where volatile and hydrophobic species are easily degraded through pyrolytic reactions as well as reactions involving participation of hydroxyl radicals with the latter being formed through water sonolysis:



(ii) the bubble-liquid interface where hydroxyl radicals are localized and, therefore, radical reactions predominate, though pyrolytic reactions to a less extent may occur and (iii) the liquid bulk where secondary sonochemical activity may chiefly happen since free radicals have escaped from the interface and migrated to the liquid bulk. It should be pointed out that hydroxyl radicals could recombine yielding hydrogen peroxide, which may in turn react with hydrogen to regenerate hydroxyl radicals:



It is quite noticeable that carrageenan is a non-volatile and soluble polysaccharide; hydroxyl radical-mediated reactions primarily take place in the liquid bulks and are likely to be the dominant degradation pathway. A polymer molecule at the vicinity of a collapsing bubble is pulled towards the cavity of the bubble, and the solvodynamic shear elongates the polymer backbone, thus leading to scission [44].

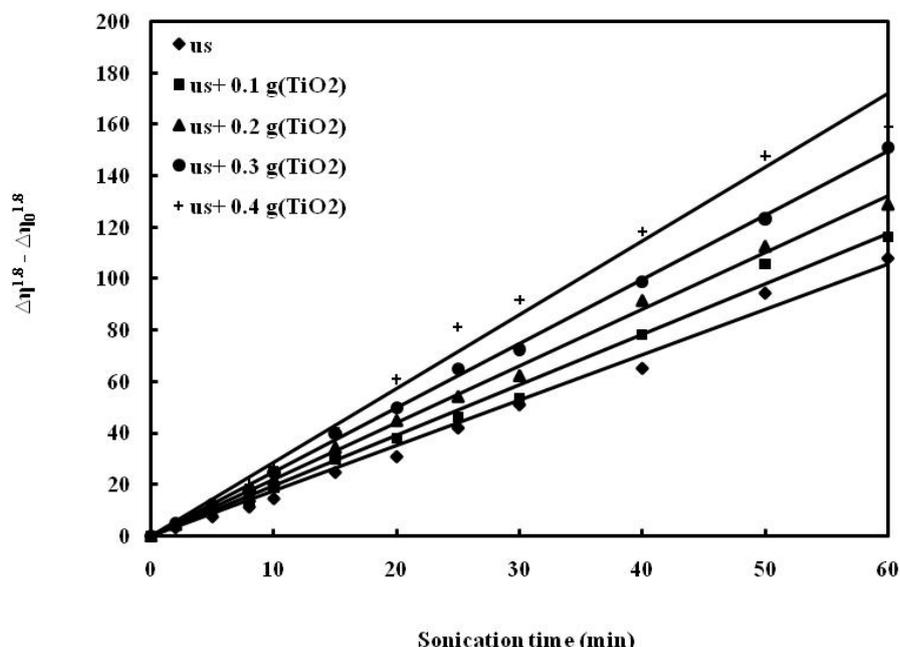


Figure 4. The plot of $\Delta\eta^{1.8} - \Delta\eta_0^{1.8}$ versus the sonication time in sonocatalytic process, for different loading of TiO_2 nanoparticles.

Table 1. The effect of power of ultrasound on the degradation rate constants at 1.5g/L concentration and 25°C.

P (W)	30	40	50	60	70	80
$K \times 10^{10} (\text{mol}^{1.8} \text{L}^{-1.8} \text{min}^{-1})$	2.111	4.004	4.625	4.990	5.759	6.102

Table 2. Initial carrageenan degradation rate constants in the presence of various values of catalyst loading and treatment conditions at 1.5g/L concentration and 25°C.

Process	TiO_2 loading (g/l)	$K \times 10^{10} (\text{mol}^{1.8} \text{L}^{-1.8} \text{min}^{-1})$
US	0.00	2.134
US	0.10	4.012
US	0.20	4.120
US	0.30	4.662
US	0.40	4.965
US + UV	0.10	4.244
US + UV	0.20	4.800
US + UV	0.30	7.455
US + UV	0.40	8.245

The plot of $\Delta\eta^{1.8} - \Delta\eta_0^{1.8}$ versus sonication time for different powers of ultrasound is presented in Fig. 4. The apparent degradation rate constant, k' , defined in Eq. (11), can be estimated from the slopes of the plots in Fig. 5. Based on these results, degradation rate constants, k , were calculated shown in Table 1. It can be observed that at the same concentration, the extent of degradation increases with an increase in applied ultrasound power. In quantitative terms, in 60 min of irradiation time the extent of degradation at 80W is three times higher compared to that at 30 W.

The effect of TiO_2 catalyst and its concentration in sustained power of ultrasound (30 W) on the degradation rates has also been investigated. As indicated, the presence of TiO_2 particles in the reaction mixture partially raised the sonochemical degradation of carrageenan. These results are

shown in Fig. 5 and Table 2. The observed phenomenon can be explained on the basis of the adsorption and desorption characteristic of carrageenan on TiO_2 catalyst. At higher catalyst concentration, the degradation rate in the solution increases, the rate of releasing of already adsorbed carrageenan also increases, thereby giving lower overall degradation rate based on the free concentration of the carrageenan in the liquid.

3.3. Sonophotocatalytic (US + UV + TiO_2) Degradation of Carrageenan

In further experiments, the degradation of carrageenan by means of simultaneous ultrasound and ultraviolet irradiation in the presence of TiO_2 was performed and temporal changes

in relative viscosity, η_r , and the rate constant of degradation reaction were studied. The reaction rate constants for applied degradation methods (sonocatalytic and sonophotocatalytic) are summarized in Table 2. Combination of ultrasound and photolysis resulted in better efficacy as compared to the individual operations and the rate of degradation does not appear to slow down with time of treatment [45]. In previous works, Gogate et al. were designed reactor based on this method as an efficient technique to remove some pollutants such as phenol and formic acid from wastewater [46-49]. As a result, the synergism between the ultrasonic and photocatalytic methods seems to be dependent on the time of

operation and hence the final selection of the treatment approach would be strongly dependant on the desired objective of using the treatment approach [50]. As shown in Table 2 and Fig. 6, sonophotocatalytic degradation generally occurs faster than sonocatalytic degradation during the respective individual processes at similar operating conditions. Comparison of reaction rate constants is presented in Fig. 7. As illustrated, the rate constants of degradation process in sonocatalysis method have a linear increasing, however in the combined method (sonophotocatalysis) the increasing shows an exponential behavior.

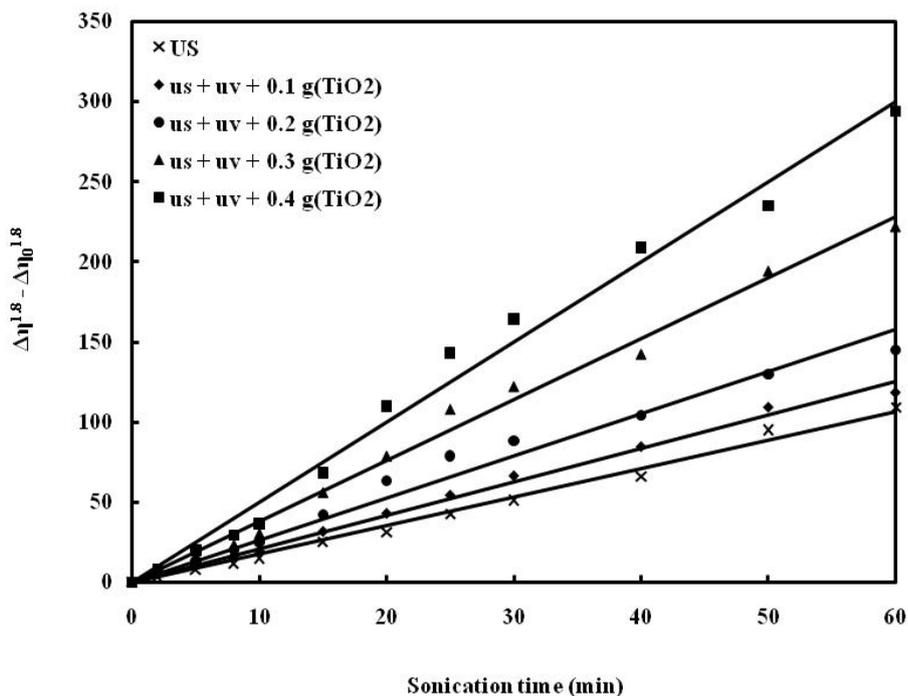


Figure 6. The plot of $\Delta\eta^{1.8} - \Delta\eta_0^{1.8}$ versus the sonication time in sonophotocatalytic process, for different loading of TiO_2 nanoparticles.

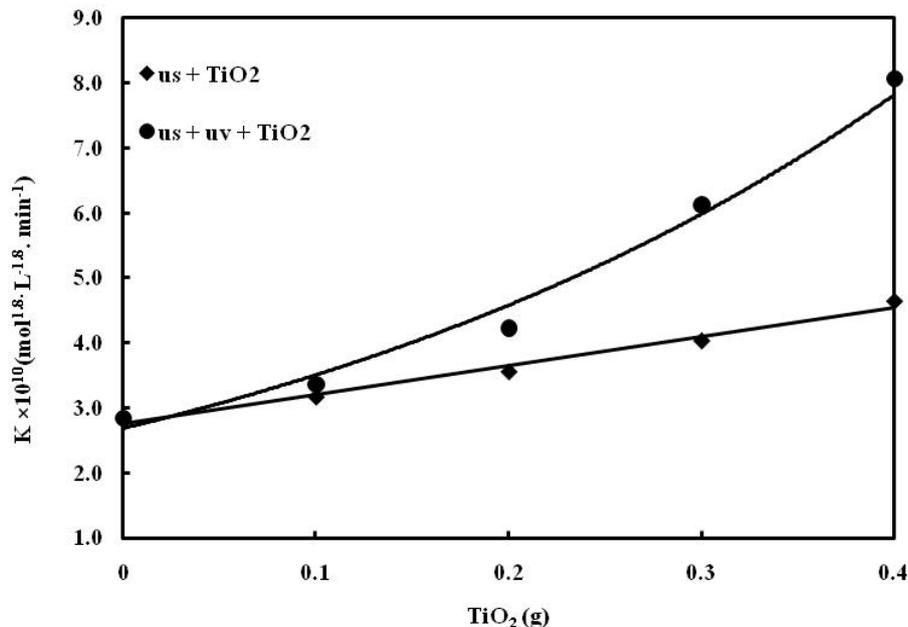


Figure 7. Comparison of increase mode of rate constants with increasing the catalyst loading for different degradation techniques.

Table 3. Results of GPC analysis for weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity of carrageenan samples for initial and degraded carrageenan by means of different applied techniques at 1.5g/L concentration and 25°C for different duration.

Applied process	Time	$M_w \times 10^3$ (kDa)	$M_n \times 10^3$ (kDa)	Polydispersity
Pure sample Sonolysis	0	126.92	10.84	1.17
	15	122.76	10.70	1.15
	30	120.45	10.57	1.14
	45	113.67	9.39	1.21
	60	107.31	8.78	1.22
Sonocatalytic	15	119.10	10.41	1.14
	30	116.92	10.15	1.15
	45	100.46	8.65	1.16
	60	93.89	8.14	1.15
Sonophotocatalytic	15	117.89	9.63	1.22
	30	105.32	8.95	1.18
	45	92.40	8.19	1.13
	60	88.24	7.43	1.19

3.4. Gel Permeation Chromatography Analysis

Data of molecular weights distribution were obtained for initial κ -carrageenan and κ -carrageenan in 15min intervals for sonolysis, sonocatalytic and sonophotocatalytic degradation in the presence of 0.1g TiO₂ and 30W power of ultrasound. Relve et al. reported GPC elution profiles for different kinds of carrageenans, after irradiation at various doses in the solid and gel state. In this case the polydispersities are decreased by increasing dose of irradiation [51]. The molecular weight loss of degraded carrageenan in diverse reaction conditions for three samples at 1h interval represented a shift toward lower molecular weights, compared to the molecular weight of initial carrageenan. These results were followed by the results of viscometry method giving the reducing order of molecular weight while the degradation processes were being done. The values of polydispersity for the degraded samples are higher than that was estimated. Table 3 presented the results for number-average molecular weight (M_n) and weight-average molecular weight (M_w) and the respect of these two parameters (M_w/M_n) that is known as polydispersity. As presented, the distribution of molecular weights is much extended and difference between M_n and M_w is remarkable. Though, the number of bonds with cleavage capability at given time (60min) remains constant, the number of available molecules reaches to high at the same time. Thus, it would consequently lead to a decrease in molecular weight since fewer bonds can be broken per available molecule [52].

4. Conclusions

It has been demonstrated that carrageenan treatment with a variety of output ultrasound powers in aqueous solution is an efficient procedure for molecular weight reduction of carrageenan. Under sonolysis conditions, degradation is

carried out by OH radicals and mechanochemical effects. On the other hand, the use of TiO₂ nanoparticles as catalyst in the presence of ultraviolet source in a constant threshold power of ultrasound (30W) retrieved the ultrasound power weakness and improved the applied degradation process. The rate of carrageenan degradation in mentioned conditions (sonophotocatalysis) increased with the increase in catalyst loading. In the case of sonocatalytic process, the rate of degradation process was not increased significantly in comparison with sonolysis technique. Remarkably, the results obtained by FT-IR spectroscopy monitored that the chemical structure of carrageenan was not altered during sonophotocatalytic degradation.

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