

## Photo-Assisted Sonodegradation of Hydrogels in the Presence of TiO<sub>2</sub> Nanoparticles

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**ABSTRACT.** The degradation of one of the commercially important hydrogel based on acrylic acid and acryl amide, (acrylic acid-co-acryl amide) hydrogels, by means of ultrasound irradiation and its combination with heterogeneous (TiO<sub>2</sub>) was investigated. 24 kHz of ultrasound irradiation was provided by a sonicator, while an ultraviolet source of 16 W was used for UV irradiation. The extent of sonolytic degradation increased with increasing ultrasound power (in the range 30-80 W). TiO<sub>2</sub> sonophotocatalysis led to complete (acrylic acid-co-acryl amide) hydrogels degradation with increasing catalyst loading, while, the presence of TiO<sub>2</sub> in the dark generally had little effect on degradation. Therefore, emphasis was totally on the sonolytic and sonophotocatalytic degradation of hydrogels and a synergy effect was calculated for combined degradation procedures (Ultrasound and Ultraviolet) in the presence of TiO<sub>2</sub> nanoparticles. TiO<sub>2</sub> sonophotocatalysis was always faster than the respective individual processes due to the enhanced formation of reactive radicals as well as the possible ultrasound-induced increase of the active surface area of the catalyst. A kinetics model based on viscosity data was used for estimation of degradation rate constants at different conditions and a negative order for the dependence of the reaction rate on total molar concentration of (acrylic acid-co-acryl amide) hydrogels solution within the degradation process was suggested.

**Key words:** (acrylic acid-co-acryl amide) hydrogels, Degradation, Sonophotocatalysis, Viscosity, TiO<sub>2</sub> nanoparticles

### INTRODUCTION

Early work in understanding the response of polymeric materials to mechanical stress was published by Staudinger, who observed a decrease in the molecular weight of polymers in response to mastication. It was suggested that the molecular weight reduction resulted from homolytic carbon-carbon bond cleavage due to mechanical force.<sup>1</sup> Mechanical stress can be in the form of ultrasound waves and the related process is named ultrasonic degradation. Ultrasound can be used to apply force to dilute polymer solutions. Since its initial use to degrade starch and agar,<sup>2</sup> this technique has also been employed to degrade cellulose,<sup>3</sup> polypeptides, polysaccharides,<sup>4,5</sup> proteins,<sup>6</sup> DNA,<sup>7</sup> transition metal-coordinated polymers,<sup>8-10</sup> and various organic polymers.<sup>11,12</sup>

Depending on the application, polymers and gels may need to be degraded to reduce their molecular weight through the shortening of the polymeric chains that can be achieved by various methods. Different methods of degradation are available such as thermal, photo and catalytic degradation.<sup>13,14</sup> Beside the ultrasonic degradation method, the methods like photocatalysis<sup>15</sup> and microwave<sup>16</sup> are also important. Polymers can be degraded thermally by

pyrolysis or in solution. But the process is energy intensive. Therefore, alternative energy reducing techniques required for degradation process are important. Ultrasound, photo and chemical methods are less energy-intensive polymer degradation. Further, the mechanism by which they interact with the polymeric systems can help get insight into the degradation pathways or mechanisms.<sup>17</sup>

Polymer chain scission results from solvodynamic shear caused by cavitation: the nucleation, growth, and collapse of bubbles in solution. A polymer molecule near the vicinity of a collapsing bubble is pulled toward the cavity of the bubble, and the solvodynamic shear elongates the polymer backbone, leading to scission.<sup>18</sup> Scission generally occurs near the midpoint of a polymer chain (approximately within the middle 15% of the chain, in the case of homopolymer), where solvodynamic forces are the greatest.<sup>19</sup> The rate of cleavage from ultrasonic irradiation of polymer solutions depends on several experimental factors, including temperature, solvent, and sonication intensity.<sup>20</sup>

The ultrasonic energy is dissipated in solution, resulting in cavitations. Cavitation produces vibrational wave energy, shear stresses at the cavitation interphase, and local high pressure and temperature. These are the major factors causing the degradation of polymers.<sup>21-23</sup> Application of high-

intensity ultrasound to dispersions of carbohydrates can lead to depolymerization because of the intense mechanical and chemical effects associated with cavitation.<sup>24-27</sup> Cavitation thermolysis may produce hydroxyl radicals and hydrogen atoms that can be followed by formation of hydrogen peroxide.<sup>28-30</sup> Some cavities exist only for one cycle of the sound field and collapse violently (transient cavities), while other are long-lived and oscillate around some equilibrium size (stable cavities).<sup>31</sup>

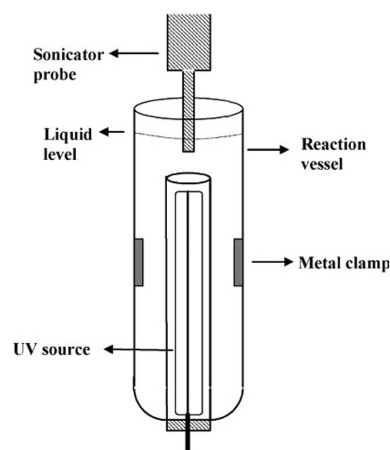
In recent years, the simultaneous use of ultrasound and photocatalysis, so-called sonophotocatalysis has been studied regarding process efficiency to degrade various organics and dyes.<sup>32-37</sup> However, some researchers were investigated this combined method on degradation of some water soluble polymers<sup>38,39</sup> and recently Saïen et al. studied the kinetic of sono-assisted photocatalytic degradation of styrene-acrylic acid copolymer and applied this technique as an enhanced degradation process.<sup>40</sup> Nano TiO<sub>2</sub> as a photocatalyst has a great many advantages such as low cost, non toxicity, high catalyst efficiency, long-term stability etc.<sup>41,42</sup> On the other hand, by using ultrasound some complicated reactions can be performed with inexpensive equipment and often in fewer steps than with the conventional methods<sup>43</sup> in this regard, researchers have used sono-photocatalysis in a variety of investigations. This process provides an excellent opportunity to reduce reaction time without the need for extreme physical conditions.<sup>44</sup>

Although photocatalysis and sonolysis have been extensively employed individually for the degradation applications, their combined use has received appreciably less attention. The aim of this work was to study the degradation of hydrogel by means of sonolysis and sonophotocatalysis, concerning the effect of catalyst presence on the kinetics of degradation process.

## EXPERIMENTAL

### Materials

Acrylic acid (AA, Merck) was used after vacuum distillation. Acrylamide (AAm, Fluka), ammonium persulfate (APs, Fluka) and methylene bisacrylamide (MBAAm, Fluka) were analytical grade and used without further purification. The hydrogel was prepared according to early works in optimum conditions.<sup>45</sup> Degussa TiO<sub>2</sub> P-25 (anatase:rutile=65:35, BET=50 m<sup>2</sup>g<sup>-1</sup>) 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.



**Fig. 1.** Schematic of the experimental setup.

All solutions were prepared using distilled and deionized water.

**Experimental setup and procedure:** Reactions were carried out in a cylindrical 100 ml Pyrex glass vessel which is schematically shown in *Fig. 1*. An ultrasound generator (Dr. Hielscher Ultrasonic Processor UP200 H) operating at a fix frequency of 24 kHz and a variable power output up to 100 W nominal value, in aqueous media was used for sonication experiments. A titanium-made H3 sonotrode ( $\phi=3$  mm) immersed in liquid and 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 lamp, which emits in the 200-300 nm wavelength range with a maximum at 254 nm. The incident photon flow of UV light, estimated under the same conditions as in the photocatalytic experiments, was  $1.8 \times 10^{-4}$  Einstein L<sup>-1</sup>min<sup>-1</sup>. The vessel was fed with a 100ml hydrogel solution and the reaction temperature in the case of sonolysis, sonocatalysis and sonophotocatalysis was kept constant at  $25 \pm 1$  °C through the use of cooling water circulating inside the double-walled compartment, thus acting as cooling jacket. The reaction vessel was covered with a dark cloth to avoid unwanted photochemical reactions induced by natural light.

Different treatments were tested, namely: sonolysis (US), sonocatalysis (US+TiO<sub>2</sub>) and combined sonolysis and photocatalysis (US+UV+TiO<sub>2</sub>). For the experiments in the presence of TiO<sub>2</sub>, a concentration range of 0.1-0.4 g/L of TiO<sub>2</sub> nanoparticles was used.

### Viscosity measurements

The intrinsic viscosities of the original hydrogel and its

degraded solutions at 25 °C were measured using the capillary viscometer (Setavic Kinematic viscometer). The internal capillary diameter was 0.5 mm. Efflux times were measured for hydrogel solutions ( $t_s$ ) and the solvent ( $t_0$ ). Measurement of efflux times were repeated two times and average efflux time was then converted to the ratio of  $t_s/t_0$ , which is proportional to relative viscosity,  $\eta_r$  of hydrogel 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,  $\eta_{sp}$  and relative viscosity,  $\eta_r$ , by the Huggins and Kramer equations.<sup>46</sup>

### Kinetic model

The rate of degradation is defined as the number of scission that occurs in 1 L in unit time and we must keep in mind that a scission in a chain yields two pieces. Thus, the rate equation of the degradation is as follows:

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

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. From the experimental data, it is clear that the degradation rate decreases with increasing solution concentration, so “n” is negative. Harkal *et al.* was found that the order of ultrasonic degradation reaction for poly (vinyl alcohol) obtained from this kinetic model is -1.<sup>47</sup> It is noted that solution concentration (g/L) is constant and the total molar concentration (mol/L) increases during the degradation of polymer. The solution of differential Eq. (3) is:

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

Where  $M_0$  is the initial total molar concentration of polymer. The total molar concentration is related to the number average molecular weight through:<sup>48</sup>

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

Moreover, viscosity average molecular weight,  $M_v$ , is related to the number average molecular weight,  $M_n$ , through.<sup>49</sup>

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

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

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

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

Finally,  $[\eta]$  can be related to the specific viscosity,  $\eta_{sp}$ , and relative viscosity,  $\eta_r$ , 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:

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

Substitution of Eq. (10) in (9) and Eq. (9) in (8) yields

$$M_n = \left[ \frac{\sqrt{2(\eta_{sp} - Ln\eta_r)}}{(1+\alpha)\Gamma(1+\alpha)KC} \right]^{1/\alpha} \quad (11)$$

Finally, the substitution Eq. (11) in (5) yields:

$$M = \left[ \frac{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}}{\sqrt{2}} \right]^{1/\alpha} \Delta\eta \quad (12)$$

In addition, substitution Eq. (12) in (4) yields:

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = (1-n) \left[ \frac{\sqrt{2}}{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}} \right]^{(1-n)/\alpha} kt \quad (13)$$

Or

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = k't \quad (14)$$

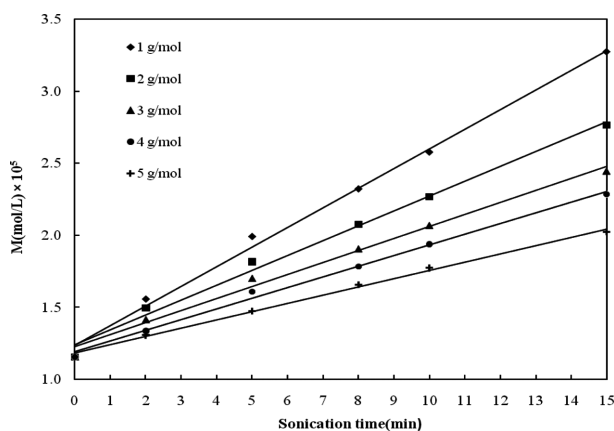
## RESULTS AND DISCUSSION

### Determination of reaction order of degradation of (acrylic acid-co-acryl amide) hydrogel

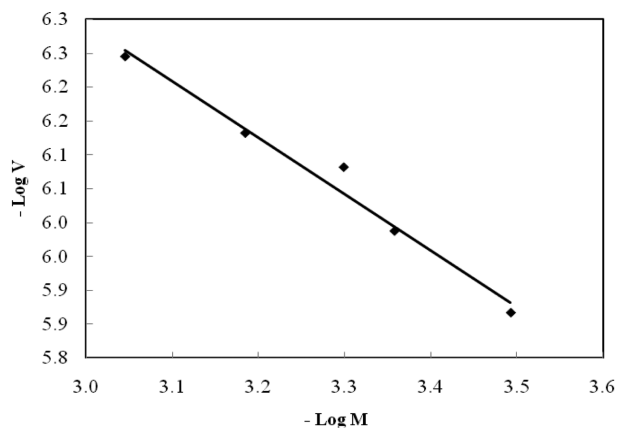
At the level of interatomic distances within the macromolecules, there is still some debate regarding the place where the bond breakage occurs. By analogy with the chemical degradation, it is expected to take place at the weakest links in the polymer backbone, but some works<sup>49</sup> suggested that it mainly 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 induced by an acoustic eld is a non-random process; for example,

the scission of polymer chains in solution occurs at a preferential position near the midpoint.<sup>50-52</sup> Moore *et al.* approved this idea by an isotope labeling experiment on 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.<sup>53</sup>

Several studies propose a random chain breakage but still consider that some bonds are more resistant, in relation to the decrease in the scission rate constant as lower values of degree of polymerization are reached.<sup>54</sup> Due to the polydisperse nature of most polymers, an accurate analysis of the degradation kinetics is almost impossible without 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.<sup>55</sup> Although, a number of different rate models have been proposed for the degradation of polymers,<sup>56,57</sup> but in this study a simple model was employed via viscometry, Using Eq. (12). A negative order for the dependence of the reaction rate on total molar concentration of hydrogel solution within the degradation process was suggested. In the initial sonication times, for different concentration of polymer we calculate total molar concentration of polymer. The results are depicted in Fig. 2. Previous studies were proved that with an increase in concentration, the rate constant,  $k$ , was decreased obviously.<sup>58,59</sup> 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



**Fig. 2.** Variation of total molar concentration with sonication time for different concentration of hydrogel aqueous solution at 25 °C.



**Fig. 3.** The plot of  $\ln R$  versus  $\ln M$  for degraded hydrogel at 25 °C.

increased threshold makes it more difficult for cavitation bubbles to form. More importantly, the velocity gradients around collapsing bubbles become smaller, and the elongation of the polymer backbone is reduced.<sup>60</sup>

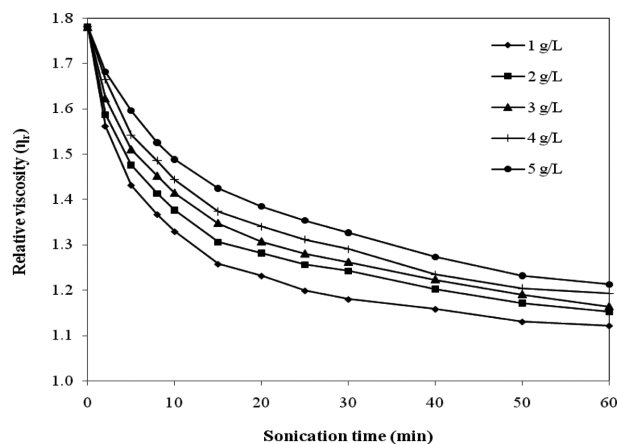
The slopes of plots give the initial rate of degradation using Eq. 3, the plot of  $\ln R$  versus  $\ln[M]$  are linear and it is shown in Fig. 3. The slope of curve is -0.8, which suggest the order of reactions with respect to total molar concentration of polymer.

From substitution of the value of “ $n$ ” in Eq. 14, we obtain the following:

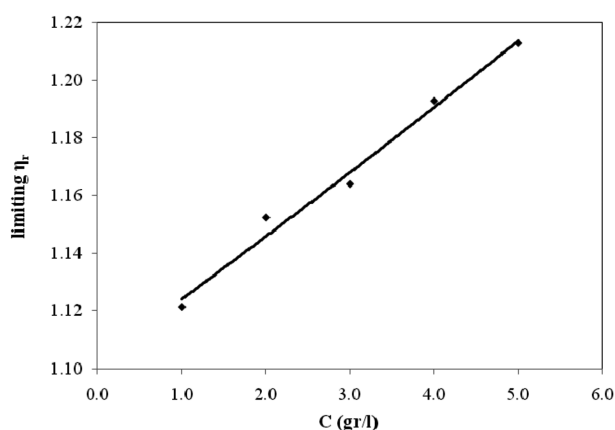
$$\Delta\eta^{1.8} - \Delta\eta_0^{1.8} = k't \quad (15)$$

#### Effect of concentration on the rate of degradation

Sonication was carried out for five different hydrogel concentrations at 25 °C. The relationship between  $\eta_r$  and sonication time are presented in Fig. 4. Based on these



**Fig. 4.** The relationship between  $\eta_r$  and sonication time in sonolytic process, for different concentrations of hydrogel aqueous solutions at 25 °C.



**Fig. 5.** The relationship between the limiting value of  $\eta_r$  and solution concentrations.

findings, it is clear that  $\eta_r$  decreases with sonication time and tends to have a constant value. It can be deduced that there is a limiting molecular weight that below which chain scission does not occur. Under the same conditions, the decrease in  $\eta_r$  of the sample with a high polymer concentration is lower than of the sample with a low polymer concentration.

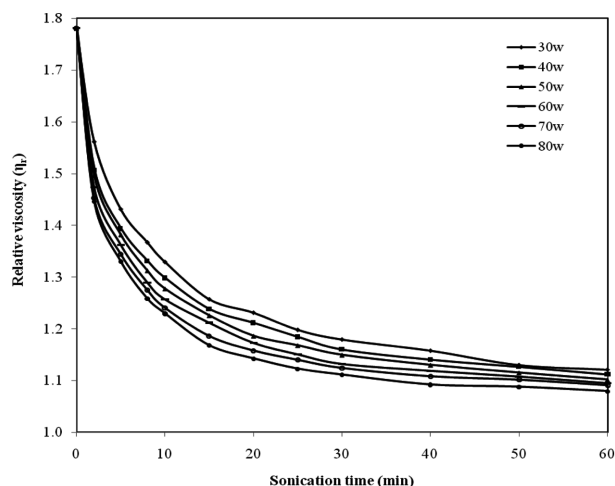
The relationship between the limiting value of  $\eta_r$  and solution concentration is presented in *Fig. 5*. These results indicate that the extent of degradation is more pronounced in more dilute solutions. This might be due to the fact that the probability of chemical bond scission caused by efficient shearing in the polymer chain is greater in dilute solution. These findings are consistent with the results of other investigators.<sup>21</sup>

#### **Sonolytic (US) and sonocatalytic (US+TiO<sub>2</sub>) degradation of (acrylic acid-co-acryl amide) hydrogel**

*Fig. 6* shows the effect of increasing changing ultrasound power on relative viscosity ( $\eta_r$ ) of hydrogel solution as a function of the sonication time at 1 g/L initial hydrogel concentration under air. As seen,  $\eta_r$  decreases with increasing the nominal applied power from 30 to 80W. In aqueous phase sonolysis, there are three potential sites for sonochemical activity, namely: (i) the gaseous region of the cavitation bubble where volatile and hydrophobic species are easily degraded through pyrolytic reactions as well as reactions involving the participation of hydroxyl radicals with the latter being formed through water sonolysis:



(ii) the bubble-liquid interface where hydroxyl radicals



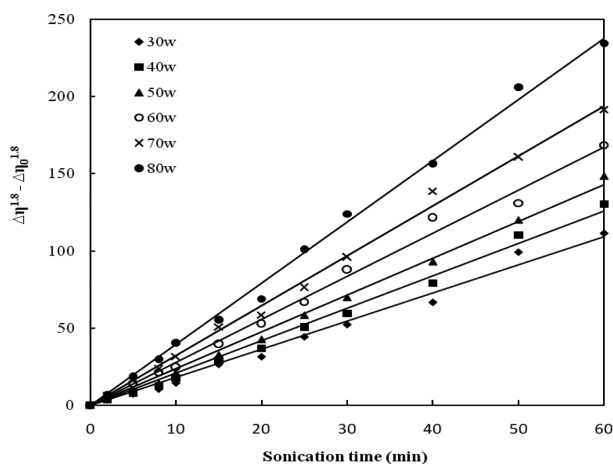
**Fig. 6.** The relationship between  $\eta_r$  and sonication time in sonolytic process, for different powers of ultrasound at 25 °C.

are localized and, therefore, radical reactions predominate although pyrolytic reactions may also, to a lesser extent, occur and (iii) the liquid bulk where secondary sonochemical activity may take place mainly due to free radicals that 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:

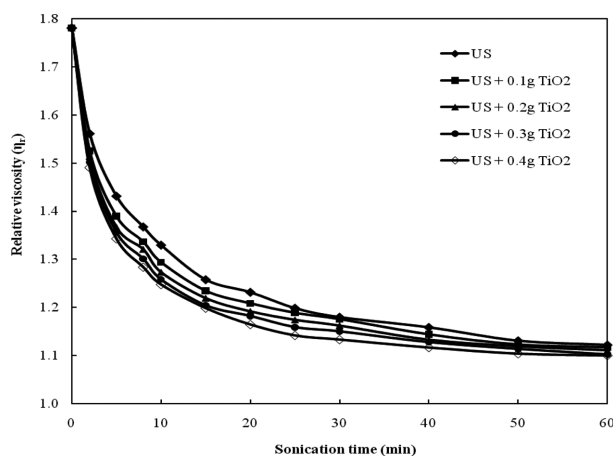


Given that hydrogel is a non-volatile and soluble copolymer, hydroxyl radical-mediated reactions occurring primarily in the liquid bulks as well as at the bubble interface are likely to be the dominant degradation pathway. A polymer molecule near the vicinity of a collapsing bubble is pulled toward the cavity of the bubble, and the solvodynamic shear elongates the polymer backbone, leading to scission.<sup>54</sup> Ulanski *et al.* have been study the effect of power of ultrasound on degradation of chitosan and found that the mechanism of ultrasonic is complex and can be mainly ascribe to radical random scissions, accompanied too some extend with mechanical breakage caused by hydrodynamic and shear forces.<sup>61</sup>

The plots of  $\eta^{1.8} - \eta_0^{1.8}$  versus sonication time for different powers of ultrasound are presented in *Fig. 7*. The apparent degradation rate constant,  $k$  defined in Eq. 14, can be estimated from the slopes of the plots in *Fig. 7*. Based on these results, degradation rate constants,  $k$ , were calculated that are shown in *Table 1*. It can be seen that at



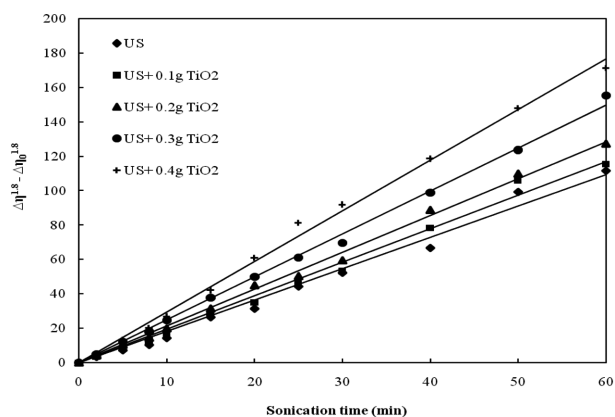
**Fig. 7.** The plot of  $\Delta\eta^{1.8}-\Delta\eta_0^{1.8}$  versus the sonication time in sonolytic process, for different power of ultrasound at 25 °C.



**Fig. 8.** The relationship between  $\eta_r$  and sonication time in sonocatalytic process, for different loading of catalyst at constant power of ultrasound (30W) at 25 °C.

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 as compared to degradation at 30W.

Effect of presence of catalyst TiO<sub>2</sub> and concentration of catalyst in constant power of ultrasound (30W) on the degradation rates has also been investigated. Fig. 8 shows the change in  $\eta_r$  versus sonication time in the sonocatalytic process (US+TiO<sub>2</sub>). In principle, particles may enhance degradation providing additional nuclei for bubble formation. However, an imperfect effect may occur because of sound attenuation. As seen, the presence of TiO<sub>2</sub> particles in the reaction mixture increased partially the sonochemical degradation of hydrogel. These results are shown in Fig. 9 and Table 1. The observed phenomenon



**Fig. 9.** The plot of  $\Delta\eta^{1.8}-\Delta\eta_0^{1.8}$  versus the sonication time in sonocatalytic process, for different loading of catalyst at constant power of ultrasound (30W) at 25 °C.

**Table 1.** Initial hydrogel degradation rate constants in the presence of various values of catalyst loading and treatment conditions at 1 g/L concentration and 25 °C

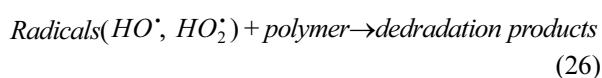
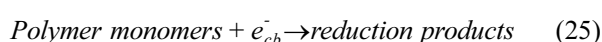
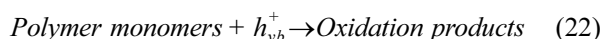
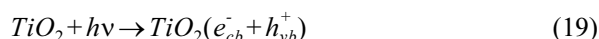
Process	US power (W)	UV power (W)	TiO <sub>2</sub> loading (g/L)	$k \times 10^9$ (mol <sup>1.7</sup> ·L <sup>-1.7</sup> ·min <sup>-1</sup> )
US	30	-	0.0	2.942
US	40	-	0.0	3.348
US	50	-	0.0	3.845
US	60	-	0.0	4.556
US	70	-	0.0	5.217
US	80	-	0.0	6.403
US	30	-	0.1	3.147
US	30	-	0.2	3.454
US	30	-	0.3	4.036
US	30	-	0.4	4.753
US+UV	30	16	0.0	3.000
US+UV	30	16	0.1	3.473
US+UV	30	16	0.2	4.461
US+UV	30	16	0.3	6.214
US+UV	30	16	0.4	8.377

can be explained on the basis of the adsorption and desorption characteristic of hydrogel on TiO<sub>2</sub> catalyst. At higher catalyst concentration, though the degradation rate in the solution increase, the rate of release of already adsorbed hydrogel also increases thereby giving lower overall degradation rate based on the free concentration of the hydrogel in the liquid.

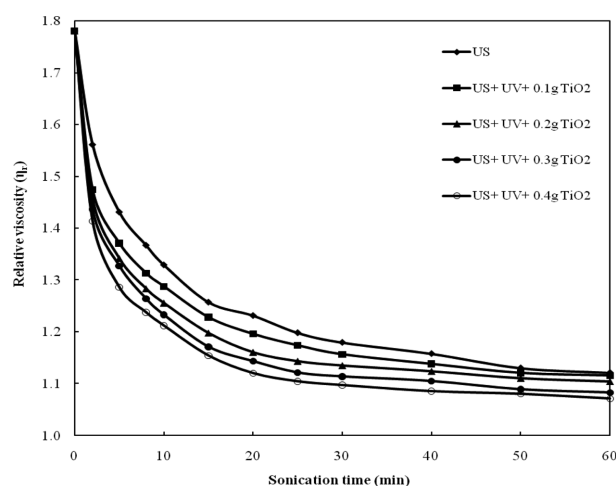
### Sonophotocatalytic (US+UV+TiO<sub>2</sub>) degradation of hydrogel

Concerning photo-assisted catalysis with titanium dioxide as the catalyst, electrons in conduction band ( $e_{cb}^-$ ) and holes in the valence band ( $h_{vb}^+$ ) are produced when the catalyst is irradiated with light energy higher than its band

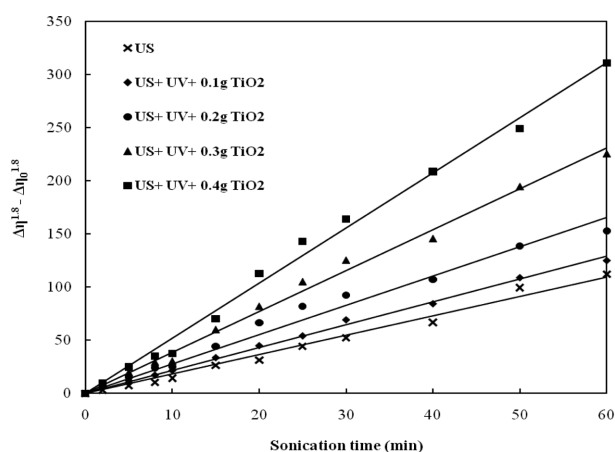
gap energy  $E_{bg}$  ( $h\nu \geq E_{bg}$ ), according to reactions (19)-(26):<sup>62</sup>



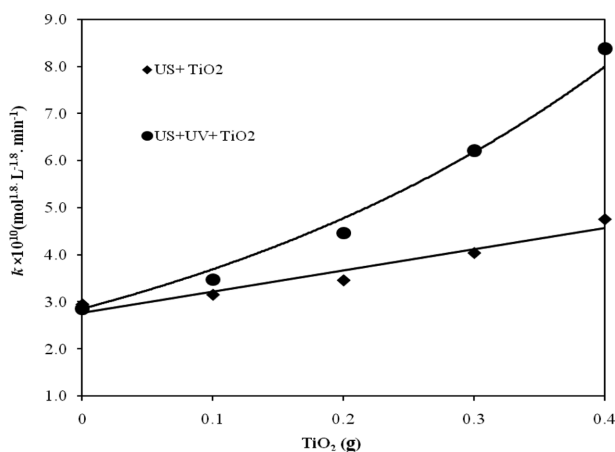
In further experiments, hydrogel degradation by means of simultaneous ultrasound and ultraviolet irradiation in the presence of  $TiO_2$  was studied and temporal changes in relative viscosity,  $\eta_r$ , and the rate constant of degradation reaction during sonophotocatalysis at 1 g/L initial concentration and various catalyst loadings under air are shown in Fig. 10 and 11, respectively. Rate constants for the various experiments are given in Table 1. As seen from Table 1, sonophotocatalytic degradation generally occurs faster than that during the respective individual processes at similar operating conditions. Comparison of reaction rate constants is presented in Fig. 12. As seen, the rate constants of degradation process in sonocatalysis method have a linear increase, but in the combined method (sonophotocatalysis) increase show an exponentially behavior. Taghizadeh *et al.* investigated the degradation of chitosan



**Fig. 10.** The relationship between  $\eta_r$  and sonication time in sonophotocatalytic process, for different loading of catalyst at constant power of ultrasound (30W) and ultraviolet (16W) at 25 °C.



**Fig. 11.** The plot of  $\Delta\eta^{1.8} - \Delta\eta_0^{1.8}$  versus the sonication time in sonophotocatalytic process, for different loading of catalyst at constant power of ultrasound (30W) and ultraviolet (16W) at 25 °C.



**Fig. 12.** Comparison of increase mode of rate constants with increasing the catalyst loading for different degradation techniques.

by means of ultrasound irradiation and its combination with heterogeneous ( $TiO_2$ ). We focused especially on the effects of the presence of catalyst  $TiO_2$  and concentration of catalyst and coupling photocatalysis with sonolysis on the degradation rates. It was observed that the use of  $TiO_2$  nanoparticles as catalyst in the presence of ultraviolet source in a constant threshold power of ultrasound (30 W) retrieved the ultrasound power weakness and improved the applied degradation process. The rate of chitosan degradation in mentioned conditions (sonophotocatalysis) increased with an increase in catalyst loading. The beneficial effect of coupling photocatalysis with sonolysis may be attributed to several reasons, namely: (i) increased production of hydroxyl radicals in the reaction mixture, (ii) enhanced mass transfer between the liquid phase and the catalyst

surface, (iii) catalyst excitation by ultrasound-induced luminescence which has a wide wavelength range below 375 nm<sup>63-66</sup> and (iv) increased catalytic activity due to ultrasound de-aggregating catalyst particles, thus increasing surface area.

## CONCLUSIONS

It has been demonstrated on hydrogel that treatment with a variety of output ultrasound powers in aqueous solution is an efficient procedure for reduction of molecular weight of hydrogel. Under sonolysis conditions, degradation is caused by OH radicals and mechanochemical effects. On the other hand, the use of TiO<sub>2</sub> 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 hydrogel degradation in mentioned conditions (sonophotocatalysis) increased with an increase in catalyst loading. In the case of sonocatalytic process, the rate of degradation process was not increased significantly in comparison with sonolysis technique. It was observed that the use of TiO<sub>2</sub> nanoparticles as catalyst in the presence of ultraviolet source in a constant threshold power of ultrasound retrieved the ultrasound power weakness and improved the applied degradation process.

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