ISSN : 0974 - 746X Volume 7 Issue 1

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 7(1), 2012 [32-38]

Sonophotocatalysis degradation of hydrogels

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Received: 19th December, 2011 ; Accepted: 12th January, 2012

ABSTRACT

One of the commercially important hydrogel based on acrylic acid and acryl amide, (acrylic acid-co-acryl amide) hydrogels have been degraded by means of ultrasound irradiation and its combination with heterogeneous (TiO_2). 24 kHz of ultrasound irradiation was provided by a sonicator, while an ultraviolet source of 16 W was used for UV irradiation. TiO_2 sonophotocatalysis led to complete (acrylic acid-*co*-acryl amide) hydrogels degradation with increasing catalyst loading, while, the presence of TiO_2 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_2 nanoparticles. TiO_2 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.

KEYWORDS

Sonolysis;
Sonophotocatalysis;
Viscosity;
Hydrogels;
Degradation.

INTRODUCTION

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[1], this technique has also been employed to degrade cellulose[2], polypeptides and polysaccharides[3], proteins[4], transition metal-coordinated polymers[5-7], and various organic polymers[8]. 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[9]. Beside the ultrasonic degradation method, the methods like photocatalysis[10] and microwave[11] are also important.

Polymers can be degraded thermally by pyrolysis in solution. Alternative energy reducing techniques required for degradation process are important, too. 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[12]. 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[13]. Scission generally occurs near the midpoint of a polymer chain, where solvodynamic forces are the greatest[14]. The rate of cleavage from ultrasonic irradiation of polymer solutions depends on several experimental factors, including temperature, solvent, and sonication intensity[15].

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[16, 17]. Application of high-intensity ultrasound to dispersions of carbohydrates can lead to depolymerization because of the intense mechanical and chemical effects associated with cavitation[18, 19]. Cavitational thermolysis may produce hydroxyl radicals and hydrogen atoms that can be followed by formation of hydrogen peroxide[20]. Some cavities exist only for one cycle of the sound field and collapse violently, while other are long-lived and oscillate around some equilibrium size[21].

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[22-26]. However, some researchers were investigated this combined method on degradation of some water soluble polymers[27, 28]. Nano TiO_2 as a photocatalyst has a great many advantages such as low cost, non toxicity, high catalyst efficiency, long-term stability etc[29, 30]. 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[31, 32] in this regard, researchers have used sono-photocatalysis in a variety of investigations. 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 sand sonophotocatalysis, concerning the effect of catalyst presence on degradation.

EXPERIMENTAL

Materials and procedure

The monomers acrylic acid (AA, Merck), 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[33, 34]. Degussa TiO_2 P-25 (anatase:rutile = 65:35, BET=$50m^2g^{-1}$) 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. Distilled and deionised water was solvent.

Reactions were carried out in a cylindrical 100ml Pyrex glass vessel. An ultrasound generator (Dr. Hielscher Ultrasonic Processor UP200 H) operating at a fix frequency of 24 kHz and a variable power output up to 100W nominal value, in aqueous media was used for sonication experiments. 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 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±1°C through the use of cooling water circulating inside the double-walled compartment, thus acting as cooling jacket. Different treatments were tested, namely: sonolysis (US), sonocatalysis ($US+TiO_2$) and combined sonolysis and photocatalysis ($US+UV+TiO_2$).

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 0.5mm. 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, η_r of hydrogel solution.

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

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

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:

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

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. 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:

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

Where M_0 is the initial total molar concentration of polymer. The total molar concentration is related to the number average molecular weight through:

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

Moreover, through[35].

$$M = \left[\frac{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}}{\sqrt{2}}\right]^{1/\alpha} \Delta\eta \qquad (6)$$

In addition, substitution Eq. (6) in (4) yields:

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = (1-n)\left[\frac{\sqrt{2}}{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}}\right]^{(1-n)/\alpha} kt \qquad (7)$$

Or

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = k't \qquad (8)$$

RESULTS AND DISCUSSION

Determination of degradation reaction order

By analogy with the chemical degradation, it is expected to take place the bond breakage occurs at the weakest links in the polymer backbone, but some works[35] 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 field is a non-random process; for example, the scission of polymer chains in solution occurs at a preferential position near the midpoint[36, 37]. Moore et al. approved this idea by an isotope labeling experiment on ultrasonic degradation of linear PEG[38]. 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[39].

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[40]. Although, a number of different rate models have been proposed for the degradation of polymers, but in this study a simple model was employed via viscometry, Using Eq. (6). 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 Figure 1. Previous studies were proved that with an increase in concentration, the rate constant, *k*, was decreased obviously[41]. At higher concentrations, the so-

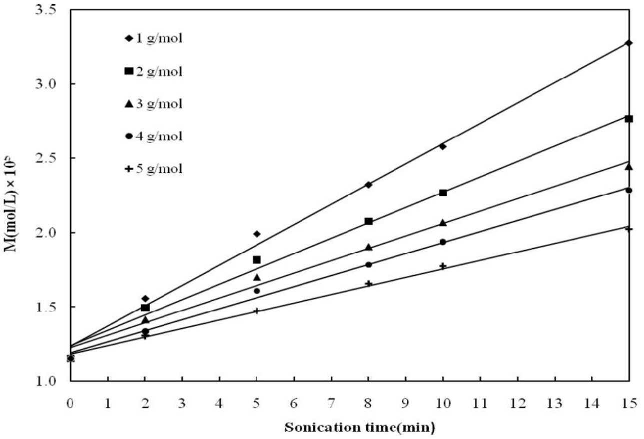

Figure 1 : Variation of molar concentration with sonication time for different concentration of hydrogel at 25°C.

lution viscosity increases. An increase in viscosity raises the cavitation threshold. This 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.

The slopes of plots give the initial rate of degradation using Eq.3, the plot of lnV versus ln[M] are linear and it is shown in Figure 2. The slope of curve is -0.8, which suggest the order of reactions with respect to molar concentration.

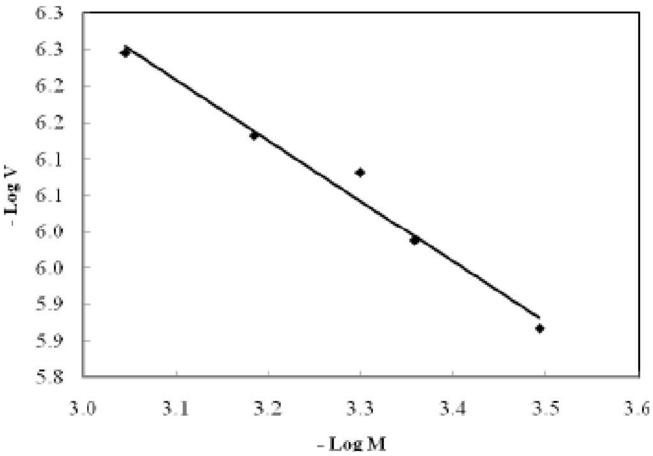

Figure 2 : The plot of lnV versus lnM for degraded hydrogel at 25°C.

From substitution of the value of "*n*" in Eq.8, we obtain the following:

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

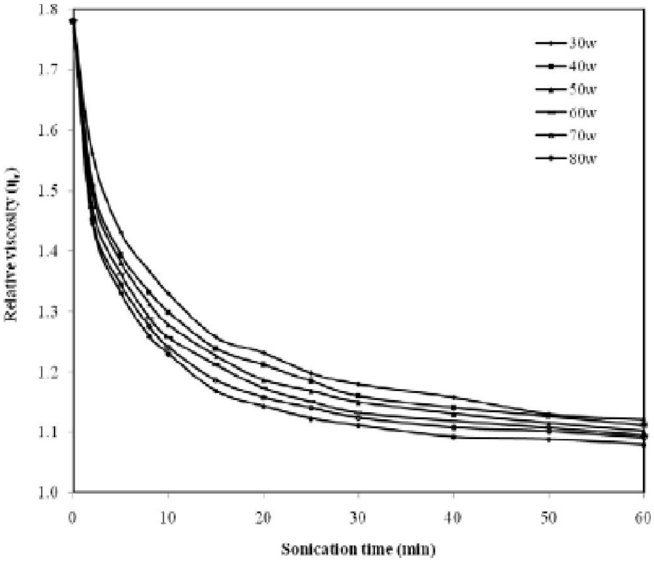

Figure 3 : The relationship between η_r and t in sonication, for different powers of ultrasound at 25°C.

Sonolytic (US) and sonocatalytic (US+TiO_2) degradation

Figure 3 shows the effect of increasing changing ultrasound power on relative viscosity (η_r) of hydrogel solution as a function of the sonication time at 1 g/L initial hydrogel concentration under air. As seen, η_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:

$$H_2O \rightarrow H^{\bullet} + OH^{\bullet} \qquad (16)$$

(ii) the bubble–liquid interface where hydroxyl radicals 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:

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \qquad (17)$$

$$H_2O_2 + H^{\bullet} \rightarrow H_2O + OH^{\bullet} \qquad (18)$$

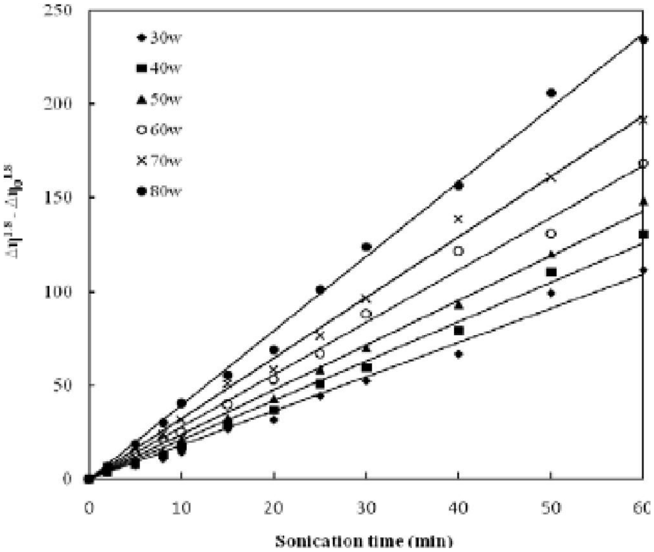

Figure 4 : The plot of $\Delta\eta^{1.8}$ - $\Delta\eta_0^{1.8}$ versus the sonication time in sonication, for different power of ultrasound at 25°C.

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[39, 42]. The plots of $\Delta\eta^{1.8} - \Delta\eta_0^{1.8}$ versus sonication time for different powers of ultrasound are presented in Figure 4. The apparent degradation rate constant, *k£½* defined in Eq. 8, can be estimated from the slopes of the plots in Figure 4.

Effect of presence of catalyst TiO_2 and concentration of catalyst in constant power of ultrasound (30W) on the degradation rates has also been investigated. Figure 5(left) shows the change in η_r versus sonication time in the sonocatalytic process (US+TiO_2). 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_2 particles in the reaction mixture increased partially the sonochemical degradation of hydrogel. These results are shown in Figure 5(right). The observed phenomenon can be explained on the basis of the adsorption and desorption characteristic of hydrogel on TiO_2 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.

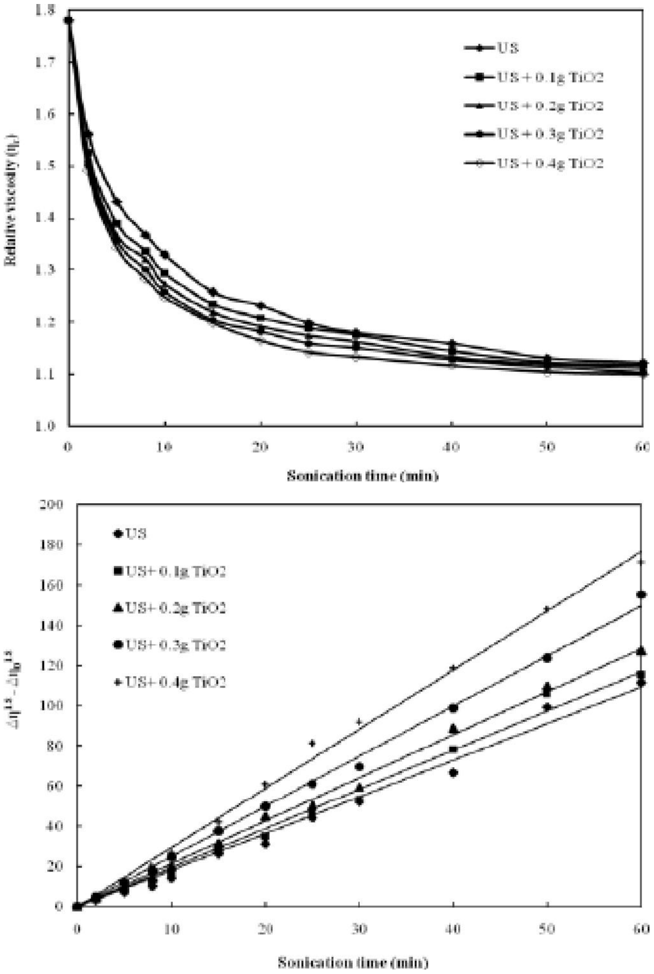

Figure 5 : The relationship between η_r and t(up) and the plot of $\Delta\eta^{1.8} - \Delta\eta_0^{1.8}$ versus t(down) in sonication, for different loading of catalyst at 30W ultrasound and 25°C.

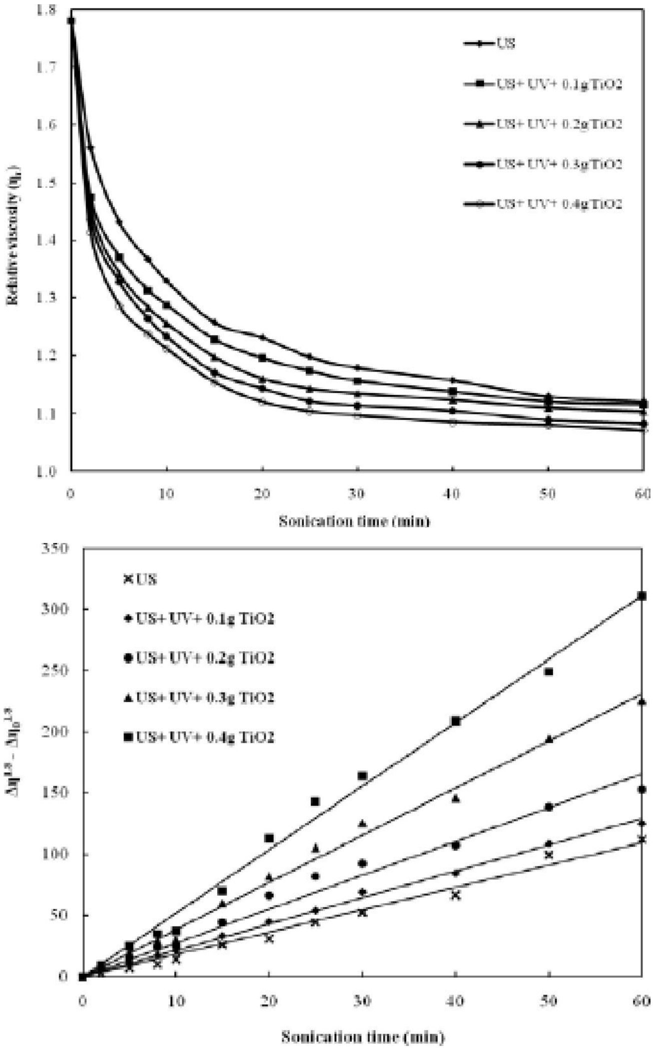

Figure 6 : The relationship between η_r and t (up) and the plot of $\Delta\eta^{1.8} - \Delta\eta_0^{1.8}$ versus t (down) in sonication, for different loading of catalyst at 30W ultrasound, 16W ultraviolet and 25°C.

Sonophotocatalytic (US+UV+TiO_2) 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} ($h\nu \geq E_{bg}$)[43]. 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, η_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 Figure 6.

Comparison of reaction rate constants is presented in Figure 7 shows Sonophotocatalytic degradation generally occurs faster than that during the respective individual processes at similar operating conditions. 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.

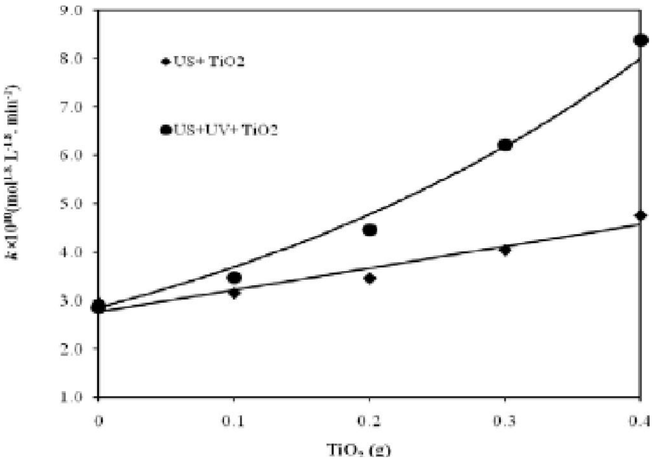

Figure 7 : Comparison of increasing of rate constants with increasing the catalyst loading for different degradation techniques.

Taghizadeh et al. investigated the degradation of chitosan 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 (sonophotoca talysis) 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[44-47] and (iv) increased catalytic activity due to ultrasound de-aggregating catalyst particles, thus increasing surface area.

ACKNOWLEDGEMENTS

This work is financially supported by Islamic Azad university research port. The authors would like to thank Mr. Mahdi Siahpoush, Mr. Tofigh Taherkhani, Mr. Mahdi Ghorbani and Mr. Ali Taherkhani for their collaboration throughout this project.

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