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Sonophotocatalytic degradation of poly (vinyl pyrrolidone) (PVP) in the presence of TiO_2 nanoparticles

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Abstract

The degradation of poly (vinyl pyrrolidone) (PVP) by means of ultrasound irradiation and its combination with heterogenous photocatalysis (TiO_2 nanoparticles) was investigated. Emphasis was given on the effect of additive on degradation rate constants. 24 kHz of ultrasound irradiation was provided by a sonicator, while an ultraviolet source of 30 W was used for UV irradiation. To increase the efficiency of degradation process, degradation system was combined with TiO_2 nanoparticles (0.1-0.6 g L^{-1}) in the presence of UV irradiation. Sonophotocatalytic process led to complete PVP degradation in 150 min with the rate increasing with increasing catalyst loading. Sonophotocatalysis in the presence of nanoparticles was always faster than the respective individual processes. A synergistic effect between ultrasound and ultraviolet irradiation in the presence of TiO_2 nanoparticles was suggested. The average molecular weight of ultrasonicated PVPs was determined by measurements of intrinsic viscosity of samples.

Keywords: Poly (vinyl pyrrolidone); Ultrasonic degradation; Viscosity; Molecular weight.

1. Introduction

The ultrasonic polymer degradation has several unique characteristics that make it interesting both from practical and theoretical viewpoints [1]. High-intensity ultrasonic treatment can be applied to degrade polymers and to facilitate emulsifying and cleaning processes in homogenous liquid phase [2]. The degradation of several polymers such as polystyrene [3], polyvinyl acetate [4], polypropylene [5], low-density poly ethylene [6], poly(methylmethacrylate) [7], dextran [8], hydroxy propyl cellulose [9], carboxymethyl cellulose [10], polyacrylamide [11] and poly(caprolactone) [12] has been investigated. These works have been summarized in a review paper by Price [13].

Poly vinyl pyrrolidone (PVP) is a unique polymer as it provides a remarkable combination of properties that no other molecule is yet able to match. PVP offers a unique variety of properties, such as good initial tack, transparency, chemical and biological inertness, very low toxicity as well as high media compatibility and cross linkable flexibility [14]. These functions undoubtedly depend upon not only their chemical structure but also the molecular weight. Therefore, it is necessary to produce different molecular weights of PVP [15]. High-intensity ultrasonic treatment can be applied to degrade polymers and to facilitate emulsifying and

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cleaning processes. 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 [16]. Cavitational thermolysis may produce hydroxyl radicals and hydrogen atoms that can be followed by formation of hydrogen peroxide [17]. In recent years, the simultaneous use of ultrasound and photocatalysis, i.e. the so-called sonophotocatalysis has been studied regarding process efficiency to degrade various organics and polymers [18].

In recent years, the simultaneous use of ultrasound and photocatalysis, i.e. the so-called sonophotocatalysis has been studied regarding process efficiency to degrade various organics and dyes [19–24]. Among semiconductor materials, TiO_2 powders have been widely studied as the photocatalyst to treat pollutants due to its strong oxidizing power, non-toxic, and low cost [25]. Many studies have been reported on combining ultrasonic with UV light irradiation in the presence of TiO_2 and sonophotolysis shows excellent remove ability [26–29]. This process provides an excellent opportunity to reduce reaction time without the need for extreme physical conditions [30].

Concerning photocatalysis 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 (1)–(8) [31]:

$$TiO_2 + h\nu \rightarrow TiO_2(e_{cb}^- + h_{vb}^+) \quad (1)$$

$$h_{vb}^+ + H_2O \rightarrow H^+ + HO^\bullet \quad (2)$$

$$h_{vb}^+ + HO^- \rightarrow HO^\bullet \quad (3)$$

$$polymer\ monomers + h_{vb}^+ \rightarrow Oxidation\ products \quad (4)$$

$$e_{cb}^- + O_2 \rightarrow O_2^{\bullet -} \quad (5)$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet \quad (6)$$

$$Polymer\ monomers + e_{cb}^- \rightarrow reduction\ products \quad (7)$$

$$Radicals(HO^\bullet, HO_2^\bullet) + polymer \rightarrow dedradation\ products \quad (8)$$

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

2. Experimental

2.1. Materials

Polyvinyl pyrrolidone (PVP) with weight-average molecular weight 1300000 kDa was purchased from Across Co. Ltd. Degussa TiO_2 P-25 (anatase:rutile = 65:35, BET: $50 m^2 g^{-1}$) 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. PVP solution preparation

PVP solutions containing 5 g L^{-1} PVP were prepared. The solutions were stirred overnight to ensure complete solubilisation of the PVP molecules, and then filtered to remove any impurities and 100 mL samples were immediately sonicated.

2.2.2. Experimental setup and procedure

Reactions were carried out in a cylindrical 100ml 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 probe 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 was a 30 W UV lamp, which emits in the 200-300 nm wavelength range with a maximum at 254 nm. The vessel was fed with a 100ml PVP 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 through 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 and for the experiments in the presence of TiO_2, a concentration range of 0.1-0.6 g L^{-1} of TiO_2 nanoparticles was used.

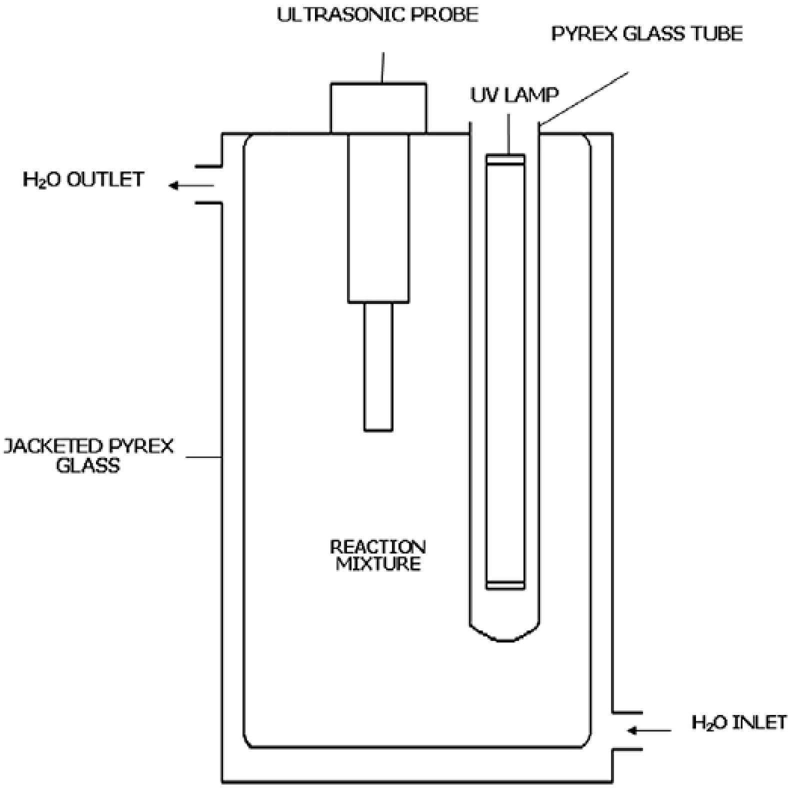

Fig. 1. Schematic of the experimental setup.

2.3. Viscosity measurements

The intrinsic viscosities of the original PVP and its degraded solutions at 25°C were measured using the capillary viscometer (Setavic Kinematic viscometer). Efflux times were measured for PVP 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 PVP solution.

$$\eta_r = \frac{t}{t_0}, \eta_{sp} = \eta_r - 1 \tag{9}$$

The intrinsic viscosity [η] values can be related to the specific viscosity, η_{sp}, and relative viscosity, η_r, by the Huggins and Kramer equations [32]. The conditions used in this work ($\alpha = 0.55$ and $k = 6.67\times10^{-5}$ l g^{-1}) were adopted on the basis of previous findings in the literature [33].

2.4. 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 [9]:

$$R = \frac{dM}{dt} = kM^n \tag{10}$$

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. It is noted that solution concentration (g L^{-1}) is constant and the total molar concentration (mol/L) increases during the degradation of polymer. The solution of differential Eq. (10) is:

$$M^{1-n} - M_0^{1-n} = (1-n)kt \tag{11}$$

where M_0 is the initial total molar concentration of polymer. The total molar concentration is related to the number average molecular weight through [32]

$$M = \frac{C}{M_n} \tag{12}$$

Moreover, viscosity average molecular weight, M_v, is related to the number average molecular weight, M_n, through [10].

$$M_v = [(1+\alpha)\Gamma(1+\alpha)]^{-\frac{1}{\alpha}} M_n \tag{13}$$

where, $\Gamma(1+\alpha) = \int_0^\infty e^{-t} t^\alpha dt$, M_v is related to the intrinsic viscosity, [η], through Marck-Houwink equation:

$$M_v = \left(\frac{[\eta]}{K}\right)^{1/\alpha} \tag{14}$$

where α and k are the Mark–Houwink constants.

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

$$\frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2 C \tag{15}$$

$$\frac{Ln\eta_r}{C} = [\eta] + (K' - 0.5)[\eta]^2 C \tag{16}$$

from Eq. (15) and (16), intrinsic viscosity is:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - Ln\eta_r)}}{C} \tag{17}$$

Substitution of Eq. (17) in (13) and Eq. (14) in (13) yields

$$M_n = \left[\frac{\sqrt{2(\eta_{sp} - Ln\eta_r)}}{(1+\alpha)\Gamma(1+\alpha)KC} \right]^{1/\alpha} \tag{18}$$

finally, the substitution Eq. (18) in (12) yields:

$$M = \left[\frac{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}}{\sqrt{2}} \right]^{1/\alpha} \Delta\eta \tag{19}$$

In addition, substitution Eq. (19) in (11) yields:

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = (1-n)\left[\frac{\sqrt{2}}{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}} \right]^{(1-n)/\alpha} kt \tag{20}$$

or

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = k't \tag{21}$$

3. Results and discussion

3.1. Determination of reaction order of degradation of PVP

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 [34, 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 [36-38]. 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 [39].

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 [40]. 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 [41]. Although, a number of different rate models have been proposed for the degradation of polymers [42], 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 PVP solution within the degradation process was suggested.

3.2. Sonocatalytic (US+TiO_2) degradation of PVP

A number of different rate models have been proposed for the degradation of polymers [43, 44], but in this study a simple model was employed via viscometry, Using Eq. (20). The plot of lnR versus ln[M] presented in Fig. 2 are linear and the slope of curve is -0.5, which suggest the order of reactions with respect to total molar concentration of polymer. From substitution of the value of "*n*" in Eq.21, we obtain the following:

$$\Delta\eta^{1.5} - \Delta\eta_0^{1.5} = k't \qquad (22)$$

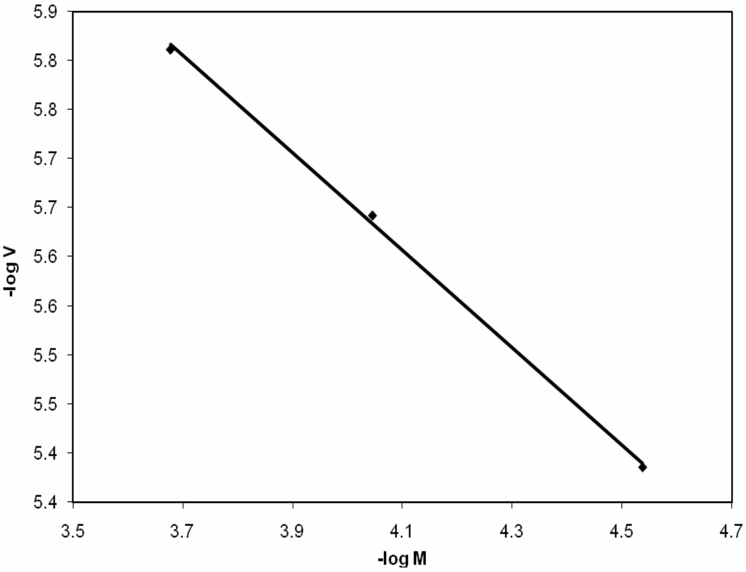

Fig. 2. The plot of lnR versus lnM for degraded PVP at 25 ˚C.

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 [45-47]:

$$H_2O \rightarrow H^\bullet + OH^\bullet \qquad (23)$$

(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:

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \qquad (24)$$

$$H_2O_2 + H^\bullet \rightarrow H_2O + OH^\bullet \qquad (25)$$

Given that PVP is a non-volatile and soluble polymer, 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 [48].

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. Fig. 3 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 [49-51].

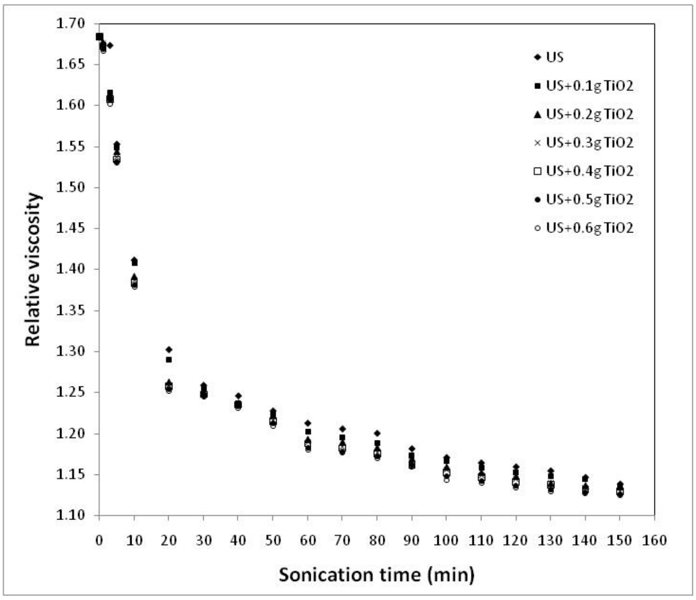

Fig. 3. The relationship between η_r and sonication time in sonocatalytic process, for different loading of catalyst at constant power of ultrasound (30W) at 25 ˚C.

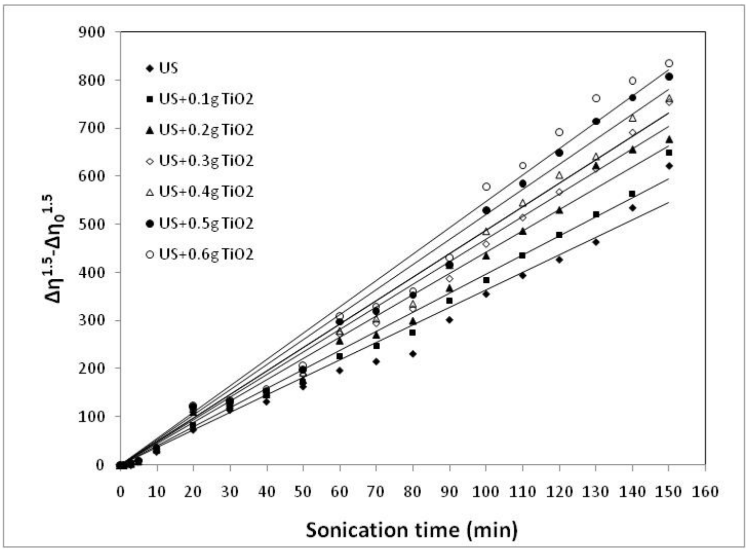

Fig. 4. The plot of $\Delta\eta^{1.5}-\Delta\eta_0^{1.5}$ versus the sonication time in sonocatalytic process, for different loading of catalyst at constant power of ultrasound (30W) at 25˚C.

As seen, the presence of TiO_2 particles in the reaction mixture increased partially the sonochemical degradation of PVP. These results are shown in Fig. 4 and Table 1. The observed phenomenon can be explained on the basis of the adsorption and desorption characteristic of PVP on TiO_2 catalyst. At higher catalyst concentration, though the degradation rate in the solution increase, the rate of release of already adsorbed PVP also increases thereby giving lower overall degradation rate based on the free concentration of the PVP in the liquid.

Table 1
Rate constants corresponding to the sonocatalytic and sonophotocatalytic degradation at 5 g L^{-1} concentration and 25 ˚C.

Process	TiO_2 loading (g/L)	$k\times10^5$ ($mol^{1.5}.L^{-1.5}.min^{-1}$)
US	0.00	4.073
US	0.10	4.440
US	0.20	4.952
US	0.30	5.253
US	0.40	5.470
US	0.50	5.831
US	0.60	6.138
US+UV	0.10	4.700
US+UV	0.20	5.007
US+UV	0.30	5.387
US+UV	0.40	6.594
US+UV	0.50	7.360
US+UV	0.60	8.356

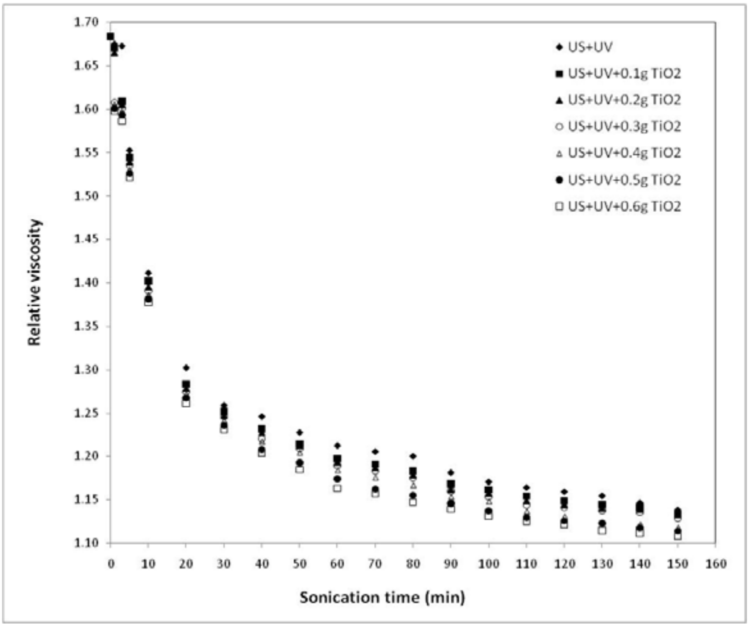

Fig. 5. The relationship between η_r and sonication time in sonophotocatalytic process, for different loading of catalyst at constant power of ultrasound (30W) and ultraviolet (30W) at 25˚C.

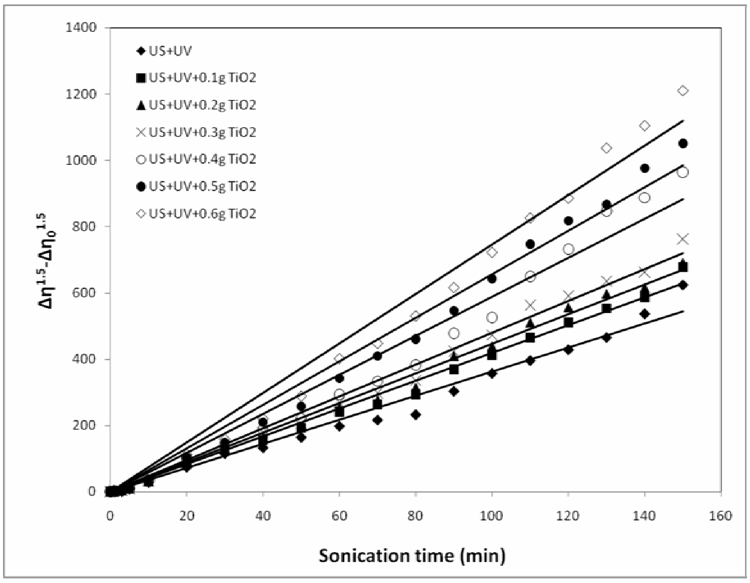

Fig. 6. The plot of $\Delta\eta^{1.5} - \Delta\eta_0^{1.5}$ versus the sonication time in sonophotocatalytic process, for different loading of catalyst at constant power of ultrasound (30W) and ultraviolet (30W) at 25°C.

3.3. Sonophotocatalytic (US+UV+TiO_2) degradation of PVP

In further experiments, PVP 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 5 g L^{-1} initial concentration and various catalyst loadings under air are shown in Fig. 5 and 6, respectively. The reaction rate constants for applied degradation methods (sonocatalytic, and sonophotocatalytic) are summarized in Table 1. As seen from these data, 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. 7.

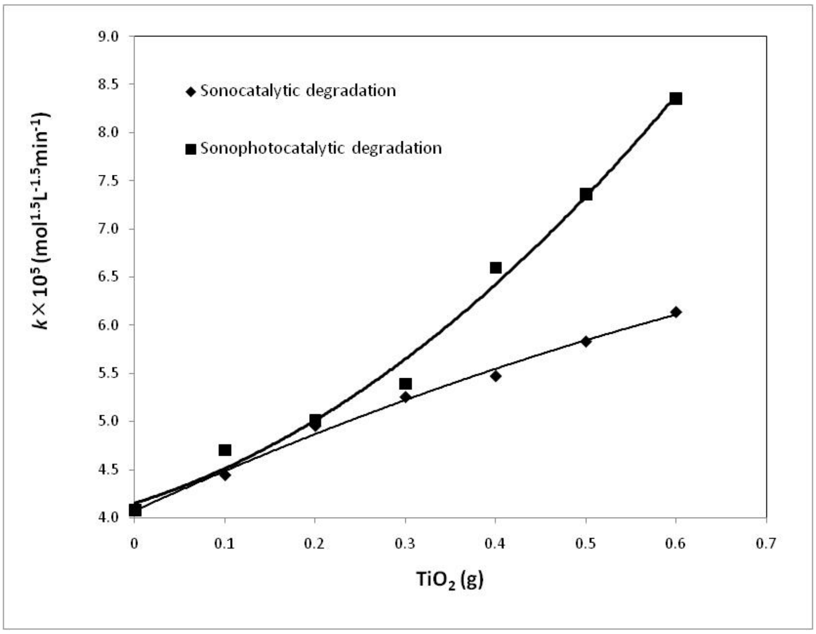

Fig. 7. Comparison of increase mode of rate constants with increasing the catalyst loading for different degradation techniques.

As seen, the rate constants of degradation process in sonocatalysis methods has a linear increase, but in the combined method (sonophotocatalysis) increase show an exponentially behavior.

4. Conclusion

It has been demonstrated on PVP the use of TiO_2 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 PVP 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.

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