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Optimization of Radiolytic Degradation of Poly(vinyl alcohol)

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Ionizing radiation-induced degradation of poly(vinyl alcohol) (PVA) in aqueous solutions was investigated. Experimental results demonstrate that PVA degradation was initiated by attack of $\cdot$OH and H$\cdot$, followed by random chain scission and formation of ketones, enols, aldehydes, acids, etc. Complete mineralization of PVA could be achieved providing that a sufficient radiation dose was supplied. The collaborative effects of initial PVA concentration, pH of the solution, and H_2O_2 dosage with irradiation dose rate on PVA degradation efficiency were evaluated by using a response surface methodology. Lower initial PVA concentrations, higher dose rates, and acidic or alkaline conditions were found to be favorable for PVA degradation. At a certain dose rate, there was an optimal H_2O_2 dosage to facilitate the PVA degradation. In addition, the presence of O_2 was beneficial for PVA degradation. Tentative interpretation and theoretical analysis on these effects are presented.

Introduction

Poly(vinyl alcohol) (PVA), a well-known water-soluble polymer, is widely used as warp-sizing and paper-coating agents, adhesives, and films. The global production of PVA is estimated as 650 000 tons per year, and the large amount of discharged PVA from industrial effluents has become a significant pollution problem.[1] Conventional biological technologies are not efficient for the degradation of PVA because the PVA-degrading capacity of most microorganisms is very limited.[1−5] By use of acclimated microorganisms, only about 40% of PVA was mineralized after a 48-day incubation.[2] Furthermore, much foam is formed when PVA-rich wastewater is treated in biological reactors, making it very difficult, or even in some cases impossible, for the biological processes to operate steadily and to achieve satisfactory results.[6] Therefore, effective methods for the removal or pretreatment of PVA from wastewaters need to be pursued.

Direct chemical oxidation,[7] photocatalytic degradation,[8,9] wet air oxidation,[10] and ionizing radiolysis have been investigated for the removal of PVA.[11−16] Among these methods, ionizing radiation has proven to be a promising approach. As a consequence of the interaction between ionizing radiation and aqueous solutions, several species, e.g., $\cdot$OH, e_{aq}^-, and H$\cdot$, are formed. These species, especially $\cdot$OH, are highly reactive and sensitive to their surroundings, such as the composition of a solution and the atmosphere.

In our previous work the radiolytic degradation of PVA in aqueous solutions was found to be influenced by several factors, such as radiation dose rate, initial PVA concentration, the solution pH, additives, and atmosphere.[15] Some preliminary results have been obtained through a conventional "change-one-factor-at-a-time" method. This is an experimentation method in which a single factor is varied while all other factors are kept fixed at a specific set of conditions. Its main disadvantage is excess number of experiments and unreliable results. To resolve this problem, the response surface methodology (RSM) has been proposed to determine the influences of individual factors and their interactive influences.[17] The RSM is a statistical technique for designing experiments, building models, evaluating the effects of several factors, and searching optimum conditions for desirable responses. With RSM, the collaborative effects of potential influencing parameters on radiolytic degradation of PVA can be evaluated with a limited number of planned experiments. Therefore, in this work, a response surface methodology was employed for the optimal experimental design for PVA radiolytic degradation.

Materials and Experimental Methods

Materials. PVA with a 1750 ± 50 average degree of polymerization (DP), boric acid, iodine, potassium iodide, sodium hydroxide, perchloric acid, hydrogen peroxide (H_2O_2), 2-propanol (*i*-PrOH), and *tert*-butyl alcohol (*t*-BuOH) were purchased from Shanghai Chemical Reagent Company. All of them were of analytical reagent grade and were used for experiments without further purification. Doubly distilled water was used throughout the experiments.

Irradiation Experiments. A ^{60}Co γ source with a radioactivity of about 60 kCi (2.22×10^{15} Bq) was used for irradiation. The dose rates varied with the distance between ^{60}Co column and dose sites and were determined by means of a Fricke dosimeter using $G(Fe^{3+}) = 15.6$. The G value, viz., radiation chemical yield, is defined as the number of formed or decomposed molecules per 100 eV absorbed energy. For conversion into SI units, multiplication of the G value by 0.1036 results in a $G(x)$ value in μmol J^{-1}. The samples were irradiated in 100-mL Pyrex glass vessels at certain dose rates and sampled at certain time intervals. All experiments performed were conducted in duplicate or triplicate at ambient temperatures.

Analytical Methods. Quantitative determination of PVA in aqueous solutions was carried out by using a UV−vis spectrophotometer (UV751-GD, Shanghai Analytical Instrument Co.) following the procedure described by Finley.[18] An aliquot of prepared PVA solution was transferred into a 50-mL volumetric flask and

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diluted with water to approximately 20 mL. It was then treated with 20 mL of boric acid solution (30 g L^{-1}). Finally, 5 mL of iodine solution (7.6 g of iodine dissolved in a concentrated solution of 15 g of potassium iodide and diluted to 1 L with distilled water) was added, and the mixture was diluted to 50 mL. The absorbance of the solution was measured at 690 nm against a reference solution prepared by diluting 20 mL of boric acid and 5 mL of iodine solution to 50 mL. A calibration curve was obtained by plotting the absorbance value at 690 nm against the PVA concentration. The PVA degradation efficiency is calculated based on such an absorbance determination. The average DP values of PVA prior to and after irradiation were determined using an Ubblehode meter according to the procedure proposed by Finch.[19] The pH of the solutions was adjusted with NaOH or HClO$_4$ solutions and was determined using a pH meter (pHS-25, Shanghai Scientific Instrument Co.). The gaseous products in sealed sample vessels after γ-ray irradiation were determined by using a gas chromatograph (model SP-6800A, Lunan Instrument Co.) equipped with a thermal conductivity detector and a 2 m stainless column packed with 5-Å molecular sieve. The temperatures of injector, column, and detector were kept at 100, 60, and 105 °C, respectively. Argon was used as the carrier gas at a flow rate of 30 mL min^{-1}. The total organic carbon (TOC) concentration was determined using a TOC analyzer (TOC-V$_{CPN}$, Shimadzu Co.).

Computational Procedure. A response surface methodology was applied to describe the collaborative influences of two factors on PVA degradation efficiency. The response variable was fitted by a second-order model in the form of a quadratic polynomial equation[17]

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum\sum b_{ij} X_i X_j \quad (1)$$

where Y is the associated response, X_i and X_j are input variables which influence the response variable Y, b_0 is the intercept term, b_i is the ith linear coefficient, b_{ii} is the quadratic coefficient, and b_{ij} is the ijth interaction coefficient.

Since different variables are usually expressed in different units and/or have different limits of variation, the significance of their effects on response can only be compared after they are coded. In development of the regression equation, the test variables were coded according to the equation

$$X_i = \frac{U_i - U_i^0}{\Delta U_i} \quad (2)$$

where X_i is the coded value of the ith independent variable, U_i is the uncoded value of the ith independent variable, U_i^0 is the uncoded value of the ith independent variable at the center point, and ΔU_i is the step change value.

MATLAB software (version 6.1) was used for regression and response surface drawing. The model fit and regression significance were assessed by Spearman's rank test, including correlation coefficient (R) and its associated probability value (P).

Results and Discussion

Radiolytic Degradation of PVA. A PVA solution with an initial concentration of 200 mg L^{-1} was irradi-
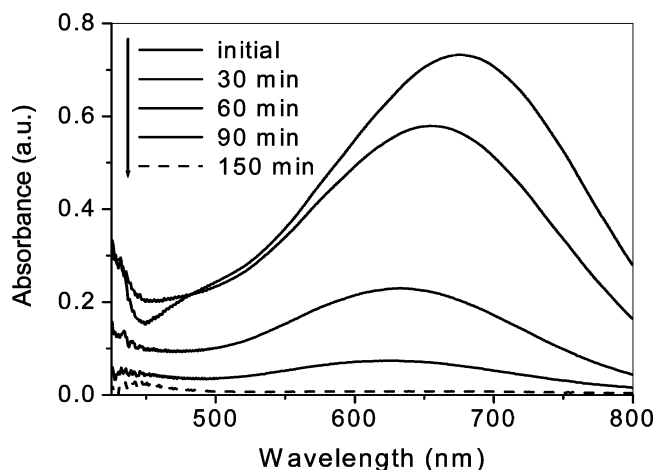

Figure 1. Absorption spectra of PVA–iodine complex versus irradiation time (D_r, 19.6 Gy min^{-1}; [PVA], 200 mg L^{-1}).
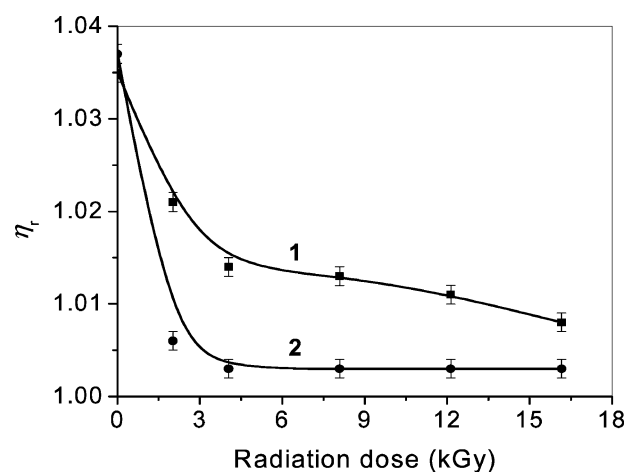

Figure 2. The relative viscosity of PVA solutions as a function of radiation dose ([PVA], 500 mg L^{-1}): line 1, original solution; line 2, with addition of 5 mmol L^{-1} H$_2$O$_2$.

ated at a dose rate of 19.6 Gy min^{-1}. The optical density of the PVA–iodine complex was significantly reduced, and the absorption band gradually shifted to shorter wavelength with increasing irradiation time (Figure 1). These might be attributed to the dependence of both molar extinction coefficient and absorption maxima of the PVA–iodine complex upon the molecular weight. Another reason for these phenomena could be the change of structure units in PVA chain due to radiolytic degradation. The interpretations above lie in the formation of the PVA–iodine complex. PVA gives a characteristic color reaction with iodine, which is used as the basis for the quantitative determination of PVA.[19] This reaction is affected by the degree of polymerization of PVA and by the presence of different monomer units in the polymer chain.[19] The color intensity decreases with increasing 1,2-glycol content and becomes almost zero when the 1,2-glycol content exceeds 5 mol %. A sequence of about 120 units of 1,3-glycol structures is necessary for the formation of the PVA–iodine complex. As shown in Figure 1, after 150 min of irradiation at a dose rate of 19.6 Gy min^{-1}, no PVA–iodine complex was observed, indicating the chain scission of PVA.

The reduction of the relative viscosity (η_r) of PVA aqueous solutions as a function of radiation dose, as shown in Figure 2, provides further support for the cleavage of polymer chains due to γ-ray irradiation. Addition of 5 mmol L^{-1} H$_2$O$_2$ significantly enhanced the
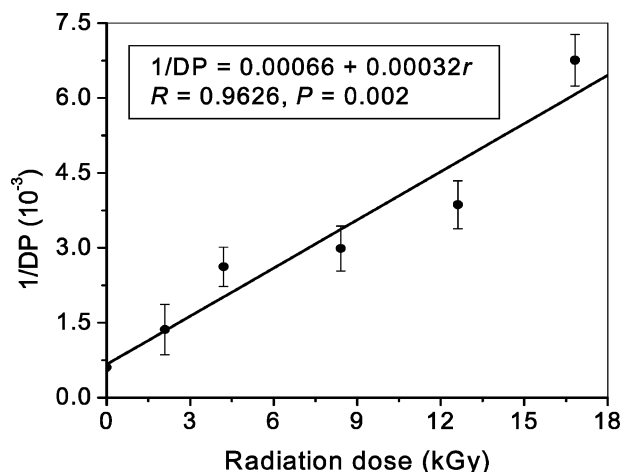
Figure 3. The reciprocal of DP versus radiation dose, with $R = 0.9626$ and $P = 0.002$. ([PVA], 500 mg L^{-1}; D_r, 55.7 Gy min^{-1}.)

reduction of η_r. With the equation between η_r and DP described by Finch,[19] the DP values prior to and after irradiation were calculated. A linear relationship was found between the reciprocal of DP and the radiation dose (r), as illustrated in Figure 3. This suggests that PVA radiolytic degradation followed the random scission mode proposed by Charlesby[16]

$$1/\bar{M}_v = (1.04 \times 10^{-6})(r + r_0)G \qquad (3)$$

where $\bar{M}_v$ is the viscosity-average molecular weight after degradation, r_0 is the "virtual" radiation dose required to fracture an infinitely long chain to give the initial molecular weight distribution, and G is the number of main chain scissions per 100 eV of energy absorbed.

The mineralization extent of PVA was evaluated by TOC determination. A sample with an initial PVA concentration of 250 mg L^{-1} was irradiated at a dose rate of 100 Gy min^{-1}. No TOC reduction was observed after irradiation up to a dose of 60 kGy. However, after absorption of a dose of 270 kGy, more than 75% of the TOC was reduced. This result suggests that complete mineralization of PVA could be achieved by utilizing ionizing radiation, but it is costly. Therefore, it might be more reasonable to employ ionizing radiation as a pretreatment method for the removal of PVA, considering the high chain scission efficiency of radiolysis.

Mechanisms of PVA Radiolytic Degradation. When dilute PVA aqueous solutions are irradiated, the energy of the ionizing radiation is principally absorbed by water, resulting in the formation of several reactive primary species and molecular products as shown in the following

$$H_2O \rightsquigarrow {}^\bullet OH\ (2.8),\ e_{aq}^-\ (2.7),\ H^\bullet\ (0.6),$$
$$H_2\ (0.45),\ H_2O_2\ (0.72)$$
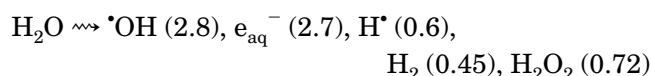
The values in parentheses are the yields of these species (G values) at pH 7. These species are sensitive to the nature of solvent, such as acid and base properties, dissolved gases, and presence of radical scavengers and other additives, as presented in Table 1. In O$_2$-saturated solutions, the reductive species H$^\bullet$ and e_{aq}^- formed will be converted to oxidative peroxyl radicals, HO$_2^\bullet$ and O$_2^{\bullet-}$, due to reactions 1 and 2. In strong acidic solutions, the e_{aq}^- formed will be converted to H$^\bullet$ as shown in reaction 3. On the contrary, when the solution

Table 1. Reactions in Irradiated Aqueous Solutions

no.	reaction	rate constant (L mol^{-1} s^{-1})	ref
1	$H^\bullet + O_2 \rightarrow HO_2^\bullet$	1.2×10^{10}	20
2	$e_{aq}^- + O_2 \rightarrow O_2^{\bullet-}$	1.9×10^{10}	20
3	$e_{aq}^- + H^+ \rightarrow H^\bullet$	2.3×10^{10}	20
4	$H^\bullet + OH^- \rightarrow e_{aq}^-$	2.2×10^7	20
5	$H_2O_2 + e_{aq}^- \rightarrow {}^\bullet OH + OH^-$	1.2×10^{10}	21
6	$H_2O_2 + H^\bullet \rightarrow H_2O + {}^\bullet OH$	5.1×10^7	22
7	$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HO_2^\bullet$	2.7×10^7	20
8	$t\text{-BuOH} + {}^\bullet OH \rightarrow {}^\bullet CH_2C(CH_3)_2OH + H_2O$	6.0×10^8	20
9	$i\text{-PrOH} + {}^\bullet OH \rightarrow (CH_3)_2{}^\bullet COH + H_2O$	1.9×10^9	20
10	$i\text{-PrOH} + H^\bullet \rightarrow (CH_3)_2{}^\bullet COH + H_2$	7.4×10^7	20

Table 2. Degradation Efficiency of PVA under Various Conditions (initial PVA concentration, 250 mg L^{-1}; dose rate, 40.6 Gy min^{-1}; irradiation time, 1 h)

additive (50 mmol L^{-1})	degradation (%)	
	O$_2$ saturated	N$_2$ saturated
i-PrOH	1	0
t-BuOH	2	8
H$_2$O$_2$	42	43
a	66	62
H$_2$O$_2^b$	100	c

[a] No additive. [b] 5 mmol L^{-1}. [c] Not determined.

is strong alkaline, H$^\bullet$ will be converted to e_{aq}^- as shown in reaction 4. The presence of H$_2$O$_2$, on one hand, can increase the yields of $^\bullet$OH owing to reactions 5 and 6. On the other hand, H$_2$O$_2$ can consume $^\bullet$OH as shown in reaction 7. Both t-BuOH and i-PrOH are $^\bullet$OH radical scavengers. The carbon-centered radicals formed in reactions 8 and 9 are less reactive, having a negligible effect on the other substances dissolved in solutions. As shown in reaction 10, i-PrOH can scavenge H$^\bullet$ as well.

All the reactions summarized in Table 1 form a complicated reaction system. By selectively generating or scavenging one or several reactive species from water radiolysis, one can elucidate the roles of the individual reactive species in substrate degradation. To clarify which species plays the key role in PVA degradation, experiments were carried out with addition of several radical scavengers and with saturation of O$_2$ or N$_2$. The results are summarized in Table 2.

In N$_2$-saturated solution with an initial PVA concentration of 250 mg L^{-1} and with 50 mmol L^{-1} of i-PrOH added, no PVA degradation was detected after 1 h of irradiation at a dose rate of 40.6 Gy min^{-1}. This indicates that hydrated electrons, as the predominant species in the solution due to reactions 9 and 10, had no contribution to PVA degradation. A limited PVA degradation was observed when the solution was saturated with O$_2$, suggesting that the peroxyl radical anion, O$_2^{\bullet-}$, from reaction 2 played a minor role in PVA degradation. Under the same conditions but with addition of t-BuOH instead of i-PrOH, the PVA degradation efficiency was higher in both O$_2$ and N$_2$ saturated solutions. This difference was more significant when the solutions were saturated with N$_2$, which can be explained by reactions 1 and 10. This result indicates that H$^\bullet$ played a role in PVA degradation and that the role of peroxyl radical, HO$_2^\bullet$, in PVA degradation was limited.

In O$_2$-saturated PVA solution without scavengers, the degradation efficiency of PVA was higher than that in N$_2$-saturated solution, suggesting that the presence of O$_2$ was beneficial for PVA degradation. Possible explanations are as follows. On one hand, the formation of O$_2^{\bullet-}$ due to reaction 2 had a contribution to PVA
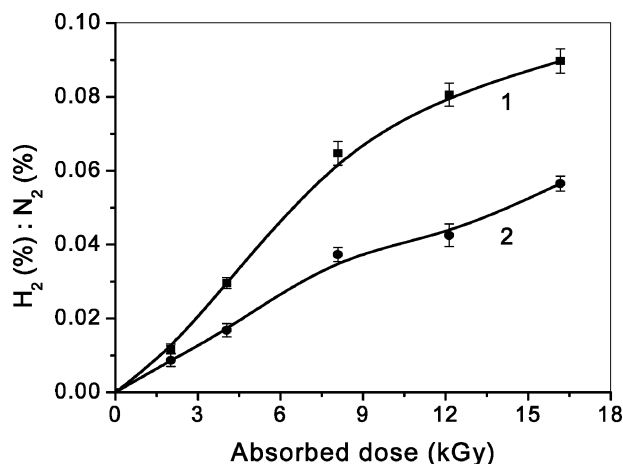
Figure 4. The volume content ratio of H_2 to N_2 as a function of radiation dose ([PVA], 500 mg L^{-1}): line 1, original solution; line 2, with addition of 5 mmol L^{-1} H_2O_2.

Figure 5. Absorbance of PVA solutions at 280 nm as a function of radiation dose: line 1, 500 mg L^{-1} PVA with addition of 5 mmol L^{-1} H_2O_2; line 2, 250 mg L^{-1} PVA; line 3, 500 mg L^{-1} PVA.

degradation. On the other hand, the presence of O_2 facilitated the scission of PVA chain through formation of peroxyl intermediate radicals.[14]

Interesting results were observed when H_2O_2 was added. In the presence of 5 mmol L^{-1} H_2O_2, the PVA degradation efficiency was significantly increased, whereas with 50 mmol L^{-1} H_2O_2 added, the PVA degradation was substantially reduced. This was due to the two-edged effects of H_2O_2 on reactive species as discussed above. At an appropriate level, H_2O_2 enhanced PVA degradation by supplying more $^{\bullet}OH$ through reactions 5 and 6. On the contrary, excessive H_2O_2 competed with PVA for $^{\bullet}OH$ through reaction 7, leading to a decrease of degradation efficiency. The significant difference of PVA degradation efficiencies between the solutions with and without $^{\bullet}OH$ scavengers demonstrates that $^{\bullet}OH$ played a key role in PVA degradation.

The analysis on gaseous products from irradiated PVA solutions, as illustrated in Figure 4, provides further evidence for the role of $H^{\bullet}$ and H_2O_2 in PVA degradation. In the presence of 5 mmol L^{-1} H_2O_2, the yield of H_2 was much lower than that obtained without H_2O_2 due to reaction 6, indicating that $H^{\bullet}$ played a role in PVA degradation by hydrogen abstracting.

The hydrogen abstraction initiated by attack of $^{\bullet}OH$ and $H^{\bullet}$ on PVA resulted in the formation of ketones, enols, aldehydes, acids etc.,[8,11,15] which have an absorption band at about 280 nm. As shown in Figure 5, the addition of 5 mmol L^{-1} H_2O_2 enhanced the formation of these products. Interestingly, the irradiated solution with a lower initial PVA concentration had a higher absorbance at 280 nm than that seen with a higher initial concentration. This suggests that the PVA degradation efficiency was influenced by its initial concentration.

As mentioned above, the attack of reactive radicals on PVA led to a scission of the main chain, yielding biodegradable intermediates such as ketones, enols, aldehydes, acids, etc. These intermediates then underwent further degradation under γ-ray irradiation until they were completely converted into CO_2 and H_2O. The effects of these products on the successive degradation of PVA are present. However, in this work the degradation efficiency of PVA is the main concern. The evolution of the solution viscosity as shown in Figure 2 shows that, up to a radiation dose of 16 kGy, the chain scission was the main reaction in irradiated PVA solutions. Even
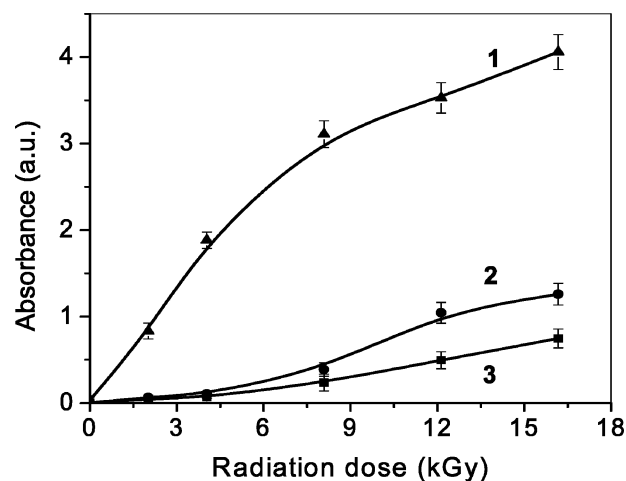
with addition of 5 mmol L^{-1} H_2O_2, a radiation dose of about 4 kGy was still needed for the completion of chain scission. Therefore, within the radiation dose applied in the RSM experiments in this work, i.e., 4.2 kGy, the chain scission of PVA was the predominant reaction in the irradiated system. From the competitive reaction kinetics point of view, the effects of degradation products on PVA degradation efficiency were limited.

On the basis of the analyses above, one can conclude that initial PVA concentration, pH of the solution, dose rate, and addition of H_2O_2 all are important factors influencing the PVA degradation efficiency. Therefore, it is of great significance to determine the appropriate H_2O_2 dosage, pH, and initial PVA concentration for the optimization of radiolytic degradation of PVA.

Optimal Experimental Design. The RSM design is especially useful if the effect of a given variable depends on the setting of another one and vice versa (interactive effect). As discussed above, the PVA degradation efficiency depends on several factors, e.g., initial PVA concentration ([PVA]), H_2O_2 dosage ([H_2O_2]), pH of the solution, and irradiation dose rate (D_r). The former three factors depend on D_r. Thus, RSM analysis was performed to evaluate the collaborative effects of [PVA], [H_2O_2], and pH of the solution with D_r on the degradation efficiency of PVA.

Six regression equations of the following form were obtained.

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_{11} X_1^2 + b_{12} X_1 X_2 \quad (4)$$

where X_1 represents [PVA], [H_2O_2], or pH of solution, X_2 always represents D_r, and Y is the degradation efficiency of PVA (DE%) calculated according to the equation

$$DE\% = \frac{[PVA] - [PVA]^*}{[PVA]} \quad (5)$$

where $[PVA]^*$ is the residue concentration of PVA after radiolysis.

The coefficient estimates and statistical analysis are summarized in Table 3. The high values of the correlation coefficient, $R > 0.904$, justify the goodness of the model fit. At the same time, the very low probability values, $P \ll 0.0001$, indicate an excellent reliability of the model. The higher coefficient estimates implies that
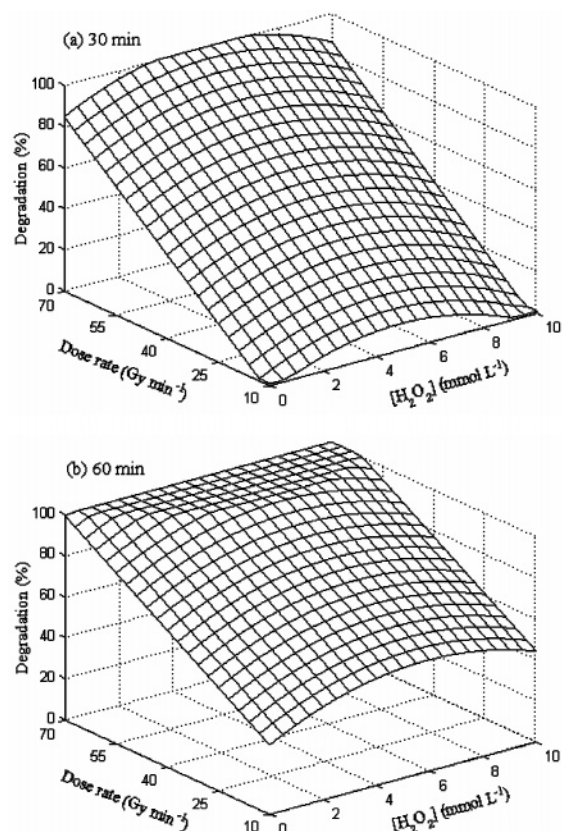
Table 3. The Parameter Estimates

X_1	t^a	b_0	b_1	b_2	b_{11}	b_{12}	R	P
[PVA]	30	47.9703	−19.3153	13.5618	2.6894	−2.7732	0.9677	≪0.0001
	60	73.9979	−17.4172	9.2886	−0.7719	3.5967	0.9801	≪0.0001
[H$_2$O$_2$]	30	57.4892	−0.0395	22.3066	−4.2215	0.1688	0.9700	≪0.0001
	60	86.3405	2.5365	16.3516	−3.6844	−0.0328	0.9041	≪0.0001
pH	30	42.3383	0.5200	20.8323	13.0464	−4.3907	0.9630	≪0.0001
	60	75.7743	0.5583	13.9783	4.6927	−3.7721	0.9285	≪0.0001

^{a} Irradiation time in units of min.
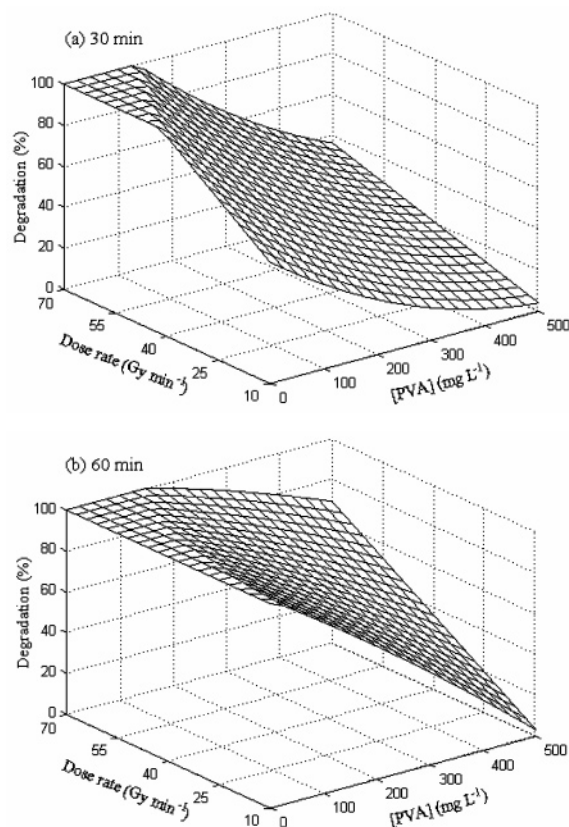
Figure 6. The landscape of DE% as a function of [PVA] and D_r: (a) 30 min of irradiation; (b) 60 min of irradiation.

Figure 7. The landscape of DE% as a function of [H$_2$O$_2$] and D_r ([PVA], 250 mg L^{-1}): (a) 30 min of irradiation; (b) 60 min of irradiation.

the effects of [PVA] and D_r are more significant than the other two factors.

In all of the six regression equations, the linear effect of D_r is significant whereas there is no quadratic effect of D_r on the degradation efficiency of PVA. Moreover, the interactive effects of D_r with the other three factors are much weaker than the linear effect of D_r. These results suggest that D_r has a direct relationship with the degradation of PVA. A higher D_r corresponds to a higher concentration of radicals generated from water radiolysis. This means that the solution irradiated at a higher D_r was attacked by more radicals than that at a lower D_r during an identical irradiation period. Consequently, a higher D_r results in a higher DE%.

The effects of [PVA] on DE% can be interpreted in terms of three aspects. First, the response chosen in this work, i.e., DE%, reflects the fractional variation of PVA. With a same reduced concentration of PVA, DE% of the solution with a higher [PVA] is lower than that with a lower [PVA], which is determined by eq 5. Second, the reactions occurring in a radiolytic system are usually diffusion-controlled. A higher [PVA], meaning a higher solution viscosity, is not favorable for the diffusion of reactive species. Consequently, [PVA] has a negative effect on its radiolytic degradation. The reduced linear

and quadratic terms in the regression equation with increased irradiation time provide support for this interpretation. Third, hydrogen-abstracted PVA can undergo recombinations, especially in concentrated solutions,[12] which deteriorates the degradation of PVA.

The effects of [H$_2$O$_2$] and pH of solution on DE% mainly indwell in the quadratic terms. This implies that the influences of them on PVA degradation are indirect. The mechanism behind the effects of [H$_2$O$_2$] on PVA radiolytic degradation has been discussed in the former section. Underlying reasons for the effect of pH on DE% are given later.

Figures 6−8 are the graphical representations of the regression equations. As illustrated in Figure 6, lower [PVA] and higher D_r were favorable for PVA degradation. This is identical to the regression results.

Figure 7 illustrates the PVA degradation efficiency as a function of D_r and [H$_2$O$_2$]. With a shorter irradiation time, e.g., 30 min, as shown in Figure 7a, 5 mmol L^{-1} H$_2$O$_2$ was an optimal dosage at the dose rates from 10 to 70 Gy min^{-1}. A significantly inhibitory effect was observed as [H$_2$O$_2$] exceeded 8 mmol L^{-1}. On the other hand, with a longer irradiation time, e.g., 60 min, H$_2$O$_2$ was partially depleted. As illustrated in Figure 7b, the
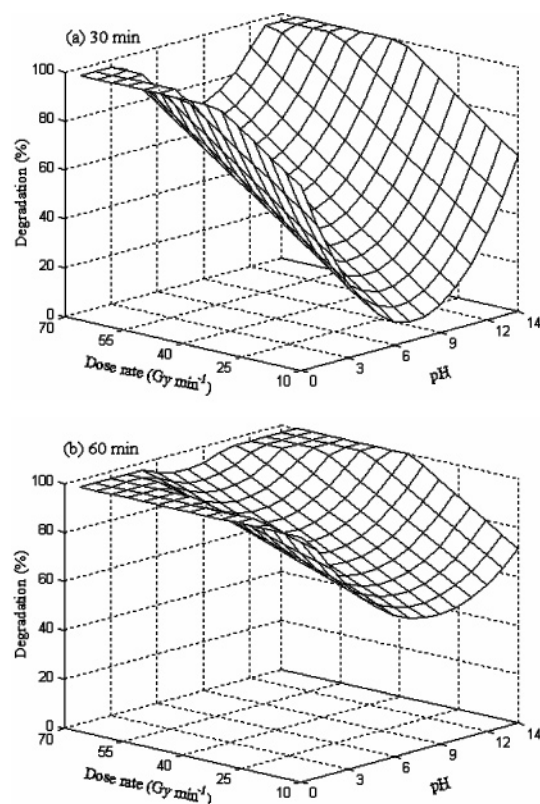
Figure 8. The landscape of DE% as a function of pH of solution and D_r ([PVA], 250 mg L^{-1}): (a) 30 min of irradiation; (b) 60 min of irradiation.

PVA solutions with over 5 mmol L^{-1} H$_2$O$_2$ achieved the maximum PVA degradation efficiency. Hence, to obtain optimal DE%, the H$_2$O$_2$ dosage should be kept at a certain concentration level.

The dependence of PVA degradation efficiency upon D_r and pH is illustrated in Figure 8. The effect of pH on DE% was significant. At the dose rates from 10 to 70 Gy min^{-1}, the lowest DE% was achieved in near neutral solutions, while the highest DE% was achieved in both strong acidic and alkaline solutions. The promotion of PVA degradation efficiency in acidic solutions is due to the enhanced role of H$^{\bullet}$ as shown in reaction 3. On the contrary, in alkaline solutions the conversion of H$^{\bullet}$ to e$_{aq}^-$ as shown in reaction 4 would reduce the degradation efficiency. However, the result obtained in this study was opposite to this assumption. This is probably attributed to the change of chemical properties of PVA due to the attack of OH$^-$ on the hydroxyl groups of PVA. Such an attack made PVA negatively charged. As a result, the approach of electrophilic species, $^{\bullet}$OH, to PVA was enhanced. On the other hand, in strong acidic or alkaline solutions the main chains of PVA, either positive or negative charged, were unwound in bulk solution due to electrostatic repulsion. This was favorable for the attack of reactive radicals on them than those being entangled in loops in neutral solutions. Further efforts should be pursued to confirm these interpretations.

Conclusions

The investigation of PVA radiolytic removal demonstrates that the degradation of PVA induced by γ-ray irradiation was initiated by attack of $^{\bullet}$OH and H$^{\bullet}$, followed by random chain scission and formation of ketones, enols, aldehydes and acids. Complete mineralization of PVA could be achieved providing that sufficient radiation dose was supplied. Initial PVA concentration, pH of the solution, irradiation dose rate, and H$_2$O$_2$ dosage all are important factors influencing the degradation of PVA. The collaborative effects of the former three factors with irradiation dose rate on PVA degradation efficiency were evaluated by using a response surface methodology. Lower initial PVA concentrations, higher dose rates, and acidic or alkaline conditions were favorable for PVA degradation. At a certain dose rate, there was optimal H$_2$O$_2$ dosage to facilitate the PVA degradation.

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