

# Heterogeneous photocatalytic oxidation of polyvinyl alcohol in water

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## Abstract

Titanium dioxide mediated photocatalytic degradation of polyvinyl alcohol (PVA) was studied in an annular photoreactor with two 6 W ( $E_{\max} = 365$  nm) UV lamps as light source. In the presence of both  $\text{TiO}_2$  and light, and initial concentration of 30 mg/l, 55.3% of PVA was found to degrade after an hour. The effects of initial concentration, pH and the addition of  $\text{H}_2\text{O}_2$  on the rate of degradation of PVA were studied. The results showed that it was more effective for PVA to be degraded under acidic or alkaline condition. The order of reaction rates was  $\text{pH } 10 > \text{pH } 9 > \text{pH } 4 > \text{pH } 5 > \text{pH } 7$ . Proper amount of  $\text{H}_2\text{O}_2$  could improve the photodegradation rate of PVA. However, the further increase of  $\text{H}_2\text{O}_2$  might inhibit the system efficiency. Fourier transformed infrared spectroscopy (FTIR) indicated that several carbon–carbon bonds were scissored, which led to the formation of short-chain compounds during the photocatalytic oxidation of PVA. These intermediates were also degraded with prolonged reaction. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Photocatalytic degradation; Polyvinyl alcohol (PVA); Titanium dioxide; Advanced oxidation process (AOP);  $\text{H}_2\text{O}_2$

## 1. Introduction

The increasing turnover and consumption of water-soluble synthetic polymers generate lots of wastes during production, use, and disposal. In addition, many materials in the production are often non-biodegradable or toxic to micro-organisms and can have very long half-life periods in the environment [1,2]. For example, polyvinyl alcohol (PVA), which is widely used in sizing process of the textile industry, is difficult to be degraded biologically without specially adapted bacteria strains [3]. Hence, search for more cost-effective methods for the removal of PVA from wastewater is in order.

Photocatalytic degradation is an emerging technology, which has been demonstrated to be able to effectively degrade various organic contaminants. These include the compounds not amendable to treatment using conventional methods such as biotreatment, carbon/resin adsorption and air stripping [4–7]. As PVA is not readily biodegradable, its interference with conventional biological treatment methods points to the necessity of an abiotic oxidative pretreatment before its release into biological treatment facilities.

For photocatalytic processes, the most suitable semiconductor is  $\text{TiO}_2$  (anatase). Chemical inertness, non-photocorrosivity, and nontoxic influence on microorganism make  $\text{TiO}_2$  interesting for the application in wastewater treatment. Photocatalytic activity of  $\text{TiO}_2$  results from the generation of highly reactive oxidant, which is generated during illumination with bandgap radiation [8]. That highly reactive oxidant is the  $\bullet\text{OH}$  radical. By using spin-trapping experiments,  $\bullet\text{OH}$  has been identified as the main radical intermediates in photocatalysis [9].

Oxidation degradation was one of effective methods to remove synthetic polymers from waters [10]. Hassan investigated the oxidation of PVA as a polymer containing secondary alcoholic groups by  $\text{KMnO}_4$  in alkaline solution. It was reported that the oxidation of PVA led to the formation of a polyvinyl ketone as a final product [11]. Recently, Lei et al. reported that  $\bullet\text{OH}$  might mineralize PVA to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in UV/Fenton system [12]. But there are still few researches on the photocatalytic degradation of PVA.

In this paper, we report the results for the photocatalytic degradation of PVA in suspension system. The effects of initial concentration and pH on the rate of degradation of PVA were examined because of the possible presence in natural water systems. The effect of the addition of  $\text{H}_2\text{O}_2$  was also discussed for enhancement of elimination of PVA. Finally, FTIR was analyzed to identify the photocatalytic degradation mechanisms of PVA in water.

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## 2. Experimental

### 2.1. Chemicals

PVA ( $M_w = 80,000$ ) was obtained from China Qidong Refined Chemical Engineering Plant.  $\text{TiO}_2$  (Shanghai, average particle size as measured by SEM about  $0.95 \mu\text{m}$ , mainly of anatase form confirmed by X-ray diffraction, not shown here) was laboratory reagent grade. Other chemicals were all reagent grade or better.

### 2.2. Photocatalytic degradation of polyvinyl alcohol

The photocatalytic oxidation reactor employed as that shown in Sabate's experiments [13]. In the center of the cylindrical reactor, two 6 W ( $E_{\text{max}} = 365 \text{ nm}$ ) UV lamps were used as the light resource. When  $\text{TiO}_2$  was present, the suspensions were equilibrated for 1 h in the dark prior to the irradiation experiment. All irradiations were carried out under constant stirring. Distilled water was used throughout the work.

For the study of the effect of hydrogen peroxide on the photocatalytic degradation of PVA, known amounts of hydrogen peroxide were added to reactor (PVA solution with  $\text{TiO}_2$ ) prior to illumination. In addition, both sodium hydroxide and nitric acid were used to adjust pH to a value of interest in the experiments. All suspensions were filtered through  $0.2 \mu\text{m}$  Millipore discs prior to further analyses.

### 2.3. PVA analyses

Quantitative determination of PVA concentration in liquid cultures was carried out by spectrophotometric analysis after addition of boric acid and iodine solutions according to the procedure described by Finley [14].

### 2.4. TOC Analyses

The analysis of total organic carbon (TOC) had been carried out using an Apollo 9000 TOC analyzer (catalytic oxidation on Pt at  $680^\circ\text{C}$ ). Calibration had been performed using oxalic acid. The calibration sample fell on a single straight line ( $r = 0.9998$ ).

### 2.5. FTIR of degraded products of PVA

The amount of 500 ml photocatalytically degraded PVA solution was enriched to 20 ml, then was dried in a  $60^\circ\text{C}$  oven. The residue was then ground with KBr. The powdered mixture was pressed (table pressing machine, model 769 YP-15, Tianjin, PR China) at 20 MPa to form a uniform disk. The IR spectra were recorded on a Nicolet 560 FTIR instrument (Nicolet Corporation, USA). The IR spectrum of the initial PVA was also measured after the similar treatment to the sample after the reaction.

## 3. Results and discussion

### 3.1. Effect of $\text{TiO}_2$ and light on the degradation of PVA

In the presence of both  $\text{TiO}_2$  and light, 55.3% of PVA (initial concentration: 30 mg/l) was found to be degraded after 1 h. This was contrast to 2.1% degradation for the same experiment performed in the absence of  $\text{TiO}_2$ , and only 1.2% when the UV lamps had switched off and reaction was allowed to occur in the darkness. These experiments suggested that PVA had negligible photo activity, both light and  $\text{TiO}_2$  were needed for the effective destruction of PVA. Thus, it could be inferred that the degradation of PVA resulted from photocatalytic oxidation. It had been proved that photogenerated holes oxidized water or adsorbed  $\bullet\text{OH}$  at the surface of semiconductor to hydroxyl radicals [15]. These highly reactive radicals could then be used to mineralize or at least partially degrade most organic pollutants.

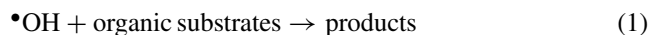


Fig. 1 displayed PVA concentrations at the effluents for various catalyst dosages. These results indicated the optimum dosage of  $\text{TiO}_2$  in the photo degradation of PVA was 2.0 g/l. For extremely few of  $\text{TiO}_2$ , the degradation rates were lower because that the limiting factor for the low rate was the lack of required amount of the catalyst. In superfluous  $\text{TiO}_2$ , the UV was diffused by  $\text{TiO}_2$  particles.

### 3.2. Effect of the initial concentration

The effect of initial PVA concentration on degradation rate was shown in Fig. 2. It was obvious that the rate increases with increasing PVA concentration. Table 1 listed the half-lives of the photodegradation of PVA as a function

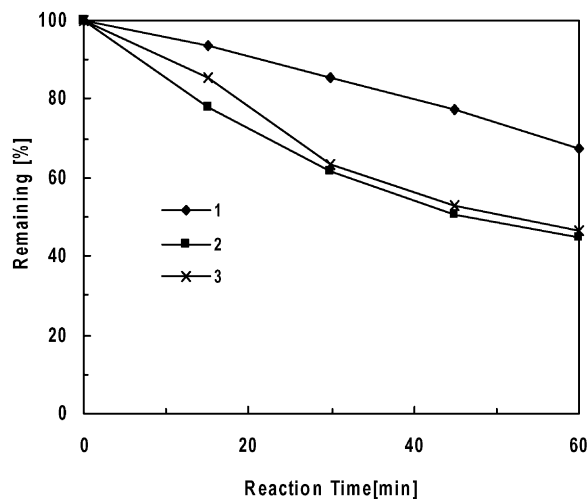


Fig. 1. PVA photocatalytic degradation for various doses of  $\text{TiO}_2$  (experimental conditions: initial PVA concentration 30 mg/l;  $\text{TiO}_2$ , 1:1.0, 2:2.0 and 3:4.0 g/l).

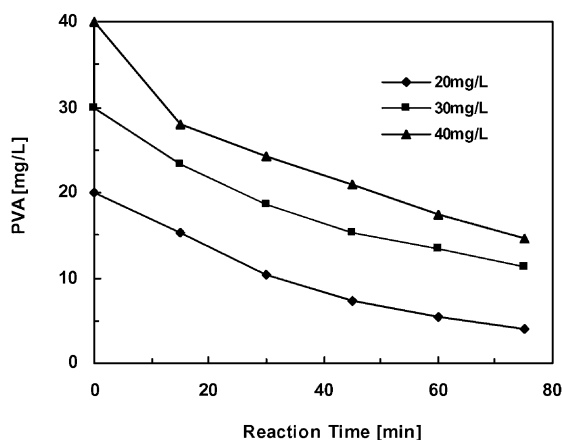


Fig. 2. Effect of initial concentration of PVA on the photocatalytic degradation (experimental conditions:  $\text{TiO}_2$ , 2.0 g/l).

Table 1  
Half-life ( $t_{1/2}$ ) for the degradation of PVA at different initial concentrations

Initial concentration (mg/l)	$t_{1/2}$ (min)
20	33.6
30	44.5
40	49.5

of initial concentration. It was observed that the half-lives increased with increasing PVA initial concentration. These could be explained by assuming that the photo-products were competing for the sites of the surface of  $\text{TiO}_2$  with PVA.

### 3.3. Effect of pH on the degradation of PVA

According to some literatures [16,17], pH value was one of the major factors influencing the rate of degradation of some organic compounds in the photocatalytic process. It was also an important operation variable in actual wastewater treatment. Fig. 3 showed the time change of residual concentration ratios  $C/C_0$  of 30 mg/l PVA at different pH

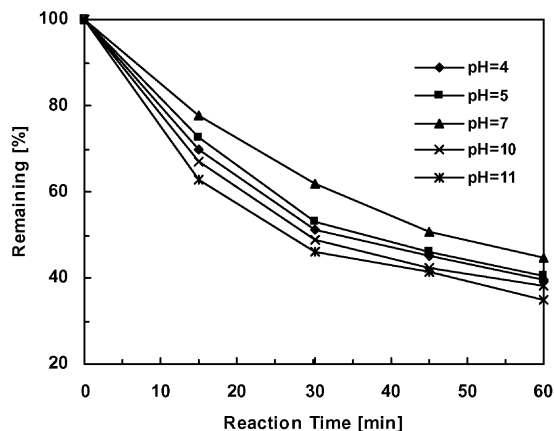
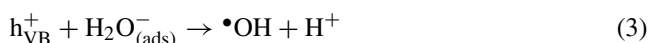


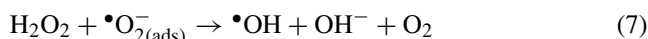
Fig. 3. Effect of the initial pH on the photocatalytic degradation of PVA (experimental conditions: initial PVA concentration 30 mg/l;  $\text{TiO}_2$ , 2.0 g/l).

values. It was interesting to note that the order of reaction rates was  $\text{pH } 10 > \text{pH } 9 > \text{pH } 4 > \text{pH } 5 > \text{pH } 7$ . It meant that it was more effective for PVA to be degraded under acidic or alkaline condition. Within 60 min, the decompositions were above 60% efficiency at acidic and alkaline conditions. Nevertheless, there was only 55.3% removal efficiency at neutral condition.

Under different pH conditions, the main pathways of producing  $\bullet\text{OH}$  are probably different, therefore, producing rate of  $\bullet\text{OH}$  are different. The increasing  $r_0$  with pH in alkaline solution could be attributed to the increase in the number of  $\text{OH}^-$  ions at the surface of the  $\text{TiO}_2$ , since  $\bullet\text{OH}$  could be formed by trapping photoproduced holes (Eqs. (2) and (3)) [18]



In acidic solution, the photocatalytic degradation of PVA is probably due to the formation of  $\bullet\text{OH}$  according to the following reactions (Eqs. (4)–(7))



### 3.4. Effect of added $\text{H}_2\text{O}_2$

Limitation to the rate of photocatalytic degradation had been attributed by most researchers to the recombination of photogenerated hole–electron pairs [19,20]. The addition of inorganic oxidant may play important roles in accelerating the degradation rate of high polymers [10]. In this work reported here, experiments were conducted to examine the effect of  $\text{H}_2\text{O}_2$  concentration on the UV/ $\text{TiO}_2$  system. This was illustrated in Fig. 4. It seemed that, the photocatalytic degradation rates of high polymers could also be increased efficiently with the addition of  $\text{H}_2\text{O}_2$ . A significant enhancement in the rate of the photocatalytic destruction was observed with the increase of  $\text{H}_2\text{O}_2$  concentration up to 5 mmol/l. In the case of the  $\text{TiO}_2/\text{UV}/\text{H}_2\text{O}_2$  system there were additional factors that needed to be considered. Firstly,  $\text{H}_2\text{O}_2$  could act as an alternative electron acceptor to oxygen (Eq. (8)) which might restrain the bulk-composite of the photo-excited electrons and holes. This should consequently increase the rate of the photocatalytic process. The reduction of  $\text{H}_2\text{O}_2$  at the conductance band would also produce hydroxyl radicals that would be available for attack on the PVA [17]. Even if  $\text{H}_2\text{O}_2$  was not reduced at the conductance band, it could accept an electron from superoxide again producing hydroxyl radicals [21] (Eq. (9))



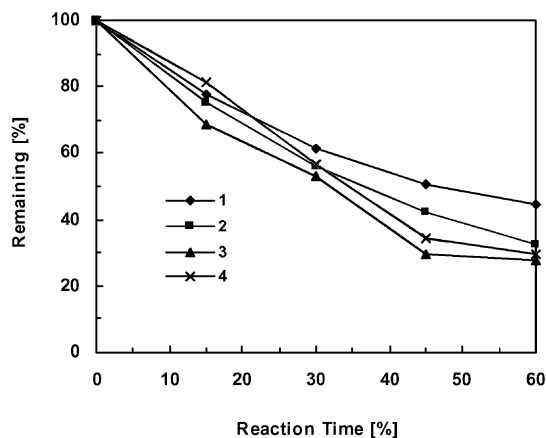
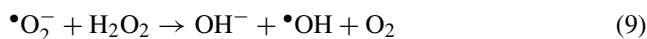


Fig. 4. Photocatalytic degradation of PVA using different  $\text{H}_2\text{O}_2$  dosages (experimental conditions: initial PVA concentration 30 mg/l;  $\text{TiO}_2$ , 2.0 g/l;  $\text{H}_2\text{O}_2$ , (1) none, (2) 2 mmol/l, (3) 5 mmol/l and (4) 8 mmol/l).



It was further observed that there was an optimum peroxide concentration on the rate of PVA destruction. From Fig. 4 it could be seen that the rate of PVA degradation was at a maximum at 5 mmol/l  $\text{H}_2\text{O}_2$ . The rate then dropped with increasing  $\text{H}_2\text{O}_2$  concentration. In previous studies, Wang and Hong had reported that the addition of  $\text{H}_2\text{O}_2$  was important in the photocatalytic degradation of 2-chlorobiphenyl [20]. Cornish et al had also reported that there was an optimum concentration of  $\text{H}_2\text{O}_2$  in the photodegradation of microcystin-LR [22]. They observed that a higher concentration hydrogen peroxide had been found to compete with microcystin-LR for surface sites on the photocatalyst. However, a lower peroxide concentration that competitive adsorption had not been observed. Therefore, the efficiency of UV/ $\text{TiO}_2$ / $\text{H}_2\text{O}_2$  system had been effected by the synthetic functions of several factors.

### 3.5. Mineralization of PVA

Much of the research on direct photocatalysis of organic pollutants focuses on illustrating complete mineralization [23–25]. The need for complete mineralization could be modified if photocatalysis is considered within an integrated treatment train. For the similar trend, the mineralization of the photocatalytic oxidation process had been investigated by the time-dependent measurement of the TOC concentration in the effluent.

Fig. 5 showed the concentration change of PVA and TOC with time in degradation. The degradation of PVA was completed in 120 min. However, the residual TOC was 98.2% at that time. From the difference between PVA and TOC change during the reaction, it was postulated that the reaction might take place in two stages [23]

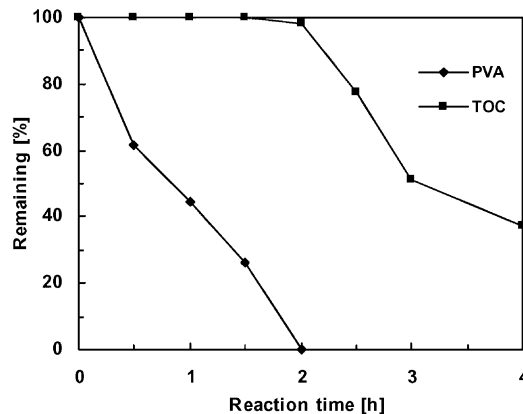
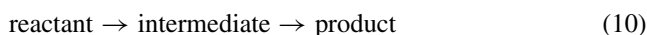


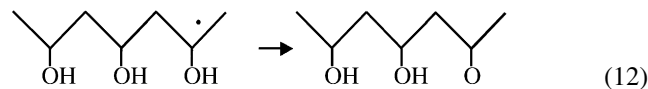
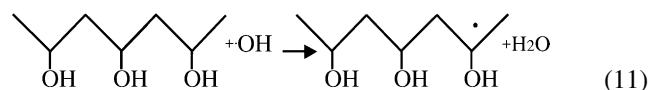
Fig. 5. Mineralization of PVA photocatalytic oxidation (experimental conditions: initial PVA concentration 30 mg/l; initial TOC concentration 16.3 mg/l;  $\text{TiO}_2$ , 2.0 g/l).

During the first stage, mineralization had not been occurred, although the concentration of PVA decreased efficiently. This was due presumably to the formation of intermediates in the first oxidation stage. After the initial PVA had been all degraded, the mineralization stages took place.

### 3.6. FTIR of PVA degradation

The degradation of PVA during photocatalytic oxidation can be closely followed by comparing spectra of solutions degraded at different times. After photodegrading 60 min, band appeared at  $1710\text{ cm}^{-1}$  (C=O stretching bonds),  $1630\text{ cm}^{-1}$  (C=C stretching in isolated double bonds),  $1380\text{ cm}^{-1}$  (symmetrical bend vibration of methyl). This observation could be explained by the photocatalytic oxidation of hydroxy bonds leading to the formation of carbonyl bonds and the scission of several carbon–carbon bonds leading to the formation of methyl. The intensity of the *n*-hydroxy stretching frequency at  $1100\text{ cm}^{-1}$  decreased after illuminated 60 min (see Fig. 6). Currently, a peak at  $1050\text{ cm}^{-1}$  appeared. It also provided evidences that the chain were broken during the photodegradation.

Consequently, hydroxyl radicals would attack PVA by hydrogen abstraction (Eqs. (11) and (12)), hence leading to the formation of carbonyl bonds [26,27]. And then several carbon–carbon bonds were scissored, which lead to the formation of short-chain compounds.



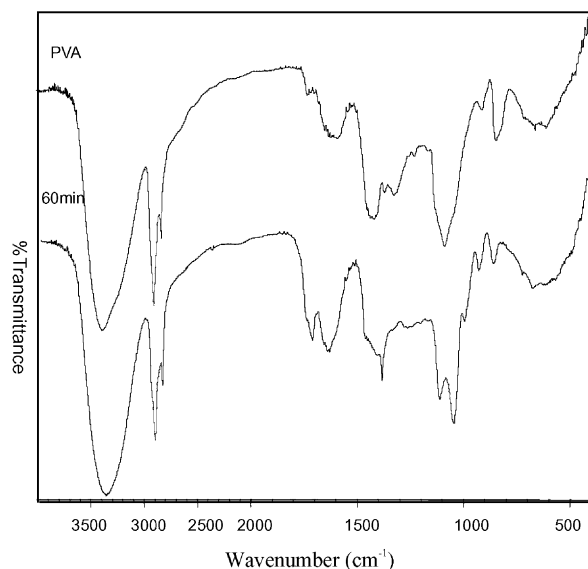


Fig. 6. Contrast of FTIR of PVA and photodegraded 60 min (experimental conditions: initial PVA concentration 30 mg/l;  $\text{TiO}_2$ , 2.0 g/l).

#### 4. Conclusions

The photocatalytic oxidative degradation of PVA had shown promising results at a laboratory scale. By this process, PVA could be destroyed to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  though mineralization needed a quite longer reaction time. The results indicated that the degradation rates of PVA were obviously affected by the initial concentrations, pH and  $\text{H}_2\text{O}_2$  addition. It was more effective for PVA to be degraded under acidic or alkaline condition. The order of reaction rates was  $\text{pH } 10 > \text{pH } 9 > \text{pH } 4 > \text{pH } 5 > \text{pH } 7$ . It was very useful in fact because the actual dyeing wastewater are always in alkaline conditions. There were some complicated factors that effected the efficiency of UV/ $\text{TiO}_2$ / $\text{H}_2\text{O}_2$  system. Therefore, there was an optimum peroxide concentration on the rate of PVA destruction.

FTIR had shown that several carbon–carbon bonds were scissored by the oxidation of hydroxyl radicals, which lead to the formation of short-chain compounds.

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