

Factorial experiment design applied to polyvinylpyrrolidone photocatalytic degradation in TiO₂ aqueous suspension

Jaqueline Suave, Mariana S. Felipe, Humberto J. José, and Regina F. P. M. Moreira*

Department of Chemical Engineering and Food Engineering, Federal University of Santa Catarina, Campus Universitário, Trindade, 88040-900, Florianópolis - SC, Brazil

ABSTRACT

Photocatalytic degradation of polyvinylpyrrolidone (PVP) was studied by the system TiO₂/H₂O₂/UV in an annular batch photoreactor. PVP solutions were tested under different conditions using a 2⁴ full factorial design. The monitoring of the degradation was evaluated by measurements of total organic carbon (TOC) and chemical oxygen demand (COD). Measurements of residual H₂O₂ concentration were also performed. The results indicated that the studied process is promising and can achieve mineralization rates of about 80% by utilizing appropriate initial concentrations of PVP, catalyst dosage and hydrogen peroxide concentration, at pH 4 or 7.

KEYWORDS: Polyvinylpyrrolidone, advanced oxidation process, titanium dioxide, factorial design

INTRODUCTION

Treatment of domestic and industrial plastics presents an unusual challenge to society. Studies on polymeric materials have typically focused on preventing degradation by physical and chemical methods, with the former implicating photodegradation with UV light, thermal and electric degradation. Chemical methods involve degradation by oxygen, ozone, water, steam, chemical oxidants and microorganisms. Polymeric materials are usually

resistant or slow to degrade by these means. The photodegradation pathway of such plastics as polypropylene (PP), polystyrene (PS), polyethylene (PE), polyvinylchloride (PVC), polyacrylate (PA) and polyvinylpyrrolidone (PVP) by UV light irradiation has recently been the object of some reports [1]. Polyvinylpyrrolidone (PVP), widely applied in the pharmaceutical, cosmetics and construction industries, is soluble in water and organic solvents [1, 2]. It is an environmentally stable synthetic polymer whose occurrence in wastewater is likely, and it is hardly biodegradable [3]. On the other hand, it has been shown that PVP is amenable to oxidation by advanced oxidation processes (AOP). Fenton and photo-Fenton processes, ultrasonic degradation and photocatalytic process are proposed as possible AOP to degrade PVP [1, 2, 4].

The photocatalytic degradation of PVP does not lead to formation of toxic final products, as confirmed by mutagenicity assays [1]. The mechanism of the photodegradation of a polymeric structure is complex and not completely known because of the uncertain extent of adsorption from the size ratio of polymer to TiO₂ particle, and from an overlap of photo-oxidation and formation of additional unidentified intermediates [1].

It has been reported that the photocatalytic mineralization of PVP by TiO₂/UV is initiated by the hydroxyl radical photogenerated attack at the N-C bond, resulting in opening of the lactam ring [1]. PVP could be adsorbed on the TiO₂ surface, where [•]OH and [•]O₂H radicals are generated by the

*Corresponding author
regina@enq.ufsc.br

UV irradiation on TiO₂. This is followed by subsequent $\cdot\text{OH}$ radical reactions at the N–C bond at the polymer backbone and leads to the formation of methylamine and propanoic acid. As oxidation progresses, the length of the polymer is reduced and the biodegradability is increased. The final major step in the mechanism involves generation and subsequent conversion of the primary amine (methylamine from opening of the lactam ring) to yield ultimately NH₄⁺ and NO₃⁻ ions, and conversion of the propanoic acid to acetic and formic acids and then to CO₂ [1].

The rate and efficiency of a photocatalytic reaction depend on a number of factors which govern the kinetics of photocatalysis, such as mass of catalyst, pH, volume of solution, radiant flux, and agitation. Design of experiments is a powerful technique used for discovering a set of process variables (or factors) which are most important to the process and then determine at what levels these factors must be kept to optimize the process performance. It has been applied as a quick and cost-effective method to understand and optimize manufacturing processes, and some studies in photocatalysis have been reported to optimize the operational conditions [5].

In the present work, the photocatalytic degradation of PVP was investigated in batch photo-reactor using TiO₂ aqueous suspension. The experimental work is carried out using a 2⁴ factorial design in order to examine the main effects and the interactions among pH, TiO₂ dosage, PVP concentration and additional oxidant H₂O₂ concentration, in order to optimize the reduction of total organic carbon (TOC) and chemical oxygen demand (COD).

MATERIAL AND METHODS

Materials

TiO₂ P-25 (Evonik Degussa) was used for the degradation process. It consists of 80% anatase and 20% rutile with a specific BET-surface area of 50 m²/g and primary particle size of 20 nm. All other chemicals used in the experiments were of laboratory reagent grade and used as received without further purification. PVP K90 (Mw = 360,000) was supplied by Termotécnica (Brazil). The molecular structure of PVP is given in Figure 1.

Factorial design 2⁴

The experimental variables studied were catalyst (TiO₂) concentration, pH, H₂O₂ concentration and PVP concentration, in two levels as shown in Table 1. Table 2 presents the experimental matrix and represents all experiments that were performed according to the combinations of factors and levels. The response variables were the TOC and COD reduction, and the residual H₂O₂ concentration after 6 h reaction time. The experiments were performed in duplicate. The polynomial equations and response surfaces were obtained using the software Statistica 8.0, considering a significance level of 5%.

Heterogeneous photocatalytic process

The heterogeneous photocatalytic process was carried out in an annular UV reactor with TiO₂ Degussa P-25 in suspension and the solution was irradiated with a medium pressure mercury vapor lamp of 80 W. The lamp was suspended vertically inside the quartz glass cylinder in the middle of the reactor. The reactor containing 1.5 L sample of the PVP solution and the pH was adjusted to the desired value. The aqueous suspension was mechanically stirred and air was bubbled through a sintered glass device placed at the bottom of the reactor, at 300 mL/min. Prior to each experiment, the lamp was stabilized for 2 min.

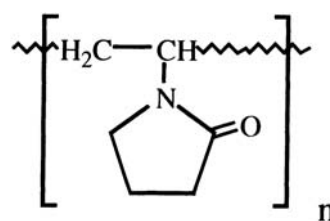


Figure 1. Molecular structure of PVP.

Table 1. Factors and levels of the factorial design 2⁴.

Factors	Lower Level (-)	Upper Level (+)
(A) PVP concentration	0.5 g/L	1.0 g/L
(B) TiO ₂ dosage	0.5 g/L	1.0 g/L
(C) H ₂ O ₂ concentration	0.2 g/L	0.4 g/L
(D) Initial pH	4	7

Samples were taken at different times until 6 hours of reaction with a 10 mL plastic syringe and then filtered in Millipore PVDP membrane (0.22 μ m).

The filtered samples obtained from the photochemical reactions were analyzed in a Shimadzu TOC-VCPH analyzer (Shimadzu, Japan). The COD determinations were performed according to the closed reflux method [6], and a Shimadzu UV 1650C spectrophotometer (Shimadzu, Japan) was used. The determination of residual hydrogen peroxide concentration was made by titration, using the iodometric method, which is less susceptible to interference from organic compounds [7]. The interference of H₂O₂ concentration on the COD analysis was performed as proposed by Kang *et al.* [8].

RESULTS AND DISCUSSION

All 16 experimental runs of factorial design were performed in accordance with Table 2, and the results are shown in Table 3. High TOC removal was observed in all experiments indicating that PVP is successfully mineralized by the TiO₂/H₂O₂/UV process. The similarity between COD and TOC removal indicates that intermediary products could be present only in small concentrations.

Figure 2 shows the Pareto chart for all study variables and their interactions. The independent variables and their interactions are on the Y axis, while the estimated absolute effect is shown on the X axis, and calculated from the ratio between the estimated effect and its respective standard deviation. All Pareto chart values greater than the

Table 2. Matrix of experimental design.

Run	A	B	C	D	Run	A	B	C	D
1	-	-	-	-	9	-	-	-	+
2	+	-	-	-	10	+	-	-	+
3	-	+	-	-	11	-	+	-	+
4	+	+	-	-	12	+	+	-	+
5	-	-	+	-	13	-	-	+	+
6	+	-	+	-	14	+	-	+	+
7	-	+	+	-	15	-	+	+	+
8	+	+	+	-	16	+	+	+	+

Table 3. Results of maximum reduction (TOC and COD) and residual concentration of H₂O₂.

Run	TOC (%)		COD (%)		Residual H ₂ O ₂ (%)		Run	TOC (%)		COD (%)		Residual H ₂ O ₂ (%)	
	I	II	I	II	I	II		I	II	I	II	I	II
1	77	72	77	71	2	6	9	79	76	80	72	3	1
2	55	55	58	60	8	3	10	52	56	66	65	3	3
3	77	73	75	72	3	3	11	81	73	78	74	3	2
4	61	66	72	77	3	1	12	61	62	65	56	3	2
5	74	73	74	73	3	5	13	79	81	81	77	2	2
6	71	73	82	81	1	1	14	64	68	65	67	2	1
7	77	74	70	71	2	4	15	72	72	77	69	5	2
8	62	64	58	57	2	1	16	60	61	67	64	2	2

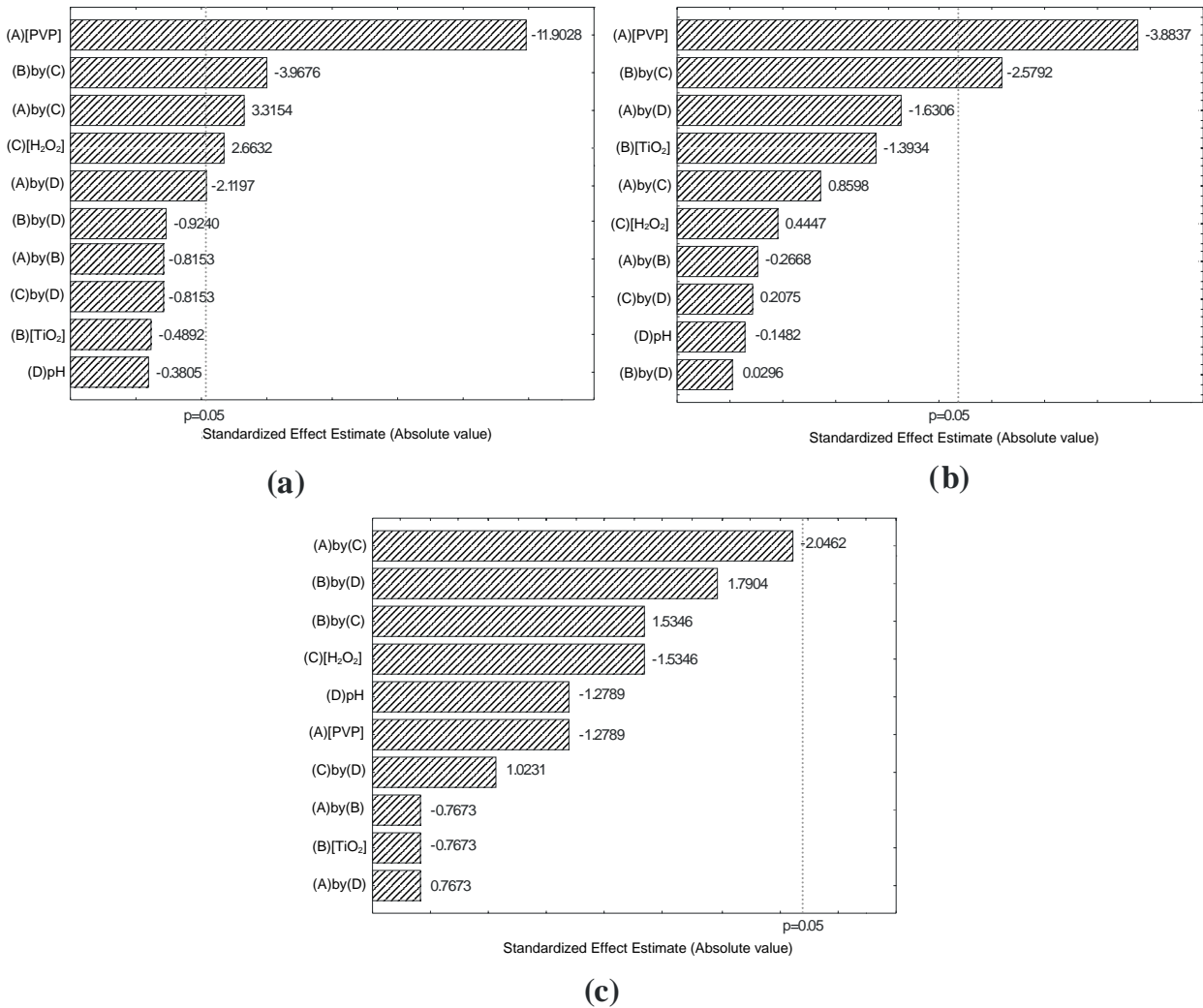


Figure 2. Pareto charts for the effects of the factors in the response: (a) TOC reduction, (b) COD reduction and (c) residual H₂O₂.

p value (0.05) are statistically significant. Thus, it can be observed in Figure 2 that initial PVP concentration as well the interaction concentration of TiO₂ and H₂O₂ have a significant effect on the TOC removal. In this case, the other variables are not statistically significant.

The PVP concentration presented a negative effect, i.e. the TOC removal decreased as the initial PVP concentration increased. The interaction between TiO₂ and H₂O₂ concentration appears with negative effect on the reduction of TOC and COD. It is known that when the H₂O₂ is in excess, it can form hydroperoxyl radicals ($\dot{\text{O}}_2\text{H}$) that can react with H₂O₂ to form hydroxyl

radicals, which can, in turn, regenerate H₂O₂ [9]. Thus, higher initial concentrations of H₂O₂ and TiO₂ can lead to higher consumption of hydroxyl radicals by decreasing the reactions.

The TOC removal is positively influenced by the interaction between PVP and H₂O₂ and by hydrogen peroxide alone. Regarding the response of H₂O₂ concentration in the end of the process, any factor or interaction between factors had statistical significance. In general, regardless of the initial reaction conditions, the residual concentration of H₂O₂ after the 6-hour period was small, ranging from 1 to 8%. H₂O₂ was completely consumed after 6 hours reaction time, in all cases.

Chong *et al.* [10] emphasized the importance of statistical analysis and the analysis of response surface for photocatalytic studies because they allow an optimization process in less time. In this study, the results indicate that the greatest mineralization rates (approximately 70-80% reduction in TOC and COD) are obtained using a PVP concentration of 0.5 g/L and dosage catalyst of 0.5 or 1.0 g/L.

The next step in this study was to observe the behavior of the experimental data on the response

surface methodology. Figure 3 presents four different surface response graphics, which represent the behavior of overall factor influence on PVP degradation. The response surfaces show similar behavior than Pareto charts, regardless of initial pH of the reaction, when comparing experiments using the same concentration of H₂O₂. However, the addition of 0.2 g/L H₂O₂ shows an increase in TOC reduction when the PVP is at its lowest level and TiO₂ with values ranging from lower to higher level. In the

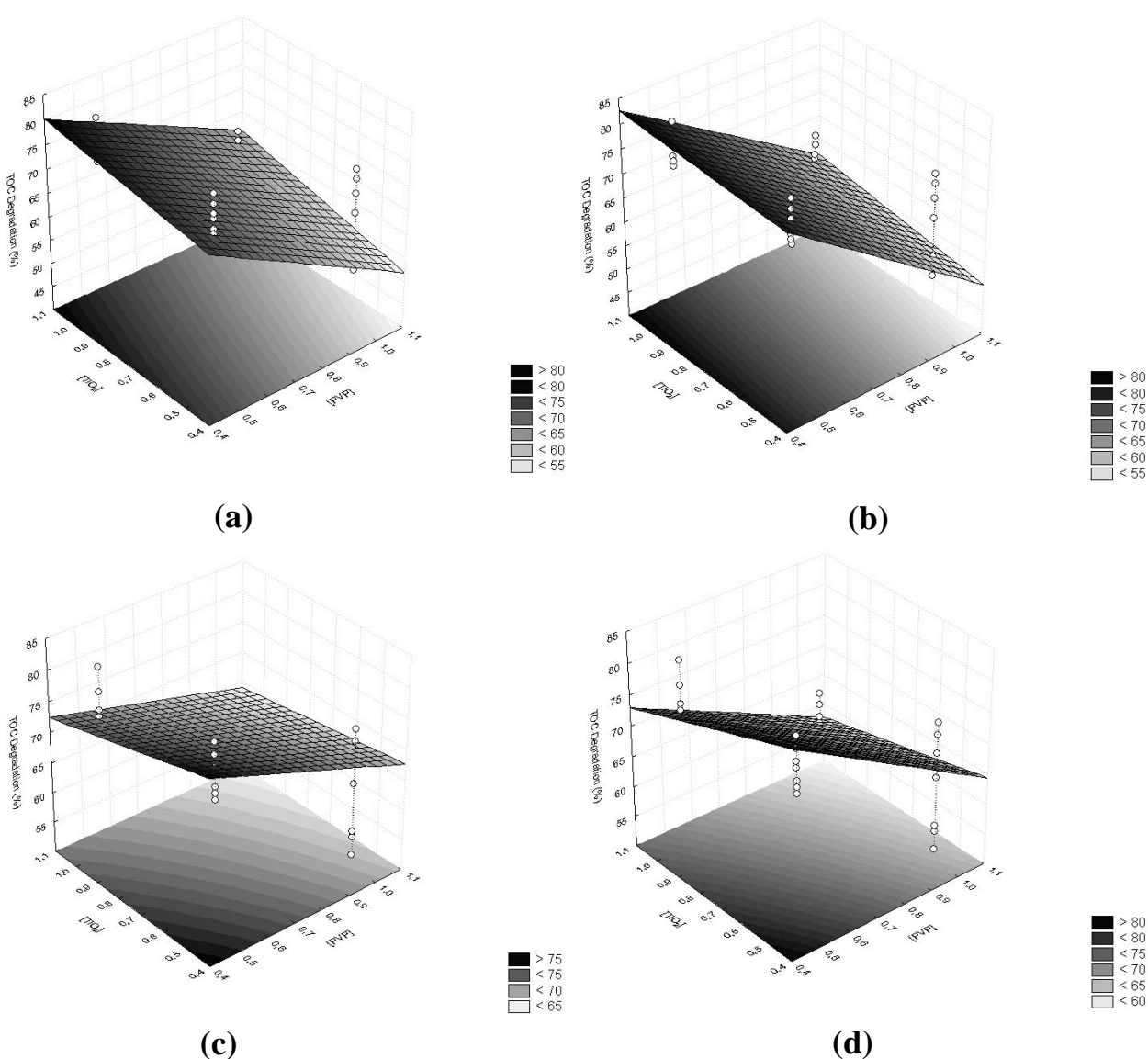


Figure 3. Response surface plots for reduction of TOC, under the conditions: (a) [H₂O₂] = 0.2 g/L and pH = 4, (b) [H₂O₂] = 0.2 g/L and pH = 7, (c) [H₂O₂] = 0.4 g/L and pH = 4, and (d) [H₂O₂] = 0.4 g/L and pH = 7.

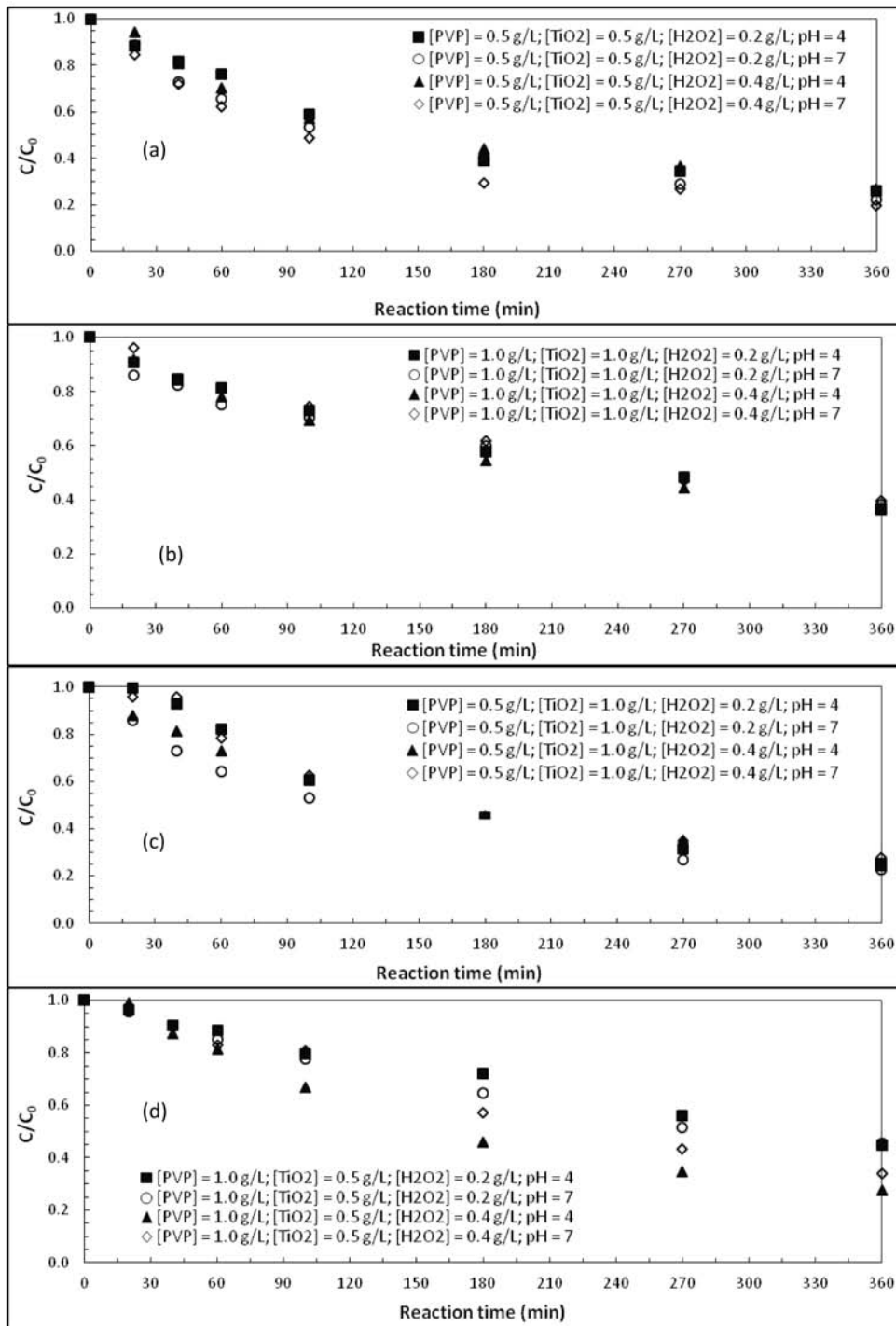


Figure 4. Kinetics of PVP mineralization under different experimental conditions.

experiments with 0.4 g/L H₂O₂, the highest mineralization occurs only when the PVP and TiO₂ concentrations are at their lowest level. The literature reports that at low doses, the removal of

organic compounds tends to increase linearly with the catalyst dosage. But, the presence of catalyst in excess in the aqueous solution may cause a protective effect on light penetration,

minimizing the removal of pollutants [1, 10]. Thus, the ideal catalyst concentration must be determined in order to avoid excess catalyst and ensure the efficient absorption of photons [11].

From the obtained data, an empirical model capable of predicting the system efficiency in terms of TOC degradation (%), applying the studied variables, was generated with the help of the Statistica Experimental Design Software (Eq. (1)).

$$\text{TOC degradation (\%)} = -35.75 [\text{PVP}] + 4.49 [\text{TiO}_2] + 7.5[\text{PVP}][\text{TiO}_2] + 86.22 \quad (1)$$

Figure 4 shows degradation curves versus time of the experiments performed. To compare the behavior of different curves, the TOC values were normalized with respect to initial concentration. The curves show that the experiments conducted with PVP/TiO₂ (g/L/g/L) in the proportion of 1.0/1.0 and 1.0/0.5 generate lower rates of mineralization. However, it can be observed that when the dosage of catalyst is half the dosage of PVP the degradation rates are improved when applying 0.4 g/L H₂O₂, which corresponds to twice the stoichiometric concentration calculated for this amount of PVP. It is noted here that the degradation is slightly higher at pH 4 than 7. The curves where the ratio PVP/TiO₂ is equal to 0.5/0.5 or 0.5/1.0 show very similar behavior and provide the best rates of degradation, and at pH 7 the mineralization tends to be faster.

Boroski *et al.* studied the treatment of liquid effluents from pharmaceutical and cosmetics industries (which probably contain PVP) and observed that the photocatalytic UV/TiO₂ assessed at pH 3.0, 7.0 and 10.0 is more successful in acidic and neutral medium. They also reported that the addition of H₂O₂ improves the treatment and TOC removal [12].

Photocatalytic degradation of polyvinylpyrrolidone using the TiO₂/H₂O₂/UV system proved to be promising. The results obtained with the factorial design indicated that degradation of PVP is influenced by the initial PVP concentration and by interactions of TiO₂ with H₂O₂ and PVP with H₂O₂. In analyzing the response surface graphs of reduction of TOC, final rates of mineralization up to 80% can be obtained using a PVP concentration of 0.5 g/L, a catalyst dosage of

0.5 g/L and a initial concentration of hydrogen peroxide of 0.4 g/L, at pH 4 or 7. Although the kinetic curves show that at pH 7 the rates are slightly higher. We also conclude that the use of 0.2 or 0.4 g/L H₂O₂ did not influence the levels of residual peroxide at the end of the process. However, the reaction time is still very long to obtain satisfactory mineralization rates, so further studies will be conducted to minimize the reaction time.

ACKNOWLEDGMENTS

The authors thank CAPES-DS for a PhD scholarship awarded to J. S and CNPq for financial support.

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