Research Article

Improvement of Biodegradable Biocide's Activity of Peroxyacetic Acid Basis Using Surfactants: Characterization and Stability

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This paper deals with the study of the kinetics decomposition reaction of the peroxyacetic acid under influence of surfactant additives. The peroxyacetic acid shows a decomposition rate of $1.70 \times 10^{-3} \text{ h}^{-1}$ and its activation energy is 66 kJ mol^{-1} . The influence of temperature on the reaction of spontaneous decomposition of peroxyacetic acid was studied at two seasonal periods. Peroxyacetic acid standard and four prototypes of biocide samples with known concentration of peroxyacetic acid and hydrogen peroxide were studied. Finally, a factorial analysis ANOVA was carried out to establish significant differences ($p < 0.003$) between the four biocide samples over time with respect to peroxyacetic acid and hydrogen peroxide concentration. From the study carried out, it can be concluded that the biocide with surfactant substances in its composition offers the best stability and its difference versus the other biocides may guarantee a better behaviour.

1. Introduction

The use of peroxyacetic acid (PAA) as sanitizer in agricultural [1, 2] and medical environments [3, 4], water and wastewater industry [5], food processing, beverage, and medical and pharmaceutical industries [5] has increased due to its efficient biocide effect: bactericidal [6], virucidal [7], and fungicidal and sporicidal [8] effectiveness, wide range of pH application [9–11], and absence of halogenated persistent by-products [12]. However, its uncontrollable decomposition rate to acetic acid and oxygen [13] is a question of concern [9, 14], as the peroxides, in general, are high-energy-state compounds and, as such, they can be considered thermodynamically unstable [15]. The common commercial sanitizer biocide samples based on PAA contain acetic acid (10% v/v), hydrogen peroxide (HP) (25% v/v), and peroxyacetic acid (5% v/v), with specific gravity being 1.10 [16]. One key parameter of these biocides is the stability versus time. It is believed that the use of surfactants greatly improves the biocide properties of the compounds [13], because cleaning and disinfection of

a hard surface comprise the step of treating the surface with a cleaning compound [17–19]. To assess the decomposition rate of their main components such as peroxyacetic acid and hydrogen peroxide, several methods have been developed and among them, double step titration [20], spectrophotometric methods [21–23], enzymatic methods [24], gas chromatography [25], liquid chromatography [26], simultaneous spectra-kinetic determination [27], and flow injection analysis (FIA) method [28] can be mentioned. The chosen method for this assessment study based on liquid chromatography has the advantage of the simultaneous determination of PAA and HP with only one previous derivatization reaction. The quantitative reaction of PAA with methyl *p*-tolyl sulphide (MTS) and the HP with triphenylphosphine (TPP) yields the corresponding methyl *p*-tolyl sulfoxide (MTSO) and triphenylphosphine oxide (TPPO), according to Pinkernell et al. [26].

The aim of this work is to study the decomposition kinetics of PAA and HP in four sanitizer biocide prototypes

TABLE 1: Analytical characteristics of the validated method.

Compound	RT (min)	Linear range (mmol·L ⁻¹)	Limit of detection (mmol·L ⁻¹)	Limit of quantification (mmol·L ⁻¹)	R ²	Recovery (%)	RSD (%)
PAA	1.39	0.023–0.800	0.002	0.005	0.9996	99.5	1.3
HP	3.79	0.008–0.270	0.001	0.002	0.9983	96.5	1.4

under environmental conditions reflecting realistic situations. These experiments were made in the laboratory and included combinations of stability time (0–63 days), environmental temperature (25–30°C), and surfactant content added (0–5%). In addition, PAA and HP concentrations were measured throughout the assessment study. For this purpose, the simultaneous determination of PAA and HP using the HPLC validated method has been applied and a kinetic model was developed. In addition, by using classified and statistical tools such as factorial ANOVA and Tukey's proof, the characteristic labelled groups in the sanitizer biocide samples were established for their distinction and differentiation. The results are shown and discussed.

2. Material and Methods

2.1. Apparatus. Analysis was performed with a Waters 2695 High Performance Liquid Chromatography (HPLC) with a Waters 2696 photodiode array detector. Compounds were separated on a SunFire C8 reversed phase column (150 mm × 2.1 mm × 3.5 μm). The injection volume was 10 μL, and the UV detection wavelength was 229 nm. The following gradient of acetonitrile (A) and water (B) was selected to achieve separation of methyl *p*-tolyl sulphide (MTS), methyl *p*-tolyl sulfoxide (MTSO), triphenylphosphine (TPP), and triphenylphosphine oxide (TPPO): initial mobile phase ratio was held at 40% A and 60% B for 10 min and then programmed at 100% A and 0% B in 0.1 min and held for 1.8 min and then 40% A and 60% B in 0.1 min and held for 3 min to final run time (15 min). The flow rate of the mobile phase was 0.45 mL min⁻¹.

2.2. Reagents and Solutions. Peroxyacetic acid (PAA) 39% and hydrogen peroxide (HP) 6% from Sigma-Aldrich Química S.A. (Madrid, Spain) were used as standards for quantitation. Peroxide solution of PAA (23.85 mmol L⁻¹) and HP (8.21 mmol L⁻¹) was prepared under gravimetric control. Standard solutions of these peroxide solutions in acetonitrile were used for calibration curves of PAA.

All chemicals for the derivatization reaction were purchased from Sigma-Aldrich Química S.A. (Madrid, Spain) in the highest quality available: methyl *p*-tolyl sulphide (MTS) 99%; triphenylphosphine (TPP) 98%; methyl *p*-tolyl sulfoxide (MTSO) 97%, and triphenylphosphine oxide (TPPO) 98%. Standard solutions of MTS (20 mmol L⁻¹) and TPP (10 mmol L⁻¹) in acetonitrile were prepared and gravimetrically controlled. Vacu-vial kit patented for CheMetrics was purchased from Instrumentación Científica Técnica, S.L., Barcelona, Spain. Ammonium metavanadate 97% was obtained from Panreac (Spain). Methanol and acetonitrile

of HPLC grade were obtained from Sigma-Aldrich Química, S.A. (Madrid, Spain).

2.3. Samples. Four sanitizer biocide samples were studied: A to D. All of them were supplied by Biocidas Biodegradables ZIX Company (Huesca, Spain) with the following properties: sample A (25% HP, 5% PAA, and 5% surfactant-1), sample B (25% HP, 5% PAA, and 2% surfactant-2), sample C (25% HP, 5% PAA, and 1% surfactant-3), and sample D (25% HP, 5% PAA, without surfactant) (for confidentiality reasons, the BZIX company cannot give information on the type of surfactant used, but in all three cases the formula was different).

For this study, 0.010 g of biocide samples was diluted in 20 mL vials with Milli-Q water. The biocide samples were analysed in triplicate during 60 days.

In the first derivatization step 100 μL of solution of MTS (20 mmol L⁻¹) and 365 μL of Milli-Q water were added to 35 μL of diluted biocide sample or work solution of PAA for the calibration curve. After 10 min at room temperature, 400 μL of acetonitrile and 100 μL of solution of TTP (10 mmol L⁻¹) were added to start the second derivatization step. The solutions were stored in the darkness for 30 min at room temperature and directly analysed by HPLC/UV.

3. Results and Discussion

3.1. Analytical Features of the Method. From the calibration curve the regression coefficient values and detection and quantification limits were calculated and are shown in Table 1. The daily measurement of blanks, standards, samples, and fortified samples with their corresponding duplicates for six days was used to calculate the recoveries, reproducibility, and repeatability of the analytical method for the determination of PAA and HP after the derivatization to MTSO and TPPO, respectively. The derivatization reaction is shown in (Figure 1).

Figure 2 shows the chromatograms obtained by HPLC/UV for calibration curve. The results show good linearity for both compounds under study and with the signal/noise ratio of the chromatograms corresponding to the blank and the first point on the calibration curve (0.023 mmol L⁻¹ for PAA and 0.008 mmol L⁻¹ for HP) the detection and quantifications limits were calculated.

Table 2 shows the recovery values, expressed as percentage of peroxyacetic acid and hydrogen peroxide standards analysed by HPLC/UV. As can be seen, the recovery values of both standards, PAA and HP, both at low concentration level (2.22 mmol L⁻¹ and 0.76 mmol L⁻¹, resp.) and at high concentration level (23.85 mmol L⁻¹ and 8.21 mmol L⁻¹, resp.) were from 90% to 103%.

FIGURE 1: Derivatization reactions of PAA and HP for their determination by HPLC.

TABLE 2: Recovery values expressed as percentage of the standards analysed with the HPLC/UV validated method.

Compound	Added (mmol L^{-1})	Recovered (mmol L^{-1})	Recovery (%)	Mean recovery (%)
PAA	2.22	2.22	100	99.5
	23.85	23.71	99	
HP	0.76	0.69	90	96.5
	8.21	8.43	103

FIGURE 2: Overlay chromatograms of the calibration curve analysed by HPLC/UV.

3.2. Validation of the Analytical Method. According to the American Chemical Society (ACS) and its validation method guidelines, the precision level III or ruggedness is evaluated taking into account other validated methodologies and comparing their results about the interesting parameters, in this case with the determination of PAA and HP. The concentrations of both standards were also independently measured by UV/Vis spectroscopy, using the patented kit Vacu-vials[®] [23] in the case of PAA determination, and by UV/Vis spectroscopy with metavanadate methodology [22]

in the case of HP determination. The commercial samples were also analysed using these methods. The results obtained for the PAA and HP are shown in Figure 3.

For the four types of biocide samples, good agreements of the results using the spectrophotometric and chromatographic methods were achieved. In the case of peroxyacetic acid the results obtained were similar in the four samples of biocides. In the case of hydrogen peroxide the results obtained by UV/Vis spectroscopy were slightly higher than those obtained by simultaneous HPLC/UV analysis. This deviation can be explained by the simultaneous presence of two oxidants in the medium, HP and PAA, which is not detected by the spectroscopic methods. Reproducibility problems with spectroscopy UV/Vis methodologies have been described [10, 11]. Therefore, the HPLC/UV method, where the surrogates were simultaneously determined, was proposed to analyze PAA and HP in real samples of disinfection control. The selectivity of HPLC-UV method is better, compared to the spectrophotometric methods, in which each oxidant should be independently analyzed.

3.3. Stability Study of Biocide Samples. During the study of stability carried out over two months it was observed that pH of the biocide samples remained stable, showing pH values between 0.6 and 0.8, with variations of 0.1–0.2 pH units. Therefore, these small variations of pH were considered negligible and did not influence the stability of the biocide samples. It is well known that changes in two pH units can accelerate the decomposition rate of peroxyacetic acid in the biocides [11, 21, 22].

The control of temperature is also a key parameter for the stability of peroxyacids and consequently very important to monitor the stability of the biocide samples, as temperature

FIGURE 3: Analysis of PAA (a) and HP (b) in biocide samples using a simultaneous HPLC/UV determination and UV/Vis spectroscopy methods.

affects the rate of decomposition of HP and PAA [9–11, 14, 29–32], especially when temperatures are above 30°. In the first 35 days of study room temperature was held at 25°, but in the period from day 42 to day 63, temperature reached up to 30°.

3.4. Peroxyacetic Acid Levels and Kinetic Study. Figure 4 shows the evolution graph of the peroxyacetic acid content during the study of four biocide samples. As can be seen, the results of the stability of peroxyacetic acid are influenced by two parameters: the temperature and the storage time [14, 29, 30]. Both parameters accelerate the decomposition reaction of peroxyacetic acid. According to the results shown in Figure 4 the following performance can be seen:

- (1) Until day 42 of study, laboratory temperature remained constant and around 25°C, so that the decomposition of peroxyacetic acid was spontaneous. The reduction of peroxyacetic acid content in this period was from 10% to 20%.
- (2) From day 42, the average temperature in the laboratory was about 30°C, showing that the rate of peroxyacetic acid decomposition increased. The reduction of peroxyacetic acid content in this period was 27% for sample A and 39% for sample B. Only sample C (with less amount of surfactant-3) and sample D (without surfactant) did not increase their decomposition rate of peroxyacetic acid in this period. These results agree with other studies from Wang et al. [30] carried out at constant temperature of 25°C in thermostatic chambers. Within the first 10 days the peroxyacetic acid reduction rate was 11% and after 30 days storage was 19%, showing the influence of storage time as the only reason for the reduction of peroxyacetic acid. This statement coincides with the results obtained in this study, where there was acceleration in the rate of reduction of peroxyacetic acid for samples A and B in the period where the temperature exceeded 25°C.

FIGURE 4: Evolution of peroxyacetic acid (PAA) in the biocide samples during stability study.

From the results obtained from the study a kinetic study was carried out in order to evaluate the main reason for the decomposition of peroxyacetic acid. Using the standard solutions the decomposition kinetic of peroxyacetic acid was obtained, showing a first-order reaction with a rate constant value (k) of $1.70 \times 10^{-3} \text{ h}^{-1}$ at 25°C with a standard solution of 2.22 mmol L^{-1} as initial peroxyacetic acid concentration. These data agree with the results obtained by Kunigk et al. [14]. Equation (1) was proposed to correlate concentration of peroxyacetic acid and time (θ) with a confidence level of 95%. Equation (1) represents the curves shown in Figure 5. Consider

$$\begin{aligned}
 [\text{PAA}] (0 \text{ to } 35 \text{ days}) &= 2.203 \cdot e^{-1.7 \cdot 10^{-3} \theta} \text{ at } 25^\circ, \\
 [\text{PAA}] (42 \text{ to } 63 \text{ days}) &= 4.858 \cdot e^{-2.25 \cdot 10^{-3} \theta} \text{ at } 30^\circ.
 \end{aligned} \quad (1)$$

Using the initial standard solution of 2.22 mmol L^{-1} Figure 5 was obtained. The percentage differences between the calculated values of peroxyacetic acid concentration with

FIGURE 5: Variation of the initial concentration of 2.22 mmol L^{-1} peroxyacetic acid at 25°C and 30°C versus time (θ).

(1) and the corresponding experimental values of peroxyacetic acid concentration varied from 0.2 to 4.2% (average of 1.6% and standard deviation of 1.3%).

With this assessment the influence of temperature and initial peroxyacetic acid concentration under decomposition kinetic of peroxyacetic acid was obtained. As expected, when temperature increased the kinetic constant increased. In Figure 5 the kinetic constant (k) increased from $1.70 \times 10^{-3} \text{ h}^{-1}$ to $2.25 \times 10^{-3} \text{ h}^{-1}$ for standard of PAA (2.22 mmol L^{-1}). According to Zhao et al. [31, 32], in this range of temperature the decomposition of PAA must be attributed to the hydrolysis process of PAA, but the temperature affects the two reactions (reversible reaction 1) in a similar degree. In addition, the hydrolysis of PAA in acidic medium is of first order with respect to PAA concentration, water concentration, and H^+ concentration [18]. Table 3 shows the influence of temperature (T) on the specific decomposition rate constants (k).

There was a good agreement between our data, the proposed model, and the experimental results from Kunigk et al. [14]. The percentage differences between the k value, calculated with the Brazilian model and the Experimental Spain, corresponding to the experimental values of k for 25°C and 30°C , varied from 3.3% to 12.0% (average of 7.6% and standard deviation of 6.1%). The equation of the Brazilian model, which correlates k and T , may be used in our case to calculate the activation energy (E_a) for the decomposition of PAA in aqueous solutions. For this purpose, the standard solutions used in this study showed that the Arrhenius law was obeyed, and the activation energy was $66.20 \text{ kJ mol}^{-1}$. This value is comparable to the intrinsic activation energies of PAA synthesis and hydrolysis from the Arrhenius plot of $57.80 \text{ kJ mol}^{-1}$ and $60.40 \text{ kJ mol}^{-1}$, respectively, obtained by Zhao et al. [31]. With this value, it is possible to compare the efficiency of different stabilizers if the concentrations of the compounds present in the sanitizer formulation remain constant.

3.5. Peroxide Hydrogen Levels. Figure 6 shows the graphical representation of the evolution of the hydrogen peroxide

FIGURE 6: Evolution of hydrogen peroxide (HP) in the biocide samples during stability study.

content during the study of four biocide samples. When analyzing the stability of hydrogen peroxide, there was a decrease in the percentage of its own spontaneous decomposition.

As can be seen from the results shown in Figure 6 samples C (with less surfactant-3 composition) and D (without surfactants) are more stable, as the reduction of hydrogen peroxide content after 63 days is only 9% and 8%, respectively. Furthermore, as in the case of the reduction in the content of peroxyacetic acid, samples A and B (with higher surfactant contents in their composition, resp.) showed higher rates of decomposition of hydrogen peroxide after 63 days, being 17% and 15%, respectively. It can be seen that the concentration of hydrogen peroxide is generally stable during the two months where its stability was evaluated, remaining around 20–25%. These results agree with those obtained by Zhao et al. [32] which showed that the thermal decomposition of hydrogen peroxide in the liquid phase is not easily reached because the energy for breaking the O-O bond is relatively high ($\sim 213 \text{ kJ mol}^{-1}$). Homolysis of hydrogen peroxide cannot happen unless it is heated above a critical temperature of 120°C .

3.6. Factorial ANOVA for Assessment of Peroxyacetic Acid and Hydrogen Peroxide. Using a factorial ANOVA or univariate analysis of variance with the help of SPSS v15 software it was possible to elucidate some differences among the four sanitizer samples, grouping them in various subgroups. The first goal was to establish that all sanitizer biocide samples were statistically different, followed by the presence of interactions between the two factors evaluated: kind of sample and time. Then, with Tukey's HSD proof (Honestly Significant Difference), the existence of other types of linkage between them was demonstrated as it is shown below. The three selected factors, sample, time, and its mutual interaction included in the model, explain more than 98% and 83% of variance of dependent variables (for peroxyacetic acid and hydrogen peroxide concentration, resp.). It can be concluded from Tables 4(a) and 4(b) that the critical levels of significance show that the four samples have different mean concentrations of HP over the time of study. The same situation

TABLE 3: The influence of temperature (T) on the rate constant value (k) for the kinetic decay PAA method developed.

T (K)	Model Braz. ^a $k (\times 10^3)$	Experimental Braz. ^b $k (\times 10^3)$	Experimental Spain ^b $k (\times 10^3)$	Error %
298	1.64	1.71	1.70	3.3
303	2.55	—	2.25	12.0
308	3.91	3.73	—	—
313	5.91	5.38	—	—
318	8.82	9.64	—	—

^a $k = e^{20.30} e^{-7959.85(1/T)}$.^bData were compared at the same initial PAA: 2.22–3.68 mol L⁻¹.

TABLE 4: (a) Intersubject effects proof for peroxyacetic acid for the factorial ANOVA analysis. (b) Intersubject effects proof for hydrogen peroxide HP for the factorial ANOVA analysis.

(a)

Source	Sum of squares Type III	D_f	RMS	F	Significance
Corrected model	28.357 ^c	27	1.050	56.491	0.000
Intersection	1293.434	1	1293.434	69571.874	0.000
Sample	1.731	3	0.577	31.032	0.000
Time	21.495	6	3.582	192.696	0.000
Sample * time	5.131	18	0.285	15.333	0.000
Error	0.521	28	0.019		
Total	1322.311	56			
Corrected total	28.877	55			

^c $R^2 = 0.982$ (corrected $R^2 = 0.965$).

(b)

Source	Sum of squares Type III	D_f	RMS	F	Significance
Corrected model	573.777 ^c	27	21.251	5.334	0.000
Intersection	29257.143	1	29257.143	7343.134	0.000
Sample	62.140	3	20.713	5.199	0.006
Time	278.940	6	46.490	11.668	0.000
Sample * time	232.698	18	12.928	3.245	0.003
Error	111.560	28	3.984		
Total	29942.480	56			
Corrected total	685.337	55			

^c $R^2 = 0.837$ (corrected $R^2 = 0.680$).

occurred for PAA. In addition, the interaction sample time has a reliable effect under HP concentration, anticipating that the differences in the HP concentrations over the time of study are not the same in the four sanitizer samples (Table 4(b)). Again the same situation was found for PAA (Table 4(a)).

For PAA behaviour and in accordance with Tukey's proof it can be observed that only sample C had differences with the rest of the samples ($p = 0.000$), while samples A, B, and D do not have differences between them (Table 5).

In addition, by using a post hoc procedure with Dunnett's proof (Table 5) and taking as control sample D (without

surfactant), only sample C (1% surfactant-3) has shown significant differences ($p < 0.000$); this demonstrates how both the type and concentration of surfactant influence the behavior of samples biocides.

The behaviour of the hydrogen peroxyacetic acid is confirmed in Table 6, where the sanitizer biocide samples C and D had been grouped in one subgroup, each one separately, whereas sanitizer biocide samples A, B, and D have not been classified in another subgroup; sample C offers the best conditions for stability.

Throughout the study of the significant interaction between sample and time (Figure 7) it is possible to confirm

TABLE 5: Post hoc proof on multiple comparisons for peroxyacetic acid (PAA) taking into account the sample as independent factor.

Multiple comparisons						
Dependent variable: PAA						
(I) Sample	(J) Sample	Mean difference (I – J)	Std. error	Sig.	95% confidence interval Lower bound	Upper bound
Tukey HSD						
A	B	–0.0566	0.05154	0.694	–0.1973	0.0841
	C	–0.4343*	0.05154	0.000	–0.5750	–0.2936
	D	–0.0364	0.05154	0.894	–0.1771	0.1043
B	A	0.0566	0.05154	0.694	–0.0841	0.1973
	C	–0.3777*	0.05154	0.000	–0.5184	–0.2370
	D	0.0202	0.05154	0.979	–0.1205	0.1609
C	A	0.4343*	0.05154	0.000	0.2936	0.5750
	B	0.3777*	0.05154	0.000	0.2370	0.5184
	B	0.3979	0.05154	0.000	0.2572	0.5386
D	A	0.0364	0.05154	0.894	–0.1043	0.1771
	B	–0.0202	0.05154	0.979	–0.1609	0.1205
	C	0.3979*	0.05154	0.000	–0.5386	–0.2572
Dunnett's test (bilateral)						
A	D	0.0364	0.05154	0.822	0.1643	0.0916
B	D	0.0202	0.05154	0.961	–0.1078	0.1482
C	D	0.3979*	0.05154	0.000	0.2699	0.5259

*The mean difference is significant at the 0.05 level.

TABLE 6: Homogeneous subsets for peroxyacetic acid (PAA) with Tukey's HDS proof.

PAA				
Sample		N	Subset	
			1	2
Tukey's HDS ^{a,b}	A	14	4.6741	
	D	14	4.7105	
	B	14	4.7307	
	C	14		5.1084
	Sig.		0.694	1.000

^aUsing the sample size of the harmonic mean = 14.000.

^bAlpha = 0.05.

that the sequential peroxyacetic acid concentration measured over the study was always lower than the earlier measurement. Sample C has shown more stability than sanitizer biocide samples A, B, and D in terms of PAA concentrations. Thus, the influence of temperature on all samples under study is evident, especially in first two samples (A and B).

4. Conclusions

The simultaneous determination by HPLC of PAA and HP is possible and reliable to assess the decomposition of these compounds in biocide samples. The method was validated and only requires conventional HPLC equipment after the chemical reaction for derivatization.

The decomposition of peroxyacetic acid is a first-order reaction, and the corresponding rate constant is affected by

temperature according to Arrhenius equation. The activation energy of the decomposition of peroxyacetic acid in aqueous standard solutions used in this work is 66.20 kJ mol^{–1}.

The factorial ANOVA analysis allowed us to establish the interaction between time and the kind of sample (surfactant type and concentration) with respect to PAA and HP concentration. From the study carried out it can be concluded that biocide C with 1% of surfactant-3 content in its composition offers the best conditions in terms of stability, and its difference with the other biocides may guarantee a better behaviour.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

FIGURE 7: Profile plot of interaction between sample and time in the assessment of sanitizer biocide sample under factorial ANOVA analysis.

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