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Water disinfection with UVC radiation and H_2O_2. A comparative study†

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A generalized kinetic model resulting from several modifications of the one originally known as the Series Event Model has been applied to describe three different disinfection processes and compare their efficiencies. The work was performed in a well-defined, versatile batch reactor employing *Escherichia coli* as a subrogate bacteria. The following systems were studied: (i) UVC radiation alone, (ii) hydrogen peroxide alone and (iii) UVC radiation combined with hydrogen peroxide. The kinetic parameters of the three models were determined. Within the range of studied operating conditions, the use of UVC alone has shown to produce the best results.

1. Introduction

Increasing concern for human health has produced an important search for safer water treatment processes, particularly for water disinfection or the removal of products resulting from the use of conventional technologies. Typical chlorination is known to produce different families of chlorinated byproducts (CBP) either from existing natural organic compounds such as humic acids or from the presence of artificial organic matter (AOM) resulting from chemical contamination. They give rise to a large group of halogenated organic mixtures known as trihalomethanes (THMs), haloacetic acids (HAAs), chlorophenols, chlorohydrates and haloacetonitriles (HANs).[1,2] The removal of natural organic matter (NOM) or AOM from surface waters has been the intent of several alternative methods such as adsorption, reverse osmosis and, more recently, some processes known as Advanced Oxidation Technologies (AOT) that constitute a group of very versatile potential operations.[3] Using UV radiation alone or UV radiation combined with oxidants other than of chlorine or ozone to disinfect domestic water, for example, seems to provide a promising option. Among them, the use of UV + H_2O_2 is one of the methods competing in the market.

Bacteria inactivation using UVC radiation results in absorption of rather high-energy photons by the cell DNA producing thymine dimers. When there is a sufficient number of these dimers inside a microorganism the duplication of DNA and RNA is inhibited, preventing the cell reproduction and, in absence of an enzymatic remediation, the outcome is the death of the bacteria.[4,5]

The existence of hydrogen peroxide inside a bacterium may be the result of an endogenous process originating in its aerobic metabolism that is usually self-controlled, or a consequence of an exogenous action. In the latter case, it is accepted that the substance in its molecular state does not produce the inactivation. Its deadly toxic properties are produced by different, very active oxidant species produced by hydrogen peroxide photolysis. This process gives rise to the production of singlet oxygen, superoxide ($O_2^{\bullet-}$) and hydroxyl ($^{\bullet}OH$) radicals that, due to their high chemical activity, are extremely toxic for the normal metabolic evolution of the cell.[6,7] These very unstable species have very strong and non-selective oxidizing capabilities (particularly the $^{\bullet}OH$ radical) and are very effective in the removal of organic and inorganic pollutants, as well as disinfection targets.[8] Thus, they can produce severe changes in macromolecules, like lipids, proteins and nucleic acids.[9] It is suggested that the main advantage of this combined process is that it seems to preclude the possibility of recovery and subsequent growth of bacteria.[10]

However, there is no consensus concerning the most certain mechanism that explains the action of H_2O_2/UV in disinfection process. One group[11] employing bacteria such as *Escherichia coli* and *Bacillus subtilis* found a beneficial effect on the rate because of the addition of hydrogen peroxide. Conversely, Rajala-Mustonen and Heinomen-Tanski[12] found the opposite result. Rincon and Pulgarin[13] found a synergistic effect of low wavelength UV radiation and low concentrations of hydrogen peroxide (less than 10 ppm). Bayliss and Waites[14] and Standard *et al.*[15] found an acceptable effectiveness of the method to inactivate vegetative cells and spores employing rather large concentrations of H_2O_2. Even more unusual are the results reported by Hartman and Eisenstark[16] and Chu.[17] They found positive results with *E. coli*, combining hydrogen peroxide with 365 nm UV radiation and the opposite result when employing 254 nm UV radiation. In this work we intend to compare rates of bacteria inactivation (*E. coli*) using UVC radiation alone, H_2O_2 alone and a combination of UVC + H_2O_2 and draw some conclusions about the observed kinetics.

2. Materials and methods

In all experiments, a well-stirred batch annular reactor having a total reaction volume of 2000 cm^3 was employed. The internal radius is r_i = 3.7 cm and the external one is r_o = 7.5 cm. Stirring was achieved with a custom made, strong, eccentrically-operated, orbital shaking device. A cooling jacket connected to a thermostatic bath (Haake) surrounds the reactor to keep the reacting system at a constant temperature of 20 °C. The system was irradiated with two different lamps placed at the centerline of the annular space and separate from the contaminated water by

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a concentric quartz tube. Both lamps were low-pressure mercury lamps having more than 85% emission at 253.7 nm (Germicidal). One was a Philips TUV (15 W) lamp and the other a UV-C Heraeus (40 W) lamp. The employed subrogate bacteria was *E. coli* ATCC 8739. The bacteria were grown in a complex nourishing broth. The working solution was prepared from a bacteria culture that had reached the stationary phase and subjected to a dilution of 1/1000 with physiological solution.

Experiments were made with (i) UVC alone, (ii) hydrogen peroxide alone and (iii) a combination of UVC and H_2O_2. In cases (ii) and (iii), the culture was mixed with the required amount of hydrogen peroxide (Merck, p.a., 30% v/v). The hydrogen peroxide concentration was varied from 45 to 350 ppm. It was exactly measured with colorimetric techniques at 350 nm, according to Allen *et al.*[18] with a Perkin Elmer 300 instrument. The initial concentration of bacteria ($t = 0$) was measured and was always in the order 10^5 CFU. Samples were taken at different time intervals according to the employed disinfection method. Runs were always duplicated and sampling measurements were always triplicated. The initial pH was 7 and remained constant during all experiments.

Every sample was subjected to the following analysis: spectrophotometric measurement of hydrogen peroxide concentration, bacteria counting (in terms of CFU) employing specific Petrifilm™ (3M Microbiology Products) for *E. coli* and coliform bacteria. Dilution of the samples for bacteria counting was made with a sterile peptone solution. Bacteria seeding on the Petrifilm™ plates were incubated for 24 h at 37 °C.

3. Results, interpretation and discussion

3.1. UVC radiation inactivation

The widely used Chick and Watson (C-W) classical model for bacteria disinfection has been known since 1908.[19,20] However, even if it is used for fast control of practical operations, its simplicity and lack of selectivity precludes its application to represent the actual behavior of a large number of microbiological species. In 1972, Hom, based on the C-W model, presented an empirical and flexible modification[21] which was also discussed by P. C. Pretorious and W. A. Pretorious in 1999.[22] Hass *et al.*[23] made an additional improvement in the C-W model including the variation of the disinfectant concentration along the process. More specifically, concerning the application of UV radiation, the most widely used models, including the representation of the initial resistance by the microorganisms, are those known as the multi-hit or multi-target type[24] and the series-event type.[25] The first case considers the existence of a certain amount of specific targets inside the microorganism that must receive a definite number of strikes or hits (n) produced by the incoming photons in order to reach a threshold limit, above which inactivation is produced. Every new hit, before reaching the critical stage (n) is affected by a probability factor that depends on the previously received hits. In the series-event model, when a bacterium is exposed to radiation is suffers a series of successive damages (disablement events) that may be accumulated till the point of reaching a similar threshold limit (n) that produces, as a final outcome, the inactivation.

All those bacteria that for a particular reason do not reach this point are called survival bacteria. In both cases, the threshold limit determines the number of events that are necessary for an almost irreversible inactivation of the microorganism. Both models were analyzed in detail by Severin *et al.*[26] in different reactors and found agreement with the experimental data in relatively short times. In this work, the series-events model is used as a background to introduce conceptual modifications in the evaluation of the effects of different involved variables; *i.e.* we depart from the consideration of a typical second order class of kinetics.

The initial approach is similar. After each damaging event, it is considered that a new species is formed. Then, the process can be represented as a series of n reactions, according to:

$$C_{\mathrm{Ec},0} \xrightarrow{k_1} C_{\mathrm{Ec},1} \xrightarrow{k_2} \ldots C_{\mathrm{Ec},i} \xrightarrow{k_{i+1}} \ldots C_{\mathrm{Ec},n-1} \xrightarrow{k_n} C_{\mathrm{Ec},n} \quad (1)$$

It should be noticed that the initial concentration of bacteria is C^0_{Ec} whereas $C_{\mathrm{Ec},0}$ is the concentration of bacteria that has not received any damage. Only at $t = 0$, $C^0_{\mathrm{Ec}} = C_{\mathrm{Ec},0}$. At any other time, $C_{\mathrm{Ec},i} < C^0_{\mathrm{Ec}}$. $C_{\mathrm{Ec},i}$ is the concentration of a given state of damage (state "i") in the microorganism that has reached the level of injury "i". "n" is the "threshold limit", equal to the number of events needed to reach inactivation (or the number of elapsed stages of damage occurring before reaching total inactivity). Thus, n represents inactivated "species" that have suffered a usually irreversible damage and can be counted as dead bacteria. Consequently, the total number of existing "species" is $n + 1$ in order to account for the species that have not yet received any injury. All bacteria, either the ones that have no damage or the others that have received some stage of damage, but have not reached the threshold limit "n", are survival bacteria: $C_{\mathrm{Ec}} = \sum_{i=0}^{n-1} C_{\mathrm{Ec},i}$. With the above considerations, in mathematical terms, it is only necessary to solve n differential equations, representing the inventory (bacteria balance) for each of the events ("reactions") involving different species, because the number of inactivated or death bacteria can be obtained from the difference between the initial concentration C^0_{Ec} and the concentration of survival bacteria C_{Ec}.

$$C_{\mathrm{Ec,dead}} = C^0_{\mathrm{Ec}} - C_{\mathrm{Ec}} = C^0_{\mathrm{Ec}} - \sum_{i=0}^{n-1} C_{\mathrm{Ec},i} \quad (2)$$

It is possible to write the equivalent to a mass balance (bacteria inventory) for each "species" (state of damage) as follows:

For $i = 0$:

$$\frac{\mathrm{d}C_{\mathrm{Ec},i}}{\mathrm{d}t} = -k_{i+1}(C_{\mathrm{Ec},i})^{\delta}\left\langle(\alpha_{\lambda}E_{\lambda,\mathrm{o}})^{\gamma}\right\rangle \quad (3)$$

For $i = 1, 2, \ldots (n-1)$:

$$\frac{\mathrm{d}C_{Ec,i}}{\mathrm{d}t} = k_i(C_{\mathrm{Ec},i-1})^{\delta}\left\langle(\alpha_{\lambda}E_{\lambda,\mathrm{o}})^{\gamma}\right\rangle - k_{i+1}(C_{\mathrm{Ec},i})^{\delta}\left\langle(\alpha_{\lambda}E_{\lambda,\mathrm{o}})^{\gamma}\right\rangle \quad (4)$$

For $i = n$:

$$\frac{\mathrm{d}C_{\mathrm{Ec},i}}{\mathrm{d}t} = k_i(C_{\mathrm{Ec},i-1})^{\delta}\left\langle(\alpha_{\lambda}E_{\lambda,\mathrm{o}})^{\gamma}\right\rangle \quad (5)$$

Note that k_0 does not exist. This is consistent with the statement that the total number of species is $n + 1$. Also let us remark, as defined above, that the survival bacteria C_{Ec} include $C_{\mathrm{Ec},0}$ but are not equal.

The radiation effect is written in terms of the spectral fluence rate (for a divergent beam), because almost monochromatic radiation is employed, [$E_{\lambda,\mathrm{o}}$ (einsteins^{-1} cm^{-2} nm^{-1})] times the linear

Napierian absorption coefficient α_λ (cm^{-1} nm^{-1}). The model can be greatly simplified if it is assumed that all the kinetic constants for all the events are equal, *i.e.* $k_1 = k_2 = \ldots k_{n-1} = k_n = k$. This constant will be called the inactivation constant. The *E. coli* concentration seems to be raised only to an exponent δ. However, since α_λ includes again the *E. coli* concentration formula, the real exponent is equivalent to a reaction order equal to $\gamma + \delta$. In some cases, the value of $\gamma + \delta$ is 1, but when the logarithmic representation of C_{Ec}/C^0_{Ec} *vs.* time shows a very characteristic "*tailing*", it may take a value that is slightly greater than 1. These equations in the general case should be always written in terms of reactor volume averages of both, $C_{Ec,i}$ and $E_{\lambda,o}$. However, since the reactor is very well mixed, bacteria concentrations are constant. This is not the case of the spectral fluence rate, which is always a function of position (particularly when the medium does not have negligible absorption); *i.e.* there is a non-uniform field of concentration of photons. Therefore, its volume average value must be applied $[(1/V_R)\int_{V_R}(\alpha_\lambda E_{\lambda,o})^\gamma \mathrm{d}V = \langle(\alpha_\lambda E_{\lambda,o})^\gamma\rangle]$. The average is represented by the symbol $\langle \ldots \rangle$.

To obtain the spectral fluence rate, one must solve the radiative transfer equation for the reactor that, for a pseudo homogeneous medium in a three-dimensional space, for any particular direction of radiation propagation given by the directional coordinate s, takes the following form:

$$\frac{\mathrm{d}L_{\lambda,\underline{\Omega}}(s,t)}{\mathrm{d}s} + \alpha_\lambda(s,t)L_{\lambda,\underline{\Omega}}(s,t) = 0 \tag{6}$$

In eqn (6), $L_{\lambda,\underline{\Omega}}$ is the spectral radiance, valid for the monochromatic radiation (λ) and a given direction of propagation $\underline{\Omega}$. From this equation, one can derive a relevant property for a photochemical system that is the fluence rate:

$$E_{\lambda,o}(\underline{x},t) = \int_\Omega L_{\lambda,\underline{\Omega}}(\underline{x},t)\mathrm{d}\Omega \tag{7}$$

Considering that almost monochromatic light is used, from now on the subscript λ will be dropped.

The radiation field inside the reactor was formulated using the Three-dimensional Source with Volumetric Emission model (Fig. 1). This is described in detail by Cassano *et al.*[27] It is based on the following assumptions:

(1) The lamp has an extension given by its used length (L_L) and its radius (r_L); in this extension, emitters are uniformly distributed.

(2) Each elementary volume of the lamp is an emitter. The radiance associated with each bundle of radiation coming from each emitter, at each wavelength, is spherical, isotropic and proportional to its extension.

(3) Each elementary differential volume of the lamp is transparent to the energy emerging by each emitter located in its surroundings.

(4) The lamp is a perfect cylinder whose boundaries are mathematical surfaces without thickness.

(5) In this case, end effects in the lamp electrodes are avoided; *i.e.* the used length is shorter that the lamp length.

(6) A spherical coordinate system located at each point of radiation reception (I) inside the reactor can characterize the arriving radiance. It is necessary to know the distance from such a point to the centerline of the lamp and two pairs of angular coordinates $[(\theta_1,\theta_2), (\phi_1,\phi_2)]$ that define the extension of the useful volume of the lamp.

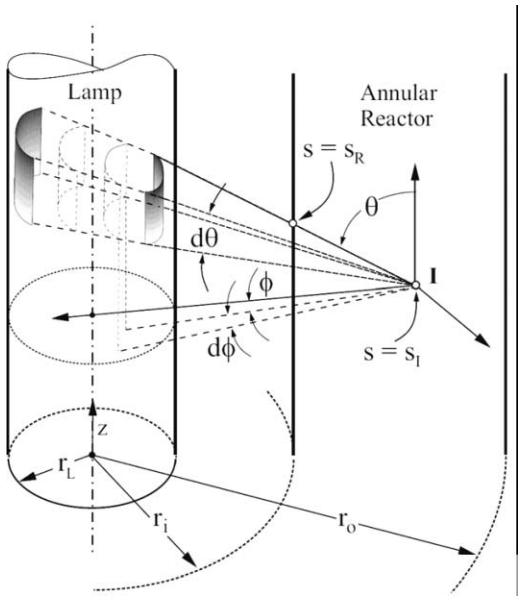

Fig. 1 Schematic diagram of the Three-dimensional Source with Volumetric Emission model. Adapted from ref. 27.

(7) The radiant power of the lamp (P, in units of einstein s^{-1}) can be calculated knowing the dimensions of the lamp and the isotropic characteristics of its emission.

Upon integration of eqn (6) and considering eqn (7) we have:

$$E_o(r,z,t) = \int_{\phi_1}^{\phi_2}\mathrm{d}\phi\int_{\theta_1}^{\theta_2}\mathrm{d}\theta\sin\theta L^0(\theta,\phi)\exp\left[-\int_{s_R}^{s_I}\alpha(s,t)\mathrm{d}s\right] \tag{8}$$

$L^0(\theta,\phi)$ is the boundary condition of eqn (6). Its value is given by:

$$L^0(\theta,\phi) = Y_W\left(\frac{P_{\lambda,L}}{4\pi^2 r_L{}^2 L_L}\right)\frac{2[r^2(\cos^2\phi - 1) + r_L{}^2]^{0.5}}{\sin\theta} \tag{9}$$

Y_W is an average value of the reactor wall transmittance.

The limiting angles for integrating eqn (8) are:

$$\theta_1(\phi) = \tan^{-1}\left\{\frac{r\cos\phi - [r^2(\cos^2\phi - 1) + r_L{}^2]^{0.5}}{L_L - z}\right\} \tag{10}$$

$$\theta_2(\phi) = \tan^{-1}\left\{\frac{r\cos\phi - [r^2\cos^2\phi - 1) + r_L{}^2]^{0.5}}{-z}\right\} \tag{11}$$

$$-\phi_1 = \phi_2 = \cos^{-1}\left[\frac{(r^2 - r_L{}^2)^{0.5}}{r}\right] \tag{12}$$

$E_o(r,z,t)$ can be written in terms of the value of the fluence rate at the inner wall of the annular reactor:

$$E_o(r,z,t) = \frac{E_o|_W}{\Psi}\int_{\phi_1}^{\phi_2}\mathrm{d}\phi\int_{\theta_1}^{\theta_2}\mathrm{d}\theta\ 2[r^2(\cos^2\phi - 1) + r_L{}^2]^{0.5} \times \exp\left[-\int_{s_R}^{s_I}\alpha(s,t)\mathrm{d}s\right] \tag{13}$$

In eqn (13) Ψ is a geometric factor that is not a function of position and defined as:

$$\Psi = \frac{1}{L_R}\int_0^{L_R} dz \int_{\phi_1(r_i)}^{\phi_2(r_i)} d\phi \int_{\theta_1(\phi,r_i,z)}^{\theta_2(\phi,r_i,z)} d\theta\, 2[r_i^2(\cos^2\phi - 1) + r_L^{\,2}]^{0.5} \qquad (14)$$

Notice the difference between eqn (13) and (14). In the second, r_i is a constant. $E_o|_W/\Psi$ gives the boundary condition just before the absorption process by the reacting medium commences at $r = r_i$. Ψ accounts for the geometrical relationship that expresses the relative location of the lamp (with all its dimensions) and the inner wall of the reactor at $r = r_i$. It is clear that, with the exception of the wall compound transmission coefficient given by Y_W, from the lamp till the point at $r = r_i$, the medium is transparent. The integral in eqn (13), on the contrary, is needed to represent the absorption process occurring at each point inside the reaction space.

$E_o|_W$ is a value that can be obtained with potassium ferrioxalate actinometry.[28] The values of the three employed boundary conditions are:

Fluence rate level 1: 15 W lamp, $E_o|_W = 44.17 \times 10^{-9}$ einstein cm^{-2} s^{-1};

Fluence rate level 2: 40 W lamp, $E_o|_W = 22.36 \times 10^{-9}$ einstein cm^{-2} s^{-1};

Fluence rate level 3: 40 W lamp with filter (17%): $E_o|_W = 14.92 \times 10^{-9}$ einstein cm^{-2} s^{-1}.

Being monochromatic light they can also be expressed in terms of CGS units as follows: 20.8×10^{-3} , 10.5×10^{-3} and 7.0×10^{-3} W cm^{-2} respectively.

As indicated before, after integration of eqn (8) with the boundary conditions given by eqn (9) to (12), in order to apply eqn (3), (4) and (5), the volume average of $E_{\lambda,o}$ must be obtained. The result is:

$$\left\langle E_o^{\gamma} \right\rangle = \frac{2}{(r_o^{\,2} - r_i^{\,2})L_R}\left(\frac{E_o|_W}{\Psi}\right)^{\gamma}\int_0^{L_R} dz \int_{r_i}^{r_o} r\,dr \times \left\{\int_{\phi_1}^{\phi_2} d\phi \int_{\theta_1}^{\theta_2} d\theta\, 2[r^2(\cos^2\phi - 1) + r_L^{\,2}]^{0.5} \exp\left[-\int_{s_R}^{s_1} \alpha(s,t)\,ds\right]\right\}^{\gamma} \qquad (15)$$

α is the total absorption coefficient of the system. Several species may contribute to its value. Two typical examples are the culture medium and the bacteria. Thus, rigorously speaking the following equations apply:

$$\alpha = \alpha_{Ec} + \alpha_c \text{ with } \alpha_{Ec} = \sum_{i=1}^{i=n} \hat{\kappa}_{Ec,i} C_{Ec,i}; \quad \hat{\kappa}\,[=]\,\text{cm}^2\ (\text{CFU})^{-1} \text{ and } C_{Ec,i}\,[=]\,\text{CFU cm}^{-3} \qquad (16)$$

The values of α_{Ec} and α_c were measured spectrophotometrically.

Employing previously mentioned spectral fluence rates at the reactor inner wall, inactivation greater than 99.99% was obtained in less than 10 s. Consequently, in transparent waters, UVC radiation is a very effective process for bacteria inactivation.

To obtain the kinetic parameters corresponding to the model described by eqn (3), (4) and (5), the experimental data are compared with simulations from the model, employing a non-linear, multiparameter estimator (Gauss-Newton routine) coupled with an optimization program (the Lebenberg-Marquart algorithm) for global convergence. The method also gives the residual values of the jacobian matrix to calculate the results within a 95% confidence interval. Eqn (3), (4) and (5) were solved with a Runge-Kutta ODE integration program. The parameter estimation was made including all the experiments, comprising the three different fluence rates calculated with the Three-dimensional Source with Volumetric Emission model. There is a special point to notice. The number of events in series is an integer number. Then, it is necessary to try with different numbers ($n = 1, 2, \ldots$ *etc.*) until the minimum error in the estimated parameters is reached. The following results were obtained:

$n = 4$

$\gamma = 0.5$

$k = (1.31 \pm 0.18) \times 10^8$ s^{-1} (cm^3 s einstein^{-1})$^{\gamma}$ (CFU cm^{-3})$^{(1-\delta)}$

$\delta = 0.70 \pm 0.02$

These results indicate that the inactivation has an induction time. The results are shown in Fig. 2. The typical initial shoulder that corresponds to the value of $n = 4$ cannot be seen clearly in the plot of the experimental results due to the difficulties in taking samples at times between $t = 0$ and $t = 2$ s. The existence of this plateau is slightly insinuated for the small value of the fluence rate (40 W lamp, with filter). The small increment in the reaction order with respect to the concentration of *E. coli*, ($\gamma + \delta = 1.2$) is related to the above-mentioned "*tailing*" in the plot.

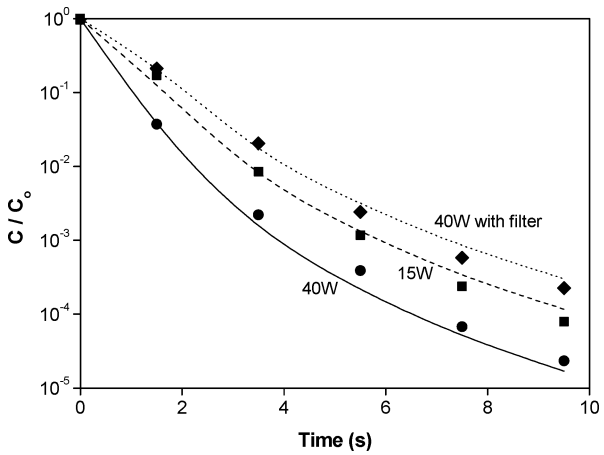

Fig. 2 Results employing UVC radiation alone. Dotted lines, broken lines and solid lines are results from the model.

3.2. Hydrogen peroxide inactivation

Published results concerning H_2O_2 are scarce as compared with the UVC irradiation process. Imlay and Linn[29] used this disinfectant with *E. coli* K-12 and concluded that there are two different ways of operation from the kinetics point of view. Mode I, that explains the results when the hydrogen peroxide concentration is lower than 2×10^{-6} mol cm^{-3} and Mode II when the said concentration is larger that 1×10^{-5} mol cm^{-3}. Lambert *et al.*[30] reported a disinfection kinetics for *Staphylococcus aureus* and *Pseudomonas aeruginosa* using a mixture of hydrogen peroxide and paracetic acid and interpreted their experimental data in terms of the Chick–Watson model and some of its more recent modifications. Yamagiwa *et al.*[31] studied the disinfection of *Legionella pneumophila* using hydrogen peroxide and found that the inactivation process can be

characterized with two different steps: the first, where there is a clear initial time lag and the second one, where the kinetics follow a first order behavior. Usually, the published disinfection literature represents the experimental results in terms of semi-logarithmic plots of survival bacteria as a function of time. One significant part of the reported information indicates the existence of one initial shoulder in the graph, which is attributed to a primary resistance of the microorganisms to the attack by the disinfectant.

Once again, to explain these results the same approach discussed previously has been used: the Muti-target model and the Series-event model described by Severin *et al.*[32] In the past, working with UVC radiation, we published some conceptual modifications to the Series-events model.[33,34] In working with chemical disinfection, we discussed that there is no reason to assume that any form of kinetics should start by proposing a first order dependence either to the bacteria concentration or to the disinfectant concentration. Moreover, after the usually observed initial time lag and, in the absence of tailing, it could be a good approximation to consider that the process has a simple linear dependence with the concentration of the existing microorganisms.[35]

In this work, the preceding approach of considering the model as an equivalent process of a series reaction sequence is proposed again:

$$C_{\mathrm{Ec},0} \xrightarrow{k_S C_P^{\beta}} C_{\mathrm{Ec},1} \xrightarrow{k_S C_P^{\beta}} \ldots C_{\mathrm{Ec},i} \xrightarrow{k_S C_P^{\beta}} \ldots C_{\mathrm{Ec},n_P-1} \xrightarrow{k_S C_P^{\beta}} C_{\mathrm{Ec},n_P} \tag{17}$$

It is possible to write once more an equivalent to a mass balance for this particular form of "reaction":

For $i = 0$:

$$\frac{dC_{\mathrm{Ec},i}}{dt} = -k_S C_{\mathrm{Ec},i} (C_P)^{\beta} \tag{18}$$

For $i = 1,2, \ldots n_P - 1$:

$$\frac{dC_{\mathrm{Ec},i}}{dt} = k_S C_{\mathrm{Ec},i-1} (C_P)^{\beta} - k_S C_{\mathrm{Ec},i} (C_P)^{\beta} \tag{19}$$

For $i = n_P$:

$$\frac{dC_{\mathrm{Ec},i}}{dt} = k_S C_{\mathrm{Ec},i-1} (C_P)^{\beta} \tag{20}$$

The subscript P refers to hydrogen peroxide. As before, "i" indicates a given state of damage. Eqn (18)–(20) must be integrated with the following initial conditions:

$$t = 0 \begin{cases} \text{For } i = 0 & \rightarrow C_{\mathrm{Ec},i} = C^0_{\mathrm{Ec}} \\ \text{For } i = 1, 2, \ldots n_P - 1 & \rightarrow C_{\mathrm{Ec},i} = 0 \end{cases} \tag{21}$$

In this case, eqn (18)–(20) with the initial conditions given by eqn (21) are amenable of an analytical integration to give:

$$\frac{C_{\mathrm{Ec}}}{C^0_{\mathrm{Ec}}} = [\exp(-k_S (C_P)^{\beta} t)] \sum_{i=0}^{n_P - 1} \frac{[k_S (C_P)^{\beta} t]^i}{i!} \tag{22}$$

Experiments at different hydrogen peroxide concentrations were made in the same laboratory reactor used for the disinfection experiences with UVC lamps explained in section 3.1. In this case, the radiation source was switched off.

To some extent, results show accordance with those reported by Imlay and Linn.[29] There is almost no activation for $C_P < 45$ ppm, since in spite of the processing time, the bacteria concentration was only reduced to 90%. Above a C_P concentration of 90 ppm the time lag for the initiation of the decrease in CFU concentration is significantly reduced and the result shows that 99.99% inactivation is achieved. However, the more striking observation is that under these operating conditions a minimum of 150 min of disinfection time was required. Results are shown in Fig. 3. The change in the concentration of hydrogen peroxide along an experimental run is very small. However, an increase in the initial concentration of H_2O_2 produces a significant increase in the inactivation rate of the *E. coli.*

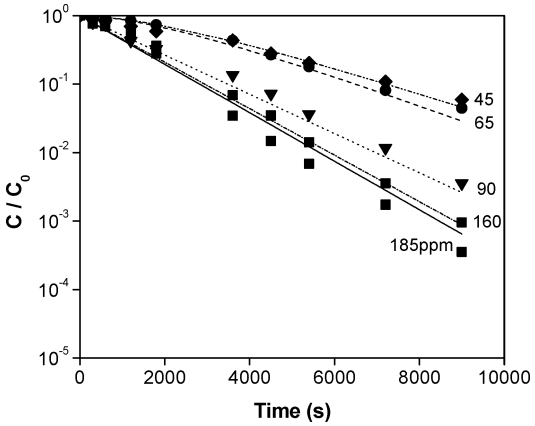

Fig. 3 Results employing hydrogen peroxide alone. Broken and dotted lines, broken lines, dotted lines and solid lines are results from the model.

Following the same procedure described before; *i.e.* using the experimental data and the simulation resulting from the model, employing the same mathematical method, the following parameters for eqn (18)–(22) were obtained:

$n_P = 1$ for $C_P \geq 90$ ppm (2.65×10^{-3} mol cm^{-3})

$n_P = 2$ for $C_P < 90$ ppm (2.65×10^{-3} mol cm^{-3})

$k_P = (3.75 \pm 0.09) \times 10^{-3}$ s^{-1} (cm^3 mol^{-1})$^{\beta}$

$\beta = (0.29 \pm 0.02)$

Clearly, the small reaction order found for the hydrogen peroxide effect, explains, to same extent, the very long processing times required by this technology.

3.3. Disinfection with UVC and hydrogen peroxide

Publications concerning kinetic studies of the combined use of UVC radiation and hydrogen peroxide are very limited. Sundstrom *et al.*[11] proposed two kinetic models: a mixed second order model and an application of the typical Series-event model. Later Gardner and Sharma[36] described the inactivation of spores of *B. subtilis* in terms of a kinetic expression derived from the Multi-target model. Just recently, Alkan *et al.*[37] studied inactivation working with coliform bacteria in superficial waters and interpreted their results calculating the coefficients of the Chick–Watson model.

In this work, we will apply the Modified Series Event model. It must be noted that according to the results shown in sections 3.1 and 3.2, the time required for bacterium inactivation are not comparable (10 s *versus* > 10 000 s). Table 1 shows the time required to reach the same level of reduction of the microbiological contamination for three of the alternatives explored before. It is clear that the effect produced by hydrogen peroxide alone is

Table 1 Processing time to reach 99.99% reduction of the CFU concentration

Process	Time/s
UVC (40 W) irradiation.	10
UVC (15.6 W) irradiation (40 W with filter)	14
Hydrogen peroxide: 100 ppm	14 400

negligible compared with the one corresponding to UVC alone. Then it is not necessary to consider the existence of two parallel, competitive reaction kinetics. However, a very significant outcome was observed. The time required to reach 99.99% inactivation increases when H_2O_2 is added. The larger the added concentration of hydrogen peroxide, the longer the time to reach the desired inactivation results.

The Series-event model was applied once more. The equations for this process are very similar to those derived for the first case. However, eqn (15) must be significantly modified according to:

$$\alpha = \alpha_{EC} + \alpha_C + \alpha_P \tag{23}$$

where $\alpha_P = \kappa_P C_P$. Experiments were conducted with the same three levels of irradiation described before and hydrogen peroxide concentration between 90 to 350 ppm. It was observed that the time required to reach a 99.99% inactivation was larger than in the case when UVC alone was used. Qualitatively it is possible to conclude that the presence of H_2O_2 has a negative effect on the process.

Employing eqn (3), (4), (5), and (15), but taking into account eqn (23), it was necessary to perform a new parameter estimation. The obtained results are:

$k = (1.56 \pm 0.25) \times 10^8$ s^{-1} (cm^3 s einstein^{-1})$^{\gamma}$ (CFU cm^{-3})$^{1-\delta}$

$\delta = 0.66 \pm 0.02$

$\gamma = 0.5$

The number of events to reach the threshold limit for the combined process and for each set of experiments is shown in Table 2. Fig. 4 and 5 show the results obtained with both lamps, employing different concentrations of hydrogen peroxide. It is clear that the hydrogen peroxide produces a detrimental effect in the process.

For the range of explored hydrogen peroxide concentrations, four main consequences are apparent: (i) the time required for inactivation is longer and (ii) the number of events (needed hits on the cell to produce the threshold limit of damage) is significantly increased, (iii) the slope of the of the lines corresponding to UVC alone and UVC + H_2O_2 are very similar and (iv) the values of k, δ, and γ show very small differences.

One explanation is immediate: hydrogen peroxide acts as an inner filter, absorbing UVC radiation (at 254 nm, its molar napierian absorption coefficient is not too high but important as compared with the other components of the "reacting" medium). Thus, the radiation field that acts on the bacteria is reduced and this diminution is a function of the applied concentration of H_2O_2. Furthermore, if the radiation field is attenuated, more events in series will be needed to reach the threshold limit.

A second possibility that cannot be totally disregarded and that would also explain the increase in the necessary number of damaging events, could be related to the possibility of the bacteria to form a protecting shell with the molecules of hydrogen peroxide, increasing in this way, the length of the initial time lag.

Table 2 Number of events required to reach the threshold limit as a function of the employed H_2O_2 concentration

40 W Lamp		15 W Lamp	
C_P (ppm)	n_C	C_P (ppm)	n_C
0	4	0	4
150	5	90	5
250	6	150	6
350	7	215	7

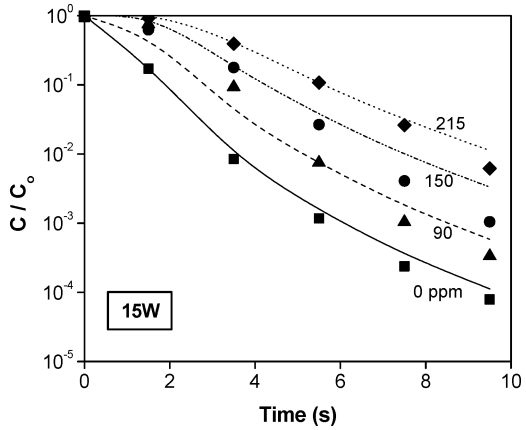

Fig. 4 Results employing UVC plus hydrogen peroxide. 15 W nominal input power lamp. Dotted lines, dotted and broken lines, broken lines and solid lines are results from the model.

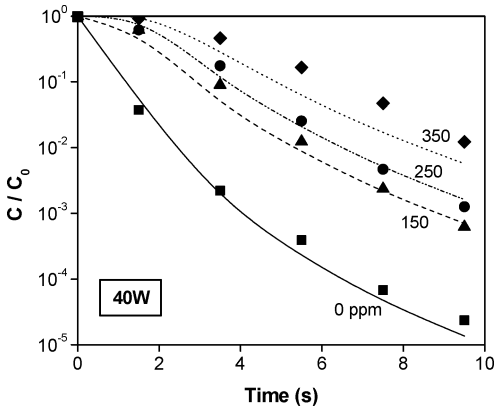

Fig. 5 Results employing UVC plus hydrogen peroxide. 40 W nominal input power lamp. Dotted lines, dotted and broken lines, broken lines and solid lines are results from the model.

4. Conclusions

From the reported information on disinfection of surface water, it can be concluded that within the range of explored variables:

1. UVC radiation alone is the most efficient process;

2. Indubitably, hydrogen peroxide alone is an impracticable process;

3. The combination of UVC and hydrogen peroxide, under the explored operating conditions, is detrimental to the UVC effectiveness performance.

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References

1 W. J. Cooper, E. Cadavid, M. G. Nickelsen, K. J. Lin, C. N. Kuruez and T. D. Waite, Removing THMs from drinking-water using high-energy electron-beam irradiation, *J. Am. Water Works Assoc.*, 1993, **85**, 106–112.
2 M. J. Nieuwenhuijsen, M. B. Toledano and P. Elliott, Uptake of chlorination disinfection by-products; a review and a discussion of its implications for exposure assessment in epidemiologic studies, *J. Exposure Anal. Environ. Epidemiol*, 2000, **10**, 586–599.
3 J. M. Symons and K. L. Worley, An advanced oxidation process for DBP precursors with catalytic-oxidation, *J. Am. Water Works Assoc.*, 1995, **87**, 66–75.
4 J. Jagger, *Introduction to Research in Ultraviolet Photobiology*, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1967.
5 Y. A. Lawryshyn and B. Cairns, UV Disinfection of Water: The Need for UV Reactor Validation, *Water Supply*, 2003, **3**, 293–300.
6 B. Halliwell and J. M. C. Gutteridge, Oxygen toxicity, oxygen radicals, transition metals and disease, *Biochem. J.*, 1984, **219**, 1–14.
7 R. J. Watts, D. Washington, J. Jowsawkeng, F. J. Loge and A. L. Teel, Comparative toxicity of hydrogen peroxide, hydroxyl radicals, and superoxide anion to Escherichia coli, *Adv. Environ. Res.*, 2003, **7**, 961–968.
8 J. Koivunen and H. Heinonen-Tanski, Inactivation of enteric microorganisms with chemical disinfectants, UV irradiation and combined chemical/UV treatments, *Water Res.*, 2005, **39**, 1519–1526.
9 A. G. Fantel, Reactive oxygen species in developmental toxicity: Review and hypothesis, *Teratology*, 1996, **53**, 196–217.
10 C. Bayliss and W. Waites, The effect of hydrogen peroxide and ultraviolet irradiation on non-sporing bacteria, *J. Appl. Bacteriol.*, 1980, **48**, 417–422.
11 D. W. Sundstrom, B. A. Wier, T. A. Barber and H. E. Klein, Destruction of pollutants and microorganisms in water by UV light and hydrogen peroxide, *Water Pollut. Res. J. Can.*, 1992, **27**, 57–68.
12 R. Rajala-Mustonen and H. Heinomen-Tanski, Effect of advanced oxidation processes on inactivation of coliphages, *Water Sci. Technol.*, 1995, **31**, 131–134.
13 A. Rincón and C. Pulgarin, Effect of pH, inorganic ions, organic matter and H_2O_2 on *Escherichia coli* K12 photocatalytic inactivation by TiO_2. Implications in solar water disinfection, *Appl. Catal. B: Environ.*, 2004, **51**, 283–302.
14 C. Bayliss and W. Waites, The combined effect of hydrogen peroxide and ultraviolet irradiation on bacterial spores, *J. Appl. Bacteriol.*, 1979, **47**, 263–269.
15 C. Standard, J. S. Abbis and J. M. Wood, Combined Treatment with hydrogen peroxide and ultraviolet irradiation to Reduce microbial contamination levels in pre-formed food packaging cartons, *J. Food Protect.*, 1983, **46**, 1060–1064.
16 P. Hartman and A. Eisenstark, Synergistic killing of *Escherichia coli* by near-uv radiation and hydrogen peroxide: distinction between RecA-repairable and RecA-non-repairable damage, *J. Bacteriol.*, 1978, **133**, 769–774.
17 C. L. Chu, The synergistic effect of hydrogen peroxide and ultraviolet irradiation in killing Escherichia coli, Project Number S1304, California State Science Fair, 2002.
18 A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, Decomposition of Water and Aqueous Solutions Under Mixed Fast Neutron and Gamma Radiation, *J. Phys. Chem.*, 1952, **56**, 575–586.
19 H. Chick, An Investigation of the Laws of Disinfection, *J. Hyg.*, 1908, **8**, 92–158.
20 H. E. Watson, A note on the Variation of the Rate of Disinfection with Change in the Concentration of the Disinfectant, *J. Hyg.*, 1908, **8**, 536–542.
21 L. W. Hom, Kinetics of Chlorine Disinfection of an Ecosystem, *J. Sanit. Eng. Div., Am. Soc. Civ. Eng.*, 1972, **98(SA1)**, 183–194.
22 P. C. Pretorius and W. A. Pretorius, Disinfection of Purified Sewage Effluent with Monochloramine, *Water SA*, 1999, **25**, 463–472.
23 Ch. Haas, *Disinfection, Chapter 14,Water Quality & Treatment-American Water Works Association (AWWA)*. Fifth Edition, McGraw-Hill Inc., 1999.
24 W. Harms, *Biological Effects of Ultraviolet Radiation*, Cambridge University Press, Cambridge, 1980.
25 B. Severin, *Kinetic Modeling of Microbial Inactivation by Ultraviolet*, Doctoral Thesis, University of Illinois at Urbana-Champaign, 1982.
26 B. Severin, M. Suidan and R. Engelbrecht, Kinetic Modeling of UV Disinfection of Water, *Water Res.*, 1983, **17**, 1669–1678.
27 A. E. Cassano, C. A. Martín, R. J. Brandi and O. M. Alfano, Photoreactor Analysis and Design Fundaments and Aplications, *Ind. Eng. Chem. Res.*, 1995, **34**, 2155–2201.
28 S. L. Murov, I. Carmichel and G. L. Hug, *Handbook of Photochemistry*, 2nd edn., Marcel Dekker Inc., New York. 1993.
29 J. A. Imlay and S. Linn, Bimodal pattern of killing of DNA-Repair-defective or anoxically grown *Escherichia coli* by hydrogen peroxide, *J. Bacteriol.*, 1986, **166**, 519–527.
30 R. J. W. Lambert, M. D. Johnston and E. A. Simons, A kinetic study of the effect of hydrogen peroxide and peracetic acid against Staphylococcus aureus and Pseudomonas aeruginosa using the Bioscreen disinfection method, *J. Appl. Microbiol.*, 1999, **87**, 782–786.
31 K. Yamagiwa, H. Shimizu, K. Takahashi, M. Yoshida and A. Ohkawa, Disinfection kinetics of Legionella pheumophila by hydrogen peroxide, *J. Chem. Eng. Jpn*, 2001, **34**, 1074–1077.
32 B. F. Severin, M. T. Suidan and R. S. Engelbrecht, Series-Event kinetic model for chemical disinfection, *J. Environ. Eng.*, 1984, **110**, 430–439.
33 M. D. Labas, C. A. Martín and A. E. Cassano, Kinetics of bacteria disinfection with UV radiation in an absorbing and nutritious medium, *Chem. Eng. J.*, 2005, **114**, 87–97.
34 M. D. Labas, R. J. Brandi, C. A. Martín and A. E. Cassano, Kinetics of bacteria inactivation employing UV radiation under clear water conditions, *Chem. Eng. J.*, 2006, **121**, 135–145.
35 M. D. Labas, C. S. Zalazar, R. J. Brandi and A. E. Cassano, Reaction Kinetics of Bacteria Disinfection Employing Hydrogen Peroxide, *Biochem. Eng. J.*, 2008, **38**, 78–87.
36 D. W. M. Gardner and G. Shama, The kinetics of Bacillus subtilis spore inactivation on filter paper by UV light and UV light in combination with hydrogen peroxide, *J. Appl. Microbiol.*, 1992, **84**, 633–641.
37 U. Alkanm, A. Teksoy, A. Atesli and H. Baskaya, Efficiency of the UV/H_2O_2 process for the disinfection of humic surface waters, *J. Environ. Sci. Health, Part A*, 2007, **42**, 497–506.

