Modelling the kinetics of UV/H$_2$O$_2$ oxidation of dichloroacetic acid

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Abstract The intrinsic reaction kinetics of the decomposition of dichloroacetic acid (DCA) using UV/H$_2$O$_2$ was studied. A complete mathematical model, including the effect of the absorbed radiation intensities and H$_2$O$_2$ concentration was developed. The results of the kinetic measurements were analysed using a complete mathematical model of the experimental device that was used for the laboratory operation (a differential reactor inside a recycle). In this way it was expected to obtain intrinsic kinetic parameters. Experimental data agree well with theoretical predictions esmploying just two kinetic parameters derived from the proposed reaction mechanism.

Keywords Dichloroacetic acid; kinetics; UV/hydrogen peroxide; water pollution

Introduction

Dichloroacetic acid (DCA) is a pollutant that can be found in water as a byproduct of chlorine disinfection (DBPs) and can also be detected in wastewaters resulting from the degradation of several chlorinated compounds. DCA is one of the haloacetic acids (HAAs) that have been classified as possible carcinogenic compounds by the US Environmental Protection Agency (USEPA).

Conventional methods such as air stripping or adsorption by activated carbon are not good alternatives for DCA due to its high solubility in water and low vapour pressure. Thus, advanced oxidation technologies seem to be a potential choice to decrease DCA concentrations within admissible limits, particularly because complete mineralisation can always be achieved. The combination of hydrogen peroxide and UV radiation should be a suitable process for treating these type of pollutants.

This work was planned to derive, from a plausible reaction sequence, a mathematical model able to represent the kinetics of DCA oxidation and validate its quality with experiments. The kinetic model must be independent of the shape, size and configuration of the laboratory reactor in order to be apt for scaling up purposes.

Methods

Experimental procedure

The employed experimental device was a cylinder, with two parallel, flat windows made of quartz. Each window was irradiated with a tubular, germicidal lamp ($\lambda = 253.7$ nm) placed at the focal axis of a parabolic reflector. The small reactor was part of a recycle that includes a pump, a heat exchanger (for temperature control) and a large volume, well stirred tank with provisions for sampling and temperature measurements (Figure 1). Experiments were carried out changing the following variables: (i) initial DCA concentration, (ii) radio of H$_2$O$_2$ to DCA concentrations and (iii) incident radiation with filters (Table 1).

Figure 1 Equipment set up
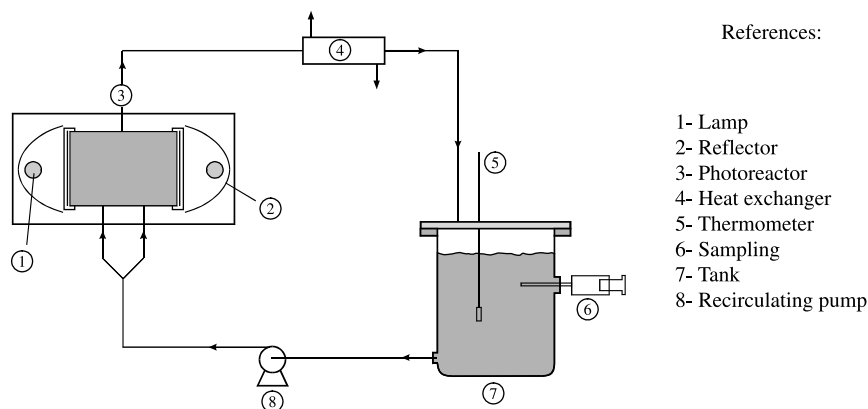
References:

1- Lamp
2- Reflector
3- Photoreactor
4- Heat exchanger
5- Thermometer
6- Sampling
7- Tank
8- Recirculating pump

Table 1 Experimental programme

Variable	Range
DCA concentration (ppm)	30–120
H_2O_2 concentration (ppm)	8–560
Incident radiation (Einstein cm^{-2} s^{-1}) $\times 10^9$	
Heraeus 40 W (100%)	29.85
Heraeus 40 W (16%) (with filter)	4.75
pH during reaction	3.4–2.9

Kinetic model

The required reaction path for the degradation of dichloroacetic acid with H_2O_2/UV is illustrated in Table 2.

It is widely accepted that the main interactions between hydrogen peroxide with UV radiation and free radicals are well represented by reactions (1)–(6) (Glaze *et al.*, 1995; Crittenden *et al.*, 1999) while the reactions (7)–(10) correspond to the decomposition of DCA and have been proposed taking into account the reported reaction steps between the $^{\bullet}$OH radical and the acetate ion in aqueous solution (Schuchmann *et al.*, 1985) which is assumed to have a similar behaviour to DCA. These steps involve the formation of phosgene ($COCl_2$), but it is well known that in water solution reaction 10 is very fast.

Using the mass action law and the micro-steady-state approximation, a kinetic model was developed. Steps 3 and 5 have been assumed negligible, compared with all the others in the proposed scheme. With this kinetic representation the following limiting behaviour can be described: (a) for high irradiation rates, the DCA reaction rate (R_{DCA}) is

Table 2 Reaction scheme

No.	Steps	Reaction	Const. (cm^3/mol s)
1	**Initiation**	$H_2O_2 \xrightarrow{\phi_P} 2^{\bullet}OH$	
2	**Propagation**	$H_2O_2 + {}^{\bullet}OH \xrightarrow{k_2} HO_2^{\bullet} + H_2O$	2.7×10^{10}
3		$H_2O_2 + HO_2^{\bullet} \xrightarrow{k_3} {}^{\bullet}OH + H_2O + O_2$	3.0×10^3
4	**Termination**	$2^{\bullet}OH \xrightarrow{k_4} H_2O_2$	5.5×10^{12}
5		$2HO_2^{\bullet} \xrightarrow{k_5} H_2O_2 + O_2$	8.3×10^8
6		${}^{\bullet}OH + HO_2^{\bullet} \xrightarrow{k_6} H_2O + O_2$	6.6×10^{12}
7	**Decomposition**	$Cl_2HCCOO^- + {}^{\bullet}OH \xrightarrow{k_7} {}^{\bullet}CCl_2COO^- + H_2O$	–
8		${}^{\bullet}CCl_2COO^- + O_2 \xrightarrow{k_8} {}^{\bullet}OOCCl_2COO^-$	–
9		$2^{\bullet}OOCCl_2COO^- \xrightarrow{k_9} 2COCl_2 + 2CO_2 + O_2$	–
10		$COCl_2 + H_2O \xrightarrow{k_{10}} 2HCl + CO_2$	–

proportional to the square root of the $e^a(x, t)$, the local volumetric rate of photon absorption (LVRPA) and (b) for low irradiation rates, the DCA reaction rate is directly proportional to $e^a(x, t)$. The same pattern is obtained for the hydrogen peroxide rate (R_P). According to the existing information (Glaze *et al.*, 1995; Stefan *et al.*, 1996; Crittenden *et al.*, 1999; Colona *et al.*, 1999) and the employed levels of $e^a(x, t)$, from the complete kinetic model the following equations were obtained:

$$R_{DCA}(x, t) = -\frac{2k_7\varphi_P C_{DCA}(t)e^a(x, t)}{2k_2 C_P(t) + k_7 C_{DCA}(t)} \tag{1}$$

$$R_P(x, t) = -\varphi_P e^a(x, t) - \frac{2k_2\varphi_P C_P(t)e^a(x, t)}{2k_2 C_P(t) + k_7 C_{DCA}(t)} + k_4\left[\frac{2\varphi_P e^a(x, t)}{2k_2 C_P(t) + k_7 C_{DCA}(t)}\right]^2 \tag{2}$$

In eqn (2), the quadratic term is negligible with respect to the other ones according to the working experimental conditions and the values in Table 2.

In these equations φ_p and k_7 are the kinetic constants to be determined. The radiation intensity effect was calculated by solving the radiation balance in the experimental reactor.

The radiation balance

For the one-dimensional radiation field, that is applicable to our experimental device and monochromatic radiation, the equation for the spectral incident radiation takes the following form:

$$\frac{dG(x, t)}{dx} + G(x, t)\kappa(x, t) = 0 \tag{3}$$

In the case of this reactor the radiation originated in lamp 1 and 2, may arrive at any point p from two opposite sides. Then:

$$G_T(x, t) = G_1(x, t) + G_2(x, t) \tag{4}$$

with

$$G_1(x, t) = G_{W,1} \exp[-\kappa_T(t)x]$$
$$G_2(x, t) = G_{W,2} \exp[-\kappa_T(t)(L_R - x)] \tag{5}$$

where G_W is the incident radiation at the reactor wall and κ_T is the total absorption coefficient of the reacting system.

The local volumetric rate of photon absorption by the radiation absorption species, at a given point in the reactor (the LVRPA) is given as follows:

$$e^a(x, t) = \kappa_R(t)G_T(x, t) \tag{6}$$

where κ_R is the volumetric absorption coefficient of the reactant absorbing species. This coefficient can be obtained by direct application of Beer's equation (for this work, $\kappa_R = \kappa_P = C_P \times \kappa_P^*$, because radiation absorption by DCA has been shown to be negligible). If $G_{W,1} = G_{W,2} = G_W$, substituting eqn (5) into eqn (4) and the resulting equation into eqn (6), gives:

$$e^a(x, t) = \kappa_P G_W\{\exp[-\kappa_P(t)x] + \exp[-\kappa_P(t)(L_R - x)]\} \tag{7}$$

The boundary condition G_W: actinometry. Incident radiation at $x = 0$ and $x = L_R$ was evaluated with actinometer measurements using potassium ferrioxalate. For the actinometer reaction:

$$R_{Fe^{+2}}(x, t) = \phi_{Act}e^a(x, t) \tag{8}$$

In eqn (8) the reactant is Fe^{+3}, the reaction product is Fe^{+2} and ϕ_{Act} the overall actinometer quantum yield in terms of the product.

In the described reactor, for low reactant conversion, the plot of (Fe^{+2}) vs. time gives a straight line. The slope of such line at $t \rightarrow 0$ is

$$\left(\frac{dC_{Fe^{+2}}}{dt}\right)_{t\rightarrow 0} = \lim_{t\rightarrow 0}\left(\frac{C_{Fe^{+2}} - C_{Fe_0^{Fe^{+2}}}}{t - t_0}\right) \tag{9}$$

Employing eqns (8) and (9) and the corresponding mass balance, integrating over the reactor volume, and considering that at initial conditions: (a) $\kappa_{Fe^{+2}}(t \rightarrow 0) \cong 0$ and (b) at 253.7 nm $\kappa_{Fe^{+3}}$ is very large, we can get:

$$G_W = \lim_{t\rightarrow 0}\left(\frac{C_{Fe^{+2}} - C_{Fe_0^{Fe^{+2}}}}{t - t_0}\right)\frac{V_T}{A_R\phi_{Act}} \tag{10}$$

where V_T is the total volume and A_R is the total area of radiation entrance.

The mass balance

A mass balance for species (i) in the batch, well-stirred tank photoreactor with recycle gives (Cabrera *et al.*, 1997):

$$\frac{d\langle C_i(x,t)\rangle_{V_R}}{dt} = \frac{V_R}{V_T}\langle R_i(x,t)\rangle_{V_R} = \frac{V_R}{V_T}\frac{1}{L_R}\int_0^{L_R} R_i(x,t)dx \tag{11}$$

with the following initial condition:

$$\langle C_i(x,0)\rangle_{V_R} = C_i^0 \tag{12}$$

Substituting the reaction rate for the stable species ($i = DCA, P$) into eqn (11) we finally get:

$$\frac{d\langle C_{DCA}(x,t)\rangle_{V_R}}{dt} = \frac{V_R}{V_T}\left\langle -\frac{2k_7\phi_P C_{DCA}(t)e^a(x,t)}{2k_2 C_P(t) + k_7 C_{DCA}(t)}\right\rangle_{V_R} \tag{13}$$

$$\frac{d\langle C_P(x,t)\rangle_{V_R}}{dt} = \frac{V_R}{V_T}\left\langle -\phi_P e^a(x,t) - \frac{2k_2\phi_P C_P(t)e^a(x,t)}{2k_2 C_P(t) + k_7 C_{DCA}(t)}\right\rangle_{V_R} \tag{14}$$

Model and experimental results

The rate of DCA degradation sensitised by the H_2O_2/UV photolysis depends on the ratio of hydrogen peroxide to DCA concentrations. For example, the optimum range of H_2O_2 concentration is about 2–4 mM for a DCA concentration of 0.48 mM. At lower concentrations, H_2O_2 absorbs only a small fraction of the incident light, and the rate of DCA removal is too slow. At higher concentrations, H_2O_2 becomes a strong scavenger for $^\bullet OH$ radicals, competing with DCA, and hence the rate of DCA degradation decreases. Others authors observed a similar effect in the treatment of different pollutants (Glaze *et al.*, 1995; Stefan *et al.*, 1996; Shu and Chang, 2005).

The mass balance for DCA degradation and chloride ion formation was closed with very small error at any time, indicating that in an aqueous medium there are no significant stable intermediate reaction products. In addition to this, the total organic carbon (TOC) determined experimentally by carbon analysis, agrees very well with that calculated considering the concentration of DCA the only stable organic compound present in the system.
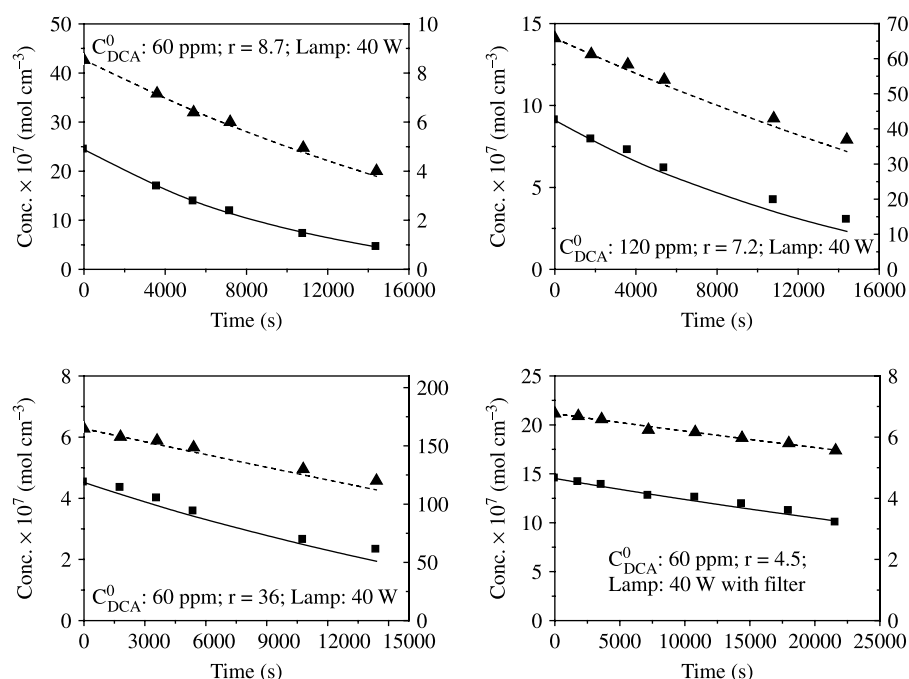
Figure 2 Predicted vs. experimental values in the DCA degradation with UV/H_2O_2: H_2O_2 experimental, H_2O_2 model, DCA experimental, DCA model, r: H_2O_2/DCA molar ratio

Using the kinetic model (that includes the radiation model for step 1), the mass balance for the recycling system, the reference values of the known kinetic constants (Buxton *et al.*, 1988) and the experimental data, upon application of the Levenberg-Marquardt optimization algorithm, the following kinetic constants were obtained:

$$\varphi_P = 0.47 \pm 0.03 \, \text{mol einstein}^{-1} \quad \text{and} \quad k_7 = (1.24 \pm 0.11) \times 10^{11} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$$

Experimental data can be compared with theoretical predictions from the reactor-reaction kinetic model. Figure 2 is an example of the quality of the developed kinetic model for the different experimental conditions employed. In addition to this, the estimated ϕ_P value differs only by 6% with respect to the reference data.

Conclusions

A kinetic model has been developed to describe the degradation of dichloroacetic acid using hydrogen peroxide plus UV radiation. It predicts with a reasonable degree of accuracy the performance of this reaction under a wide variety of experimental conditions, i.e., different ratios of H_2O_2 to DCA concentrations, initial DCA concentrations and irradiation levels. Hence this kinetic model could be directly used for scaling-up purposes.

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