

Development of a Kinetic Model for the Photodegradation of 4-Chlorophenol using a XeBr Excilamp

M. Gomez, M. D. Murcia, E. Gomez, J. L. Gomez, and N. Christofi

Abstract—Excilamps are new UV sources with great potential for application in wastewater treatment. In the present work, a XeBr excilamp emitting radiation at 283 nm has been used for the photodegradation of 4-chlorophenol within a range of concentrations from 50 to 500 mg L⁻¹. Total removal of 4-chlorophenol was achieved for all concentrations assayed. The two main photoproduct intermediates formed along the photodegradation process, benzoquinone and hydroquinone, although not being completely removed, remain at very low residual concentrations. Such concentrations are insignificant compared to the 4-chlorophenol initial ones and non-toxic. In order to simulate the process and scale-up, a kinetic model has been developed and validated from the experimental data.

Keywords—4-chlorophenol, excilamps, kinetic model, photodegradation.

NOMENCLATURE

a_1 = model parameter defined in (47), dimensionless
 a_2 = model parameter defined in (61), dimensionless
 b_1 = model parameter defined in (47), dimensionless
 b_2 = model parameter defined in (61), dimensionless
 BQ = benzoquinone
 c_1 = model parameter defined in (47), dimensionless
 c_2 = model parameter defined in (61), dimensionless
 4CP = 4-chlorophenol

HQ = hydroquinone

k = pseudo-first order rate constant for 4-chlorophenol

photodegradation, min⁻¹

k_1 = kinetic constant for HQ formation from 4CP, min⁻¹

k_2 = kinetic constant for BQ formation from 4CP, min⁻¹

k_3 = kinetic constant for HQ decomposition to final products, min⁻¹

$k_{3.1}$ = kinetic constant for final products partial conversion to HQ, min⁻¹

k_4 = kinetic constant for BQ decomposition to final products, min⁻¹

$k_{4.1}$ = kinetic constant for final products partial conversion to BQ, min⁻¹

s = Laplace variable

t = reaction time, min

X_{BQ} = benzoquinone conversion, dimensionless

X_{4CP} = 4-chlorophenol conversion, dimensionless

X_{HQ} = hydroquinone conversion, dimensionless

[BQ] = concentration of benzoquinone at time t , mM

[BQ]₀ = initial concentration of benzoquinone, mM

[4CP] = concentration of 4-chlorophenol at time t , mM

[4CP]₀ = initial concentration of 4-chlorophenol at time t , mM

[HQ] = concentration of hydroquinone at time t , mM

[HQ]₀ = initial concentration of hydroquinone, mM

I. INTRODUCTION

CHLOROPHENOLS are common pollutants widely found in wastewaters of numerous industries. These pollutants are often released from industry without appropriate treatment, which causes negative effects on both human beings and the environment [1, 2, 3].

Although a wide variety of physical, chemical and biological methods has been utilised in the removal of these toxic compounds, a definitive solution remains [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. Technology utilising advanced oxidation processes (AOPs) has proven to be an efficient alternative to biological treatments when dealing with high pollutant concentrations [17, 18, 19, 20, 21]. Among these methods, photodegradation of the contaminants with UV radiation has shown great potential.

The high-, medium- and low-pressure UV mercury lamps, at a wavelength of primarily 254 nm, are typically used in photolysis of chlorophenols [22, 23, 24], and, frequently,

M. Gomez was with the Department of Chemical Engineering, Murcia University, 30071 Murcia, Spain (corresponding author, phone: 0034- 968-367351, Fax: 0034- 968-364148; e-mail: maria.gomez@um.es). She is currently with the Pollution Research Unit, School of Life Sciences, Edinburgh Napier University, Merchiston Campus, Edinburgh EH10 5DT, Scotland UK.

M. D. Murcia was with the Department of Chemical Engineering, Murcia University, 30071 Murcia, Spain (e-mail: md.murcia@um.es). She is currently with the Pollution Research Unit, School of Life Sciences, Edinburgh Napier University, Merchiston Campus, Edinburgh EH10 5DT, Scotland UK.

E. Gomez is with the Department of Chemical Engineering, Murcia University, 30071 Murcia, Spain (e-mail: egomez@um.es).

J. L. Gomez is with the Department of Chemical Engineering, Murcia University, 30071 Murcia, Spain (e-mail: carrasco@um.es).

N. Christofi is with the Pollution Research Unit, School of Life Sciences, Edinburgh Napier University, Merchiston Campus, Edinburgh EH10 5DT, Scotland UK (e-mail: n.christofi@napier.ac.uk).

catalysts have been used to improve the process efficiency, titanium dioxide being the most common [25, 26, 27, 28].

The development of excimer lamps as new UV radiation sources and their use in the destruction of toxic organic pollutants from wastewater has turned out to be an attractive alternative to commonly used mercury lamps [29, 30]. Excimer lamps, or excilamps, are a class of spontaneous radiation sources based on transitions of exciplex (rare gas halides) or excimer molecules (rare gas or halogen dimers). Their main advantage is the emission of a narrow-band ultraviolet radiation. Other advantages include the absence of elemental mercury, long lifetime (from 1000 to 10000 h), geometric freedom and high photon flux [31].

As far as we are aware there are no kinetic studies related to excilamps. However, numerous studies can be found in the area of photocatalytic processes based on UV mercury lamps and the use of catalysts such as titanium dioxide [25, 26, 27, 28]. The kinetic models proposed are basically of two types: the lineal model based on first order kinetics and the Langmuir-Hinshelwood non-linear model, which involves a prior adsorption process of the photocatalytic substrate on the catalyst surface and its subsequent degradation. The initial reaction rate, expressed as the variation of the initial photocatalytic substrate concentration, C_0 , over time is given as follows:

First order kinetic model:

$$\frac{dC_0}{dt} = -k_r C_0$$

Langmuir-Hinshelwood model:

$$\frac{dC_0}{dt} = -\frac{k_r K_s C_0}{1 + K_s C_0}$$

where k_r is the kinetic constant, in both models, and K_s is the apparent adsorption constant in Langmuir model.

It is known that a thorough understanding of degradation processes and their simulation is vital in order to predict the behaviour of treatment systems and their scaling up [32, 33]. From this point of view, in the present work a XeBr excilamp has been used for 4-chlorophenol photodegradation and, additionally, a simplified photocatalytic kinetic model has been developed based on the experimental data.

II. MATERIALS AND METHODS

4-chlorophenol (99%), p-benzoquinone (98%) and hydroquinone (99%) were all purchased from Sigma-Aldrich.

A XeBr excilamp with output power of 5 W and emitting maximum UV radiation at 283 nm was used for photodegradation experiments. The excilamp was of cylindrical geometry covered by a metal case having a UV exit window with an area of 75 cm² [31]. The exit window was oriented vertically in close proximity to a quartz tube with an operating length of 22 cm and external diameter of 2.6 cm. 4-chlorophenol at the required concentrations, ranging from 50 to 500 mg L⁻¹ (0.389 to 3.891 mM) was dissolved in 10 ml of distilled water, placed into the quartz tube covered with a reflector and irradiated at room temperature (23–25 °C) under

static conditions and for exposure times ranging from 20 to 90 minutes depending on the initial 4-chlorophenol concentration.

The output power of the excilamp was measured with a H8025-222 photodetector (Hamamatsu Photonics KK) and was tested using an electrochemical actinometer. The average radiation intensity delivered to the solution was 17.12 mW cm⁻².

Any 4-chlorophenol remaining after the treatment and the two main photoproducts of the photodegradation process, benzoquinone and hydroquinone, were determined by HPLC analysis, at 283 nm, using a Varian Prostar 210 chromatograph with UV-vis detector and a C18 reverse phase column. The mobile phase was a mixture of methanol, acetic acid and water (6: 2.5: 37.5 v/v) with a constant flow rate of 1 ml min⁻¹. Retention times were 6.2, 2.1 and 2.4 min for 4-chlorophenol, hydroquinone and benzoquinone, respectively.

III. EXPERIMENTAL RESULTS

A. 4-Chlorophenol Photodegradation

The results obtained in the photodegradation process with the XeBr excilamp, for the series of initial 4-chlorophenol concentrations ranging from 50 to 500 mg L⁻¹, (0.389–3.891 mM) are shown in Fig. 1-(A) to 1-(D).

Changes of 4-chlorophenol, hydroquinone and benzoquinone concentrations with time are shown in Fig. 1-(A), 1-(B) and 1-(C), respectively. The temporal evolution of the sum of these three components, being approximately the equivalent of the total organic load that has not been degraded to low molecular weight compounds, is shown in Fig. 1-(D).

As can be seen from Fig. 1-(A), the excilamp can achieve total 4-chlorophenol degradation with exposure times between 5 minutes, for an initial concentration of 50 mg L⁻¹ (0.389 mM), and 90 minutes, for 500 mg L⁻¹ (3.891 mM).

As for the two main intermediates of the photodegradation process, hydroquinone and benzoquinone, it can be seen from Fig. 1-(B) and 1-(C) that, at the beginning of the process, an increase of their concentration takes place, reaching maxima and, thereafter, decreasing up to a constant value. Although hydroquinone concentration is slightly higher than benzoquinone, both of them present at low concentrations compared to the initial chlorophenol concentration and considered insignificant with respect to toxicity.

It is seen in Fig. 1-(D), that the curves corresponding to the total sum of 4-chlorophenol, hydroquinone and benzoquinone concentrations, regardless of the initial concentration of 4-chlorophenol, show a continuous decreasing trend, which suggests that the excilamp is capable of completely degrading the compounds following an appropriate period of operation. With the exposure time used in the present work, the residual organic load remains below 10% of the initial 4-chlorophenol concentration in most cases.

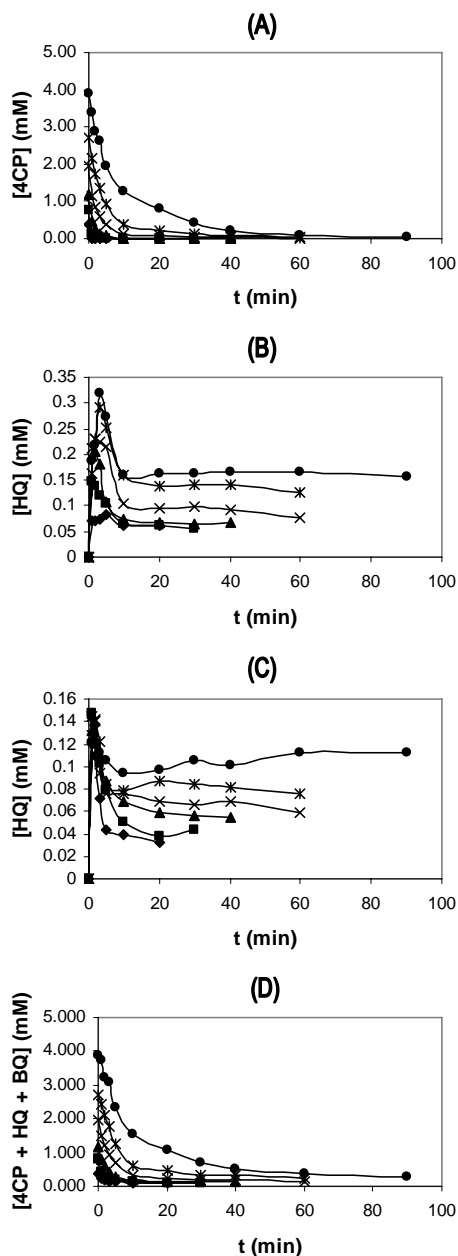


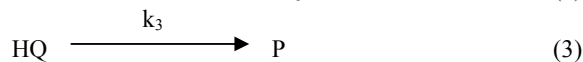
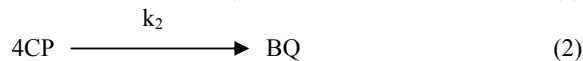
Fig. 1 Progress curves for 4-chlorophenol, (A), hydroquinone, (B), benzoquinone, (C), and for the sum, (D), for the different 4-chlorophenol concentrations tested: \blacklozenge 0.389 mM; \blacksquare 0.778 mM; \blacktriangle 1.167 mM; \times 1.946 mM; \bullet 2.724 mM and \bullet 3.891 mM

IV. THEORETICAL ANALYSIS: KINETIC MODEL FOR THE PHOTODEGRADATION OF 4-CHLOROPHENOL

According to the experimental results obtained, as well as to a previously proposed mechanism [34], a kinetic model has been developed for the photodegradation process and applied to the main components of the degradation system: 4-chlorophenol, hydroquinone and benzoquinone. A simplified scheme of the process is shown and the kinetic equations are

developed and integrated as follows:

A. Reaction Scheme



Where:

4CP = 4-chlorophenol

HQ = hydroquinone

BQ = benzoquinone

P, Q = other compounds that degrade to low molecular weight species

B. Mass Balance Equations

$$\frac{d[4\text{CP}]}{dt} = -(k_1 + k_2)[4\text{CP}] \quad (5)$$

$$\frac{d[\text{HQ}]}{dt} = k_1[4\text{CP}] - k_3[\text{HQ}] + k_{-3}[\text{P}] \quad (6)$$

$$\frac{d[\text{BQ}]}{dt} = k_2[4\text{CP}] - k_4[\text{BQ}] + k_{-4}[\text{Q}] \quad (7)$$

$$\frac{d[\text{P}]}{dt} = k_3[\text{HQ}] - k_{-3}[\text{P}] \quad (8)$$

$$\frac{d[\text{Q}]}{dt} = k_4[\text{BQ}] - k_{-4}[\text{Q}] \quad (9)$$

With the initial conditions:

$$t = 0; \quad [4\text{CP}] = [4\text{CP}]_0; \quad [\text{HQ}] = [\text{BQ}] = [\text{P}] = [\text{Q}] = 0 \quad (10)$$

C. Definition of Conversion

The following equations apply for the conversions of the different species mentioned above:

$$X_{4\text{CP}} = \frac{[4\text{CP}]_0 - [4\text{CP}]}{[4\text{CP}]_0} \quad (11)$$

$$X_{\text{HQ}} = \frac{[\text{HQ}]}{[4\text{CP}]_0} \quad (12)$$

$$X_{BQ} = \frac{[BQ]}{[4CP]_0} \quad (13)$$

$$X_P = \frac{[P]}{[4CP]_0} \quad (14)$$

$$X_Q = \frac{[Q]}{[4CP]_0} \quad (15)$$

Applying the previous definitions of conversion to the mass balance equations the following expressions are obtained:

$$\frac{dX_{4CP}}{dt} = (k_1 + k_2)(1 - X_{4CP}) \quad (16)$$

$$\frac{dX_{HQ}}{dt} = k_1(1 - X_{4CP}) - k_3X_{HQ} + k_{-3}X_P \quad (17)$$

$$\frac{dX_{BQ}}{dt} = k_2(1 - X_{4CP}) - k_4X_{BQ} + k_{-4}X_Q \quad (18)$$

$$\frac{dX_P}{dt} = k_3X_{HQ} - k_{-3}X_P \quad (19)$$

$$\frac{dX_Q}{dt} = k_4X_{BQ} - k_{-4}X_Q \quad (20)$$

With the initial conditions:

$$t = 0; X_{4CP} = X_{HQ} = X_{BQ} = X_P = X_Q = 0 \quad (21)$$

D. Final Integrated Equations

Solving the previous equation system, the following expressions are obtained:

$$X_{4CP}(t) = 1 - e^{-kt} \quad (22)$$

$$X_{HQ}(t) = a_1 \left(1 - (1 + b_1)e^{-c_1t} + b_1e^{-d_1t} \right) \quad (23)$$

$$X_{BQ}(t) = a_2 \left(1 - (1 + b_2)e^{-c_2t} + b_2e^{-d_2t} \right) \quad (24)$$

where the parameters k , a_1 , b_1 , c_1 , a_2 , b_2 y c_2 are related to the kinetic constants as indicated in the appendix.

The result of fitting the 4CP, HQ and BQ conversion values to (22), (23) and (24) is shown in Fig. 2-(A), 2-(B) and 2-(C), respectively. The points correspond with the experimental conversion data and the solid continuous lines with the values calculated with the model.

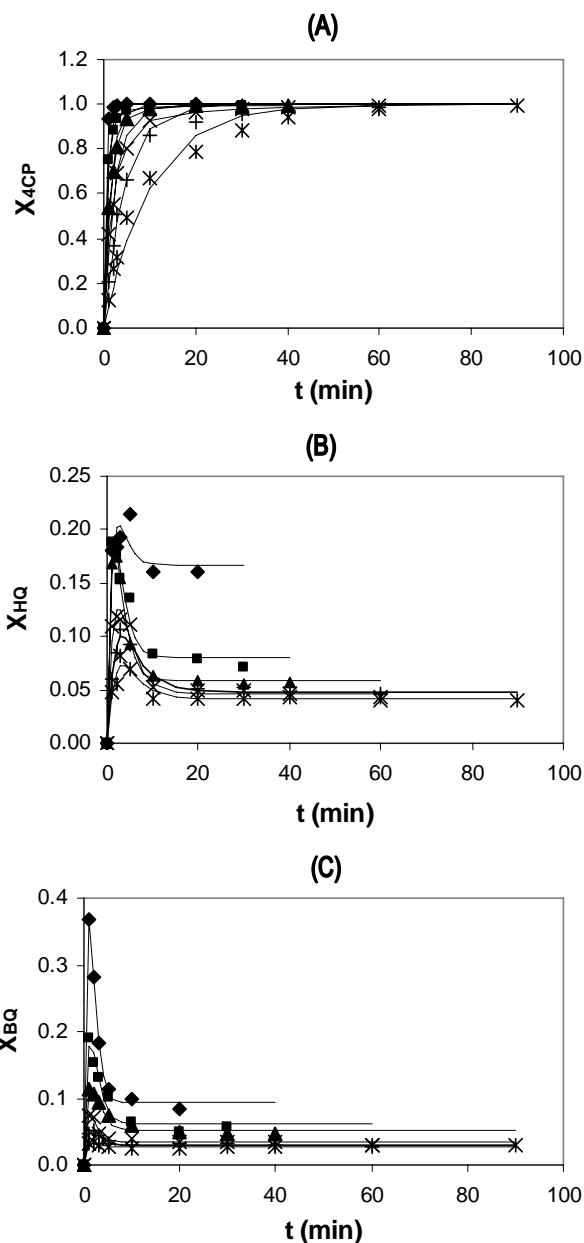


Fig. 2 Temporal variation of 4-chlorophenol, (A), hydroquinone, (B), and benzoquinone, (C), for the different 4-chlorophenol concentrations tested: \blacklozenge 50 mg L⁻¹; \blacksquare 100 mg L⁻¹; \blacktriangle 250 mg L⁻¹; \times 500 mg L⁻¹; $+$ 350 mg L⁻¹; $*$ 500 mg L⁻¹; — model

Additionally, for all the mentioned compounds, the conversion values obtained with the model have been plotted versus those from experimental observations (Fig. 3). An excellent degree of agreement is obtained, with $R^2 = 0.9967$.

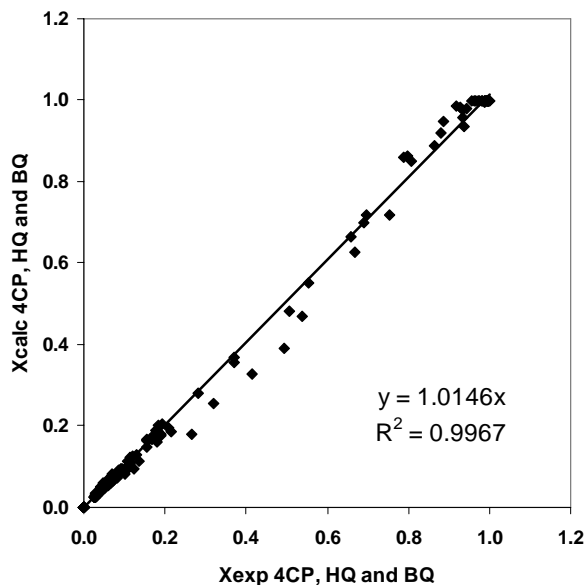


Fig. 3 Experimental and calculated conversion of 4-chlorophenol, hydroquinone and benzoquinone, for all experimental conditions assayed

The values of the model parameters corresponding to (22), (23) and (24) are shown in Tables I to III, as well as their confidence intervals for a significance level of 95%.

TABLE I

MODEL PARAMETERS FOR 4-CHLOROPHENOL

$[4CP]_0$ (mg L ⁻¹)	$[4CP]_0$ (mM)	k (min ⁻¹)
50	0.389	2.73 +/- 0.06
100	0.778	1.27 +/- 0.09
150	1.167	0.63 +/- 0.04
250	1.945	0.40 +/- 0.03
350	2.724	0.22 +/- 0.01
500	3.891	0.10 +/- 0.01

TABLE II

MODEL PARAMETERS FOR HYDROQUINONE

$[4CP]_0$ (mg L ⁻¹)	$[4CP]_0$ (mM)	a_1	b_1	c_1	d_1
50	0.389	0.17 +/- 0.03	46.42 +/- 26.36	0.70 +/- 0.06	0.68 +/- 0.06
100	0.778	0.08 +/- 0.01	44.42 +/- 6.44	0.78 +/- 0.06	0.71 +/- 0.05
150	1.167	0.06 +/- 0.00	48.65 +/- 8.54	0.77 +/- 0.09	0.67 +/- 0.08
250	1.945	0.05 +/- 0.01	48.38 +/- 3.89	0.51 +/- 0.23	0.46 +/- 0.21
350	2.724	0.05 +/- 0.00	48.54 +/- 6.15	0.39 +/- 0.19	0.36 +/- 0.19
500	3.891	0.04 +/- 0.00	49.19 +/- 19.92	0.42 +/- 0.05	0.39 +/- 0.05

TABLE III

MODEL PARAMETERS FOR BENZOQUINONE

$[4CP]_0$ (mg L ⁻¹)	$[4CP]_0$ (mM)	a_2	b_2	c_2	d_2
50	0.389	0.09 +/- 0.01	48.13 +/- 6.46	1.24 +/- 0.16	1.03 +/- 0.13
100	0.778	0.06 +/- 0.01	38.14 +/- 2.55	0.96 +/- 0.45	0.81 +/- 0.39
150	1.167	0.05 +/- 0.00	46.65 +/- 6.03	0.84 +/- 0.46	0.76 +/- 0.42
250	1.945	0.03 +/- 0.00	50.87 +/- 7.31	1.09 +/- 0.68	1.01 +/- 0.62
350	2.724	0.03 +/- 0.00	49.77 +/- 10.95	0.88 +/- 0.57	0.83 +/- 0.55
500	3.891	0.03 +/- 0.00	48.35 +/- 11.09	1.08 +/- 0.37	1.05 +/- 0.36

V. CONCLUSION

Total 4-chlorophenol removal was achieved for all the experimental conditions tested, with the residual organic load reducing to lower than 10% of the initial concentration in most cases, and, with hydroquinone and benzoquinone as main reaction products.

With the aim of process simulation and scale-up, a kinetic model has been developed and validated with the experimental data, the model parameters being determined from the fitting of the experimental data to the model. A good fitting between experimental and calculated data was obtained confirming the validity of the model and the parameters used.

APPENDIX

The resolution of the differential equation system shown above, from (16) to (20), was carried out using the Laplace Transform, as follows:

$$sX_{4CP}(s) = (k_1 + k_2) \left(\frac{1}{s} - X_{4CP}(s) \right) \quad (25)$$

$$sX_{HQ}(s) = k_1 \left(\frac{1}{s} - X_{4CP}(s) \right) - k_3 X_{HQ}(s) + k_{-3} X_P(s) \quad (26)$$

$$sX_{BQ}(s) = k_2 \left(\frac{1}{s} - X_{4CP}(s) \right) - k_4 X_{BQ}(s) + k_{-4} X_Q(s) \quad (27)$$

$$sX_P(s) = k_3 X_{HQ}(s) - k_{-3} X_P(s) \quad (28)$$

$$sX_Q(s) = k_4 X_{BQ}(s) - k_{-4} X_Q(s) \quad (29)$$

From these new equations, the different conversions corresponding to the different species can be calculated as follows:

A. 4-Chlorophenol Conversion

From (25):

$$X_{4CP}(s) = \frac{(k_1 + k_2)}{s(s + (k_1 + k_2))} \quad (30)$$

This can be expressed as simple fractions:

$$X_{4CP}(s) = \frac{1}{s} - \frac{1}{s + (k_1 + k_2)} \quad (31)$$

And the inverse transform gives the 4CP conversion:

$$X_{4CP}(t) = 1 - e^{-(k_1 + k_2)t} \quad \text{where:} \quad (32)$$

$$k = k_1 + k_2 \quad (33)$$

Thus (32) can be expressed as:

$$X_{4CP}(t) = 1 - e^{-kt} \quad (34)$$

B. Hydroquinone Conversion

From (28):

$$X_P(s) = \frac{k_3}{s + k_{-3}} X_{HQ}(s) \quad (35)$$

And, from (31):

$$\frac{1}{s} - X_{4CP}(s) = \frac{1}{s + (k_1 + k_2)} \quad (36)$$

substituting (35) and (36) in (26) gives:

$$sX_{HQ}(s) = \frac{k_1}{s + (k_1 + k_2)} - k_3 X_{HQ}(s) + \frac{k_3 k_{-3}}{s + k_{-3}} X_{HQ}(s) \quad (37)$$

giving:

$$X_{HQ}(s) = \frac{k_1(s + k_{-3})}{s(s + k_1 + k_2)(s + k_3 + k_{-3})} \quad (38)$$

This can be converted into the sum:

$$X_{HQ}(s) = \frac{B_{11}}{s} + \frac{B_{21}}{(s + k_1 + k_2)} + \frac{B_{31}}{(s + k_3 + k_{-3})} \quad (39)$$

And (39) can be solved applying the inverse transform:

$$X_{HQ}(t) = B_{11} \left(1 + \frac{B_{21}}{B_{11}} e^{-(k_1 + k_2)t} + \frac{B_{31}}{B_{11}} e^{-(k_3 + k_{-3})t} \right) \quad (40)$$

Where the coefficients B_{11} , B_{21} and B_{31} can be calculated in the following way:

$$B_{11} = \left[s \frac{k_1(s + k_{-3})}{s(s + k_1 + k_2)(s + k_3 + k_{-3})} \right]_{s=0} = \frac{k_1 k_{-3}}{(k_1 + k_2)(k_3 + k_{-3})} \quad (41)$$

$$B_{21} = \left[(s + k_1 + k_2) \frac{k_1(s + k_{-3})}{s(s + k_1 + k_2)(s + k_3 + k_{-3})} \right]_{s=-(k_1 + k_2)} = -\frac{k_1((k_1 + k_2) - k_{-3})}{(k_1 + k_2)((k_1 + k_2) - (k_3 + k_{-3}))} \quad (42)$$

$$B_{31} = \left[(s + k_3 + k_{-3}) \frac{k_1(s + k_{-3})}{s(s + k_1 + k_2)(s + k_3 + k_{-3})} \right]_{s=-(k_3 + k_{-3})} = \frac{k_1 k_3}{(k_3 + k_{-3})((k_1 + k_2) - (k_3 + k_{-3}))} \quad (43)$$

From the previous values the following relations can be obtained:

$$\frac{B_{21}}{B_{11}} = -\frac{(k_3 + k_{-3})((k_1 + k_2) - k_{-3})}{k_{-3}((k_1 + k_2) - (k_3 + k_{-3}))} \quad (44)$$

$$\frac{B_{31}}{B_{11}} = \frac{k_3(k_1 + k_2)}{k_{-3}((k_1 + k_2) - (k_3 + k_{-3}))} \quad (45)$$

Where:

$$\frac{B_{21}}{B_{11}} + \frac{B_{31}}{B_{11}} = -1 \quad (46)$$

And by defining some new parameters:

$$a_1 = B_{11}; \quad b_1 = \frac{B_{31}}{B_{11}}; \quad c_1 = k_1 + k_2; \quad d_1 = k_3 + k_{-3} \quad (47)$$

(37) can be rewritten as:

$$X_{HQ}(t) = a_1 (1 - (1 + b_1)e^{-c_1 t} + b_1 e^{-d_1 t}) \quad (48)$$

C. Benzoquinone Conversion

From (29):

$$X_Q(s) = \frac{k_4}{s + k_{-4}} X_{BQ}(s) \quad (49)$$

And from (31):

$$\frac{1}{s} - X_{4CP}(s) = \frac{1}{s + (k_1 + k_2)} \quad (50)$$

Substituting (49) and (50) in (27):

$$sX_{BQ}(s) = \frac{k_2}{s + (k_1 + k_2)} - k_4 X_{BQ}(s) + \frac{k_4 k_{-4}}{s + k_{-4}} X_{BQ}(s) \quad (51)$$

This can be rewritten as:

$$X_{BQ}(s) = \frac{k_2(s + k_{-4})}{s(s + k_1 + k_2)(s + k_4 + k_{-4})} \quad (52)$$

And the fraction can be converted into the following sum:

$$X_{BQ}(s) = \frac{C_{11}}{s} + \frac{C_{21}}{(s + k_1 + k_2)} + \frac{C_{31}}{(s + k_4 + k_{-4})} \quad (53)$$

Applying the inverse transform:

$$X_{BQ}(t) = C_{11} \left(1 + \frac{C_{21}}{C_{11}} e^{-(k_1 + k_2)t} + \frac{C_{31}}{C_{11}} e^{-(k_4 + k_{-4})t} \right) \quad (54)$$

Where the coefficients C_{11} , C_{21} and C_{31} can be expressed as follows:

$$C_{11} = \left[s \frac{k_2(s + k_{-4})}{s(s + k_1 + k_2)(s + k_4 + k_{-4})} \right]_{s=0} = \frac{k_2 k_{-4}}{(k_1 + k_2)(k_4 + k_{-4})} \quad (55)$$

$$C_{21} = \left[(s + k_1 + k_2) \frac{k_2(s + k_{-4})}{s(s + k_1 + k_2)(s + k_4 + k_{-4})} \right]_{s=-(k_1 + k_2)} = -\frac{k_2((k_1 + k_2) - k_{-4})}{(k_1 + k_2)((k_1 + k_2) - (k_4 + k_{-4}))} \quad (56)$$

$$C_{31} = \left[(s + k_4 + k_{-4}) \frac{k_2(s + k_{-4})}{s(s + k_1 + k_2)(s + k_4 + k_{-4})} \right]_{s=-(k_4 + k_{-4})} = \frac{k_2 k_3}{(k_4 + k_{-4})((k_1 + k_2) - (k_4 + k_{-4}))} \quad (57)$$

These values lead to the following relations:

$$\frac{C_{21}}{C_{11}} = -\frac{(k_4 + k_{-4})((k_1 + k_2) - k_{-4})}{k_{-4}((k_1 + k_2) - (k_4 + k_{-4}))} \quad (58)$$

$$\frac{C_{31}}{C_{11}} = \frac{k_4(k_1 + k_2)}{k_{-4}((k_1 + k_2) - (k_4 + k_{-4}))} \quad (59)$$

Where:

$$\frac{C_{21}}{C_{11}} + \frac{C_{31}}{C_{11}} = -1 \quad (60)$$

And by defining some new parameters:

$$a_2 = C_{11}; \quad b_2 = \frac{C_{31}}{C_{11}}; \quad c_2 = k_1 + k_2; \quad d_2 = k_4 + k_{-4} \quad (61)$$

(51) can be rewritten as follows:

$$X_{BQ}(t) = a_2 \left(1 - (1 + b_2) e^{-c_2 t} + b_2 e^{-d_2 t} \right) \quad (62)$$

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