



Optimization of a continuous pulsed corona reactor

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Abstract

Pulsed corona discharge processes utilize chemical radicals, ions, and highly reactive molecules produced from a high-voltage pulsed electrical discharge. Recently, these processes have been used for treating organic contaminants in wastewater. The chemistry induced by the pulsed streamer corona in the aqueous phase involves several reactions and is based on hydrogen peroxide. The principal objective of this work is to minimize the amount of hydrogen peroxide needed in a plug-flow reactor to degrade phenol to a prespecified level. A simplified model of the corona reactor is utilized in conjunction with dynamic optimization. Scaling analysis and quasi-steady-state assumptions are used to derive analytical expressions for calculating the optimal hydrogen peroxide concentration profile. Simulations are performed to verify the performance of this optimization strategy. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

There is a continuing need for the development of efficient and cost-effective processes to remove organic contaminants from groundwater and wastewater. In the process of removing waste contaminants, it is also desirable to degrade them to harmless products. Advanced oxidation processes (AOTs) are a class of processes that degrade (usually through oxidation pathways) a range of organic contaminants. Over the past decade, an advanced oxidation technology that utilizes a pulsed streamer corona discharge in the liquid phase (Clements, Sato & Davis, 1985; Sharma, Locke, Arce & Finney, 1993; Joshi, Locke, Arce & Finney, 1995; Sun, Sato & Clements, 2000) has been found to be effective at removing and degrading organic contaminants from aqueous solutions.

Pulsed corona discharge processes utilize chemical radicals and ions (e.g. e_{aq}^- , HO^\cdot , H^\cdot , HO_2^\cdot , $O^1(D)$) and highly reactive molecules, (e.g. O_3 , H_2O_2) produced from a high-voltage pulsed electrical discharge that is sustained in an aqueous phase medium. Preliminary studies have demonstrated the complete degradation of

phenol in solution (Sharma et al., 1993; Sunka et al., 1999; Sun et al., 2000) and the production of ozone when oxygen or air is sparged through the needle electrodes immersed in water (Clements et al., 1985). The combination of activated carbon particles with the pulsed corona discharge also leads to enhanced power efficiency and possible surface-phase-induced catalytic chemical reactions (Grymonpré, Finney & Locke, 1999b).

Initial work has only been done in batch reactors, with a corona discharge produced by a single point to plane electrode system. However, for large-scale applications, such a reactor would be inadequate and a different reactor configuration is necessary. One such reactor configuration is a *flow reactor* which would allow for a contaminated water sample to flow continuously through the corona region, thereby increasing the amount of sample that can be treated.

The principal objective of this work is to optimize the hydrogen peroxide needed in the flow reactor to degrade the phenol to a prespecified level with respect to the chemistry induced by the pulsed streamer corona. This will involve the use of a simplified model of the phenol degradation in combination with dynamic optimization. It will be shown that the optimum solution is a constraint and analytical expressions for the input can be obtained. The case where the inlet phenol concentration is varying will be considered and two types of solution will be

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proposed depending on whether or not the measurement of the phenol concentration is available.

2. Modelling of the reactor

Initial models of the bulk phase corona-induced chemical reactions were reported by Joshi et al. (1995). In that study, it was assumed that the pulsed corona discharge leads to the formation of hydrogen peroxide, hydroxyl radicals, and aqueous electrons. Of these reactive species, the hydroxyl radical is the dominant reactive species, but quickly recombines to form hydrogen peroxide. In combination with ferrous ions (Fe^{2+}), hydrogen peroxide reacts to form hydroxyl radicals in the bulk solution. For this reason, the present model will predict hydrogen peroxide concentrations to optimize the oxidation products of phenol.

2.1. Model formulation

The reactions used in this simplified model are given in Table 1 along with the reactions rate constants. The first two reactions are the Fenton reactions, which involve the production of hydroxyl radicals from hydrogen peroxide. The third reaction is the phenol oxidation reaction which, for this simplified model, will produce only oxidation products. The final three reactions are a few of the many possible radical termination and combination reactions, which are well known from radiation chemistry (Buxton, 1987; Magee & Chatterjee, 1987). The rates of various corona-induced reactions have been determined experimentally (Joshi et al., 1995) and those of the other reactions are taken from radiation chemistry and advanced oxidation technology literature.

The general material balance for a plug-flow reactor is

$$\frac{dc_i}{dV} = \frac{1}{v} r_i, \quad (1)$$

where c_i is the molar concentration of the i th species, V is the coordinate associated with the volume of the reactor, v is the volumetric flow rate, and r_i is the global reaction rate for the i th species. Applying this equation to the

Table 1
Pulsed corona chemistry

$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \xrightarrow{k_1} \text{Fe}^{3+} + \text{OH}^- + \text{HO}^\cdot$	$k_1 = 76 \text{ mol}^{-1} \text{ s}^{-1}$
$\text{Fe}^{2+} + \text{HO}^\cdot \xrightarrow{k_2} \text{Fe}^{3+} + \text{OH}^-$	$k_2 = 5 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$
$\text{Phenol} + \text{HO}^\cdot \xrightarrow{k_3} \text{Products} + \text{H}^\cdot$	$k_3 = 6.5 \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$
$\text{H}^\cdot + \text{HO}^\cdot \xrightarrow{k_4} \text{H}_2\text{O}$	$k_4 = 2.4 \times 10^{10} \text{ mol}^{-1} \text{ s}^{-1}$
$2\text{HO}^\cdot \xrightarrow{k_5} \text{H}_2\text{O}_2$	$k_5 = 4 \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$
$\text{H}^\cdot + \text{H}_2\text{O}_2 \xrightarrow{k_6} \text{H}_2\text{O} + \text{HO}^\cdot$	$k_6 = 1.0 \times 10^{10} \text{ mol}^{-1} \text{ s}^{-1}$

chemical reactions given in Table 1, the following equations arise:

$$\frac{dc_1}{dV} = \frac{1}{v} [-k_3 c_1 c_2], \quad c_1(0) = 10^{-3} \text{ mol/l}, \quad (2)$$

$$\frac{dc_2}{dV} = \frac{1}{v} [k_1 c_4 u - k_2 c_2 c_4 - k_3 c_1 c_2 - k_4 c_2 c_6 - 2k_5 c_2^2 + k_6 c_6 u], \quad c_2(0) = 0 \text{ mol/l}, \quad (3)$$

$$\frac{dc_3}{dV} = \frac{1}{v} [k_3 c_1 c_2], \quad c_3(0) = 0 \text{ mol/l}, \quad (4)$$

$$\frac{dc_4}{dV} = \frac{1}{v} [-k_1 c_4 u - k_2 c_2 c_4], \quad c_4(0) = 4.85 \times 10^{-4} \text{ mol/l}, \quad (5)$$

$$\frac{dc_5}{dV} = \frac{1}{v} [k_1 c_4 u + k_2 c_2 c_4], \quad c_5(0) = 0 \text{ mol/l}, \quad (6)$$

$$\frac{dc_6}{dV} = \frac{1}{v} [k_3 c_1 c_2 - k_4 c_2 c_6 - k_6 c_6 u], \quad c_6(0) = 0 \text{ mol/l}, \quad (7)$$

where $c_1 = [\text{Phenol}]$, $c_2 = [\text{HO}^\cdot]$, $c_3 = [\text{Products}]$, $c_4 = [\text{Fe}^{2+}]$, $c_5 = [\text{OH}^-]$, $c_6 = [\text{H}^\cdot]$, and $u = [\text{H}_2\text{O}_2]$. Also, the case where the concentration of phenol at the inlet varies between $0.9 \times 10^{-3} \text{ mol/l}$ and $1.1 \times 10^{-3} \text{ mol/l}$ for a typical waste stream is considered in this paper. With the volumetric flow rate $v = 1 \text{ l/s}$ and the reactor volume of $V_{\text{max}} = 10 \text{ l}$, the residence time in the reactor is 10 s. No balance is given for hydrogen peroxide as the optimization seeks to find the optimal peroxide trajectory in the reactor. The implementation of this trajectory is a separate problem which requires a mathematical relation between peroxide generation and consumption and is not considered here.

2.2. Model reduction

The system of Eqs. (2)–(7) can be simplified by noting the following facts.

1. $c_1 + c_3 = \text{constant}$ and $c_4 + c_5 = \text{constant}$. This allows us to remove c_3 and c_5 from the system of equations. Moreover, c_3 and c_5 do not appear in the reaction rates r_i for any i .
2. Due to the difference in speed of the various reactions, two of the states, c_2 and c_6 , are in a pseudo-steady state with their values being around 10^{-11} M . This has been verified experimentally in Grymonpré, Finney and Locke (1999a).

It can be seen from the numerical values of the different constants and states, that $k_4 c_2 c_6 (\approx 10^{-12})$ is several orders of magnitude smaller than $k_3 c_1 c_2 (\approx 10^{-4})$ and

$k_6 c_6 u$ ($\approx 10^{-4}$). Since c_6 is in a pseudo-steady state,

$$\frac{dc_6}{dV} = 0 \Rightarrow k_3 c_1 c_2 = k_6 c_6 u. \quad (8)$$

Substituting this into Eq. (3) and removing terms which are of magnitude 10^{-10} we get

$$k_1 c_4 u = k_2 c_4 c_2. \quad (9)$$

Using the two relations (8) and (9), we get

$$c_2 = \left(\frac{k_1}{k_2}\right)u \quad \text{and} \quad c_6 = \frac{(k_1 k_3)}{(k_2 k_6)}c_1. \quad (10)$$

Thus, the system equations (2)–(7) are completely described by

$$\frac{dc_1}{dV} = \left(\frac{-k_3 k_1}{vk_2}\right)c_1 u, \quad (11)$$

$$\frac{dc_4}{dV} = \left(\frac{-2k_1}{v}\right)c_4 u. \quad (12)$$

Also, unlike the system of Eqs. (2)–(7), Eqs. (11) and (12) are completely decoupled. Only the first one is related to the optimizing objective of reducing the concentration of phenol. Hence, only the c_1 profile will be studied.

2.3. Analytical expression for phenol profile

An analytic expression for the solution of c_1 can be easily obtained by using the following length scaling. Let a new length scale τ be chosen such that $d\tau/dV = u$ implying $\tau = \int_0^V u(\mu) d\mu$. τ is the coordinate proportional to the length of the reactor. In this new length scale the system of equations is written as

$$\frac{dc_1}{d\tau} = -\alpha c_1, \quad c_1(0) = c_{in} \quad (13)$$

where $\alpha = (k_3 k_1 / vk_2)$. The system is linear and homogeneous in the new length scale and the solution is given by

$$c_1(V) = c_{in} e^{-\alpha\tau} = c_{in} e^{-\alpha \int_0^V u(\mu) d\mu} \quad (14)$$

2.4. Time-varying phenol concentration at reactor inlet

Next, we will consider the fact that c_{in} can vary with time. This is typically the case in a waste water stream where the contaminant concentration changes due to changes in upstream conditions. In such a case, c_1 will be a function of space and time and the analytical solution can be written as

$$c_1(V, t) = c_{in} \left(t - \frac{V}{v}\right) e^{-\alpha \int_0^V u(\mu, t - \frac{V-\mu}{v}) d\mu}. \quad (15)$$

The above expression can be obtained by noting that the contents of the reactor move along the column with the volumetric flowrate v . In the absence of any reaction along the column, $c_1(V, t) = c_{in}(t - V/v)$. The exponential term represents the consumption of phenol along the column as a function of the concentration of H_2O_2 .

3. Reactor optimization

To run the reactor optimally, it is necessary to calculate the minimum amount of hydrogen peroxide present in the reactor in order to bring the phenol concentration below a prespecified limit at the exit of the reactor. In this section, this amount of hydrogen peroxide will be computed by formulating the problem as a dynamic optimization problem and by performing a simple time-scale analysis.

3.1. Problem formulation

The optimization problem can be mathematically stated as follows:

$$\min J = \int_0^{V_{max}} u dV, \quad (16)$$

subject to dynamic equations (2)–(7) and the terminal constraint:

$$c_1(V_{max}) \leq c_{out,max}, \quad (17)$$

where $c_{out,max}$ is the maximum allowable concentration of phenol in the exit stream of the reactor. This class of optimization problems can be solved, in general, using dynamic optimization methods which involve the solution of a two-point boundary value problem (Bryson & Ho, 1975). Usually, such problems are computationally expensive to solve. However, in this example, since an analytical expression is available for the spatial phenol concentration profile, closed-form solutions will be used to calculate the optimum hydrogen peroxide concentration necessary to degrade phenol.

3.2. Optimal hydrogen peroxide calculation

From Eq. (14), the cost function for a given c_{in} is

$$J = \int_0^{V_{max}} u(V) dV = \frac{1}{\alpha} \log\left(\frac{c_{in}}{c_1(V_{max})}\right). \quad (18)$$

This implies that the larger the value of $c_1(V_{max})$, the smaller is the cost. On the other hand, the constraint $c_1(V_{max}) \leq c_{out,max}$ prevents the choice of a large $c_1(V_{max})$ and so the optimum is at $c_1(V_{max}) = c_{out,max}$. Hence

$$J_{opt} = \frac{1}{\alpha} \log\left(\frac{c_{in}}{c_{out,max}}\right) \quad (19)$$

and the optimal input is any u which guarantees $\int_0^{V_{\max}} u(V) dV = J_{\text{opt}}$. Note that the particular profile of the input is immaterial as long as the condition on the integral is satisfied. Hence, to bring the phenol concentration to $c_{\text{out,max}}$ at the end of the reactor, we choose a u which is independent of V such that

$$u_{\text{opt}} = \frac{1}{\alpha V_{\max}} \log\left(\frac{c_{\text{in}}}{c_{\text{out,max}}}\right). \quad (20)$$

Despite the variation of the inlet phenol concentration, the optimum still lies at $c_1(V_{\max}) = c_{\text{out,max}}$. The optimum input $u_{\text{opt}}(V, t)$ corresponding to keeping $c_1(V_{\max}) = c_{\text{out,max}}$ is given by

$$u_{\text{opt}}(V, t) = \frac{1}{\alpha V_{\max}} \log\left(\frac{c_{\text{in}}(t - \frac{V}{v})}{c_{\text{out,max}}}\right). \quad (21)$$

If $c_{\text{in}}(t)$ can be measured, then the feedback law (21) can be implemented. However, if the measurement of phenol concentration is not available, one has to adopt a conservative strategy and use an input which will guarantee that the outlet phenol concentration is less than $c_{\text{out,max}}$ even for the maximum value of $c_{\text{in}}(t)$, $c_{\text{in,max}}$. Then the conservative constant optimal input is given by:

$$u_{\text{conservative}} = \frac{1}{\alpha V_{\max}} \log\left(\frac{c_{\text{in,max}}}{c_{\text{out,max}}}\right). \quad (22)$$

The advantage of the conservative feedback is its simplicity — a constant peroxide concentration for all values of space and time. The disadvantage, however, is that in the presence of large variations, one uses excess hydrogen peroxide, thus leading to a larger cost of operation. In actual operation, the cost of the excess hydrogen peroxide has to be compared with the cost of implementing a measuring system for phenol.

4. Simulation results

Fig. 1 shows the implementation of the conservative optimal input scheme for several values of $c_{\text{in}}(t)$. It is observed that the concentration of phenol at the outlet is indeed below the prespecified limit of 5×10^{-5} mol/l. For $c_{\text{in,max}} = 1.1 \times 10^{-3}$, the conservative optimal input is given by $u_{\text{conservative}} = 3.13 \times 10^{-4}$ mol/l constant for all time and space. This leads to a total consumption of H_2O_2 , $J = 3.13 \times 10^{-3}$ mol.

Fig. 2 shows the implementation of the feedback scheme where on-line measurement of the inlet phenol concentration is available. In this case, the hydrogen peroxide concentration is adjusted using Eq. (21). It is observed that in this case, the phenol concentration at the reactor outlet is exactly at the prespecified limit of 5×10^{-5} mol/l. In this case, the average consumption of H_2O_2 , averaged over 100 s, $\frac{1}{100} \int_0^{100} J dt = 3.03 \times 10^{-3}$ mol.

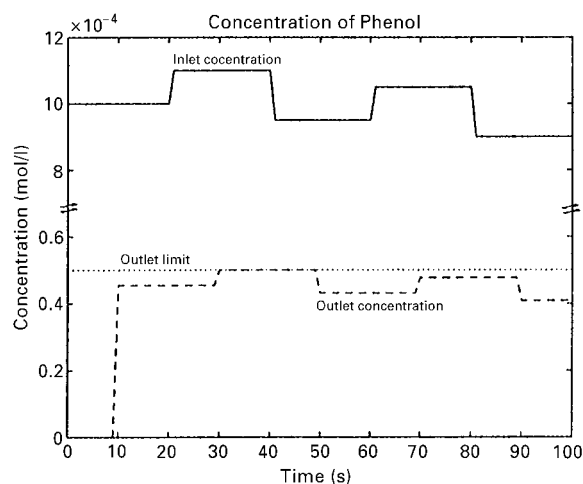


Fig. 1. Conservative Optimization — constant u .

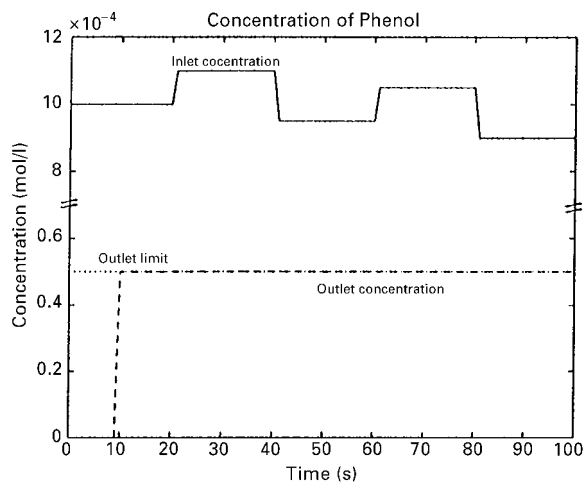


Fig. 2. Optimization with inlet phenol concentration measurements.

5. Conclusions

The minimum amount of hydrogen peroxide necessary to degrade phenol below a prespecified limit is calculated by considering a mathematical model of a pulsed corona reactor. The model described here is based on the chemistry of the pulsed corona. It is shown that the corona model can be simplified considerably by introducing quasi-steady-state assumptions and simple scaling. This simplification enables the calculation of a closed-form solution for the hydrogen peroxide concentration profile. Simulations are performed to verify that the derived closed-form solution results in the degradation of phenol to a level below a prespecified limit. It is shown that, when measurement of inlet phenol concentration is available, the concentration of hydrogen peroxide can be adjusted to guarantee that the concentration of phenol at the reactor outlet is at the prespecified limit. In the absence of this on-line measurement, a conservative

input strategy, based on the “worst case” level of phenol at the inlet, is presented, which guarantees that the concentration of phenol at the reactor outlet is below the prespecified limit.

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