

A Model Study of Phenolic Ozonation Applied to Industrial Wastes

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บทคัดย่อ

ในงานวิจัยนี้ ได้มีการพัฒนาแบบจำลองเพื่อใช้ กำจัดสารพิษที่เกิดจากโรงงานอุตสาหกรรม (ฟีนอล) โดยให้ทำปฏิกิริยากับก๊าซโอโซนในถังปฏิกิริยาชนิด Bubble Column แบบจำลองดังกล่าวอาศัยทฤษฎีของ ถังปฏิกิริยาซึ่งเชื่อมต่อกันแบบอนุกรม (Tanks-inseries) ด้วยวิธีการนี้สามารถทำนายความเข้มข้นของ ฟีนอลและก๊าซโอโซนทุกระยะความสูงของถังปฏิกิริยาได้ โดยที่ความเข้มข้นของฟีนอลลดลงจากด้านบนไปยัง ด้านล่างของถังปฏิกิริยา อันเนื่องมาจากการทำ ปฏิกิริยากับก๊าซโอโซน นอกจากนี้ยังพบว่า ปฏิกิริยา เกือบทั้งหมดเกิดในฟิล์มของของเหลว

Abstract

A computational model study of ozone-phenol reaction in bubble column has been developed. By applying the concept of the tanks-in-series arranged in counter-current flow, the concentration of ozone and phenol in the liquid bulk at the exit of the reaction vessel as well as at the intermediate stages through the reactor have been calculated. Along the height of the reaction vessel, the concentration of phenol in the bulk of liquid decreases rapidly from the top to the base of the vessel due to the reaction with ozone and by virtue of the continuous operation. Additionally, the simulation shows that reaction occurs almost entirely in the liquid film. Keywords: Counter-current Flow, Enhancement Factor, Film and Bulk Reaction, Ozonephenol Reaction, Bubble Column

1. Introduction

Phenols are some of the most common aqueous pollutants. They are toxic to aquatic life and may pose a health hazard to humans. Phenols impart obnoxious taste and odor to water, particularly after chlorination. Furthermore, chlorination of water contaminated with phenols may lead to formation of even more toxic compounds [1], [2].

As phenols are expected to be present in the effluents from gasification and liquifaction complexes, the phenol pollution problem will be exacerbated. Effective methods to remove phenol are needed. Biological oxidation and adsorption on activated carbon can be used, but uneconomically long residence times are required to reduce the phenol concentration to the discharge level allowed by emission regulations, especially for wastes with initially high phenolic content.

Another way to remove phenol is by chemical oxidation. However, phenolic compounds are refractory to oxidation by air or oxygen at ambient conditions. Heating the waste stream in order to

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oxidize phenols is not feasible because of very high heating costs. Thus, a strong oxidant applicable at ambient conditions is desirable. Ozone is a possible candidate because of its high oxidation strength, reasonable cost, ability to break down into harmless oxygen and likelihood of not forming more toxic compounds. Thus, ozonation appears to be an attractive method for treatment of industrial effluents [2].

According to the literature survey, it was found that several attempts have been made in recent years to develop models of bubble column reactors. Most of these studies were restricted to gas hold up, gas and liquid velocity, bubble characteristics, heat transfer, etc. Only some papers have been focussed on mass transfer in bubble column [3], [4]. In addition, it is rarely found the mass transfer with reaction to be reported in term of the proportion of film and bulk reaction.

Then, a study of ozonation for treatment of phenol in water in the bubble column becomes the main objective in this research work. Moreover, one of the objectives in this research is to properly calculate the precise extent of film and bulk reaction without making any prior assumption which is imposed upon the reaction-diffusive regime within the mass transfer film (fast, slow, etc.).

2. Model Formulation and Method of Solving

Figure 1 illustrates a series of backmixed zones in counter-current flow. For this case the gas stream and the liquid stream flow in parallel, but in opposite directions. At the bottom of the reactor, the gas stream containing a high concentration of component **A** (ozone) comes to contact with a relatively low concentration of substrate **B** (phenol)



Figure 1 A schematic of a series of backmixed zones arranged in counter-current flow.

in the liquid stream whist at the top of the reactor the liquid stream containing a high concentration of substrate B comes to contact with a low concentration of component A in the gas stream.

A single backmixed zone (each zone) is connected together in series with other zones as shown in Figure 1 therefore we can consider this series of backmixed zones to be a plug flow reactor of which the total volume is equal to the summation of the volume of each zone. On the other hand, for the case of a plug flow reactor having a total volume V, if the reactor is divided into N equal volume backmixed elements (volumes), each volume is actually equal to $\frac{V}{N}$. Moreover, the property of each zone before operating is exactly the same.

If dissolved gas **A** (ozone) reacts with a dissolved reactant **B** (phenol) by an irreversible second-order reaction with stoichiometry:

$$A + zB \xrightarrow{k_{r_2}} yR \tag{1}$$



where

considerations of the interactions of mass transfer and chemical reaction in both the film and the bulk of liquid phase require additional material balances for the reactive component B contained in the liquid phase. The diffusion reaction equations for firstorder reaction with respect to A and B are now:

$$D_{A} \frac{d^{2}C_{A}}{dx^{2}} - k_{r2}C_{A}C_{B} = 0$$

$$D_{B} \frac{d^{2}C_{B}}{dx^{2}} - zk_{r2}C_{A}C_{B} = 0$$
(2)

with imposed boundary conditions

$$C_{A} = C_{A}^{*}, x = 0$$

$$C_{A} = C_{Abo}, x = \delta$$

$$C_{B} = C_{Bbo}, x = \delta$$

$$\frac{dC_{B}}{dx} = 0, x = 0$$
(3)

(no transfer of reactant B to gas phase)

In providing a general approach to the solution of a single backmixed element, it is essential that the direct solution of the two second order nonlinear equation, ODE's, which are embedded in the algebraic equations governing the overall material balances, are avoided. To do this, it is possible to provide some suitable approximation to the enhancement factor. At low reaction speed, the approximation is to use a value of unity. However, under "infinitely" fast reaction conditions, the overall reaction rate is governed by the diffusion of both A and B to a reaction plane within the liquid film. Thus, at this condition the nature of the kinetics is irrelevant, and the enhancement factor has reached an ultimate asymptotic value.

Considering equation (2), an analytical solution of this set of equations is not available,

however, van Krevelen and Hoftijzer [5] computed an approximate set of solutions for the case $C_{Abo}=0$ and showed that they could be fitted within about 10% by simple empirical relationships, thus

$$\overline{R} = k_L C_A^* V \overline{a} E_A \tag{4}$$

$$E_{A} = \frac{\sqrt{E_{i} - 1}}{\tanh \sqrt{\left(M \frac{E_{i} - E_{A}}{E_{i} - 1}\right)}}$$
$$M = \frac{D_{A}k_{r2}C_{Bbo}}{k_{L}^{2}};$$
$$E_{i} = \left(1 + \frac{D_{B}C_{Bbo}}{zD_{A}C_{A}}\right)$$

The flux of reactant A across the gas-liquid interface into liquid film can be written:

$$N_{A}|_{x=0} = -D_{A}(\frac{dC_{A}}{dx})_{x=0}\bar{Va} = k_{L}\bar{Va}(C_{A}^{*} - \frac{C_{Abo}}{\cosh\sqrt{M}})E_{A}$$
(5)

The molar flow rate of component A from the film-bulk interface into the bulk of liquid is expressed as:

$$N_{A}\Big|_{x=\delta} = -D_{A}\left(\frac{dC_{A}}{dx}\right)_{x=\delta}V\bar{a} = k_{L}V\bar{a}\left(\frac{C_{A}^{*}}{\cosh\sqrt{M}} - C_{Abo}\right)E_{A} \quad (6)$$

Mass balance over a single perfectly-mixed zone for the case of bimolecular-type reaction can be written:

$$N_A|_{x=\delta} + QC_{Abi} = k_{r2}C_{Abo}C_{Bbo}V + QC_{Abo}$$
(7)

Substituting equation (6) into equation (7) gives:

$$C_{Abo} = \frac{C_A^* + \frac{QC_{Abi}Cosh\sqrt{M}}{V\overline{a}k_L E_A}}{k_1}$$
(8)



where

$$k_1 = (1 + \frac{k_{r2}C_{Bbo}}{\bar{a}k_L E_A} + \frac{Q}{V\bar{a}k_L E_A})\cosh\sqrt{M}$$

Eliminating C_{Abo} by substituting equation (8) into equation (5) and rearranging for C_A^* gives:

$$C_{A}^{*} = \frac{N_{A}|_{x=0} + k_{3}}{k_{2}}$$
(9)

where

$$k_{2} = V k_{L} \overline{a} [1 - \frac{1}{k_{1} \cosh \sqrt{M}}] E_{A}$$
$$k_{3} = \frac{Q C_{Abi}}{k_{1}}$$

From Henry's law, the solubility relationship between the partial pressure of component A (p_A) and the concentration of component A (C_A^{\bullet}) at gasliquid interface can be expressed by:

$$p_A = H_A C_A^{*} = y_{Ao} P \tag{10}$$

Substituting C_A^* from equation (9) into equation (10) gives:

$$N_{A}\Big|_{x=0} = \frac{y_{Ao}Pk_{2}}{H_{A}} - k_{3}$$
(11)

According to the material balance of reactant A over the gas phase,

$$N_{A}\Big|_{x=0} = G_{i} \frac{(y_{Ai} - y_{Ao})}{(1 - y_{Ao})}$$
(12)

Equating equation (11) with equation (12) and rearranging gives:

$$\left(\frac{k_2P}{H_A}\right)y_{Ao}^2 - \left(G_i + \frac{k_2P}{H_A} + k_3\right)y_{Ao} + \left(k_3 + G_iy_{Ai}\right) = 0 \quad (13)$$

If the inlet conditions are given, the quadratic equation above can be solved for outlet gas compositions. However, for the reaction between component A and component B, the value of E_i depends on the outlet composition, then, it is necessary to initially estimate by using the inlet composition and then update with each iteration until it converges within a specified tolerance. In order to calculate other parameters, it can be then back substituted into the previous equations.

For the step of solving the strings of backmixed zones, the program will solve the problem for just one zone first which is not involved with the direction of flow and use that outlet composition as the initial guess for the next simulation. This continues through to the final simulation (N zones) which uses the converged outlet gas composition from the N-1 zone simulation as it's initial guess. To see how well this model can predict the behavior of ozone-phenol reaction in a simple bubble column, the research work of Anderson [6] has been chosen. Anderson studied ozonation of high levels of phenol in water. In his study, a continuous reactor (counter-current flow) was used. The setup for ozonation experiments is illustrated in Figure 2. Oxygen passed through an ozone generator to produce an ozone concentration in the oxygen of about 30 mg/litre.

At the beginning of each run, the ozone content of the feed gas was determined by bypassing the gas through a 10 percent by weight potassium iodide solution. After determining the ozone concentration in the reactor feed gas, the valve was rotated so that the gas could flow to the reaction vessel. Liquid was fed using a peristaltic pump, and the level of liquid in the reactor was maintained at a





Figure 2 Reaction vessel setup for ozonation experiment. Source: Anderson [6].

constant level. During the course of a run, the liquid product was collected and analyzed for pH, chemical oxygen demand (COD), and phenol content by conventional analytical methods. In addition, the off-gas ozone was reacted with another 10 percent by weight potassium iodide solution to determine the concentration. Flow rates of the liquid and gas were estimated during the run from the calibration of the liquid pump and wet test meter speed, respectively.

As discussed by Danckwerts and Kennedy [7], Yocum [8] and others, in the absorption of a gas of low solubility such as ozone into an aqueous solution, the transport process is mainly controlled by molecular diffusion of the gas into liquid and chemical reactions taking place in a region between the interface and the bulk of the liquid. Along the path of diffusion, the reactions below occur simultaneously [9]-[12].

$$\begin{array}{ccc} A & \stackrel{k_d}{\longrightarrow} & S \\ A + zB & \stackrel{k_r}{\longrightarrow} & R \end{array}$$
(14)

The first reaction represents the decomposition of ozone (A) while the second one illustrates an ozonation reaction between ozone and an organic constituent (B) in the liquid. Bearing the model formulation in mind, ozone decomposes and reacts (with the organic substances) in water following a complex chain mechanism. Ignoring the complexity of these mechanisms, the overall reaction for the case of phenolic ozonation can be simply expressed as:

$$2O_3 \xrightarrow{k_d} 3O_2$$

$$5O_3 + C_6H_5OH \xrightarrow{k_r} \text{Product}$$
(15)

and the rate expression for these two reactions can be stated in a simplified general form:

$$-\frac{dC_A}{dt} = k_d C_A^{\ m}$$
$$-\frac{dC_A}{dt} = k_r C_A^{\ m} C_B^{\ n} \qquad (16)$$

where k_d and k_r are the reaction rate constant for the decomposition and the phenolic ozonation reaction, respectively. C_A is ozone residual concentration whereas C_B is the concentration of phenol at time *t*. The parameters *m* and *n* are the kinetic reaction orders corresponding to ozone and phenol, respectively.

Considering the reaction order, there is no consensus among different authors for the order of the ozone decomposition reaction in water. For example, for a temperature of 30-60°C and a pH range of 2-4, *m* is equal to 2 [13]. On the other hand for temperatures ranging from 19 to 22.5°C and pH values 7, *m* equals 0 [14]. Table 1 shows the range of variables covered by various investigators and their conclusions concerning the reaction order relative to ozone.



However, for many ozonation systems commonly encountered in practice, the decomposition reaction can be considered first order (m=1) and the ozonation reaction second order (with first order in both concentration of ozone and the constituent in the liquid, m=n=1) [11], [16], [17], particularly, in the case of phenolic derivatives, as has been suggested by several authors [18]-[22]; reporting in most cases thus gives global second order reactions, and first order with respect to each reactant.

Table 1	Summary of research on ozone decomposition
	in water

Researchers	pH range	Temperature range (⁰ C)	Reaction order with respect to $O_3(m)$
Rothmund & Burgstaller (1913)	2 to 4	0	2
Sennewald (1933)	5.3 to 8	0	2
Weiss (1935)	2 to 8	0	3/2
Alder & Hill (1950)	1 to 2.8	0 to 27	1
Stumm (1954)	7.6 to 10.4	1.2 to 19.8	1
Kilpatrick et al. (1956)	0 to 6.8	25	3/2
Kilpatrick et al. (1956)	13	25	2
Raukas et al. (1962)	5.4 to 8.5	5 to 25	3/2
Czapski et al. (1968)	10 to 13	25	1
Rogozhkin (1970)	9.6 to 11.9	25	1
Hewes & Davision (1971)	2 to 4	30 to 60	2
Hewes & Davision (1971)	б	10 to 50	3/2-2
Hewes & Davision (1971)	8	10 to 20	1
Kuo et al. (1977)	2.2-11	15-35	3/2
Sullivan and Roth (1979)	0.5-10	4-60	1
Sheffer and Esterson (1982)	7	19-22.5	0
Gurol and Singer (1982)	2-10	20	2

Source: Adapted from Hewes and Davision [13] and Farooq and Ahmed [15]

According to the kinetic data investigated by Li, Kuo and Week [11] and Li and Kuo [12], the rate of ozonation is much faster than that of decomposition in acidic solution, but the decomposition reaction may not be negligible in strong alkaline solution. Table 2 shows the comparison between the values of specific decomposition rate constant, k_d , determined by other investigators.

Table 2 Comparison between the values of k_d obtained by some investigators for the

reaction	$2O_3$	$\xrightarrow{\kappa_d}$	3O ₂	when $m = 1$
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Investigators	pН	Temperature ([°] C)	k _d (min ⁻¹)	Type of water used
Stumm (1954)	8.3	19.8	0.1	tap water
Hews and Davision (1971)	8.0	20.0	0.2	tap water
Sullivan and Roth (1980) ***	7.8	22.0	0.0095	tap water
Farcog and Ahmed (1989)	7.8	22.0	0.087	secondary <u>effuent</u>

Source: Farooq and Ahmed [15] Note: *** Calculated from

$$k_d = 9.811 x 10^7 \exp(\frac{-5606}{T}) [OH^-]^{0.123}$$

T = temperature (K)

Table 3 summarizes the kinetic data for some ozonation reactions at 25°C. Rizzuti, Augugliaro and Marrucci [23] and Hoigne, et al. [20] reported that especially in basic solution, the ozone can be consumed through its self decomposition reaction without involving phenolic ozonation. Moreover, Mehta, George and Kuo [24] studied the enhancement of mass transfer by ozonation of organic compounds and also reported that in the acid solution, the ozonation reaction is much faster than the decomposition reaction and most of the absorded ozone is utilized in reacting with an organic compound.

Both reaction order and reaction rate constant are generally different depending on the water quality. The reaction rate constant increases with



solution pH and decreases in the presence of hydroxyl radical scavengers such as carbonate. Moreover, suspended solids, dissolved inorganic and organic matter in solution may affect k_d .

However, in this system (Average pH^{-4.66} and temperature=25°C), the order of magnitude of the rate of ozone decomposition ($^{-6.70x10^{-2} s^{-1}}$) is several orders lower than that of the ozonation reaction rate (9.0x10³ m³ kmol⁻¹ s⁻¹). Accordingly, the rate of ozone decomposition probably plays a negligible, if any, role.

Table 3	Kinetic	data	for	some	ozonation	reactions
	at 25°C					

	Ozonation rate constant				Diffusivity, D_{B}	(D_B / D_A)
$\operatorname{Compound}(B)$	pH = 3	pH = 5	pH=7	pH = 10	((<i>cm</i> ² / sec) <i>x</i> 10	⁵)
formic acid **	47	61	140	1500	1.58	0.718
phenol 🎞	2.6X10 ³	2.0X10 ⁴	2.0X10	⁶ -	0.92	0.418
benzene *	1.2X10 ⁻²	1.10	12.0	-	1.2	0.545

Source: Adapted from Mehta, George and Kuo [24]

** Second order reaction $\left(\left(\frac{kmol}{m^3}\right)^{-1}s^{-1}\right)$

* First order reaction (*s*⁻¹)

Since in this case, the value of reaction rate constant is quite high, the absorption of ozone in phenolic solution enhanced by the chemical reaction should occur. According to the geometry of the reaction vessel in Figure 2, if the height of the vessel is divided into four, the reaction vessel will have four equal small cubic volumes connected together in series. In each cubic volumes (or zones), the concentration of both ozone and phenol can be calculated by applying the concept of tanks-in-series arranged in counter-current. By means of this method, not only can the concentration of ozone and phenol in the liquid bulk at the exit of the reaction vessel be calculated but also the ones at intermediate stages through the vessel. The operating parameters for an ozonation experiment in this system [6] are listed in Table 4.

Table 4 Operating parameters for ozonation experiment

Parameters	Values
Ν	4 zones
D_A	2.2009x10 ⁻⁹ m ² s ⁻¹
D_B	0.92x10 ⁻⁹ m ² s ⁻¹
\overline{a}	$70 \text{ m}^2 \text{ m}^{-3}$
k_L	2.1428x10 ⁻⁵ m s ⁻¹
$H_{\scriptscriptstyle A}$	7.6x10 ⁶ N kmol ⁻¹ m ⁻⁵
Р	1.01x10 ⁵ N m ⁻²
V	1.30x10 ⁻³ m ³
\mathcal{Y}_{Ai}	0.0236
G_i	2.78x10 ⁻⁹ kmol s ⁻¹
C_{Abi}	0 kmol m ⁻³
C_{bi}	1.09x10 ⁻² kmol m ⁻³
Q	7.83x10 ⁻⁸ m ³ s ⁻¹
k _r	9.0x103 m3 kmol-1 s-1
pH_{Avg}	4.66
Temperature	25°C
Reaction order	m=n=1

3. Results and Discussion

With the aid of the phenolic ozonation reaction rate constant in Table 3 (by interpolating the value







of k_r between pH 3 and pH 5 giving $k_r \approx 9.0 \times 10^3 \text{ m}^3$ kmol⁻¹s⁻¹) and the input parameter values listed in Table 4, the phenolic concentration profile in the vessel can be calculated by the strings of perfectly mixed zones model.

Considering Figure 3, along the height of the reaction vessel (or zone number), the concentration of phenol in the bulk of liquid is predicted to decrease rapidly from 1030 mg/l (fresh feed) to 1015.21, 987.03, 827.29 and 448.10 mg/l at the 1st, 2nd, 3rd and 4th zone, respectively, whereas the observed phenol concentration from the experiment (see Figure 2) by Anderson [6] is shown to decrease to 450 mg/l at the base of the vessel (see Table 5).

Along the reactor axis, the percentage film reaction is calculated to be 99.29, 99.76, 99.92 and 100% at the 1st, 2nd, 3rd and 4th zone, respectively. Figure 4 shows the reaction factor (enhancement factor) increasing along the reaction vessel height. This factor increases from 11.72 at the 1st zone to



Figure 4 Predicted enhancement factor in ozone absorption process.

Table 5 Experimental results : Run No.3

Parameters		Values	
gas flow		0.258	l/min
liquid flow		0.0047	l/min
phenol concentration	- feed	1030	mg/l
	- product	450	mg/l
COD	- feed	2360	mg/l
	- product	1748	mg/l
pН	- feed	6.60	
	- product	2.72	

Source: Adapted from Anderson [6]

18.50, 21.09 and 21.63 at the 2^{nd} , 3^{rd} and 4^{th} zone, respectively. Under this continuous operating condition, again, the mole fraction of ozone in the gas phase decreases along the reaction vessel from 0.0236 (fresh feed) to 0.006336, 0.001417, 0.000256 and 0.0000423 at the 1^{st} , 2^{nd} , 3^{rd} and 4^{th}



zone, respectively (see Figure 5). As the gas stream first comes into contact with the liquid stream there is a little absorption of ozone until it reaches the later stage of the reactor. Nearly all ozone in the gas stream is absorbed when it leaves the outlet of the reactor. The extent of absorption of ozone gas in the phenolic solution along the reactor axis equals 73.62%, 94.13%, 98.94% and 99.83% at the 1st, 2nd, 3rd and 4th zone, respectively.

In the absorption and reaction of ozone gas into an aqueous solution (water), actually, the mechanism can be visualized as consisting of several steps. These include diffusion of ozone through the gas phase into the interface between the gas and liquid phase, transport across the interface to the liquid-phase boundary, and transfer into the bulk liquid. The dissolved ozone may be depleted in each of the step by decomposition or ozonation if reacting with any pollutants in the water.

In this simulation the dissolved ozone at each intermediate stage in the reactor is very low which is equal to 5.6077×10^{-13} , 1.2298×10^{-16} , 1.5805×10^{-18} and 1.5002×10^{-19} kmol m⁻³ at the 1st, 2nd, 3rd and 4th, respectively. This predicted result is similar to that by Li and Kuo [12]. Li and Kuo utilized a gas-liquid contacting reactor to study the absorption of ozone through a gas disperser into aqueous solution containing phenol. According to the data from their experiments, Li and Kuo reported that the reaction between ozone and phenol is rapid and no trace of ozone was detectable in the main liquid stream.

Actually, the transport of ozone across the film is a result of a concentration gradient. The concentration of ozone in the surface film falls linearly from $C_A^*(_{o3})$ at the gas-liquid interface to $C_{Ab}(_{o3})$ at the outer liquid-film interface. However,



Figure 5 Decrease in calculated mole fraction of ozone in the gas phase along the reaction vessel height.

when a chemical reaction is associated with mass transfer (such as the case of phenolic ozonation), both the rate of transfer and the mass transfer coefficient may be affected [25], [26]. There is some evidence that aqueous-phase ozone reactions increase the rate of mass transfer [16], [27], [28].

In considering how the chemical reaction of ozone with organic substance affects the rate of mass transfer, Grasso, Flizabeth and Weber [29] explained that chemical reaction normally reduces bulk aqueous-phase ozone concentration , leading to a greater difference between the actual liquid bulk concentration and the interface saturation limit (higher ozone concentration gradient across the liquid film: $C_A^*(_{o3})$ - $C_{Ab}(_{o3})$). Additionally, the reaction may be sufficiently fast that a substantial conversion percentage could occur in the liquid boundary film. This could lead to a nonlinear gradient across the film and a decrease in the effective film thickness. Then, an increase in the local liquid-side mass



transfer coefficient (k_L) may result. Consequently, it may result in a further enhancement of the rate of transfer.

Considering the Hatta number mentioned, for an irreversible 1st order reaction it is defined in the form Ha = $\sqrt{\frac{D_A k_r}{k_L^2}}$. For the case of an irreversible *m,n*-order reaction between gas (A) and substance (B) such as that between ozone and phenol ($A_{(O_3)} + zB_{(phenol)} \xrightarrow{k_r} product$), however, the Hatta number has a more complex:

$$Ha = \frac{1}{k_L} \sqrt{\frac{2}{m+1} k_r D_A C_A^{*(m-1)} C_B^{\ n}}$$
(17)

Since in this case the reaction is bimoleculartype second-order of which m and n are equal to 1 (first order with respect to both ozone and phenol concentration), the Hatta number from the above equation is deduced by

$$Ha = \sqrt{\frac{D_A k_r C_B}{k_L^2}} = \sqrt{M} , \qquad (18)$$

M= the film conversion parameter

According to this theory, Dankwerts [25] has shown that the amount of diffusing gas which reacts in the film will be negligible in comparision to that which reacts in the bulk liquid if:

$$\frac{D_A k_r C_B}{k_L^2} \ll 1 \ll \frac{k_r C_B}{k_L a}$$
(19)

If this condition is not met, a significant fraction of the diffusing gas will react in the film. This simultaneous diffusion and reaction will cause the rate mass transfer to be enhanced by a factor Ea, the enhancement factor.

More precisely, it has been found that the



Figure 6 Increase in film conversion parameter along the vessel height.

reaction can occur in the liquid bulk (the slow kinetic regime, $E_A < 1$ and Ha <0.3), in the liquid film (the fast kinetic regime, $E_A > 1$ and Ha >3), or in both the liquid bulk and the diffusion film (moderately fast kinetic regime, E_A around 1 and Ha between 0.3 and 3).

Referring to the computed results in this case study (Figure 6), the value of film conversion parameter $\left(\frac{D_A k_r C_B}{k_L^2}\right)$ is much greater than one. In addition, as can be seen in this case the E_A values are always much higher than 1. As a result of this, it can be implied that the kinetic regime is fast and the ozonation reaction develops almost exclusively in the liquid film which corresponds to the simulated results (obtained from the strings of backmixed zones model). Additionally, the values of the Hatta number obtained from this simulation are ranged from 14.38 to 21.67 which also confirms that nearly all the ozone should react with phenol in the diffusion film, a common situation for many reactions among ozone and organics in the water [18], [21].



Thus, it is quite reasonable that in this system, the decomposition reaction has been neglected. Again, if considering the film conversion parameter $(M=Ha^2)$, the film conversion parameter for phenolic ozonation (M_2) is much greater than that for only decomposition reaction (M_1) which is about 6.97x10⁻⁶. Under the condition $M_2 \gg M_1$, the dissolved ozone is utilized efficiently in reacting with the liquid constituent. This behavior suggests that a combination of low decomposition and high ozonation rates is essential to the success of a waste water treatment program. Since the decomposition and ozonation rates in aqueous systems are controlled by the same variables such as temperature, pH value and ionic strength, it is critical to operate an ozonation treatment process under optimal conditions favorable to the required ozonation reaction.

It is well known that the rate of decomposition increases with temperature and pH value and is affected very little by ionic strength of the solution [13], [27]. The increase in the decomposition rate with temperature is moderate but the rate increases very rapidly with pH value, especially in strong alkaline solutions [27].

It should be noted that if the decomposition reaction is much faster than the ozonation reaction, a build-up of dissolved ozone in the bulk liquid may occur. Such a system, however, is of little interest in applications of ozone absorption processes in air and water pollution abatement. For cases in which the liquid contaminants are not very reactive with ozone, the ozonation reactions may occur mainly in the bulk of liquid following the buildup of dissolved ozone. For many cases of practical interest, nevertheless, the ozonations are relatively fast without any trace of dissolved ozone in solutions as confirmed by experimental evidence [12], [23].

4. Conclusion

By applying the concept of tanks-in-series arranged in counter-current flow, not only have the concentration of ozone and phenol in the liquid bulk at the exit of the reaction vessel been calculated but also at all intermediate stages through the vessel. Along the height of the reaction vessel, the concentration of phenol in the bulk of liquid decreases rapidly from the top to the base of the vessel due to the reaction. Additionally, the simulation shows that the reaction between phenol and ozone occurs almost entirely in the liquid film. The phenolic ozonation enhances the absorption of ozone by consuming ozone and reducing its local concentration, giving a larger possible driving force for mass transfer.

Nomenclature

\overline{a}	Interfacial area	$m^2 m^{-3}$
A	Reactant A	
В	Reactant B (non-volatile substance)	
C_A	Concentration of reactant A	kmol m
C_A^{*}	Concentration of A at gas-liquid inter	face
		kmol m ⁻³
C_{Ab}	Initial concentration of reactant A	kmol m ⁻³
C_{Abc}	Liquid bulk concentration of reactant	А
		kmol m ⁻³
C_{Bi}	Initial concentration of reactant B	kmol m ⁻³
D_A	Diffusivity of reactant A	m ² s ⁻¹
D_B	Diffusivity of reactant B	$m^2 s^{-1}$
E_A	Enhancement factor, reaction factor	-
E_i	Enhancement factor for an infinitely	fast
	reaction	_



Total gas molar flow rate (inlet)	kmol s ⁻¹
Total gas molar flow rate (outlet)	kmol s ⁻¹
Hatta number	-
Henry constant	N kmol ⁻¹ m ⁻⁵
k_2, k_3 Constant	-
Reaction rate constant for 2 nd order	reaction
	m ³ kmol ⁻¹ s ⁻¹
Liquid side mass transfer coefficient	nt m s ⁻¹
Film conversion parameter	-
Number of zones	
$_{=0}$ Molar flow rate of A at	
gas-liquid interface	kmol s ⁻¹
$_{=\delta}$ Molar flow rate of A at	
outer-liquid film interface	kmol s ⁻¹
Total pressure of the system	N m ⁻²
Partial pressure	N m ⁻²
Liquid volumetric flow rate	$m^3 s^{-1}$
Local rate of reaction	kmol m ⁻³ s ⁻¹
Liquid volume	m ³
Mole fraction of reactant A (inlet)	-
Mole fraction of reactant A (outlet)) -
	Total gas molar flow rate (inlet) Total gas molar flow rate (outlet) Hatta number Henry constant k_2 , k_3 Constant Reaction rate constant for 2 nd order Liquid side mass transfer coefficie Film conversion parameter Number of zones $=_0$ Molar flow rate of A at gas-liquid interface $=_{\delta}$ Molar flow rate of A at outer-liquid film interface Total pressure of the system Partial pressure Liquid volumetric flow rate Local rate of reaction Liquid volume Mole fraction of reactant A (inlet) Mole fraction of reactant A (outlet)

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