

Ozone transfer from gas to water in a co-current upflow packed bed reactor containing silica gel

V. Farines^a, S. Baig^b, J. Albet^{a,*}, J. Molinier^a, C. Legay^a

^a ENSIACET, Laboratoire de Chimie Agro-Industrielle, UMR INRA 1010, Equipe Génie Chimique,
118 Route de Narbonne, 31077 Toulouse Cedex 04, France

^b Ondeo-Degrémont SA, 183 Avenue du 18 Juin 1940, 92508 Rueil-Malmaison Cedex, France

Abstract

The effect of superficial gas and liquid velocities upon ozone mass transfer in a co-current upflow reactor filled with granular silica gel is studied. A concentration of dissolved ozone at steady state is observed depending on technological and operating conditions of the reactor. Increase of gas velocity is found to increase both the overall mass transfer coefficient and the concentration of dissolved ozone at steady state. Increase in liquid velocity at fixed gas velocity decreases the concentration of dissolved ozone at steady state. Ozone decomposition in the presence of silica gel is investigated and shown limited to self decomposition in liquid bulk. Ozone mass transfer is modelled from experiments carried out under different conditions of bed height, gas flow rate and liquid flow rate in order to predict the overall mass transfer coefficient involved in further simulations of ozone concentration profiles along the length of packed bed.

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Keywords: Ozone; Mass transfer; Decomposition; Fixed bed reactor

1. Introduction

Ozone is known as the most powerful chemical oxidant available for water treatment [1]. However, the removal of organic matter is often limited during direct ozone treatment due to the stable by-products formation. Then, application of advanced oxidation processes may be required to achieve high oxidation yields of organic pollutants when their reactivity towards molecular ozone is low. In this field, many processes have been developed using ozone with activating systems to promote the organic matter oxidation. Two types of activating systems are found. The first one includes hydrogen peroxide, catalysts and UV radiation whose reaction with ozone generates highly reactive secondary oxidants such as free radical species in the medium [2,3]. The second one involves solid materials such as activated alumina or active carbon acting as adsorbents to concentrate the organic matter in solid phase and then to promote its oxidation, leading to an exothermic reaction [4,5]. The aim of this paper is therefore to study ozone mass transfer and decomposition in a co-current upflow reactor packed with granular silica gel that is another potential adsorbent to be used for low organic pollutants concentration followed by oxidation with ozone at ambient temperature.

2. Materials and methods

A simplified scheme of the experimental equipment used in this study is shown in Fig. 1 lists the main physical characteristics of the granular silica gel used. The packed bed was disposed on a support grid located above a ceramic porous distributor to gas introduction. The liquid flow was injected using a peristaltic pump and a pulsation limiter through two inlet points set under and at each side of the gas diffuser. Liquid flow rate (20, 30, 40, 60 ± 0.6 l/h) was measured by a flowmeter. Liquid passed through the column co-currently with the gas bubbles. The reactor was equipped with outlets at the top of the packed bed for solution analysis and for liquid and gas discharge. On-line monitoring was performed for ozone concentrations in the liquid phase and in the gas phase. Ozone concentration in the gas phase was analysed by the UV method [6] (BMT Messtechnik 961 analyser) while the ozone concentration in the aqueous phase was obtained (±0.5%) using an electrochemical probe fed at a high enough liquid flow rate to prevent ozone depletion (Orbisphere Laboratories analyser 26506 with sensor 2301). Experiments were conducted using demineralised water at pH 6 at 289 K. Ozone was produced from pure oxygen and its concentration in the gas phase at the outlet of the generator was fixed to 100 g/m³ NTP (±2%). Gas flow rate (10, 20 ± 1 l/h NTP) was roughly measured by a flowmeter at the inlet of the column and adjusted using a volumetric counter

* Corresponding author. Tel.: +33-562-88569-7; fax: +33-562-885600.
E-mail address: joel.albet@ensiacet.fr (J. Albet).

Nomenclature

a	specific interfacial area (m^2/m^3)
C	ozone concentration (g/m^3)
C_G	ozone concentration of the gas phase (g/m^3)
C_{Gi}	ozone concentration of the gas at column inlet (g/m^3)
C_L	ozone concentration of the liquid phase (g/m^3)
C_L^*	concentration of dissolved ozone at the equilibrium (g/m^3)
C_L^∞	concentration of dissolved ozone at steady state (g/m^3)
d_c	diameter of column (m)
d_b	diameter of gas bubble (m)
d_p	particle diameter (m)
D_{O_3}	ozone diffusivity in water (m^2/s)
G	superficial gas velocity in empty column (m/h)
H	bed height (m)
He	Henry's constant (atm)
k	first-order rate constant (s^{-1})
k_d	kinetic constant of decomposition reaction (s^{-1})
$K_L a$	overall mass transfer coefficient in liquid phase (s^{-1})
L	superficial liquid velocity in empty column (m/h)
M	water molecular weight (18 g/mol)
$[\text{OH}^-]$	hydroxide ions concentration (mol/l)
Q_G	gas flow rate (l/h)
Q_L	liquid flow rate (l/h)
R	gas constant (0.082 l atm/mol K)
S	column cross section area (m^2)
T	temperature (K)
Z	distance along tubular reactor (m)
ε_g	gas holdup (dimensionless)
ρ	water density (kg/m^3)

located in the vent gas line after the ozone analyser. The residual ozone in gas was destroyed by a potassium iodide solution absorber followed by thermal destruction. The relative gas pressure at the top of the column was maintained at 0.2 bar to favour ozone dissolution in aqueous phase. Ozone gas transfer measurements were carried out at different conditions of bed height, gas flow rate and liquid flow rate.

A 0.05 m diameter column was carefully packed from the bottom to a given height (0.20, 0.35, 0.50 m) with the granular silica gel (Prolabo Granulated Silica gel). Table 1

Additional experiments in semi-batch mode were carried out using a 21 stirred vessel filled with 1.5 l of ultra-pure water containing when needed $81 \text{ g}/\text{m}^3$ of powdered silica gel (Merck Silica gel, grade 10180). The silica gel particle size range is 80–130 μm with an average pore diameter of 40 Å. Ozone was produced at a concentration of 40 g/m^3 NTP ($\pm 2\%$). The gaseous flow (60 ± 0.5 l/h NTP) contin-

Table 1

Main characteristics of the packing material (Prolabo Granulated Silica gel)

Medium screen (mm)	2–5
Average diameter of particles (mm)	3.33
Bulk density	0.75
Density of packed bed (kg/m^3)	370
Void fraction of bed	0.24
Surface area (m^2/g)	≈ 500
External surface area per volume of bed (m^2/m^3)	1370

uously entered the bottom of the reactor through a diffuser located under the impeller axis. The relative gas pressure in the reactor was maintained at 0.2 bar. The agitation speed was fixed at 500 rpm and the temperature of the solution was kept at 293 K using an immersion thermostat with a circulating water flow. Ozone gas was applied for at least the required time to obtain the equilibrium state in the liquid phase (8 min) to then allow stopped-flow measurements of dissolved ozone concentration. Dissolved ozone concentration was determined by the indigo dosage method ($\pm 1\%$), based on indigo trisulfonic acid discoloration by ozone in acid medium condition [7].

3. Results and discussion

Variation with time from start-up of ozone concentration in the liquid phase at the top of the fixed bed was studied for different gas velocities, liquid velocities and bed heights. Fig. 2 presents typical ozone absorption curves obtained for a 0.2 m bed height with superficial gas velocity of approximately 5 or 10 m/h (± 0.5 m/h) and superficial liquid velocity of approximately 10, 15, 20 or 30 m/h (± 0.3 m/h). Each experiment shows a start-up period of 5–6 min depending on ozone transfer rate after which a concentration of dissolved ozone at steady state C_L^∞ is reached. For each operating condition, the constant dissolved ozone concentration value obtained is the result of a dynamic equilibrium between the mass transfer of ozone coming from the gaseous phase and the ozone decomposition in the liquid phase. From these data, it can be noticed that the ozone dissolved concentration at steady state increases with the superficial gas velocity. In addition, the increase of liquid velocity is shown to lower the concentration of dissolved ozone at steady state. Variation with time of the ozone concentration in the liquid phase at the top of the packed bed for different bed heights with fixed flows of gas and liquid at, respectively 5 and 10 m/h is given in Fig. 3. Comparison of the curves shows that concentration of dissolved ozone at steady state increases with bed height while ozone transfer rate is clearly unaffected. Figs. 4 and 5 highlight the influence of operating conditions on the ozone concentration in aqueous phase at steady state. The dissolved ozone concentration reached at steady state linearly increases with bed height and varies as a function of gas–liquid flow ratio.

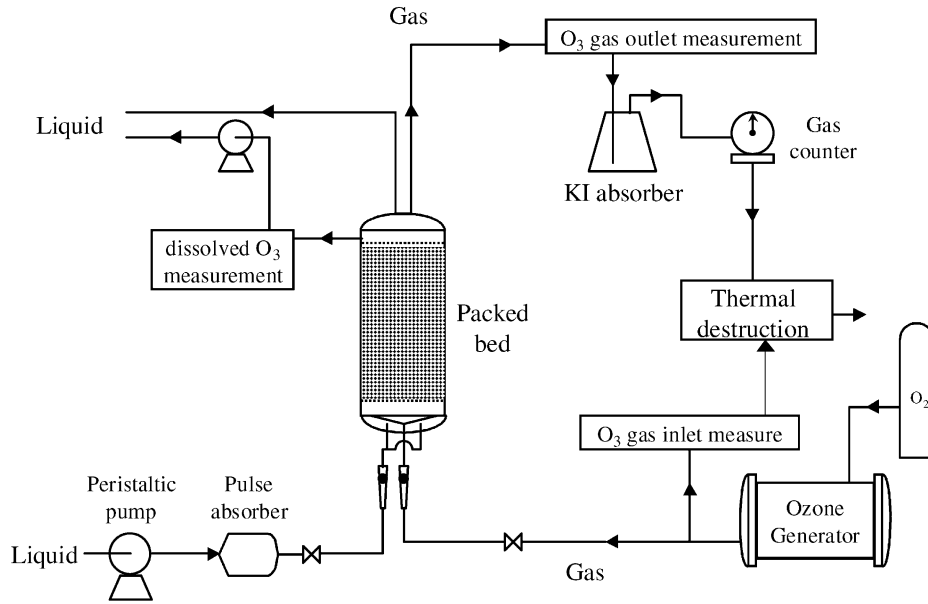


Fig. 1. Scheme of the experimental apparatus.

Ozone absorption in water results from both gas–liquid mass transfer and from dissolved ozone decomposition reaction. Following the Whitman and Lewis film theory and because of non-resistance to ozone mass flux in the gas film, the ozone transfer rate can be defined using the overall volumetric mass transfer coefficient $K_L a$ and the equilibrium concentration of dissolved ozone C_L^* . This second parameter is given by Henry’s law expressed in Eq. (1) when considering ozone as an ideal gas. The Henry’s constant (He in atmosphere) is calculated by means of the correlation (2) proposed by Sullivan [8]. This correlation takes into account pH effect on ozone solubility by means of hydroxide ions

concentration $[OH^-]$ expressed in mol/l.

$$C_L^* = \frac{\rho RT}{M He} C_G \tag{1}$$

$$He = 3.84 \times 10^7 [OH^-]^{0.035} \exp\left(\frac{-2428}{T}\right) \tag{2}$$

Ozone mass transfer in the fixed bed reactor can be modelled according to a mass balance in both gas and liquid phases given the following considerations:

- For the gas velocities used, the reactor operates in bubble-type regime characterized by gas bubbles highly

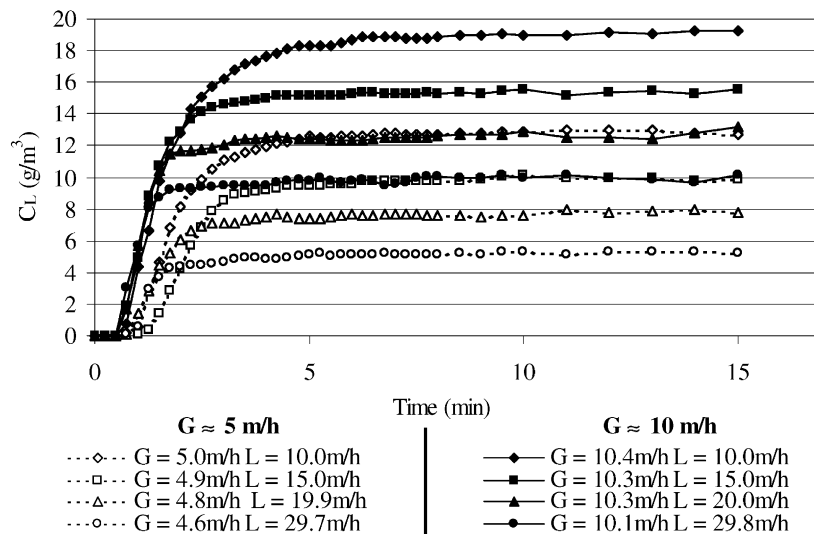


Fig. 2. Ozone absorption at different gas and liquid velocities for a bed height of 0.2 m.

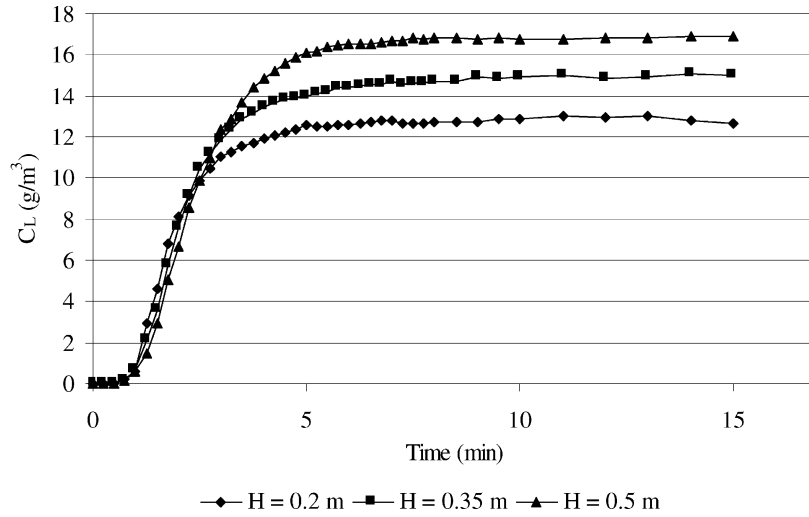


Fig. 3. Ozone absorption at different bed heights for given gas and liquid velocities ($G \approx 5$ m/h, $L \approx 10$ m/h).

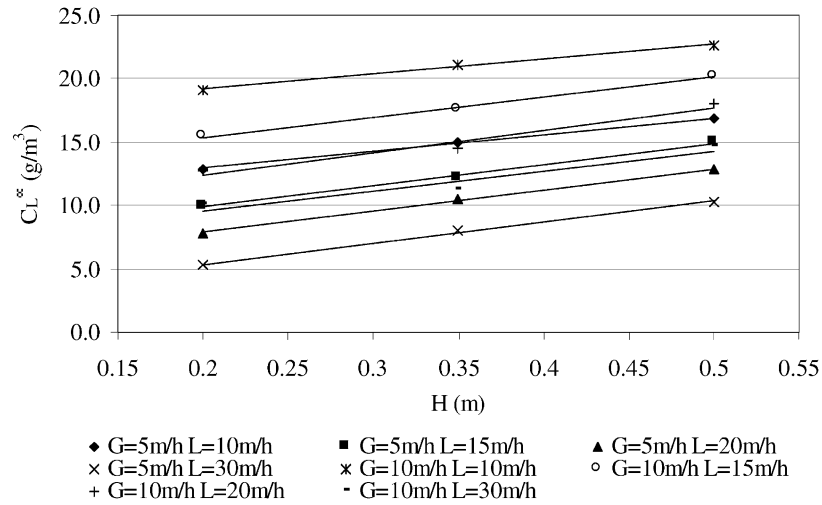


Fig. 4. Effect of bed height on concentration of dissolved ozone at steady state for different gas and liquid velocities.

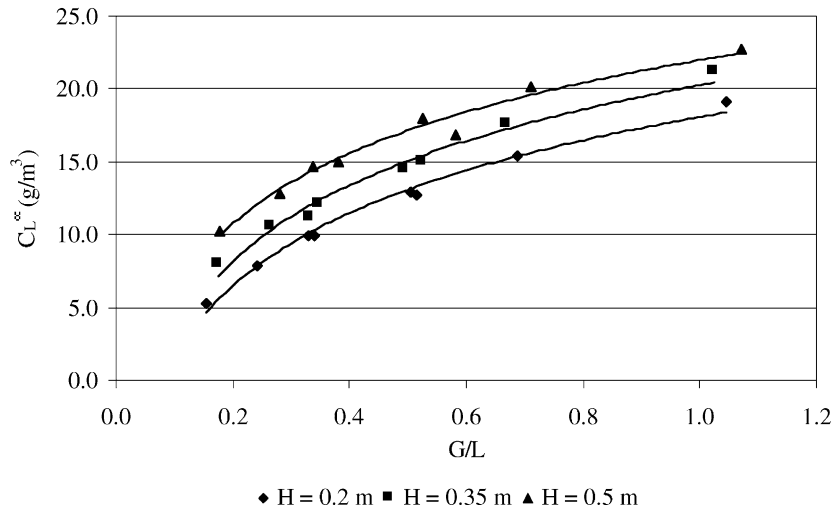


Fig. 5. Effect of gas-liquid flows ratio on concentration of dissolved ozone at steady state for different bed heights.

dispersed in a liquid flow [9]. This consideration is supported by visual observation.

- The dimensions of the reactor and solid particles ($H/d_p \geq 50$ and $H/d_c > 0.5$), the linear variation with height of the dissolved ozone concentration, and the constant pressure drop per packing height are all consistent with plug-flows of water and gas through the bed.
- The intra-particle diffusion effects are not considered.
- The ozone absorption process is assumed to be isothermal and isochoral.

The ozone mass balance developed for a unit volume of cross-section area S and height dZ is then given at steady state for the gas and liquid phases by, respectively, Eqs. (3) and (4). Ozone mass balance in Eq. (3) is limited to ozone mass transfer without ozone decomposition in the gas phase. For the liquid phase, Eq. (4) includes the gas to liquid mass transfer term and in addition a kinetic decomposition term with constant rate coefficient k_d for dissolved ozone decomposition.

$$\frac{Q_G}{S} \frac{dC_G}{dZ} = -K_L a (C_L^* - C_L) \quad (3)$$

$$\frac{Q_L}{S} \frac{dC_L}{dZ} = K_L a (C_L^* - C_L) - k_d C_L \quad (4)$$

Ozone decomposition in water has been investigated by numerous authors. Kinetic expressions have been proposed taking into account the initiator role of hydroxide ions in the radical mechanism [10–12]. A previous study confirmed that for a solution pH ranging from 3 to 10 at 293 K, ozone decomposition in water occurs according to a first-order reaction with respect to ozone [13]. To make sure that silica gel is unreactive towards ozone, experiments in batch mode were performed using an aqueous solution containing 81 g/m^3 powdered silica gel to minimise the intra-particle diffusion effect. Further to the saturation of the solution by ozone, stopped-flow measurements of dissolved ozone concentration were made. Ozone decomposition takes place according to a pseudo-first-order reaction with respect to the ozone concentration. The kinetic constant k_d is compared to the one evaluated from the reference test carried out using only water and corresponding to ozone self decomposition. The results reveal that the constant rate coefficient k_d for dissolved ozone self decomposition is equal to $1.6 \times 10^{-4} \text{ s}^{-1}$ and remain unchanged when powdered silica gel is present in the reactor. In addition, the Hatta number has been calculated in order to establish the zone of water where the reaction is taking place. For a first-order irreversible reaction, Hatta number is defined as:

$$Ha = \frac{(k_d D_{O_3})^{0.5}}{K_L} \quad (5)$$

with k_d and D_{O_3} , respectively the first-order rate constant and the ozone diffusivity in water. With these parameters, the kinetic regime of absorption can be established. By checking this, Ha was calculated from value of first-order

rate constant k_d equal to $1.6 \times 10^{-4} \text{ s}^{-1}$, taking D_{O_3} as $1.3 \times 10^{-9} \text{ m}^2/\text{s}$ at 293 K [14] and two values of K_L : $2 \times 10^{-4} \text{ m/s}$ and $2 \times 10^{-5} \text{ m/s}$. These K_L values are valid, approximately, for reactors in which ozone is fed through two different devices: a diffuser plate and a bubble column [15]. In any case, they represent the orders of magnitude K_L has in agitated tanks and bubble columns [16]. The Ha numbers obtained with and without powdered silica gel in the reactor are the same and, respectively equal to 0.0023 and 0.023 for $K_L = 2 \times 10^{-4} \text{ m/s}$ and $2 \times 10^{-5} \text{ m/s}$. The Ha is much lower than 0.1 and according to Charpentier [16], this result indicates that the reaction of ozone decomposition is very slow and takes place in the water bulk. Accordingly, the ozone absorption is controlled by the reaction rate of ozone decomposition. As well, silica gel does not enhance ozone decomposition in the liquid phase and the ozone reaction in water through the fixed bed can be considered limited to self decomposition in the liquid bulk. The kinetic constant (k_d) of $1.6 \times 10^{-4} \text{ s}^{-1}$ can be used for $K_L a$ determination.

Considering that there is no self-decomposition of ozone in the liquid film near the gas–water interface, the overall mass transfer coefficients were identified by solving Eqs. (3) and (4) simultaneously using a Runge–Kutta 4th order numerical integration method in order to minimise a least squares criterion of the difference between the measured values and the calculated ones. The boundary conditions adopted were at $Z = 0$, $C_G = C_{Gi}$ and $C_L = 0$. Table 2 shows that the increase of the superficial gas velocity from 5 to 10 m/h results in a nearly proportional increase of the $K_L a$ value while the liquid velocity effect remains low. These observations fit previous ones described and suggest that the overall mass transfer variation is mainly controlled by the specific interfacial area variation (a) linked to the gas hold-up change which strongly depends on the superficial gas velocity [17–20]. Experimental data from Roustan et al. [18] shows that the gas holdup (ϵ_g) linearly increases with the gas flow rate while the bubble size (volume-to-surface mean bubble diameter) is independent of the liquid flow rate and increases little with the gas flow rate. The specific in-

Table 2
 $K_L a$ values identified for ozone absorption through a fixed bed of 0.5 m height at different gas and liquid velocities

G (m/h)	L (m/h)	$K_L a \times 10^3$ (s^{-1}) ($\pm 2\%$)
5.4	10.0	6.40
5.3	15.0	7.56
5.2	19.9	8.09
5.0	29.7	8.64
10.5	10.0	10.53
10.3	15.0	12.04
10.2	20.0	12.42
10.0	29.8	13.79

pH = 6, $T = 289 \text{ K}$, $He = 4545.2 \text{ atm}$, $C_L^* = 32.4 \text{ g/m}^3$, $C_{Gi} = 111.9 \text{ g/m}^3$.

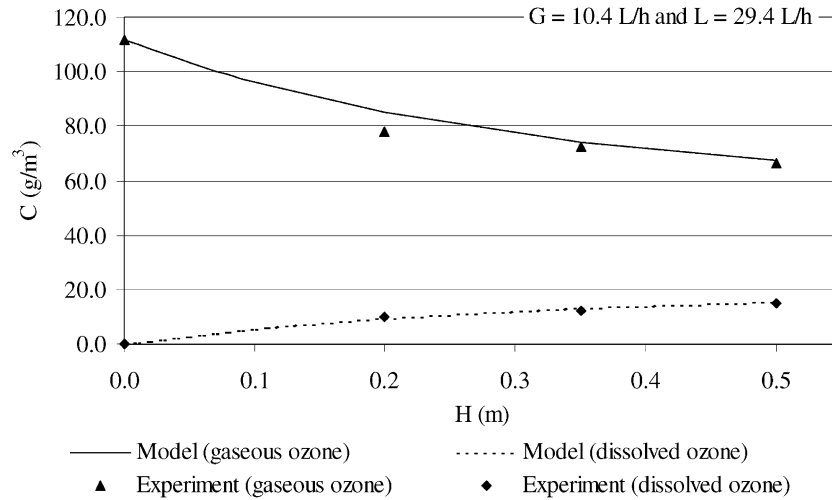


Fig. 6. Numerical simulation results for $G = 5.3 \text{ m/h}$, $L = 15.0 \text{ m/h}$, $K_L a = 7.56 \times 10^{-3} \text{ s}^{-1}$ and $k_d = 1.6 \times 10^{-4} \text{ s}^{-1}$.

terfacial area is related to the gas holdup and the diameter of bubble (d_b) by Eq. (6):

$$a = \frac{6}{d_b} \frac{\varepsilon_g}{1 - \varepsilon_g} \quad (6)$$

As well, the gas holdup linearly increases with the gas flow rate while the bubble size is less affected, resulting in a positive variation of the specific interfacial area.

Moreover, Roustan et al. [18] have proposed two experimental correlations for $K_L a$ determination in an empty bubble column operating in co-current upflow of gas (ozone) and water for two liquid flow regimes described by the Reynolds number (Re):

- Laminar flow ($Re = 680$):

$$K_L a = 0.092 \times G^{0.516} \quad (7)$$

- Turbulent flow ($Re = 1912\text{--}2985$):

$$K_L a = 0.110 \times G^{0.615} \quad (8)$$

with $K_L a$ in min^{-1} and G in m/h .

In our study, the superficial liquid velocity varies between 10 to 30 m/h corresponding to Reynolds number in the range 615–1845. Using the correlations (7) and (8), respectively, for the laminar and the turbulent liquid flow, we found that $K_L a$ values in empty bubble column are on the average 50% lower than those obtained with the silica gel packed bed for the two liquid flow regimes. In addition, our $K_L a$ values are in agreement with the gas–liquid mass transfer coefficients for co-current upflow in packed beds obtained by Alexander and Shah [17] with various packing materials such as standard cylindrical extrudates (3.17 mm diameter) and rings (6.35 mm diameter).

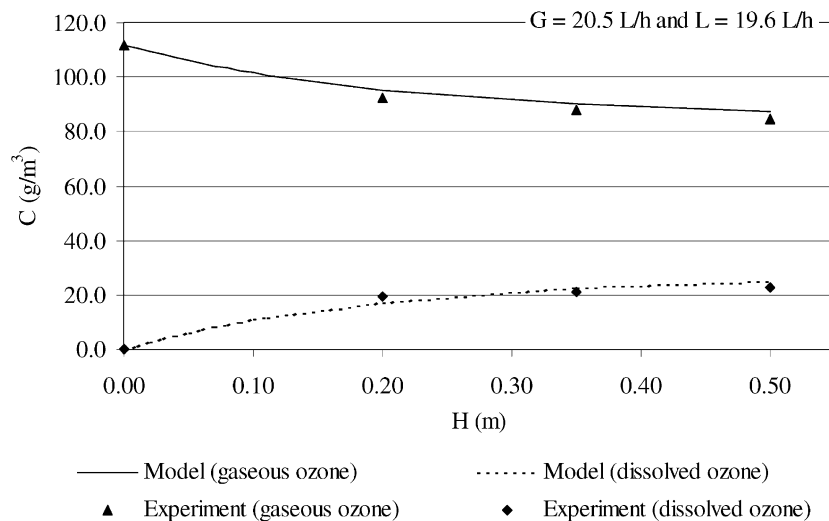


Fig. 7. Numerical simulation results for $G = 10.4 \text{ m/h}$, $L = 10.0 \text{ m/h}$, $K_L a = 10.53 \times 10^{-3} \text{ s}^{-1}$ and $k_d = 1.6 \times 10^{-4} \text{ s}^{-1}$.

In order to prove the model suitability for prediction of ozone concentrations profiles along bed length, numerical simulations were carried out involving the average $K_L a$ value relative to each gas velocity. Figs. 6, 7 show that good agreement is reached between experimental and model results.

4. Conclusion

The influence of gas and liquid flows on ozone mass transfer in a reactor containing a fixed bed of granular silica gel operating with co-current upflow is examined considering the concentration of dissolved ozone at steady state and the overall mass transfer coefficient. The concentration of dissolved ozone at steady state is found to increase with gas velocity and bed height. Liquid velocity is shown to cause the opposite effect. Whereas ozone decomposition in the presence of silica gel is shown limited to self decomposition in liquid bulk, the overall mass transfer coefficient is mainly affected by gas velocity. The mathematical model based on ozone mass balance is shown able to reproduce the experimental observations concerning the effects of gas and liquid velocities.

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