

Mass transfer of ozone in purified water

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Abstract

This work presents the study of ozone mass transfer in water in bubble column with 0.5cm inside diameter and 2 m height. The volumetric mass transfer, rate constant of ozone decomposition and mass transfer efficiency were studied with different gas flow rates (50,100, 150, 200, 250) L/min.

The volumetric mass transfer as well as rate of decomposition of ozone was found to increase with increasing gas flow rate. They were ranged between 0.21-0.41min⁻¹ and 0.018-0.036min⁻¹ respectively.

Mass transfer efficiency was increased from 77 to 98% with increasing gas flow rate.

A mathematical model was numerically solved to describe the liquid ozone concentration with time. The model and experimental results agreed well.

Keywords: Ozone, rate of decomposition of ozone, volumetric mass transfer, modelling.

انتقال كتلة الاوزون في الماء النقي

الخلاصة

هذا البحث يقدم دراسة عن انتقال كتلة الأوزون في الماء داخل عمود التفقيع بقطر 5 سم وارتفاع 2م. تم دراسة انتقال الكتلة الحجمي، ثابت سرعة تحلل الأوزون و كفاءة انتقال الكتلة بسرعات جريان مختلفة من الغاز (50, 100, 150, 200, 250) لتر/دقيقة. وجد إن انتقال الكتلة الحجمي و ثابت سرعة التحلل يزدادان بازدياد سرعة الجريان وتتراوح قيمهما بين 0.21-0.41 دقيقة⁻¹ و 0.018-0.036 دقيقة⁻¹ على التوالي. كفاءة انتقال الكتلة ازدادت من 77% إلى 98% بازدياد سرعة الجريان. تم حل موديل رياضي بصورة عددية لوصف تركيز الأوزون في السائل مع الزمن. كان هناك تطابق جيد بين قيم النتائج العملية وبين قيم نتائج الموديل.

Introduction

Ozone is one of the strongest oxidants technically applied. It utilized in a variety of chemical processes, as well as in the treatment of both drinking and wastewater.

Aims of ozonation in water treatment include the removal of color and smell and the disinfecting of biologically polluted water in order to destroy or inactivate microorganisms and event viruses n (Janknecht, et.al, 2001).

In addition, ozone can be effective degradation of organic compounds. Thus, ozonation can be used to increase the biodegradability of

biologically refractory compounds. Even small doses of ozone can be sufficient to change the structure of the compounds and make them more amenable to biological breakdown (Chang and Chian, 1981). The kinetic of reaction with organic compounds depends on the nature of them (Hoigne and Bader, 1983), (Beltran, et.al, 2001), and (Von Gunten, 2003).

When ozone is to be applied to water it needs to be transferred from the gas phase mixture into the liquid phase. The necessary condition for that is the surface between the two

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phases to enable the phase transfer, usually prepared by the formation of contactors including; bubble column, packed towers, deep U tube contactors, submerged turbines, gas inducing column and pipeline injectors (Hsu,etal., 2002), (Murayama, et al., 2005).

In this work a bubble column ozone contactor was used, which is very popular for ozone application and more traditional contactor. An orifice diffuser was used to introduce the gas at the bottom of the column. The size of the bubbles depends on the size of the hole used and type of liquid.

Theory

The transfer of ozone to water without chemical reaction is currently accepted as occurring according to the double-film model (Sotelo, et al., 1989), in which the driving force is the difference of ozone concentration between liquid and gas phase. The general form of mass balance is given as:

$$\frac{dC}{dt} = K_{La}(C^* - C) - r_A \quad \dots (1)$$

In organic free-purified water, ozone self decomposition reaction is the only reaction could be undergoing since no organic compounds exist for ozonation reaction. It's assumed that, for very clean water, the ozone decomposition can be approximated as first order process (Zhou, 1995; Roustan, 1996). The rate law is formulated as:

$$\frac{dC}{dt} = K_D C \quad \dots (2)$$

The volumetric mass transfer constant K_{La} is a key parameter for the description of gas/liquid contactor. It's a function of the physicochemical properties of the liquid, the bubble and the hydrodynamic conditions (Wu et al, 2000). At steady state, after the ozonation started, the dissolved ozone concentration constant

gas bubbles within the water. There are several types of ozone with time. According to this equation (1) and (2) will be:

$$K_{La}(C_{ss}^* - C_{ss}) = K_D C_{ss} \quad (3)$$

and it can be calculated from Henrys law (6) in which:

$$C_{ss}^* = H C_{ss} \quad (4)$$

Hence, equation (3) will be:

$$K_{La} = \frac{C_{ss}}{C_{ss}^* - C_{ss}} K_D \quad \dots (5)$$

Once steady state achieved, the ozone production stopped then the gas introduced contains no ozone i.e. $C^*=0$, so equation (1) and (2) will be:

$$\frac{dC}{C} = -K_D \left(\frac{C_{ss}^*}{C_{ss}^* - C_{ss}} \right) dt \quad \dots (6)$$

Plotting equation (6), the term $-K_D(C_{ss}^*/C_{ss}^* - C_{ss})$ is the slope of $[\ln C=f(t)]$, so the values of K_{La} and K_D can be calculated.

In order to compare the values of K_{La} and K_D , all of these values have been corrected to 20°C, because some of the physical properties depend on temperature, such as viscosity, density, surface tension.

K_{La} and K_D at 20°C are (Ting, et al., 2001):

$$K_{D(20^\circ C)} = 4 * 10^{-9} K_{D(T)} \exp(5606/T) \quad \dots (7)$$

$$K_{La(20^\circ C)} = K_{La(T)} * 1.024^{(20-T)} \quad \dots (8)$$

Experiment

The schematic diagram of the process is shown in figure (1), it consists of; a glass bubble column with 5 cm inside diameter and 2m height. Ozone generator device made by Fisher Company generating about 10 mg/L of ozone as maximum using pure oxygen.

The flow rate of oxygen controlled and measured by manual control valve and calibrated flow meter. The electrical consumed by the device also had been watched as an indication for the discrepancy of any fluctuation in amount of ozone generated in the device may occur.

First the column filled with 1.5 liter of water (its quality given in table (1)) then the generated gas dispersed at the bottom of the column through an orifice plate with fine holes to insure forming small bubbles.

Different gas flow rates of 50, 100, 150, 200,250L/min were used in this work with 10 mg/L of ozone concentration. To estimate the amount of ozone concentration in the inlet and outlet gas stream, the gas stream first lead to two traps connecting in series. Each trap contained Potassium Iodide (KI) with few drops of acetic acid to react with ozone. The solution in two traps then collected and titrated with Sodium Thiosulphite $\text{Na}_2\text{S}_2\text{O}_3$ using starch as an indicator. A sample of water with drew each 5 minute to determine ozone concentration.

Results and Discussion

Volumetric Mass Transfer

The effect of gas flow rate on volumetric mass transfer is shown in table (2). The values of KLa were found to be in the range of 0.2141min^{-1} to 0.41min^{-1} at 30°C and from 0.16 to 0.3min^{-1} at 20°C . These values are lower than those calculated by Chedeville,et.al (2007) ranged between $0.7-1.2\text{min}^{-1}$, while they are close to those obtained by Ting, et.al (2001).

It could be seen from table (2) that the volumetric mass transfer increases with increasing gas flow rate due to the increase in the velocity of bubble and number of bubbles that causes greater specific surface area. This phenomenon is similar to other

workers (Zhou and Smith, 2000 and Ting, et al., 2001). While this effect is different on mass transfer coefficient since the last is mainly controlled by the diffusion of ozone in liquid film. The liquid film is not accelerated by the velocity of gas bubble, therefore the rate of diffusion will not be effected by the increase in the gas velocity.

It was assumed that the relationship between volumetric mass transfer and superficial gas velocity (U_g) takes the form of a power law as follows:

$$KLa=aU_g^b \quad \dots\dots (9)$$

The relationship is determined from a linear regression of the logarithms of KLa and U_g as below with correlation coefficient equals to 0.94:

$$KLa=0.0404U_g^{0.414} \quad \dots (10)$$

The rate of ozone decomposition shows similar behavior i.e. these values increase with increasing gas flow rate. They rise from 0.018 to 0.036min^{-1} at 30°C and from 0.0081 to 0.016min^{-1} at 20°C . These values are lower than those obtained by Ting, et.al (2001) and Chedeville,et.al (2007). This can be explained by the mix use; purified water used in this study which was more basic in $\text{pH}=7$ than process water used by these workers. Moreover, the process water contains more competing lead to ozone decomposition.

Mass Transfer Efficiency

Mass transfer efficiency can be calculated from the amount of ozone in feed gas and in the off gas as follows:

$$TE = (\text{ozone in} - \text{ozone out}) / \text{ozone in} \quad (11)$$

The effect of detention time on mass transfer efficiency is shown in figure (2) . This figure shows that the

transfer efficiency increases with increasing detention time for all gas flow rates and 90% transfer efficiency achieved with detention time only 5 minutes and this value increases to 98% with 20 minutes.

The effect of gas flow rate on overall mass transfer efficiency can be shown in figure (3) which indicates that increasing gas flow rate caused an increase in mass transfer efficiency.

Ozone Concentration profile

The experimental results of the liquid phase ozone concentration with time are shown in figure (4). This figure shows that the ozone concentration increases with gas flow rate and time till it reaches a plateau level; i.e the ozone concentration reaches a steady state level. Different values has been expected from different experimental condition instead of constant values as would be expected since this plateau level doesn't correspond to the equilibrium value because of the impact of the simultaneous decomposition reaction occurring during the absorption process.

In order to estimate the concentration profile of liquid phase ozone concentration theoretically equation (1) had been solved with Matlab program and compared with the experimental results as illustrated in figures 5 to 8. Good agreement can be noticed from these figures.

Conclusions

Mass transfer rates were measured in purified water at different gas velocities. The mass transfer rates were roughly proportional gas velocity. It was found that the volumetric mass transfer as well as rate of ozone decomposition increase with increasing gas flow rate from 50 mg/L to 250 mg/L. Also, mass transfer efficiency increases with gas flow rate.

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Nomenclature

C	is the liquid phase ozone concentration, mg/L
C^*	is the steady state saturation liquid phase ozone concentration, mg/L
C_{ss}	is the steady state liquid phase ozone concentration, mg/L
C_{ss}^*	is the steady state saturated liquid phase ozone concentration, mg/L
H	Henry's constant
K_D	is the rate constant of ozone decomposition reaction, min^{-1}
K_{La}	is the volumetric mass transfer coefficient, min^{-1}
r_A	is the rate of ozone decomposition, mg/Lmin
t	is the time, min

Table (1): The main characteristics of water

Characteristic	
TDS	0.449-0.594 g/L
TSS	Nil-0.249 g/L
pH	7
Conductivity	984 microcem/cm
Total Hardness	116 mg/L

Table (2): The volumetric mass transfer and decomposition rate constant at different temperature for different gas flow rate

Gas Flow Rate (L/min)	K_{La} (min^{-1}) at 30°C	K_D (min^{-1}) at 30°C	K_{La} (min^{-1}) at 20°C	K_D (min^{-1}) at 20°C
50	0.21	0.0189	0.1672	0.00819
100	0.24	0.0216	0.1911	0.00936
150	0.30	0.027	0.2389	0.01171
200	0.35	0.0315	0.2788	0.01366
250	0.41	0.0369	0.3266	0.01600

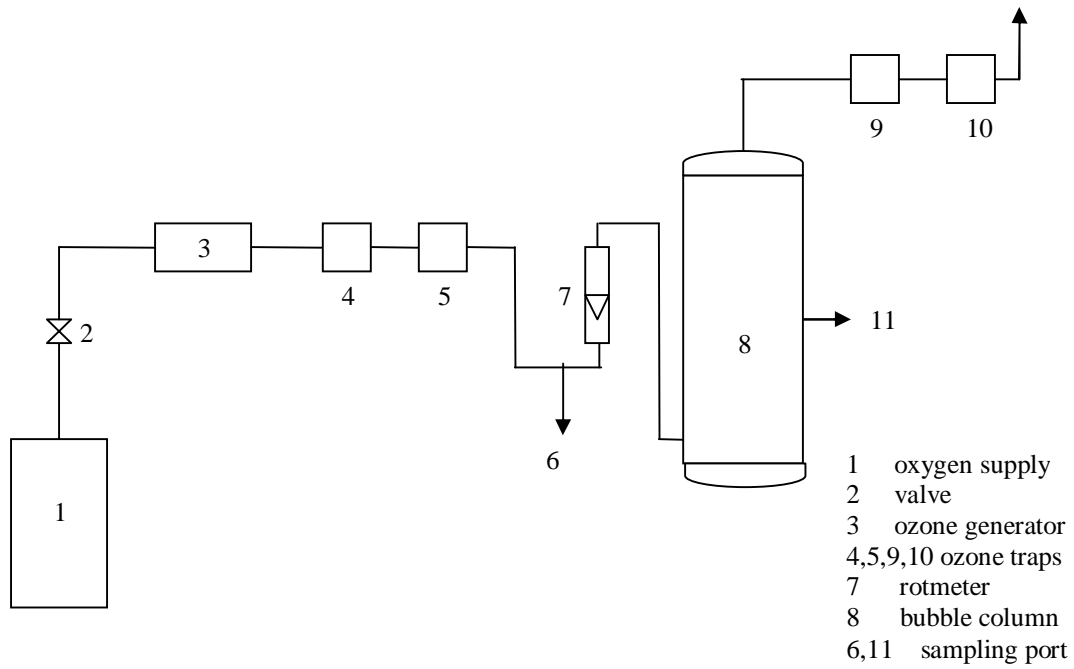


Figure (1): The schematic diagram

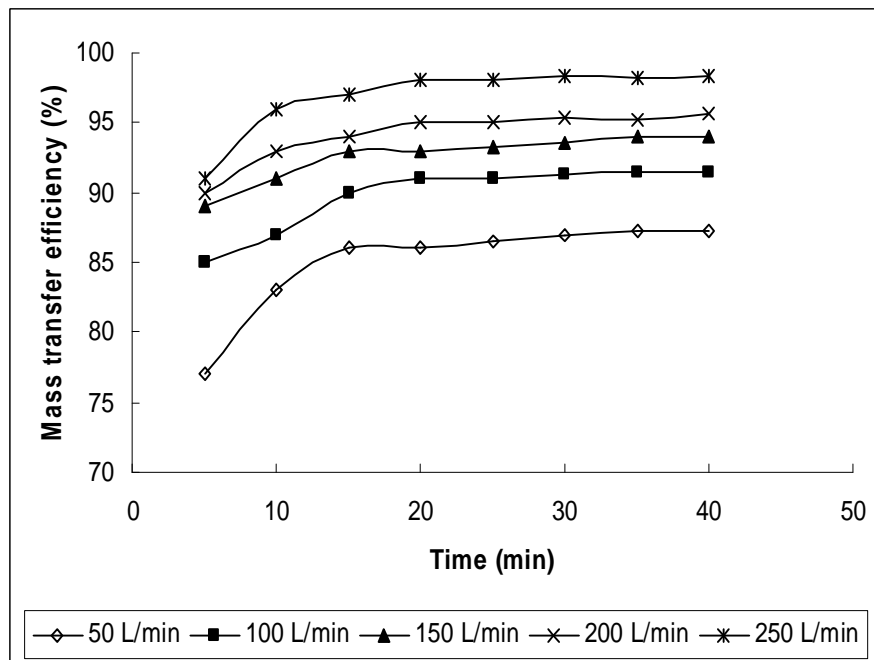


Figure (2): Mass transfer efficiency with time for different gas flow rate.

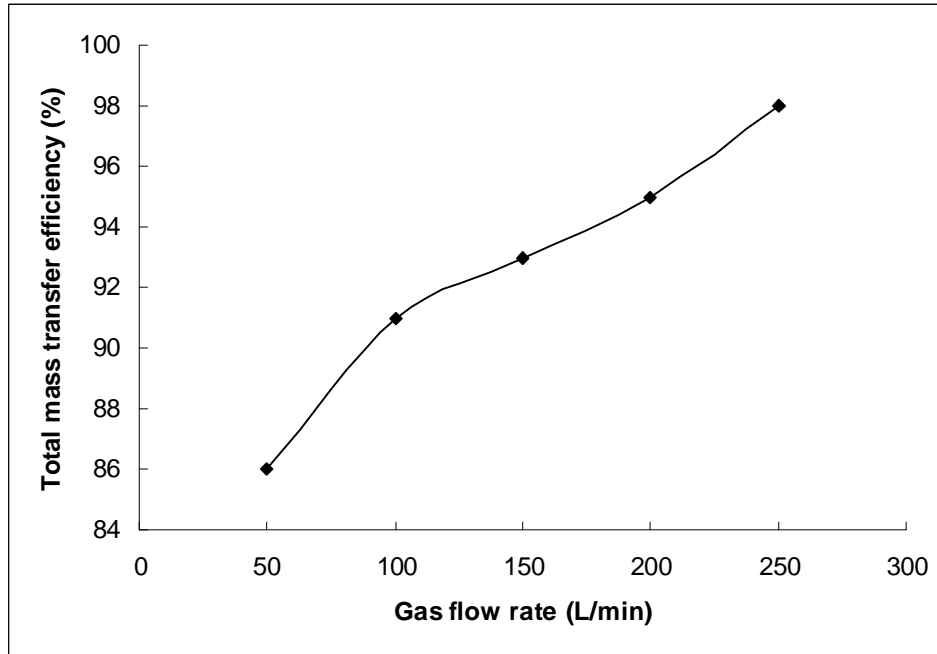


Figure (3): Total mass transfer efficiency versus gas flow rate

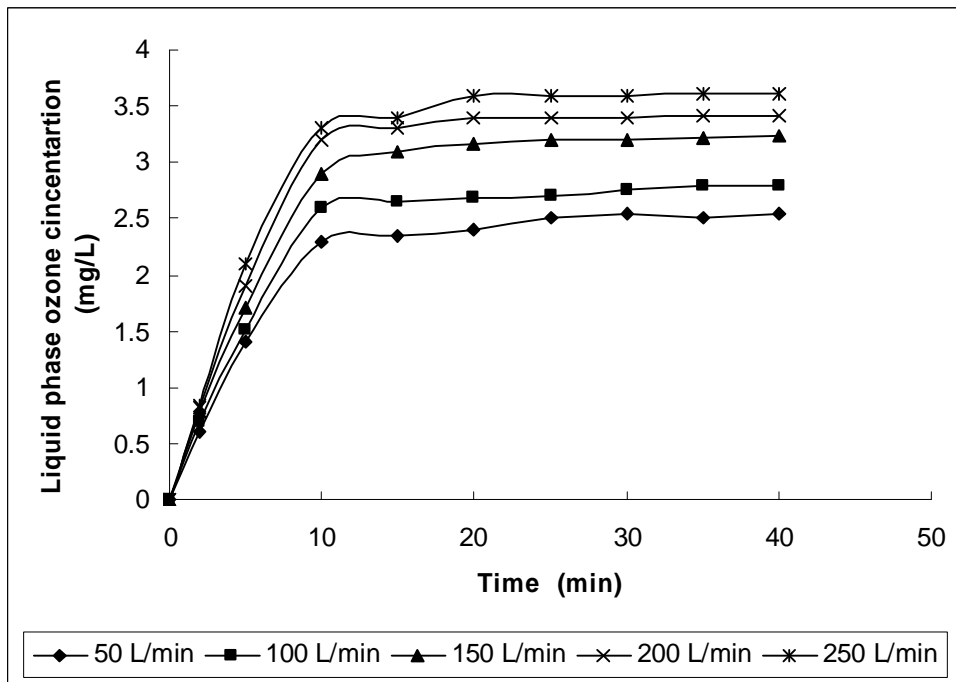


Figure (4): Liquid phase ozone concentration with time at different gas flow rate

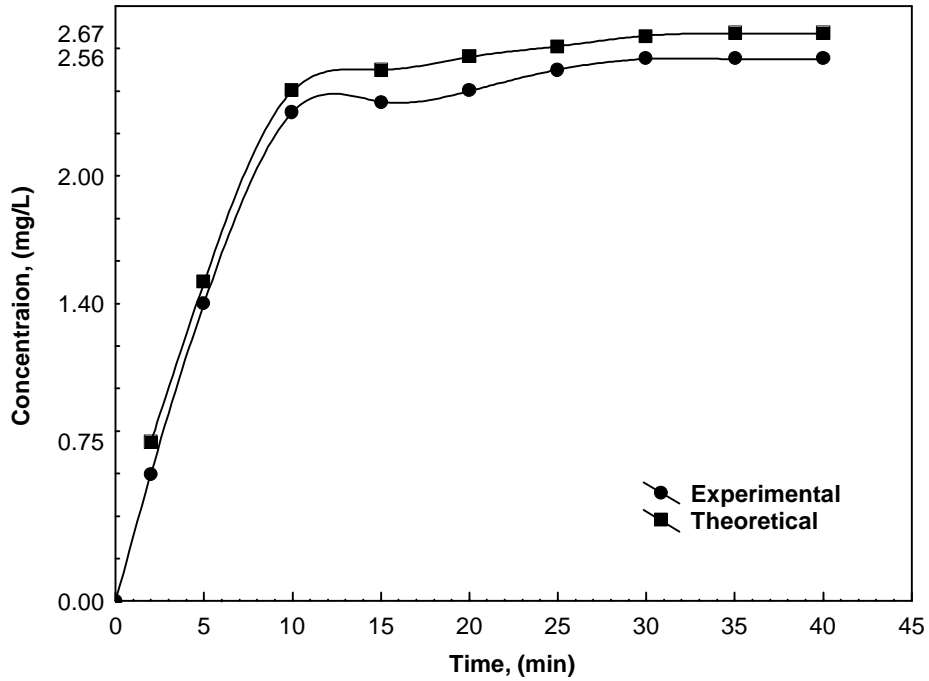


Figure (5): Theoretical and experimental results of liquid phase concentration with time at 50 l/min gas flow rate.

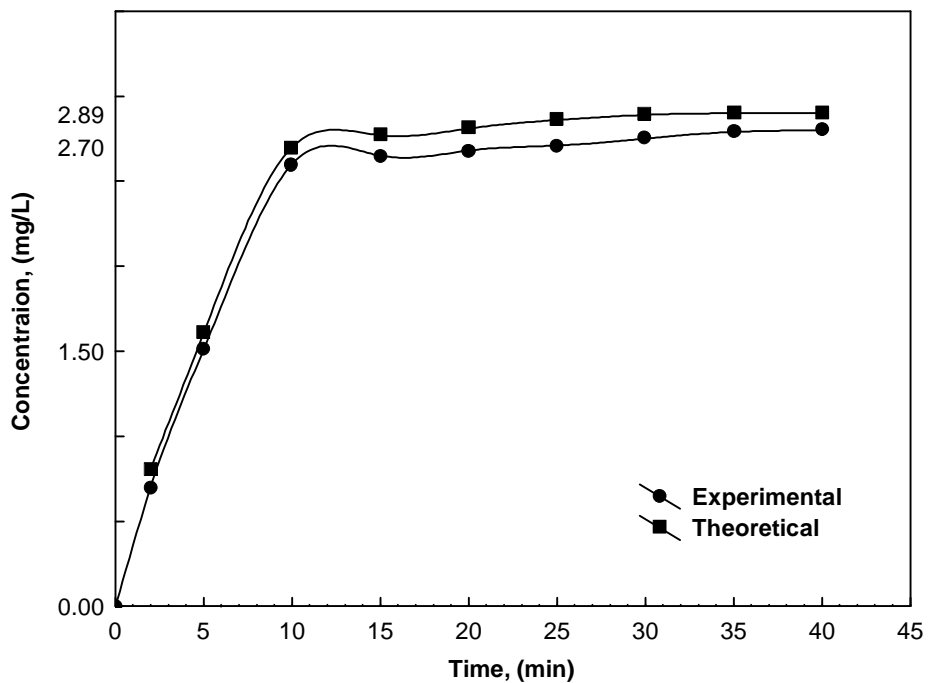


Figure (6): Theoretical and experimental results of liquid phase concentration with time at 100 l/min gas flow rate

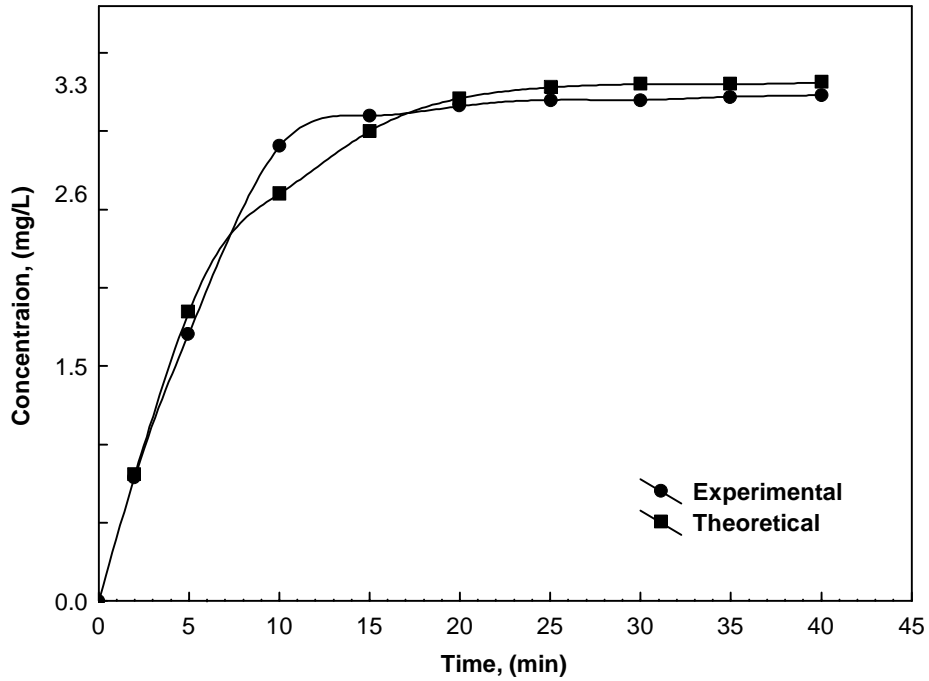


Figure (7): Theoretical and experimental results of liquid phase concentration with time at 150 l/min gas flow rate.

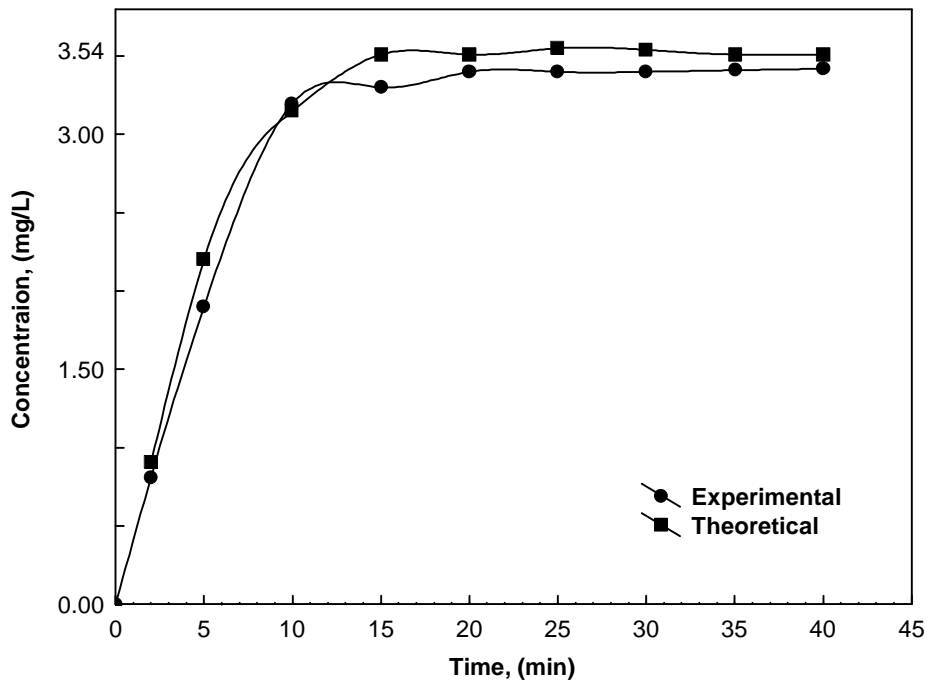


Figure (8): Theoretical and experimental results of liquid phase concentration with time at 200 l/min gas flow rate.

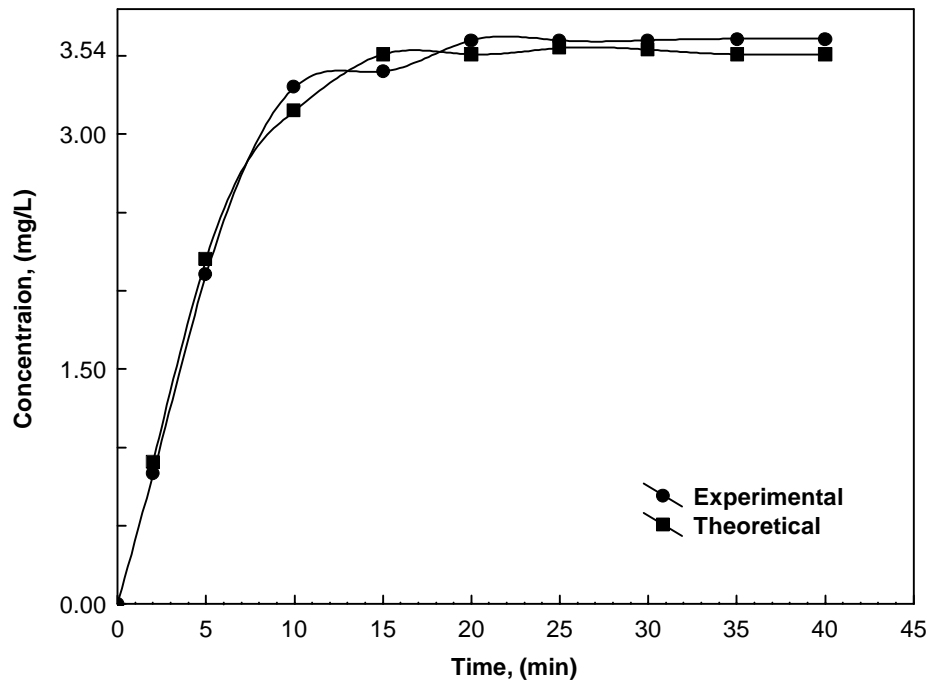


Figure (9): Theoretical and experimental results of liquid phase concentration with time at 250 l/min gas flow rate.