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Kinetics of cyanide oxidation by ozone in cassava starch production process

W. Somboonchai [a], M. Nopharatana [a,*], W. Songkasiri [b]

[a] Food Engineering Department, Faculty of Engineering, King Mongkut's University of Technology Thonburi, 126 Pracha-utit Road,
Bangkok 10140, Thailand
[b] National Center for Genetic Engineering and Biotechnology (BIOTEC), Biochemical Engineering and Pilot Plant R&D Unit (BEC),
83 Moo 8 Thakham, Bangkhuntien, Bangkok 10150, Thailand

Abstract

This research investigated the kinetics of cyanide oxidation by ozone in cassava starch production process. An acrylic column, equipped with a gas sparger located at the bottom of the column, were used as a reactor. Cassava starch solutions with the cyanide concentrations of 10, 20, 30, 40 mg/l were prepared from fresh cassava roots. The experiments were performed at the ozone generation rates of 7.4, 15.0, 22.6, and 30.0 g O_3/h. The results showed that the cyanide concentration sharply decreased during the first 30 s of the reaction time, and after that the concentration slightly decreased. Moreover, cyanohydrin, which could not be oxidized by ozone, was not completely converted to hydrogen cyanide. The kinetics of cyanide oxidation was first order with respect to cyanide and zero order with respect to ozone. The rate constant obtained from the first order equation of cyanide oxidation with ozone was 2.76 min^{-1}.
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1. Introduction

Cassava (*Manihot esculenta* Crantz) or tapioca is a perennial plant widely grown in many tropical countries. As its defense mechanism, cassava is capable of producing hydrogen cyanide (HCN) by the cyanogenesis pathway. Cassava can be classified into three main classes based on the amount of cyanide content – innocuous, moderately poisonous, and dangerously poisonous levels with the cyanide content of <50, 50–100, and >100 mg/kg of fresh weight, respectively (Balagopalan, Padmaja, Nanda, & Moorthy, 1988). HCN is synthesized from cyanogenic glucosides presented in tissues of cassava. When the plant tissue is broken down, cyanogenic glucosides, composing of linamarin and lotaustralin, are hydrolyzed to glucose cyanohydrin compounds by linamarase, a specific enzyme found in the plant cell wall (Hughes et al., 1992; McMahon, White, & Sayre, 1995). The cyanohydrin is decomposed by enzyme or alkaline condition (pH > 5) to hydrogen cyanide (Hughes, Carvahlo, & Hughes, 1994; White, McMahon, & Sayre, 1994).

During the cassava starch production process, cyanogenic glycosides in the root are first converted to HCN and dissolved into the liquid in the rasper. Fresh rasped roots are then pumped through a series of coarse and fine extractors to produce starch slurry. The starch slurry is then passed to separators, dewatering centrifuges, and flash dryers (Sriroth, Piyachomkwan, Wanlapatit, & Oates, 2000). To produce food grade native cassava starch, the cyanide from cassava root must be eliminated during processing so that the cyanide content in starch is less than a safety level. World health organization (WHO) specification stated that the cyanide content in starch should be lower than 10 mg/kg (FAO/WHO, 1991), while the total amount of cyanide content entering the process ranges

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Nomenclature

C_G	gas concentration in reactor (mg/l)	$k_L a$	liquid phase volumetric mass transfer coefficient (min^{-1})
CN	free cyanide concentration at any given time (mg CN/l)	O_3	ozone concentration in liquid at any time (mg/l)
CN_R	residual cyanide concentration at any given time (mg CN/l)	O_3^*	equilibrium ozone concentration in liquid phase (mg /l)
CN_T	total cyanide concentration at any given time (mg CN/l)	r_{CN}	reaction rate of cyanide oxidation (mg CN/ l min)
CN_0	initial cyanide concentration (mg CN/l)	r_L	ozone consumption in the liquid phase (mg O_3/ l min)
H_C	dimensionless Henry's law constant		
k_1	rate constant of cyanide decomposition (min^{-1})	y_{CN/O_3}	the ratio of ozone reacted with cyanide (mg O_3/ mg CN)
k_{O_3}	half-saturated concentration of ozone (mg O_3/l)		

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from 28 to 43 kg HCN equivalent per day or 280–430 mg HCN per kg root based on the production capacity of 100 tons starch per day (Piyachomkwan, Wanlapatit, Chotineeranat, & Sriroth, 2005).

To minimize water usage in starch production process, water from the dewatering centrifuge is normally recycled to the separators, from the separators to the root washer, and from the coarse extractor to the rasper. The cyanide content of this recycled water ranged from 10 to 50 mg/l, causing the accumulation of cyanide in the process and, subsequently, in the finished products (Piyachomkwan et al., 2005).

Ozone is known as the most powerful chemical agent with a redox potential of 1.24 V in alkaline solution (Barriga-Ordonez, Nava-Alonso, & Uribe-Salas, 2006). Cyanide oxidation with ozone is rapid, and complete decomposition of cyanide can be obtained without harmful residue. Carrillo-Pedroza, Nana-Alonso, and Uribe-Salas (2000) studied the reaction kinetics of NaCN oxidation by ozone in wastewater from the gold mining industry. Cyanide oxidation at two ozone additional rates of 0.085 and 0.114 g O_3/min was investigated. The cyanide oxidation reaction was a zero order reaction with respect to cyanide concentration and first order reaction with respect to ozone concentration in the aqueous phase with the rate constant of 0.24 min^{-1}.

This research, therefore, utilized the prior knowledge on cyanide oxidation by ozone emphasizing on the behavior and the reaction kinetics of organic cyanide oxidation by ozone in cassava starch processing with the aim of the low-cyanide cassava starch production.

2. Material and methods

2.1. Solution preparation

Starch solutions with similar starch contents as that of recycled water in the cassava starch process were prepared in the laboratory. Cassava roots were washed and chopped into smaller pieces. Chopped roots were mixed with water at the ratio of 1:1 (w/w) and ground by food blender (Hamil-

ton Beach model 911). The rasped fresh pulp was filtered out with filter cloth to separate starch solution from fiber and pulp. The starch solution was left to stand for 1 h in order to precipitate out the starch cake. The cyanide content of clarified solution was measured by enzymatic method (O'Brien, Tatlor, & Poulter, 1991). In order to obtain the starch solution which represents the recycled water from the separation unit, the starch solution was diluted with distilled water to obtain the cyanide content ranged from 10 to 40 mg/l. The starch content in the solution was approximately 0.2–0.8% (w/v). The starch solution was prepared daily before the experiment and to ensure a certain initial cyanide concentration, cyanide content of the sample was measured again before being treated with ozone.

2.2. Reactor

Two-litres bubble column reactor with a 6.4-cm internal diameter and a 100-cm height was constructed from acrylic. The reactor was equipped with a gas sparger (0.02 pore size, 1.4 cm diameter) located at the bottom of the column. The ozone generator (Prominent, model OZVa 5), which has a maximum ozone generation of 30 g O_3/h, was used. Ozone was produced from pure oxygen and the volumetric flow rate at the outlet of the generator was fixed to 0.3 m^3 NTP/h. The residual ozone in gas was destroyed by potassium iodide solution.

2.3. Experimental procedure

In order to determine liquid phase volumetric mass transfer coefficient ($k_L a$) and ozone solubility, four sets of experiments were performed to investigate the mass transfer of ozone from gas to liquid phase. The ozone generation rate of 7.4, 15.0, 22.6, and 30.0 g O_3/h were used. The gaseous mixture of oxygen and ozone was bubbled in 2 l water for 20 min. The samples were collected from the sampling port located at a height of 0.5 m from the bottom of reactor and analyzed for dissolved ozone concentration by photometer (Dulcotest, model DT1) (Shin, Mirmiran, Yiacoumi, & Tsouris, 1999).

To study the cyanide oxidation by ozone, experiments were performed by bubbling oxygen–ozone gas mixture through 2 l of starch solutions at various cyanide and ozone concentrations. The gaseous ozone was produced at the rate of 7.4, 15.0, 22.6, and 30.0 g O_3/h. The initial cyanide concentrations in starch solution of 10, 20, and 40 mg/l were used. The samples were collected from the sampling port located at 0.5 m from the bottom and analyzed for residual ozone concentration and cyanide content by using enzymatic methods (O'Brien et al., 1991). The control samples with the initial cyanide concentration of 10, 20, 30 and 40 mg/l were prepared and left for the same period of time without ozone application.

3. Results and discussion

3.1. Mass transfer coefficient and equilibrium concentration of ozone

The ozone concentrations in water during sparging with various ozone generation rates are illustrated in Fig. 1. Higher ozone generation rate increased the rate of ozone transfer to liquid phase resulted in higher ozone concentration in water.

The ozone transfer rate was calculated from the following equation (Gottschalk, Libra, & Saupe, 2000).

$$\frac{dO_3}{dt} = k_L a(O_3^* - O_3) \tag{1}$$

Eq. (1) fits reasonably well with the experimental data with r^2 between 0.992 and 0.996. The liquid phase volumetric mass transfer coefficient ($k_L a$) and equilibrium ozone concentration (O_3^*) obtained from the model are shown in Table 1.

$k_L a$ values of this system were almost constant with an average value of 1.1 min^{-1} due to the physical and process parameters, such as bubble size, volumetric flow rate of gas, reactor volume, were constant (Gottschalk et al., 2000; Shin et al., 1999). The results showed that the equi-
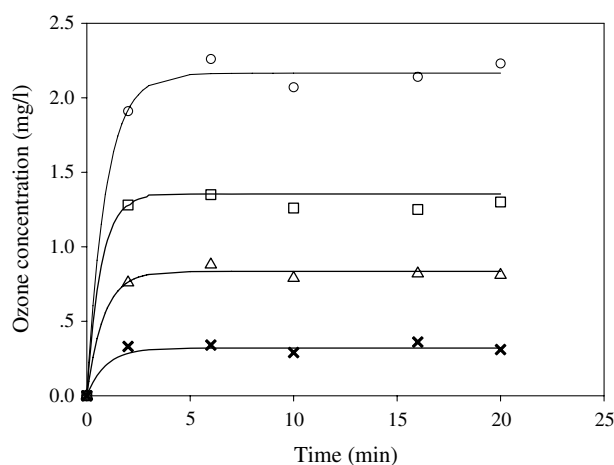
Table 1
Liquid phase volumetric mass transfer coefficient ($k_L a$) and equilibrium concentration of ozone (O_3^*) estimated from Eq. (1)

Ozone generation rate (g O_3/h)	$k_L a$ (min^{-1})	O_3^* (mg/l)	R^2
7.4	1.10 ± 0.05	0.35 ± 0.02	0.996
15.0	1.12 ± 0.05	0.85 ± 0.03	0.992
22.6	1.10 ± 0.04	1.36 ± 0.02	0.995
30.0	1.09 ± 0.04	2.16 ± 0.02	0.992

librium ozone concentration in liquid phase or solubility of ozone increased with increasing ozone generation rate. This can be described by Henry's Law (Gottschalk et al., 2000).

$$H_C = \frac{C_G}{O_3^*} \tag{2}$$

In this experiment, ozone generation rate was varied with the same volumetric oxygen flow rate. At the ozone generation rates of 7.4, 15.0, 22.6, and 30.0 g O_3/h, ozone gas concentrations were 25, 50, 75, 100 mg/l gas, respectively.

Dimensionless Henry's lw constant (H_C) is a function of temperature, pH, and ionic strength (Gottschalk et al., 2000). In this research, as these parameters were constant, dimensionless Henry's Law constant was assumed to be constant. Besides, the dimensionless Henry's Law constant has a linear correlation with the solubility ratios of ozone (S). This solubility ratio is given as mg/l in water to mg/l in gas. This factor is the inverse of the dimensionless Henry's Law constant and can be estimated from the following equation (Gottschalk et al., 2000).

$$\log_{10}s = 3.302 - 0.013\,T[K] \tag{3}$$

The experiments were performed at 27 °C. The theoretical solubility ratio of ozone calculated from Eq. (3) was 0.252 mg/l in water to mg/l in gas, whereas the measured ozone solubility was 0.02 mg/l in water to mg/l in gas. This may be because the partial pressure of ozone in gas phase was quite low due to the fact that the reactor was an open tank and gas decomposition occurred during the process (Gottschalk et al., 2000).

3.2. Reaction kinetics of cyanide oxidation

The effects of cyanide concentration and ozone generation rate on cyanide oxidation by ozone are shown in Fig. 2. Cyanide concentrations sharply decreased during the first 30 s of the reaction, after that the concentrations slightly decreased. The trends were quite similar at every initial cyanide concentration. In contrast, cyanide concentration of the control samples remained almost constant after 10 min of experiment.

From Fig. 2, it can be observed that the final cyanide concentration after treatment was not zero. Theoretically, after cassava root tissue is damaged, linamarin (bound cyanide) becomes in contact with linamarase and the result of the reaction is a chemical called cyanohydrin.
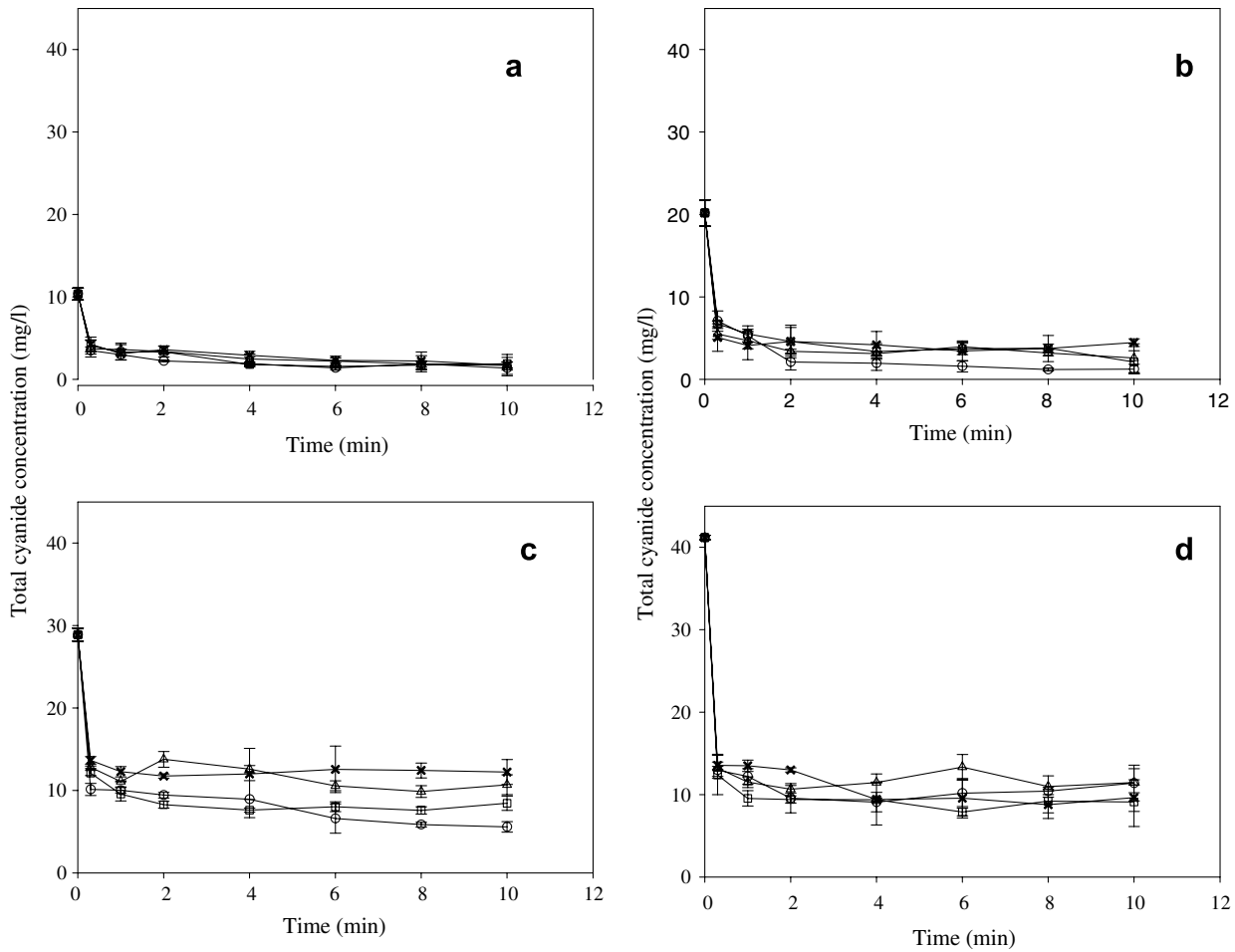

Fig. 1. Concentration of ozone in water at ozone generation rates of 7.4 (×), 15.0 (△), 22.6 (□) and 30.0 (○) g O_3/h.

Fig. 2. Cyanide oxidation at different ozone generation rates of 7.4 ($\times$), 15.0 ($\triangle$), (22.6) ($\square$) and 30 ($\bigcirc$) g O_3/h with initial cyanide concentrations of (a) 10 mg/l, (b) 20 mg/l, (c) 30 mg/l, (d) 40 mg/l.

Then, cyanohydrin is spontaneously converted to hydrogen cyanide (free cyanide). This reaction occurs at the temperatures greater than 30 °C or at pH higher than 5. Moreover, cyanohydrin can also be broken down by enzyme hydroxynitrile lyase (HNL) into acetone and volatile hydrogen cyanide, which is non-toxic (Siritunga & Sayre, 2004). The concentration of HNL, which catalyses the conversion of cyanohydrin to cyanide, is very low in cassava root. Without the suitable level of HNL, cyanohydrin may not be completely converted to hydrogen cyanide (free cyanide). The results in Fig. 2 indicated that residual cyanides still remain in the process. These residual cyanides could be cyanohydrin, which was not converted to hydrogen cyanide, and some portions of linamarin (bound cyanide), which could not converted to cyanohydrin. From the experiments, the ratio of average residual cyanide to initial cyanide content was 0.2553. Total cyanide content in cassava starch solution was classified into residual cyanide and free cyanide

$$CN_T = CN + CN_R \tag{4}$$

where

$$CN_R = 0.2553 CN_0 \tag{5}$$

An attempt has been made to characterize the rate of free cyanide oxidation with ozone based on the modified Menchaelis–Menten equation as follows:

$$-r_{CN} = -\frac{d(CN)}{dt} = k_1 \cdot CN \cdot \frac{O_3}{k_{O_3} + O_3} \tag{6}$$

Change in ozone concentration during cyanide oxidation was calculated using

$$\frac{dO_3}{dt} = k_L a(O_3^* - O_3) - r_L \tag{7}$$

Ozone consumption rate in the liquid phase (r_L) in Eq. (7) is equal to the rate of cyanide consumption during the process as shown

$$r_L = -y_{CN/O_3} \cdot r_{CN} \tag{8}$$

As one mole of ozone reacts with one mole of cyanide, the value of y_{CN/O_3} is 1.33 mg O_3/mg cyanide. The values of rate constants of cyanide decomposition (k_1) estimated from 12 experiments were within the range of 2.27–3.01 min^{-1} with the average value of 2.76 ± 0.21 min^{-1} (Table 2). The values of half-saturated concentration of ozone (k_{O_3}) were within the range of 1.12×10^{-9}–

Table 2
Rate constant of cyanide decomposition (k_1) and half-saturated constant of ozone k_{O_3} obtained from the model for 12 treatments

Cyanide concentration (mg/l)	Ozone generation rate (g O₃/h)	k_1 (min⁻¹)	k_{O_3}	R^2 (mg O₃/l)
10	15.0	2.87	3.17×10^{-9}	0.979
	22.6	2.70	2.77×10^{-9}	0.980
	30.0	2.85	1.12×10^{-8}	0.985
20	7.4	3.01	2.63×10^{-9}	0.996
	22.6	2.93	2.28×10^{-9}	0.992
	30.0	2.84	2.20×10^{-9}	0.991
30	7.4	2.27	3.91×10^{-9}	0.990
	15.0	2.64	2.46×10^{-9}	0.977
	22.6	2.47	2.91×10^{-9}	0.994
40	7.4	2.91	2.85×10^{-9}	0.992
	15.0	2.78	3.35×10^{-9}	0.993
	30.0	2.88	3.28×10^{-9}	0.995

3.91×10^{-8} mg O₃/l with the average value of $2.74 \times 10^{-9} \pm 0.71 \times 10^{-9}$ mg O₃/l (Table 2). The value of k_{O_3} was rather low compared to the ozone concentration in water; thus, it may be concluded that the rate reaction of cyanide was zero order with respected to ozone concentration. Therefore, Eq. (6) can be simplified into

$$-r_{CN} = -\frac{d(CN)}{dt} = k_1 \cdot CN \qquad (9)$$

Rate constant of cyanide decomposition (k_1) of 2.76 min⁻¹, liquid phase volumetric mass transfer coefficient ($k_L a$) of 1.1 min⁻¹ and the ozone solubility of 0.02 mg/l in water to mg/l in gas were used for model validation.

3.3. Model validation

To validate this kinetics model, the prediction data and the experimental data of cyanide concentration of four
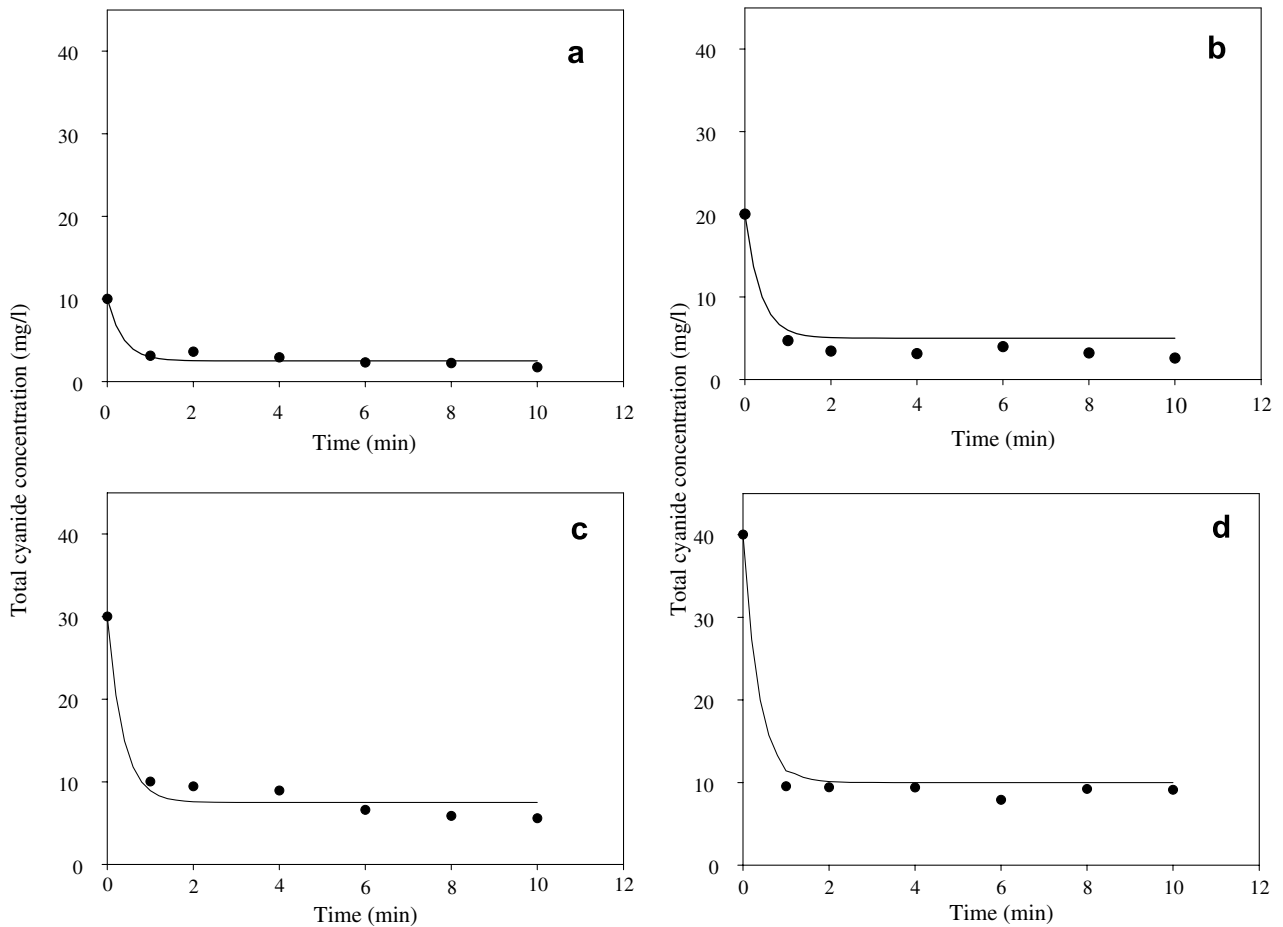

Fig. 3. Experimental (scatter plot) and predicted (line plot) cyanide concentration at initial cyanide concentration (mg/l) and ozone generation rate (g O₃/h) of (a) 10 and 7.4, (b) 20 and 15.0, (c) 30 and 30.0, (d) 40 and 22.6.

experiments at different initial cyanide concentrations and ozone generation rates were compared as shown in Fig. 3. The predicted data fitted well with the experimental data in every treatment with correlation coefficient r^2 within the range of 0.980–0.998.

4. Conclusions

During ozone oxidation, cyanide content was sharply decreased at the first 30 s of reaction and after that the cyanide concentration was almost constant. Moreover, it was found that cyanohydrin was not completely converted to hydrogen cyanide and some portions of bound cyanide also remained in the process. The value of liquid phase volumetric mass transfer coefficient ($k_L a$) was 1.1 min^{-1} and the values of equilibrium ozone concentration (O_3^*) increased with increasing ozone generation rate. The solubility factor of ozone in the open reactor was 0.02 mg/l in water to mg/l in gas, which was lower than theoretical solubility factor. The results from reaction kinetics indicated the cyanide oxidation by ozone was quite fast and controlled by the liquid phase volumetric mass transfer coefficient ($k_L a$). The oxidation of cyanide was first order with respect to cyanide and zero order with respect to ozone. The rate constant obtained for first order equation of cyanide oxidation with ozone was 2.76 min^{-1}.

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