Monitoring of pH inhibition on microbial activity in a continuous flow reactor by pseudo toxic concentration (C_{PT}) concept and time delay model

J.H. Ko*, S.H. Lee, J.R. Kim**, Y.J. Kim**, I.S. Hwang**, T.H. Lee*** and C.W. Kim****

*Research and Engineering Division, Posco Engineering & Construction, 445-810, Korea

**Department of Environmental Engineering, Pusan National University, Pusan, 609-735, Korea

***Department of Environmental Engineering, Andong National University, Andong, Korea
(E-mail: *cwkim@pusan.ac.kr*)

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Abstract The pseudo toxic concentration (C_{PT}) concept was introduced as a quantification method to describe pH as an inhibitor concentration. In this research, the applicability of the C_{PT} concept model for the detection of pH inhibitions was expanded for a continuous flow activated sludge reactor. A pilot equipped with an inhibition detection system was installed. Inhibitory wastewater was injected for 1 h and the relative activity was calculated by the maximum respiration rate. At the same time, the coefficients for the C_{PT} concept model were estimated. At the dynamic conditions, the estimated relative activity by the C_{PT} concept model showed time lag compared to the measured one. However, the time lag problem was successfully resolved by introducing a transfer function into the C_{PT} concept model. The C_{PT} concept model combined with a transfer function (C_{PT} + TF model) successfully tracked the variation of the relative activity under dynamic conditions. The C_{PT} + TF model could detect 50% inhibition faster than the respirometry based method by approximately 10 min. Moreover, it had additional advantages such as being inexpensive, easy to install and simple to operate. In conclusion, the C_{PT} + TF model was an effective and convenient detection method of pH inhibition.

Keywords Detection; inhibition; pH; pseudo toxic concentration; transfer function

Introduction

It is generally accepted that the pH inhibition on the activated sludge follows the noncompetitive inhibition kinetic which decreases the maximum specific growth rate (μ_{max}). However, pH inhibition on microbial growth is difficult to express by this kinetic equation, because pH is hardly described as inhibitor concentration. Therefore, many empirical equations were developed to describe pH inhibition on μ_{max} (U.S. EPA, 1975; University of Capetown, 1984; Siegrist and Gujer, 1987; Tyagi *et al.*, 1993; Han *et al.*, 2003). Ko *et al.* (2001a) introduced the pseudo toxic concentration (C_{PT}) concept to describe pH as an inhibitor concentration in the noncompetitive inhibition kinetic equation. The C_{PT} was defined as the squared difference between a threshold pH value and a measured pH value in a reactor. It was shown that the C_{PT} concept model was applicable to not only acidic but also basic conditions, and not restricted to any specific microorganism group (Ko *et al.*, 2005). However, this technique has been tested in the batch reactor or under static conditions. This concept may be applicable to the continuous flow reactor in field scale reactors to control pH inhibition on-line.

The aim of this research was to validate the C_{PT} concept model for model-based detection and evaluation of pH inhibition in a continuous flow activated sludge reactor. The results were compared with a technique based on the maximum respiration rate (r_{max}), which has been used widely for influent toxicity or inhibition detection in activated sludge (Kim *et al.*, 1994; Spanjers *et al.*, 1997; Ko *et al.*, 2001b; Copp *et al.*, 2002). The C_{PT}

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concept model was further improved to expand its applicability for monitoring and controlling the pH inhibition on-line in a field-scale activated sludge plant.

Methods

Pilot plant and inhibition detection system

A pigment wastewater treatment plant with an extended aeration process was scaled down to a pilot plant 1/1200 in size. The pilot plant consisted of three aeration tanks and a clarifier with 3.1 m^3 of total effective volume. The pH of raw wastewater was usually strongly acidic and varied greatly, depending on the type and mass of daily products. It was pretreated in the neutralization tank before being introduced to the biological reactors. The pH of pretreated wastewater generally ranged within 5.5–6.2, but sometimes dropped to 5.0 or lower.

The pilot plant operated at weak acidic condition (pH 5.7–6.2), just like a field plant, so that the effect of influent pH could not be directly evaluated only with the influent pH. Therefore, an inhibition detection system with a respirometer was installed as shown in Figure 1. To measure r_{max}, some portion of the influent and the sludge from the first compartment of the biological reactors were mixed in the contact chamber, which had 12.7 min of HRT. The mixed liquor was introduced to the respirometer. The flowrate ratio of the influent and the sludge was 1:1. Such a high influent ratio guaranteed the stable r_{max} measurement regardless of load variation (Choi *et al.*, 1999; Ko *et al.*, 2001a,b). DO in the contact chamber was kept over 5 mg/L.

Experimental conditions

The influent conditions for the experiments were four sets of acidic influents (pH 5.5, 5.0, 4.5 and 4.0) and four sets of basic influents (8.5, 9.0, 10.0 and 11.0). The desired influent pH was adjusted by adding H_2SO_4 or NaOH. The inhibitory wastewater was injected into the contact chamber and the biological reactors for 1 h during each experiment. The effluent from the contact chamber and the respirometer returned to the last biological reactor.

C_{PT} concept model

The variations of the relative activity were estimated with the C_{PT} concept model and compared with measured data by r_{max}. The relative activity was defined as Equation (1).

$$\text{Relative activity} = \frac{\mu_{max,I}}{\mu_{max}} = \frac{r_{max,I}}{r_{max}} = \frac{K_I}{C_{PT} + K_I} \qquad (1)$$

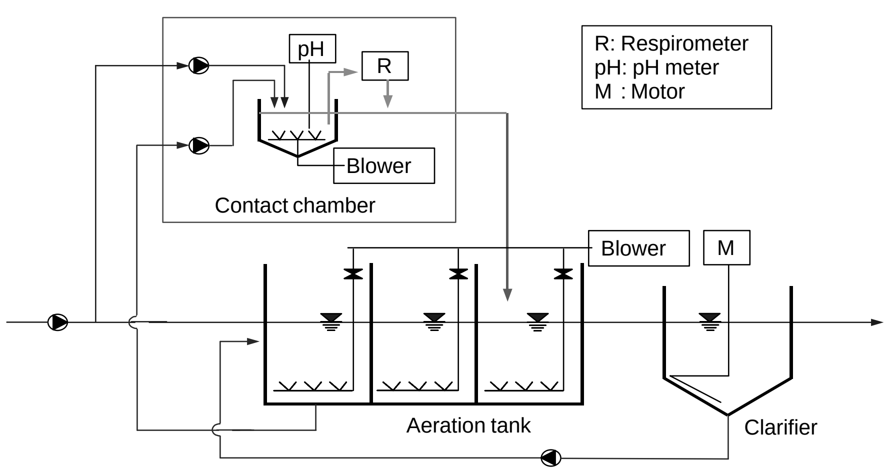

Figure 1 The pilot plant equipped with the inhibition detection system

where C_{PT} = pseudo toxic concentration, $(pH_{th}\text{-}pH)^2$; K_I = inhibition coefficient; pH_{th} = threshold pH, pH which inhibition effect begins.

Usually, the relative activity should be calculated with the maximum specific respiration rate, R_{max}. However, the variation of MLVSS concentration during one experimental period for 2.5 h was negligible, so the use of r_{max} was quite acceptable.

Dynamic modeling approach

The aim of this research was to validate the C_{PT} concept model for model based detection and evaluation of pH inhibitions. Therefore, it was essential to verify whether the relative activity estimated with the C_{PT} concept model could represent the measured value by r_{max} in dynamic situations. Basically, the C_{PT} concept model was a static model, the same as other pH inhibition models. It could show how much the relative activity decreased but not how fast it might decline.

A transfer function was introduced and combined with the C_{PT} concept model to make possible dynamic applications, by compensating for the time lag between the estimated and the measured relative activity. In the first step, the relative activity was calculated with the C_{PT} concept model where the pH changed dramatically in the contact chamber when acidic or basic wastewater was injected. However, this value could not represent the biological status of the contact chamber, because the change of pH was much faster than that of r_{max} which corresponded with the microbial activity. As a next step, a transfer function between the estimated and the measured relative activity was calculated. Last, the relative activity was re-estimated by the C_{PT} concept model combined with the transfer function (C_{PT} + TF) and compared with a measured one.

The transfer function was a simplified modeling approach, generally used for process kinetic identification and controller design. It was easier than the statistical modeling approaches such as the time series or the artificial neural network. The quantified information on time lag was given by the time constant (τ) and the dead time (θ). The relationship between the estimated and the measured relative activity was regarded as first order plus dead time system. The input and output were the estimated relative activity by using the C_{PT} concept model only and a measured one, respectively. Therefore, the process gain (K_P) would be close to unity in the Equation (2).

$$G_P(s) = \frac{(\Delta \text{Relative activity})_{\text{by } r_{max}}}{(\Delta \text{Relative activity})_{\text{by } C_{PT}}} = K_P \cdot \frac{e^{-\theta_P s}}{\tau_P s + 1} \qquad (2)$$

From the viewpoint of process kinetic identification, the estimated relative activity can hardly be regarded as the input of transfer function because it has no effect on output, the measured value. However, the transfer function was served as a tool for time lag compensation, not for cause–effect relationship development nor controller design, in this research.

Results and discussion

Parameter estimation for the C_{PT} concept model

The inhibition coefficient, K_I, was estimated by the Lineweaver–Burk method, together with pH_{th}. The estimated K_I values were 0.748 and 1.194 for acidic and basic conditions, respectively. The greater K_I value in basic conditions meant that the relative activity was less sensitive to basic influent. The reason was that the pilot plant was operated at weakly acidic conditions. Therefore, the weak basic influent might cause neutralisation rather than inhibition. The pH_{th} was estimated as 6.77 and 7.80 for the acidic and the basic conditions, respectively. It meant that no pH inhibition occurred within that range. The $pH_{th,base}$ was much higher than neutral pH, for the same reason described above.

Parameter estimation for transfer function

Two kinds of transfer functions were examined. One was an individual transfer function (individual TF) which fit best with each influent pH condition. The other was a general transfer function (general TF) which fit best with combined data of every influent pH under acidic or basic conditions. Process gain (K_P) of general TF was forced to be unity. A software tool called Control Station (http://controlstation.com/) was used to calculate parameters for the transfer functions. The objective function was to minimize the sum of squared error (SSE). The results are shown in Table 1. No significant variation was found in the relative activity at influent pH of 5.5 and 8.5, so those were not exhibited in the following tables and figures.

Data at influent pH of 9.0 was excluded when calculating the general TF of basic conditions, because it showed quite different behavior. The K_P value was only 0.604, which meant that the inhibition effect was overestimated by approximately 65%. In the basic condition, the dead time (θ) was approximately 4.5 min. It meant that the decrease of r_{max} started 4.5 min later than the pH increase. It was regarded as both low K_P at influent pH of 9.0 and long dead time at basic conditions originated from a neutralisation effect, as mentioned previously. The slight increase of the r_{max} was observed when a neutralisation effect occurred; 40–50 min at influent pH of 9.0 and 120–140 min at influent pH of 10.0 and 11.0, as shown in Figure 2. A short time constant (τ) meant fast response after the inhibition effect began under basic conditions.

Application to continuous flow activate sludge reactor

The estimated and measured relative activities are shown in Figure 2. Without considering the transfer function, the C_{PT} concept model could not represent a dynamic change in relative activity, because of its static characteristics, as one can see, "C_{PT} only" in Figure 2. There was a time lag between the estimated and the measured relative activities, and it was compensated by the transfer function. Combined with a transfer function, the C_{PT} concept model could successfully estimate the relative activity variation. It should be noted that the general TF, as well as the individual TF, showed excellent results except when the influent pH was 9.0. In that situation, the individual TF had quite a different process gain and time constant from other cases, as a result, which could finely interpret unique variations of the relative activity.

Figure 3 shows the estimation errors of the relative activity at influent pH of 4.5 and 10.0. It was clear that the transfer function could significantly reduce the estimation error due to a time lag. More accurate results could be obtained by introducing the individual TF than the general TF, but the individual TF was quite complicated for field application. The results determined with "C_{PT} + general TF" also tracked the variation tendency or relative activity closely, and the estimation error was not seriously different from that with the individual TF, as shown in Figure 3 and Table 2. It could be concluded that "C_{PT} + general TF" was the correct choice for the detection of pH inhibition.

Table 1 Constants of transfer functions under the acidic and the basic conditions

Influent pH	Acidic condition				Basic condition			
	General	Individual			General	Individual		
		5.0	4.5	4.0		9.0	10.0	11.0
K_P (−)	1.0	1.09	0.988	1.08	1.0	0.604	0.953	0.894
τ (min)	11.0	11.9	9.08	12.38	2.5	5.21	2.77	2.02
θ (min)	0.3	0.0	2.06	0.0	4.5	4.06	4.57	4.72

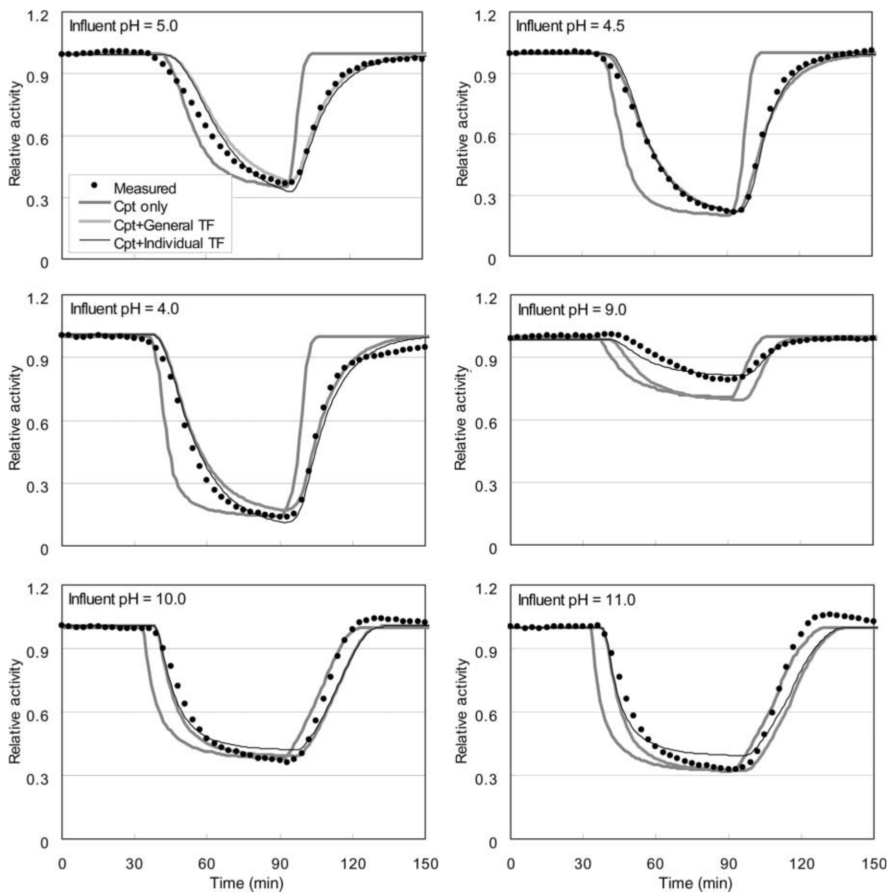

Figure 2 Estimated and measured relative activities at dynamic conditions

Inhibition detection time

The variation of pH occurred faster than that of r_{max} in the contact chamber. Consequently, the estimated relative activity when using the C_{PT} concept model changed more rapidly than the measured one. It implied that the C_{PT} concept model could detect pH inhibition earlier than the respirometry based method. Table 3 shows the detection time for 20 and 50% inhibition of μ_{max} by the C_{PT} concept model and r_{max}, respectively. The C_{PT} concept model could detect 50% inhibition faster than the r_{max} by more than 10 min. After detection, the precise value of μ_{max} can be estimated by combining it with the transfer function, and then used to simulate effluent quality deterioration.

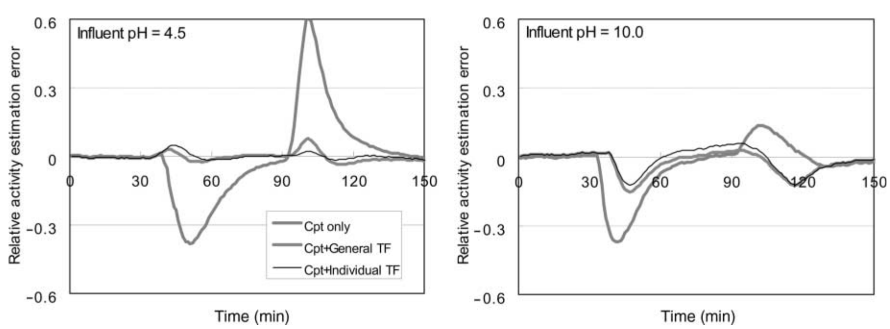

Figure 3 Estimation errors for relative activities

Table 2 Estimation errors of relative activities after inhibitory wastewater injection (30–150 min); mean absolute error ± standard deviation

pH	C_{PT} + general TF	C_{PT} + individual TF
5.0	0.033 ± 0.030	0.027 ± 0.025
4.5	0.017 ± 0.015	0.010 ± 0.011
4.0	0.041 ± 0.019	0.026 ± 0.016
9.0	0.060 ± 0.054	0.016 ± 0.016
10.0	0.043 ± 0.041	0.046 ± 0.033
11.0	0.070 ± 0.059	0.063 ± 0.043

Table 3 Detection time for 20 and 50% inhibition (min)

Influent pH	Acidic condition			Basic condition		
	5.0	4.5	4.0	9.0	10.0	11.0
20% inhibition (notice level)						
r_{max}	22	19	16	48	16	15
C_{PT}*	19	12	10	19	5	4
50% inhibition (warning level)						
r_{max}	40	30	23	–	28	25
C_{PT}	30	17	13	–	15	11

*C_{PT} + general TF

Advantages and constraints of "C_{PT} + TF model"

Advantages. The C_{PT} concept model has some virtue, basically as shown below (Ko *et al.*, 2001a, 2005):

- easy to estimate parameters
- applicable to acidic and basic wastewater without reformation of the equation
- suitable to various kinds of microorganism groups.

It was shown that the C_{PT} concept model can be applied for the detection of pH inhibition in this research. Compared with the respirometry based method, the model-based technique has some advantages as shown below:

- faster detection
- cheap and easy installation; additional pipeline is required to install the respirometer for permanent use, while only a pH meter is needed to apply the C_{PT} concept model
- simple operation; the respirometer is a complicated instrument, so delicate maintenance is necessary.

Constraints. On the other side, the constraints should be considered as shown below:

- it is not applicable for detecting the effect of heavy metals, toxic organics and other inhibitory materials
- the respirometer is needed for model setups. The measurement of r_{max} is the most reliable and convenient method to establish the relative activity variation according to pH, which is essential to calculate the transfer function
- large estimation errors can occur under specific conditions. It was shown that the inhibitory effect could be overestimated when weak basic wastewater flowed into the plant which operated at weak acidic conditions. However, this problem can be solved by adding the checking algorithm, whether pH in the contact chamber is weak basic or not.

Conclusions

The C_{PT} concept model could estimate the relative activity in the dynamic conditions in the activated sludge reactor. The time lag between the estimated and the measured values was successfully compensated by introducing the transfer function. Two kinds of transfer functions were examined. The use of individual TF could increase estimation accuracy, but the general TF was preferred because of its convenient application. The "C_{PT} + general TF" also tracked the variation tendency closely, and the estimation error with general TF was not seriously different from that of the individual TF. Detection of pH inhibition by the "C_{PT} + general TF" was faster than by the respirometry based method by about 10 min. Moreover, it had more advantages such as easy installation and simple operation. The conclusion was made that the C_{PT} concept model was suitable for the plant where the pH inhibition occurred often by strong acidic or basic influent as an effective and convenient detection method.

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