Modeling and Control of pH Process for Weak Acid-Weak Base System

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ABSTRACT

This paper studies the model and control of pH neutralization process of waste water system using different control schemes. An experimental investigation was conducted for the dynamic behavior of neutralization process of waste water in a continuous stirred tank reactor (CSTR).

A dynamic model for pH neutralization process in a continuous stirred tank reactor (CSTR) is described by a first order plus dead time (FOPDT).

The pH value is calculated by solving the charge balance of the mixture. Good agreement is obtained between the simulated and experimental responses. However, a small differences between the responses due to the error in the measurements.

The conventional feedback control was studies in this work and the controller parameters was tuned by Ziegler-Nichols reaction curve method to find the best values of proportional gain (K_c), integral time (t_I) and derivative time (t_D). Artificial Neural Network Model Predictive Control (ANN MPC) was used as another strategy to compare with above strategy.

The ANN controller was compared with conventional controller and it was found that ANN controller provides better control for the set point changes with low settling time and lower overshoot. Whereas the conventional controller provides sluggish behavior in set point change. Also it was found that the ANN controller provides better response to regulated change than the conventional controllers where the PI and PID controllers provide sluggish disturbance responses because the approximate FOPTD model has relatively small time delay. As non-linear process the conventional feedback controller was unable to control this system adequately.

Keywords: Process Control, Neutralization Process, pH Control, Nonlinear Dynamic, ANN Control.

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النمذجة والسيطرة على عملية التعادل لنظام حامض ضعيف – قاعدة ضعيفة

الخلاصة

يتناول هذا البحث دراسة النموذج الرياضي و السيطرة على عملية التعادل للدالة الحامضيه للماء الملوث باستخدام نوعين من المسيطرات. وقد تم إجراء التجارب العملية لاختبار السلوك الديناميكي لعملية المعادلة للماء الملوث في المفاعل الكيمياوي ذي الخلط المستمر.

الموديل الديناميكي لعملية التعادل في المفاعل الكيمياوي ذي الخلط المستمر وصف بواسطة معادلة من الدرجة الاولى مع زمن تاخير. قيمة الدالة الحامضية حسبت من خلال موازنة الشحنات السالبة و الموجبة لخليط من حامض ضعيف و قاعدة ضعيفه. تم الحصول على توافق جيد بين النتائج العملية والنظرية وكان هناك اختلاف بسيط سببه الخطأ في قراءة جهاز القياس (قطب الهيدروجين). السيطره التقليديه درست في هذا العمل و تم تضبيط مغيرات السيطره بطريقة (**Ziegler- Nichols reaction curve**) لأيجاد أفضل قيم لمغيرات المسيطرات التقليدية. مسيطر الشبكات العصبيه أستخدم كستراتيجيه للمقارنه مع المسيطرات التقليدية. لقد تمت المقارنه بين السيطرة التقليديه و سيطرة الشبكات العصبيه و قد وجد بان مسيطر الشبكات العصبيه يزودنا بافضل سيطره للتغير الحاصل في **disturbance** و **set point** حيث يصل النظام الى حالة الاستقرار بأقل وقت بينما المسيطر التقليدي يصل الى حالة الاستقرار بوقت اطول. هذه العملية غير خطية (**High non linear**) لذلك فالمسيطر التقليدي غير قادر على السيطرة على هذه الأنظمة بشكل ملائم.

INTRODUCTION

Neutralization is an important operation in chemical plants, such as biological, wastewater treatment, and electrochemistry and precipitation systems. The purpose of neutralization is to adjust the pH value to neutrality for a certain requirement, for example, to minimize the environmental impact in wastewater treatment systems [1]. Control of the pH neutralization process plays an important role in different chemical plants, such as biological, wastewater treatment, electrochemistry and precipitation plants. However, it is difficult to control a pH process with adequate performance due to its nonlinearities, time-varying properties and sensitivity to small disturbances when working near the equivalence point [2].

PH PROCESS CHARACTERISTICS

By definition, pH as the negative logarithm of the hydrogen-ion concentration in aqueous solution. Acids are either "strong" or "weak." This relates to the amount of free hydrogen ions in the solution of a given concentration. Thus, nitric acid is a Strong acid, since all of the nitric-acid molecules are dissociated into active hydrogen ions and nitrate ions. However, acetic acid is a weak acid. A solution of acetic acid of the same molar concentration as nitric acid would have a very different pH value, since most of the acetic acid molecules do not dissociate into hydrogen ions and acetate ions [3]. Yet both the nitric and acetic acids have the same total acidity and, therefore, each require the same amount of neutralizing base. Similarly, there are strong and weak bases.

Sodium hydroxide is a strong base, while ammonia or soda ash are weak bases. Equal molar concentrations of these bases will all have the same capacity to neutralize a given quantity of acid. Titration is the popular method for determining total acidity or basicity of a solution. An acid/base titration curve is a plot of pH vs. reagent addition and graphically shows how pH changes per unit addition of reagent. It also gives an indication of the degree of control obtainable. Figure (1) illustrates the diverse shapes a single acid/single base titration curve can take. The point of greatest change (also called the equivalence point, or inflection point) is the point where pH changes most greatly per unit of reagent added and the process gain is at a maximum at this point. For the strong acid/strong base system, the gain at the equivalence point is extremely high and it occurs at pH 7 which is neutral pH. Control of this system near pH 7 would place very high demands both on the accuracy of the control system and on the rangeability of the reagent delivery system. Clearly, the weak acid/weak base system is easier to control because of the lower gain near neutrality. While the pH logarithmic non-linearity can be severe, it should be possible to remove it, since the relationship between pH and $[H^+]$ is defined [4].

PH CONTROL TECHNIQUES

Some techniques of intelligent control have been implemented to solve pH processes control problem by many researchers, such as applying fuzzy control, neural networks or different combination of intelligent and model-based methods. For example, fuzzy logic [2] and neural networks [5] have been implemented on pH control. Fuzzy self tuning PI control [6] and fuzzy internal model control [7] have also been implemented to control pH processes. Neural networks and adaptive controller [8], PID using linearization through neural networks [9], and Genetic Algorithm combined with Internal Model Control [10] have also been reported to address the problem of proper control of pH in a chemical process with limited success [3].

THE MATHEMATICAL MODEL

A simplified schematic diagram of the pH neutralization system is shown in Figure (2). The process consists of two input streams, one containing acetic acid (CH_3COOH) and the other ammonium hydroxide (NH_4OH) that are mixed in the tank, effluent pH are measured variables. In this study, the pH is controlled by manipulating the base flow rate. The dynamic model of the pH neutralization system shown in Figure (2) is derived using conservation equations and equilibrium relations. Modeling assumptions include perfect mixing, constant density and constant temperature of 25^0C where dissociation constants and pH electrode potential are both temperature dependent and this should be accounted for high temperature applications. The model is presented briefly below;
The chemical equilibria for the weak acid/weak base system are:

$$CH3COOH \Leftrightarrow CH3COO^{-} + H^{+} \quad \dots (1)$$

$$NH_4OH \Leftrightarrow NH_4^{+} + OH^{-} \quad \dots (2)$$

$$H2O \Leftrightarrow H^{+} + OH^{-} \quad \dots (3)$$

and the equilibrium relations are:

$$K_A [CH_3COOH] = [CH_3COO^{-}][H^{+}] \quad \dots (4)$$
$$K_B [NH_4OH] = [NH_4^{+}][OH^{-}] \quad \dots (5)$$
$$K_W = [H^{+}][OH^{-}] \quad \dots (6)$$

Where K_A is the dissociation constant of CH3COOH, K_B is the dissociation constant of NH_4OH and K_W is the dissociation constant of water.
Two reaction invariants for the reactions of equations (1) and (2) are the total ionic concentration of the acid and the total ionic concentration of the base:

$$\alpha = [CH_3COOH] + [CH_3COO^{-}] \quad \dots (7)$$

$$\beta = [NH_4OH] + [NH_4^{+}] \quad \dots (8)$$

Equations (4, 5, 7 and 8) can be rearranged to give

$$[CH_3COO^{-}] = \frac{K_A a}{[H^{+}] + K_A} \quad \dots (9)$$

$$[NH_4^{+}] = \frac{K_B b}{[OH^{-}] + K_B}. \quad \dots (10)$$

Electro neutrality yield…

$$[NH_4^{+}]+[H^{+}]= [CH_3COO^{-}]+[OH^{-}] \quad \dots (11)$$

From equations (9), (10) and (11) we get:

$$A_4[H^{+}]^4 + A_3 [H^{+}]^3 + A_2[H^{+}]^2 + A_1[H^{+}] + A_O = 0 \quad .. (12)$$

Where:

$A_4 = K_B$
$A_3 = K_B\, \beta + K_W + K_A\, K_B$
$A_2 = K_A\, K_W + K_A\, K_B\, (\beta - \alpha) - K_B\, K_W$

$A_1 = -K_A K_B K_W - (K_W)^2 - K_A K_W \alpha$
$A_0 = -K_A (K_W)^2$

The reaction invariants, α and β, are found from the following mass balances:

$$V\frac{da}{dt} = F_A C_A - a(F_A + F_B) \quad ...(13)$$

$$V\frac{db}{dt} = F_B C_B - b(F_A + F_B) \quad ...(14)$$

Subtraction equation (12) from (13) to get:

$$V\frac{d\varphi}{dt} = F_B C_B - F_A C_A - \varphi(F_A + F_B) \quad ...(15)$$

where φ is the distance from neutrality and is given by:

$$\varphi=\beta-\alpha \quad ...(16)$$

V is the tank volume, C_A is the concentration of acid, C_B is the concentration of base, F_A is the flow rate of acid, F_B is the flow rate of base. Finally the pH is calculated using:

$$pH=-\log[H^+] \quad ...(17)$$

The simulated model comprises equations (11) to (17). Equations (13), (14) and (15) are bilinear differential equations which are essentially linear for small perturbations of F_B with constant F_A, while equations (11) and (17) are highly non-linear static equations. Hence, the model can be regarded as having linear dynamic characteristics and highly non-linear steady-state characteristics.

EXPERIMENTAL

Figure (2) shows a simplified schematic diagram of experimental waste water system. A wastewater stream is formed by merging a feed acid stream (solution of acetic acid, CH3COOH), which is pumped at a flow rate (F_A), with a feed base stream (ammonium hydroxide, NH4OH), at a flow rate (F_B). The weak acid and weak base were chosen for laboratory safety reasons. The dynamic responses were studied for different step change in both acid flow rate (disturbance) and base flow rate (manipulated variables) in order to study the effect of each change on the controlled variable (pH) and compared with the theoretical results. The values of step change are:

+ (20 %, 40 % and 60 %) step change in the base flow rate (F_B).
+ (20 %, 40 % and 60 %) step change in the acid flow rate (F_A).

The parameters of CSTR pH process are listed in table (1).

CONTROL STRATEGIES

Conventional Feedback Control

There are three basic types of feedback controllers:

1. Proportional.
2. Proportional-integral.
3. Proportional-integral-derivative.

The details of construction may differ among the various manufactures, but their functions are essentially the same.

The standard form transfer functions of feedback controllers are:

Proportional only:

$$G_C(s) = K_C \qquad \ldots (18)$$

Proportional plus integral:

$$G_C(s) = K_C\,(1 + \frac{1}{t_I\, s}) \qquad \ldots (19)$$

Proportional, integral and derivative:

$$G_C(s) = K_C\,(1 + \frac{1}{t_I\, s} + t_D\, s) \qquad \ldots (20)$$

The tuning of control parameters: proportional gain (K_c), integral time (t_I) and derivative time (t_D) was found by Ziegler Nichols open loop tuning method, to find the best values of proportional gain (K_c), integral time (t_I) and derivative time (t_D). (K_c), (t_I) and (t_D) values are calculated using equations in table (2).

Modern Control

Artificial Neural Network (Ann) Predictive Control

The neural network predictive controller that is implemented in the Neural Network Toolbox uses a neural network model of a nonlinear plant to predict future plant performance. The controller then calculates the control input that will optimize plant performance over a specified future time horizon. The first step in model predictive control is to determine the neural network plant model (system identification). Next, the plant model is used by the controller to predict future performance. The first stage of model predictive control is to train a neural network to represent the forward dynamics of the plant. The prediction error between the plant output and the neural network output is used as the neural network training signal. The process is represented by the figure (3). The neural network plant model uses previous inputs and previous plant outputs to predict future values of the plant output [11]. The neural network predictive controller does not require an inverse process model and has some important properties, which make it particularly suitable for control of the in-line pH process. In particular, the ability of MPC to handle time delays and anticipate the effects of measured disturbances was considered important [4].

$$J = \sum_{i=p1}^{i=p2} \begin{array}{l} (y_r(t+j) - y_m(t+j))^2 + \\ \lambda \sum_{j=1}^{P_u} (u(t+j-1) - u(t+j-2))^2 \end{array}$$

Where J is the cost function to be minimised, $P1$, $P2$ and P_u define the horizons over which the tracking error and the control increments are evaluated. The u variable is the tentative control signal, y_r is the desired response and y_m is the network model response. The l value determines the contribution that the sum of the squares of the control increments has on the performance index [11].

DISCUSSION

The experimental and model responses are studied for step change in the manipulated variable (base flow rate) and in the disturbance variable (acid flow rate) in order to study these effect on the controlled variable (pH).

Fig. (4) shows experimental and model responses for pH of the solution of waste water, with time by step change in the volumetric flow rate for inlet ammonium hydroxide, NH4OH, while Fig. (5) shows experimental and model responses for pH with time by step change in the volumetric flow rate for inlet acetic acid, CH3COOH.

In figure (4), it can be seen that the increase in the input flow rate of base is directly proportional to pH value of waste water mixture in reactor, while the increase in the input flow rate of acid (figure 5) was found a lead to decrease in pH value.

The dynamic and model responses are studied for step change in the manipulated ariables (FB) and in the disturbance variables (FA) in order to study these effect on the controlled variable (pH) as shown in figures (6 and 7). The tuning of control parameters: proportional gain (K_c), integral time (t_I) and derivative time (t_D) are found from figure (6). This parameters were found by Ziegler Nichols open loop tuning method.

Figure (8) represents unit step change in the set point of pH of reactor. This figure indicates to the comparison among set point response of all used controllers for control on the neutralization process. It shows that the ANN controller provides an excellent set point response, while PID controller provides sluggish behavior in set point change with high response time. The PI controller provides the worst set point change of all controllers because of significant overshoots and longer settling time. Figure (9) shows that the control action of the ANN controller manipulates the actuator in a smoother way than the PI and PID controllers.

Figure (10) represents unit step change in the disturbance of acid flow rate in the reactor. This figure shows the comparison for disturbance change of all used controllers. From this figure it was seen that the ANN controller provides the best control behavior for disturbance change, also the figure (11) shows that the control action of the ANN controller manipulates the actuator in a smoother way than the other controllers.

Tables (3 and 4) present values of ISE for unit step change in set point and disturbance. From these tables we note, the ISE of the ANN controller is less than the other controllers.

CONCLUSIONS

In this work, the mathematical model of the dynamic behavior of pH neutralization process in a continuous stirred tank reactor (CSTR) was studied and developed.

The unit step change was employed in the set point and disturbance of pH within reactor using PI, PID and ANN controllers.

A control system designed for process should provide fast and accurate changes for both set point changes as well for load changes.

The following conclusions can be drawn:

1. The ANN controller was compared with conventional controller and it was found that the ANN controller provides the best results for the set point change with low settling time and lower overshoot, while the conventional controllers provide sluggish response in the set point change with high settling time.
2. ANN controller provides better response to disturbance change than the conventional controllers where the PI and PID controllers provide sluggish behavior in regulated problem because the approximate FOPTD model has relatively small time delay.

Results obtained show that the performance of the ANN controller is very adequate to control highly non-linear processes, such as a pH process.-

NOMENCLATURE

ANN MPC	Artificial Neural Network Model Predictive Control
C_A	Acid concentration (mol/lit)
C_B	Base concentration (mol/lit)
CSTR	Continuous Stirred Tank Reactor
F_A	Acid flow rate (ml/min)
F_B	Base flow rate (ml/min)
FOPDT	First Order Plus Dead Time
G_C	Transfer Function
J	Cost Function
K_A	Acid dissociation constant
K_B	Base dissociation constant
K_C	Proportional Constant
K_W	Water dissociation constant
t	Time

P	Proportional
PI	Proportional-Integral
PID	Proportional-Integral-Derivative
u	Tentative Control Signal
y_m	Network Model Response
y_r	Desired Response
α	The Total Ionic Concentration of The Acid (mol/lit)
β	The Total Ionic Concentration of The Base (mol/lit)
τ_I	Integral Constant
τ_D	Derivative Constant
φ	Distance from Neutrality
t	Time

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PI	Proportional-Integral
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β	The Total Ionic Concentration of The Base (mol/lit)
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Table (1). Parameters of CSTR pH process.

Parameters	Symbol	Value
CSTR liquid volume	V	1 Liter
Acid flow rate	F_A	35 ml/min
Base flow rate	F_B	17 – 40 ml/min
Acid concentration	C_A	0.1 M
Base concentration	C_B	0.1 M
Acid dissociation constant	K_A	1.8×10^{-5}
Base dissociation constant	K_B	1.8×10^{-5}
Water dissociation constant	K_W	10^{-14}

Table (2): Constant of Ziegler Nichols open loop tuning method.

	Kc	τ_I	τ_D
P	**τ/(Kp*Td)**		
PI	**(0.9*τ)/(Kp*Td)**	**3Td**	
PID	**(1.2*τ)/(Kp*Td)**	**2Td**	**0.5 Td**

Table (3) ISE values for unit step change in set point of system

Controllers	ISE
PI controller	0.2863
PID controller	0.1721
ANN controller	0.0392

Table (4) ISE values for unit step change in disturbance of system

Controllers	ISE
PI controller	5.0514
PID controller	5.0237
ANN controller	1.3378

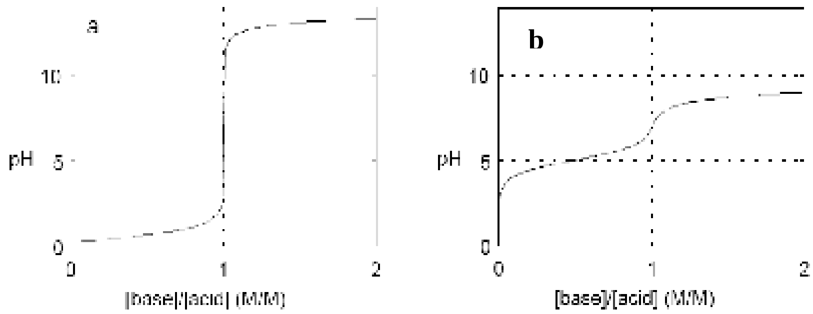

Figure 1. Titration curves. a) Strong acid/strong base, b) weak acid/weak base.

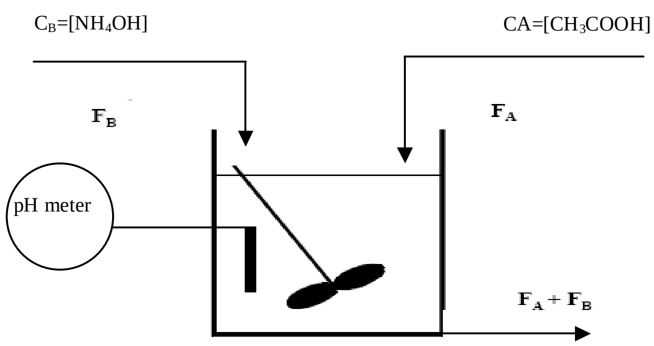

Figure (2). A simplified schematic diagram of experimental of waste water system.

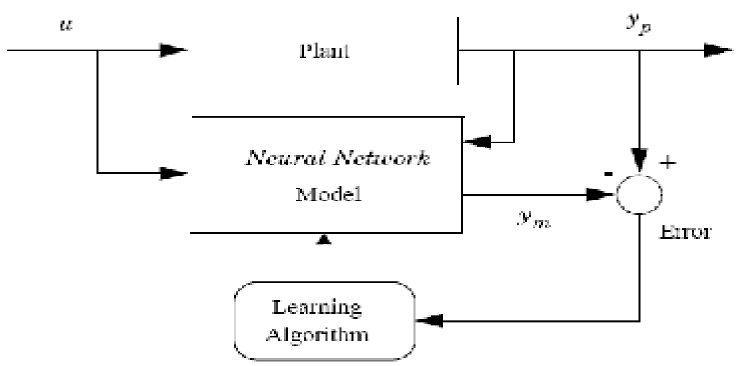

Figure (3) ANN MPC Structure

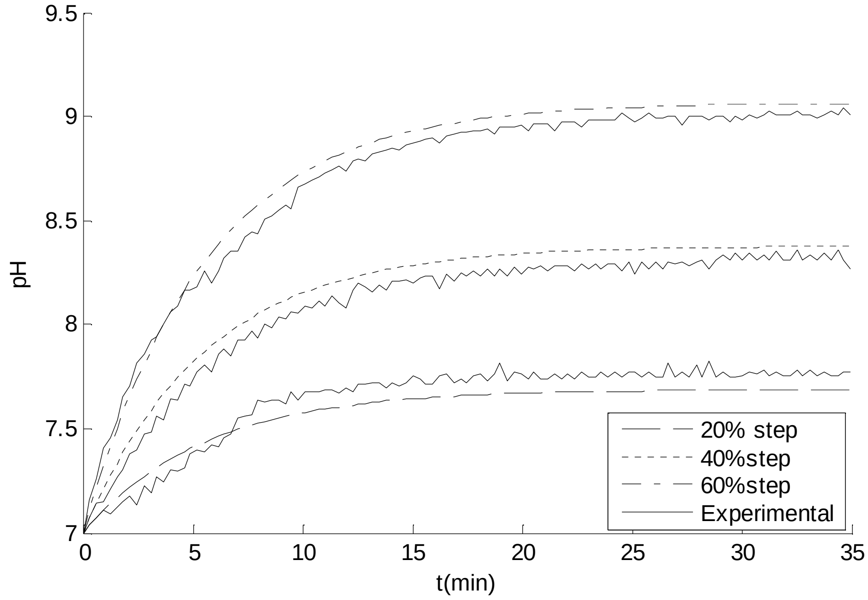

Figure (4) Experimental and theoretical responses of pH value for step change in the base flow rate.

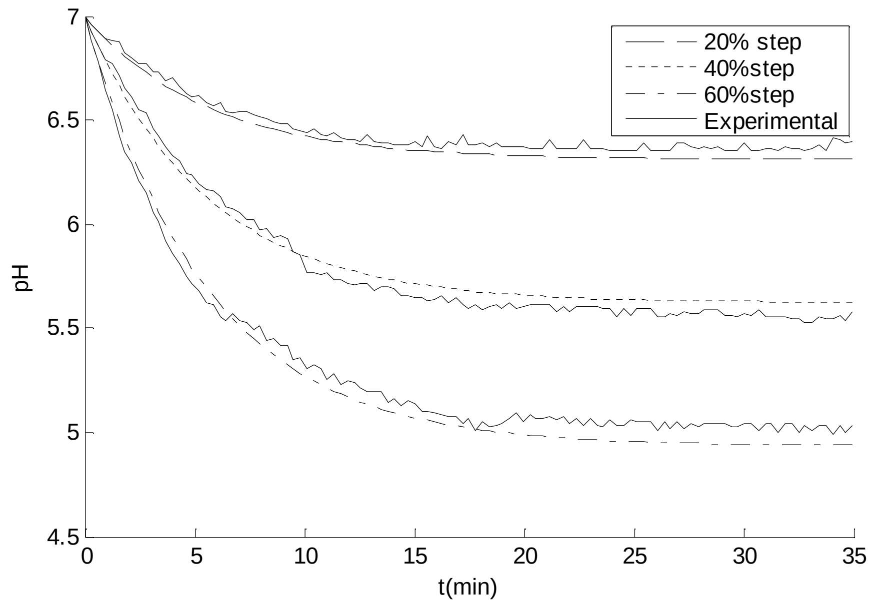

Figure (5) Experimental and theoretical responses of pH value for step change in the acid flow rate.

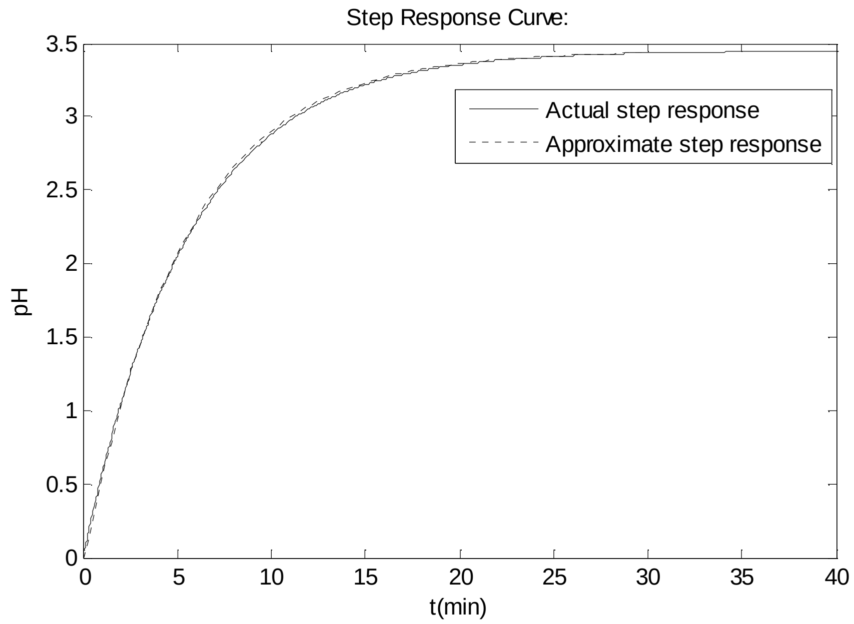

Figure (6) pH versus time at step change in input base flow rate

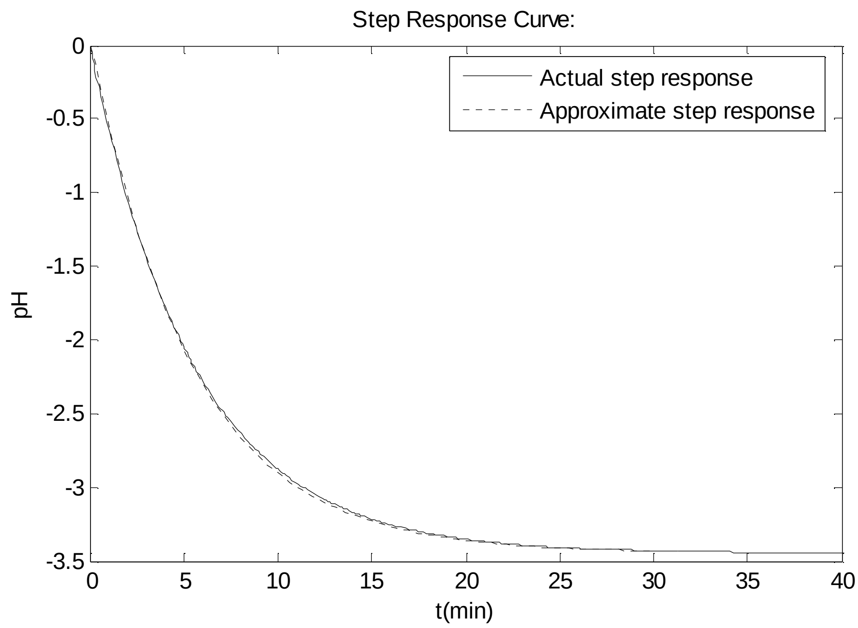

Figure (7) pH versus time at step change in input acid flow rate

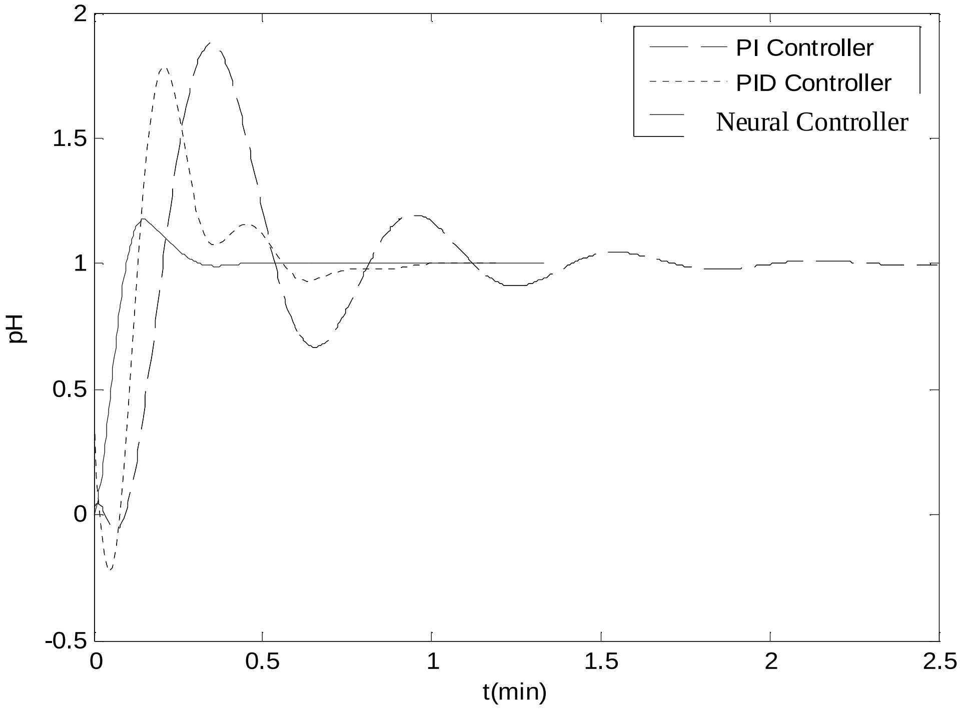

Figure (8) A comparison among set point change response of PI, PID and Neural controllers for control of pH

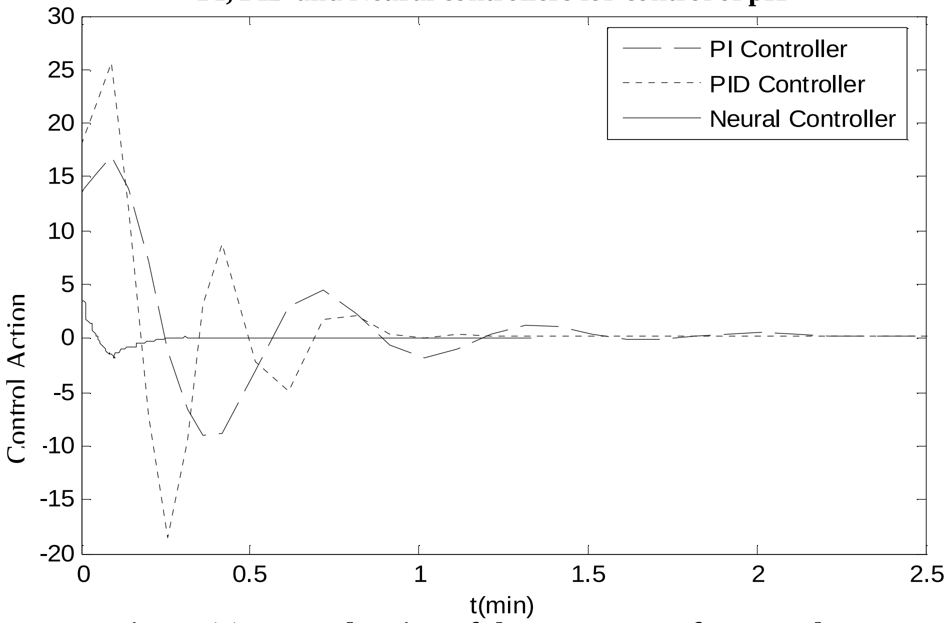

Figure (9) Control action of the pH process for step change in the set point.

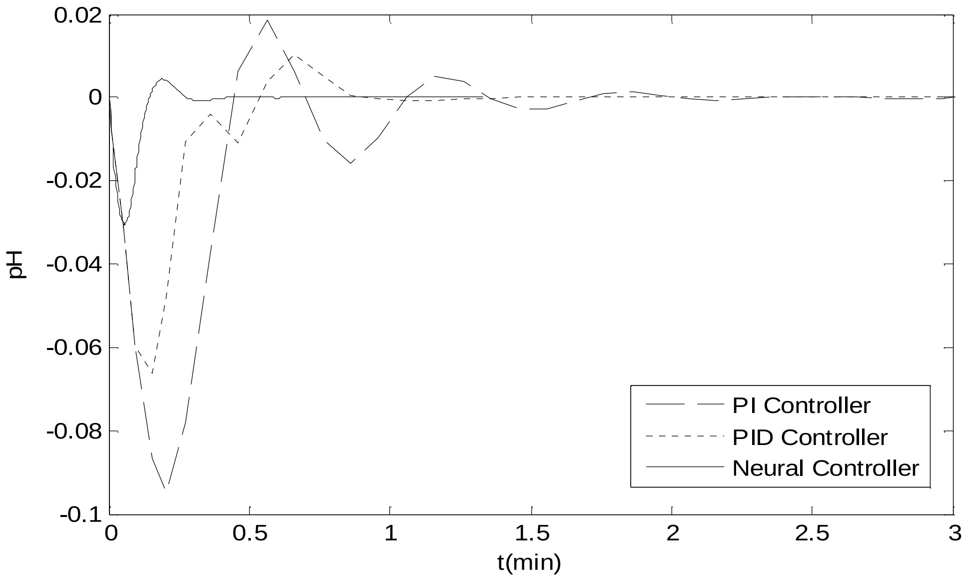

Figure (10) A comparison among load disturbance response of PI, PID and Neural controllers for control of pH

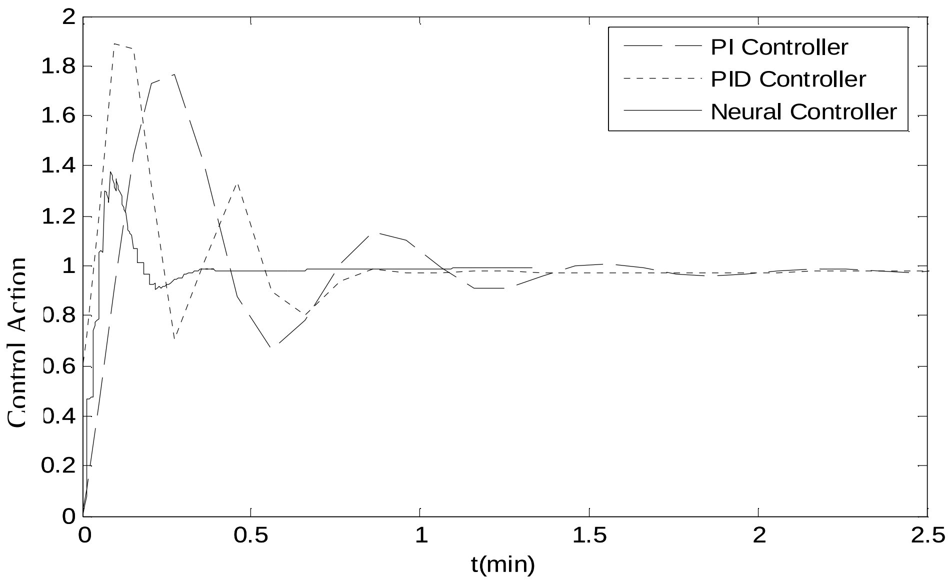

Figure (11) Control action of the pH process for step change in load disturbance.