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pH-Control Problems of Wastewater Treatment Plants

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Abstract

Experimental investigations have been carried out to investigate the pH-control problems of industrial electroplating wastewater treatment plants. The accurate and sensitive PID control system could treat most problem and disturbances in the normal operation of the water treatment. However, conventional treatment was replaced by proprietary treatment agent called a QUASIL which was found to be more effective for a wide range of pH.

Key words: Wastewater, Heavy metals, Precipitation, pH-control.

Introduction

The wastewater from metal plating facilities contains contaminants such as heavy metals, oil and grease, and suspended solid at levels which are considered hazardous to the environment and could pose risk to public health. Because of the high toxicity and corrosivity of metal plating waste streams, they require to pre-treatment of their wastewater prior to releasing them to municipal sewers or receiving waters.

Conventionally, precipitation is the method of choice for removal of heavy metals. Of the few precipitation methods, hydroxide and sulfide are the main two methods currently in use and hydroxide precipitation is by far the most widely used method, **Durhamd and Patria, (2006)**.

The control of water-PH plays an important role in these treatments, since each step takes place in a separate tank and the entire treatment requires several control loops to adjust the PH and to get perfect separation of toxic metals.

Experiment Set-Up

The present work studied several industrial electroplating wastewater treatment plants located in Iraq with capacities ranging from (5-20) m^3/day.

The streams of wastewater contain heavy metals such as (Cu, Fe, Cr, Cd and Ni), oil and grease, suspended solids and chelating or complexing agents.

The experimental data were obtained on-site and the water samples were analyzed at the laboratories of the ministry of Industry in Baghdad. The results of the analysis are given in Tables (1&2) showing average concentrations taken from several wastewater stations.

pH-Control

The acidity or the alkalinity of any solution can be indicated by the term of PH which stands for the power of the hydrogen ions H^+.PH is related to the concentration (or more strictly the activity) of hydrogen ions by the following equation **Pirece et al, (1970)**:

$$pH = -\text{Log}_{10}[H^+] \quad \ldots(1)$$

Also, alkalinity indication relates with hydroxide ion as:

$$POH = -\text{Log}_{10}[OH^-] \quad \ldots(2)$$

For neutralization process, the measurement equation **Kwok et al., (2003)** is:

$$pH = -\log_{10}\left[G + \left(G^2 + 4k_w\right)^{0.5}\right] + log_{10}\,2 \quad \ldots(3)$$

The value of G is zero at neutral point (PH =7).

The PH process control is one of great importance in the chemical industry especially wastewater treatment plants. PH process control is widely used as the end point control in the wastewater treatment plants **Shinsky, (1973)**.

The control loop mainly includes; sensor, controller and final control element which is almost a control valve. The PH-sensor (electrode) is a primary measuring element and like other primary element its dynamic response characteristics can play a significant role in control loop accuracy and stability. PH electrode dynamically behaves as a first order lag system **Giusti and Hougen, (1961)**.

Dynamic Modeling of Treatment process

It is difficult to formulate and identify a mathematical model for the PH process as small amounts of polluting elements will change the process dynamics considerably **Shinsky, (1973)**.

A general dynamic model of the PH process had been discussed earlier by **McAvoy, et al., (1972)**. They have derived a mathematical model from the first principle, i. e., mass balances for species and by combining their balances with equilibrium and electro-neutrality conditions.

Honson and Dale, (1994) have proposed the dynamic model of the PH system using conservation equations and equilibrium relations. Modeling assumptions include perfect mixing, constant density, and complete solubility of the ions involved.

However, in the present work, the dynamic model of the single stage PH process is proposed as a first order lag system, i. e., of the type:

$$\tau \frac{d\left(PH\right)}{dt} = kU - PH \qquad \ldots(4)$$

depended upon the conservation equations of the process and using modeling assumptions which include; perfect mixing, isothermal conditions and complete solubility of the ions.

From the control engineer's point of view, a linearized model where both the time constant (τ) and process gain (k) vary with PH and with the buffer concentrations in the system, and U indicate the input feed rate of acid and base solutions.

So, the transfer function of the single neutralization stage becomes:

$$G_p(s) = \frac{PH(s)}{U(s)} = \frac{k}{\tau s + 1} \qquad \ldots(5)$$

Since the wastewater treatment contains several stages of neutralization processes, the overall dynamics model will be:

$$G_o(s) = \frac{k_1 \ k_2 \ \ldots . k_n}{(\tau_1 s + 1)(\tau_2 s + 1) \ldots . .(\tau_n s + 1)} \qquad \ldots(6)$$

where n indicates the number of neutralization stages.

In the present work, the values of the time lag (τ) were determined between (3-4) hours and the process gain (k) between (1.5-2.0) PH/(m^3/hr) for each stage, which always varies depend upon the size of tanks and the operating conditions.

Dynamic of pH Electrode

In a continuous flow cell, the PH electrodes responses can be generally, represented by two time constants **Gusiti and Hougen, (1961)**, one arising from the rate of diffusion of ions into and out of the glass electrode surface, the other from solution mixing within the flow cell. The cells performance function, or transfer function can be written as:

$$G_e(s) = \frac{1}{(\tau_1 s + 1)(\tau_2 s + 1)} \qquad \ldots(7)$$

where:

τ_1 is the mixing time constant

τ_2 is the diffusion time constant.

The diffusion time constant is primarily a function of dynamic response of the measuring electrode itself. The mixing time constant is a function of the continuous flow cell in which the electrode measures the PH of the solution.

In the present work and by analyzing the experimental responses of the electrodes (process reaction curve method, **Stephanopouls,1984**), the PH-electrode could be represented by the first order lag system as follows:

$$G_e(s) = \frac{1}{\tau s + 1} \qquad \ldots(8)$$

where the time constant (τ) between (1-2) seconds.

However, since the time constant of PH-electrode was very small when compared to that of the process, it does not affect the response speed of the PH process.

The dynamic model of the process has direct effect on the design of closed-loop control system. Then the tuning of selected PID control which depends upon the values of dynamic characteristics of the process (process gain and time constant) gives agreement results with the operating of the wastewater treatment system. To increase the efficiency of the processes, it is better to use computer control system to detect and control directly any disturbances in the process variables in the system (Figures 3 & 4).

pH Control Problems

Several problems occur as a result of using the PH process control in wastewater treatment plants, these are:

1. The precipitation of heavy metals from the wastewater needed adjusting the alkalinity and acidity of water depend upon the nature of ions while another group of ions is precipitated in both conditions as shown in Figure (1). For example, Fe ion is precipitated in the acidity condition at PH of (3.0 to 4.0), while ions of Cu and Cr are precipitated in both conditions at PH of (5.0 to 8.5). Other ions of heavy metals such as (Zn, Cd, and Ni) are precipitated in alkalinity condition. These behaviors indicate that the process is required in the multistage process to neutralize and separate the heavy metals and also needing to use automatic control system for each stage.
   Additionally many apparent PH problems are really measurement problems rather than process problems due to the presence of complex agents or chelating, oil and grease and dissolved solid which contaminat the surface of sensor and could affect response and sensivity of PH-detectors. So the sensors are always cleaned and calibrated.
2. The PH process is highly non-linear Richter et al, (1974), for any small change in PH of the wastewater means a big change in the bulk concentration. For example, at PH 7 there is 10 times acidity as much as PH 8, and that at PH 7 there is 100 times as much acidity as at PH 9. Then, the adjustment of PH with high accuracy is now recommended.
   The above problem could grow to a complex situation when the wastewater has more than three types of heavy metals Bakkaloglu et al, (1998).
   Advanced and accurate control system now is needed to adjust the dosing flow of acid / base solution.
   The experimental results have proved that the regulating PID controller is shown in Figure (2), more effective than on-off type, since PID action has operate in regulated characteristics which give it enough time to correct the error.
3. Since the wastewater streams have various values of PH regarding the conditions of industrial process, the acidity of water must be monitored directly before any treatment. The PH of a mixed solution (wastewater and acid / base solution) is not just an average of the two solutions of PH values, but is also determined by the power of the solutions, and to a lesser extent by more esoteric factors Bailey, (1980). For example, when a solution of caustic soda with PH of 8.3 is added to the wastewater of PH 8, the mixed solution would actually be below PH 8.
   In the present work, the optimum PH of hydroxide precipitation was between 8.5 to 9.5 while for sulfide was between 3.0 to 4.5. These values were limited experimentally through several sets of experimental runs. It is recommended to use sensitive electrode to detect any small change in measurements. Also perfect noise-filter is implemented with the sensor to reject any undesirable signals to the controller.
4. It is difficult to formulate and identify a mathematical model for the PH process as small amounts of polluting elements in the wastewater would change the process dynamics considerably.
   Consequently, interpreting PH problems and solution requires knowledge of more than just the PH of the solutions involved.
   The entire treatment involves other processes such as, flocculation with a polymeric material, settling…etc, to get acceptable concentration limit of the heavy metals as shown in Table (2). This technique is time consuming and requires extensive set-up.
   Several private communications were made with international companies to get better design. Finally the result was, new technique called "Aquasil" treatment. This technology is commercially introduced in 1995 as an efficient alternative to conventional practices.

Aquasil Wastewater Treatment

Aquasil technology is an innovative treatment process that takes up and removes contaminants from wastewater. In the present work, several experiments were made by using Aquasil solution which proved good efficiency of separation as shown in Table (2). The aquasil agent is a single product, simultaneous process that utilizes the principles of fast kinetics and synergy for the removal of the most contaminants from the waste stream by using only single separator (Figure5). So the PH-control problems could minimize as a result of reduced process stages because the Aquasil agent was effective in the wide range of PH from 2 to 12. Also it lowers the level of COD and TDS.

Conclusions

1) The precipitation of heavy metals from the wastewater is achieved through several values of PH-solution depending upon the nature of ions.
2) It is difficult to formulate and identify a mathematical model of wastewater treatment process. It behaves dynamically as a multicapacity system and the approach dynamics model of each stage taken to be a first order lag system.
3) Automatic control of water-PH plays an important role in the waste treatment process.
4) Advanced on-line PID control has better efficiency than on-off type for the nonlinear PH process which can measure and treat directly any undesirable process signals.
5) PH control problems great with the conventional treatment of multistage process compared the modern and efficient single stage aquisil treatment.

Table 1
Analysis of heavy metals in the raw wastewater.

Constituent	Concentration (mg/liter)
Cd	60.0
Cr	50.0
Cu	15.0
Fe	20.0
Ni	50.0
Zn	40.0

Table 2
Analysis of heavy metals after treatment by (conventional and Aquasil technique).

Constituent	Concentration (mg/liter)	
	Conventional	aquasil
Cd	1.0	0.6
Cr	0.7	0.3
Cu	0.3	0.1
Fe	0.9	0.6
Ni	0.4	0.2
Zn	0.3	0.1

Nomenclature

COD: Chemical oxygen demand.
G: Distance from neutrality given by $[H^+] - [OH^-]$.
$G_{(S)}$: Transfer function.
$G_{e(S)}$: Transfer function of PH – electrode.
$G_{o(S)}$: Overall Transfer function of process.
$G_{p(S)}$: Transfer function of PH – process tank.
k: Process gain(PH/(m^3/hr)).
k_w: Dissociation constant of water. (mole/ liter)
H^+: Concentration of hydrogen ion (mg / liter).
OH^+: Concentration of hydroxide ion (mg / liter).
PH: Acidity indication.
PHI: Acidity indicator (sensor).
PID: Proportional, integral and derivative controller.
POH: Alkalinity indication.
s: Laplace transform.
TDS: Total dissolved solids.
t: Time (hours).
τ: Time constant.

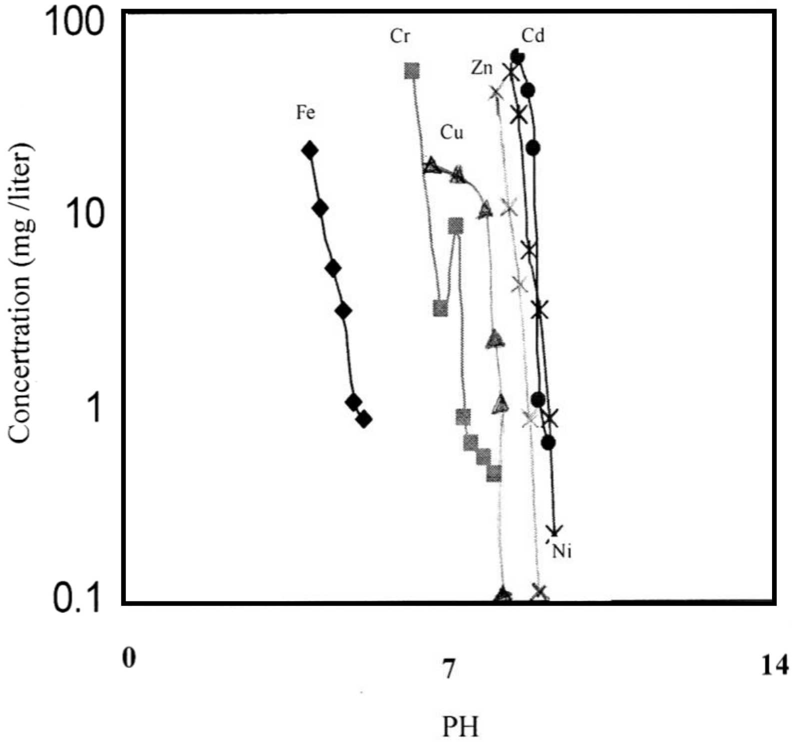

Fig. 1. Precipitation of Heavy Metals.

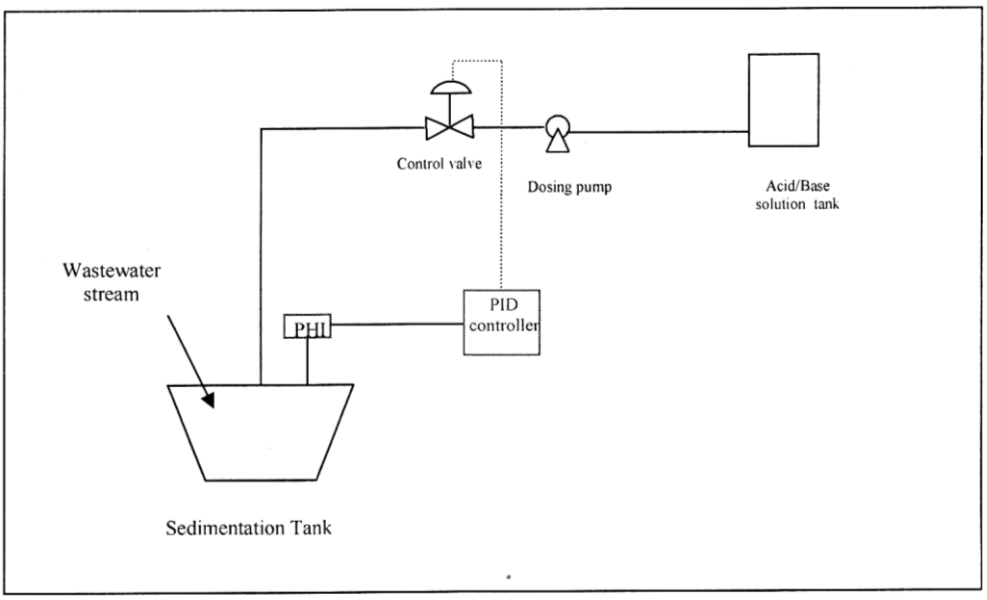

Fig. 2. Flow Diagram of PID Control System.

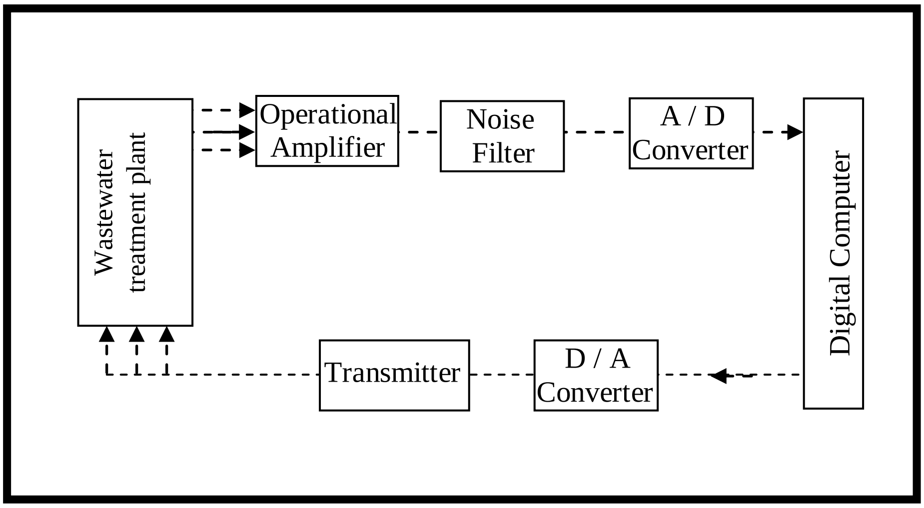

Fig. 3. Hardware Components of On-Line Control System.

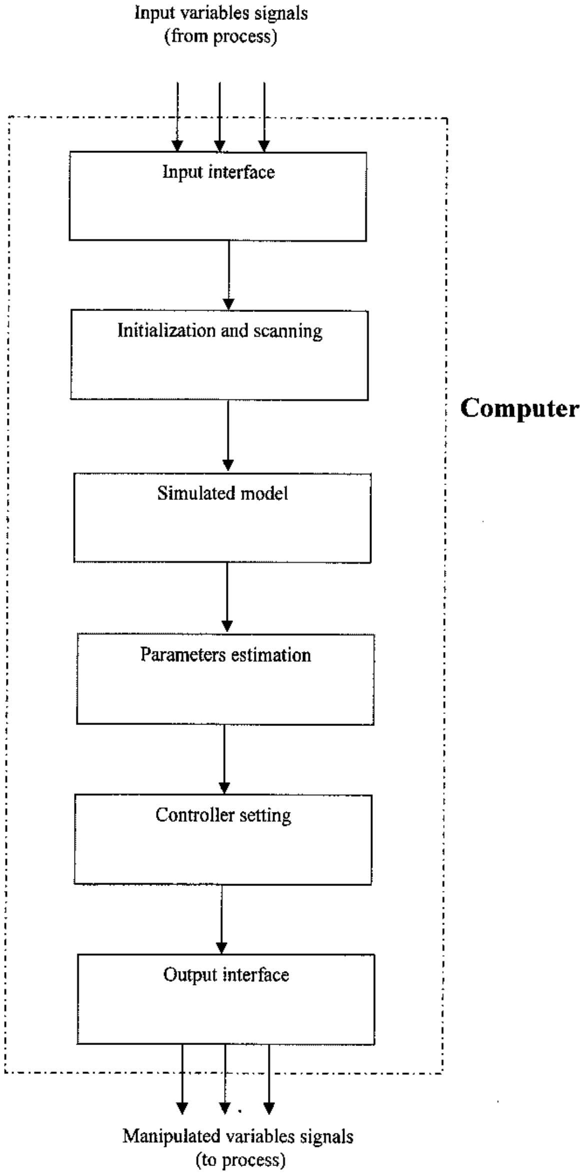

Fig.4. Block Diagram of the Computer Control Function.

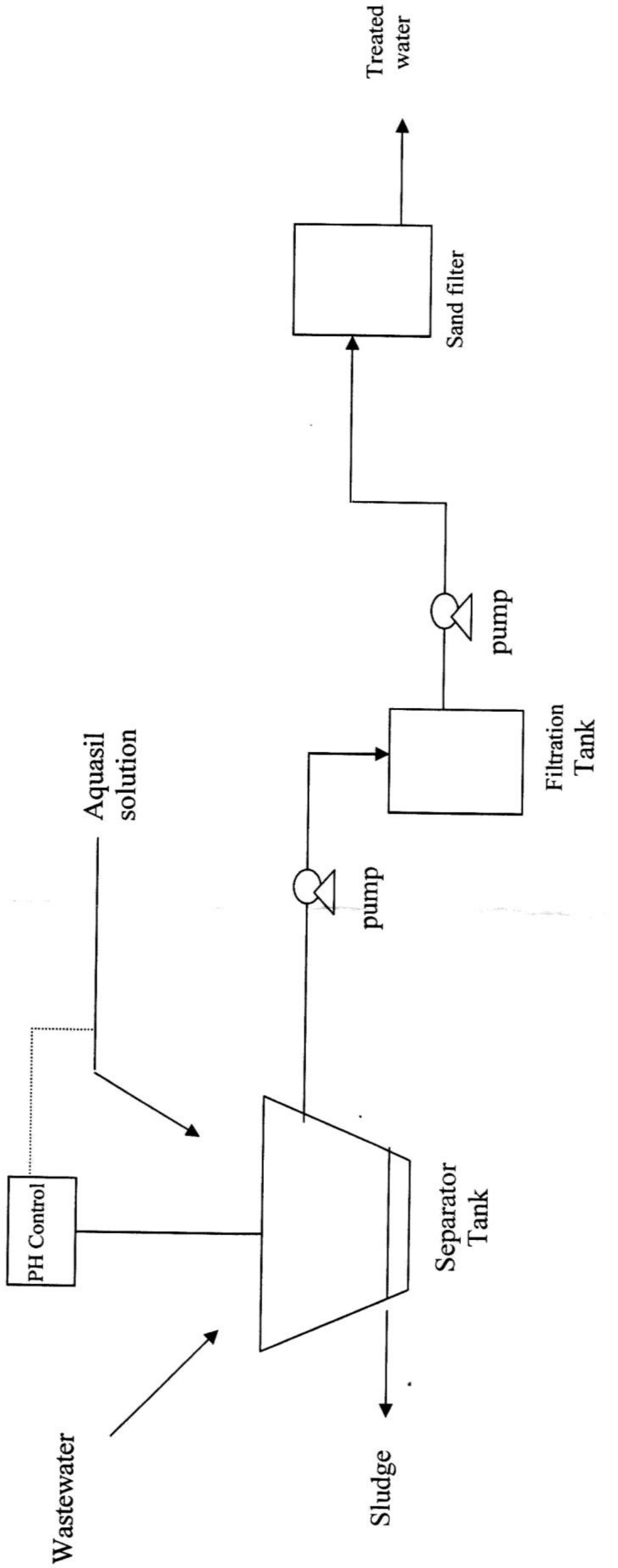

Fig. 5. Flow Diagram of Aquasil Treatment.

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