Dynamic Model of Wastewater Treatment for a Chromium Plating Process

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Electroplating processes are significant waste producers, inclusive of metal waste, alkali and acid waste and in some instances cyanide constituted effluent. Typical electroplating facilities conduct wastewater treatment processes via basic, in-house measurements and dosing. This kind of treatment results in overdosing / under-dosing of treatment chemicals due to various limitations. It would be ideal to predict, in advance, the efficiency of wastewater treatment based on variability of concentrations, flow rates, volume, concentration, complexing agents and dosing quantities. The traditional challenge regarding information availability has resulted in limited work having been undertaken in process models for predictions of waste water treatment. This paper proposes a model for the treatment of typical wastewater from chromium plating processes. This includes wastewater from degreaser, acid and the plating tank. The paper includes a study of pH adjustment and chromium treatment. The model developed was simulated and the results show the response of the treatment process to changing waste conditions including composition, volumes, etc.

Keywords: *Wastewater treatment, chromium plating, pH adjustment, process modeling*

Introduction

The metal finishing sector provides an essential service of coating metal products that are manufactured from cost effective material. A highly resistive metal surface is coated onto the products to augment the product surface. Some of the aims of surface coating are to protect surfaces against corrosion, produce attractive finishes and preserve engineering products.[1]

The metal finishing sector encompasses various industries including electroplaters, powder coaters, hot dip galvanizers, etc. Prior to 1996, there was no statistical data on the numbers of metal finishers in South Africa. A recent study by Keofeod has shown the estimated number of metal finishers to be between 600 and 1200. Results also indicated that metal finishing plants vary from small to medium size enterprises, with some operating in backyards.[2]

Electroplaters are the most predominant metal finishers, making up to 40% of the total,[3] consuming significant amounts of water and hence producing large volumes of wastewater.[1,4] About 80% of the water consumed is used for rinsing, which is essential for the removal of "drag out."[3] Rinse water is disposed of as wastewater when it gets used up, *i.e.*, when its ability to effectively rinse decreases significantly.

The electroplating process has three main stages, which are (1) cleaning / preparation, (2) plating and (3) rinsing. The properties of waste generated at these stages correspond to the process bath[5] compositions at the specified stage.

Cleaning/ preparation is comprised of acid pickling and alkaline cleaning. The acid pickling process removes oxides of corrosion from the surface of the object. Generally, 10 wt% hydrochloric acid is used. The waste from this process is the acidic solution with metal salts. The alkaline degreasing process removes oil and grease from the surface of an object. A weak solution of sodium hydroxide is used. The waste from this process is alkaline solution, oil and grease. Water rinsing is conducted after each process.

The plating process is conducted in an electrolytic bath of metal salts, with the metals to be deposited on the surface of the object. Water rinsing occurs after the object has been removed and hung over the plating process tank, thus removing excess chemical drag-out. Thereafter clean water is used to rinse the residual chemical off the plated surface.[1,4,5] Waste from the plating process rinse water contains metal ions and salts.

In general, wastewater from the electroplating industry contains metal ions (Cr^{+6}, Zn^{+2}, Cu^{+2}, Ni^{+2}, Cd^{+2}, Fe^{+2}, etc.), toxic substances (ammonia and cyanide), acids, alkalis, oil and grease, usually at higher levels than legal discharge limits. This kind of waste is hazardous and toxic to the environment.[6] The accumulation of metal ions in the environment poses a serious threat to human health, living resources and ecological systems.[7]

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There exist various treatment technologies to treat plating process waste efficiently and effectively for reuse or in order to meet discharge limits. Conventional chemical treatment is the predominant method involving precipitation, coagulation, settling and filtration.

Common features of these conventional treatments are:[8]

- Simple engineering hardware
- Convenience of operation
- Capability of effectively treating large volumes of wastewater containing high concentrations of metal ions
- Low operational cost

Various studies have indicated that electroplating wastewater treatment in the metal finishing sector can be classified as either formal or informal, depending on the level of environmental responsibility of the company concerned together with legislation. Informal treatment implies that wastewater treatment is conducted without proper measurement and controls. Thus the actual effectiveness of the treatment system is not quantified. Formal treatment of electroplating waste results in effectively treated wastewater.

The problem of effective treatment is compounded by the inconsistent volumes and chemical compositions sent to the wastewater treatment facility. This is due to periodic dumping, purging, spills and cleaning operations. Typical dosing at the wastewater treatment plant occurs on a typical load, *i.e.*, the operator doses a certain quantity based on experience. The effectiveness of this dosing regime is not quantified. The ability of the existing hardware for effective wastewater treatment is also unknown. This treatment approach could result in overdosing and/or under-dosing of treatment chemicals.

Overdosing or under-dosing results in high levels of metal ions, cyanide, ammonia and the high risk of serious secondary pollution caused by treatment reagents. Secondary pollution hazards include excess metallic sludge, formation of chlorine sub-products, etc.[9] If this unacceptably treated wastewater is released into rivers or any surface water, the result would be detrimental to the immediate environment. If released into municipal systems, it can cause problems for the treatment processes in those systems. In most instances, the municipal systems are not designed to handle such waste.

In this study, a generic mathematical model has been developed for a typical chromium wastewater treatment plant. The model is positioned to assist in predicting effluent composition based on the influent composition and load. The scope of this model includes quantification of the treatment chemicals required to treat specified wastewater loadings effectively. The model output includes residence time for specifically sized equipment, final conversion and pH. The model indicates the effects of variation in capacity of process hardware.

The key aim of this study was to provide a tool that can be used by electroplaters to predict the effectiveness of wastewater treatment facilities. The envisaged strengths of the model lie in its ability to predict the effectiveness of wastewater treatment under different operating scenarios. This could prove beneficial to the company concerned as overdosing / under-dosing can be prevented at the appropriate times. This could produce cost /environmental savings and would ensure effective treatment of wastewater.

Model development

For the purpose of model development, a typical chromium plating facility was considered. The plant consists of a degreaser, acid pickling and chromium plating system. Each process tank is followed by rinse tanks.

The waste treatment processes are modeled separately. Firstly, a typical pH adjustment is detailed, followed by a model to predict the conversion of hexavalent chromium to trivalent chromium. This chromium treatment model is capable of predicting the effectiveness of treatment based on the load, pH, temperature and concentration (*i.e.*, the concentration of both treatment reagents and metals in wastewater).

Degreasing and pickling process

The degreasing process entails the removal of oils, greases and soil from the surface of the object to be plated. The pickling process aims to remove scale and oxides from the surface of the object to be plated. These two processes ensure the integrity of the plating process. The chemicals involved in degreasing and acid cleaning include caustic and strong acids such as hydrochloric and sulfuric acid.

The acid pickling process uses high acid concentrations, for scale and corrosion removal. Corrosion scale is removed in the form of chlorides of the metal pickled and the metal ions are in a dissolved state. For example, the pickling of iron results in the formation of iron chloride ($FeCl_2$) solution. Typical concentrations of iron chloride solutions after pickling are 40 to 100 g/L.[10]

Wastewater from the degreaser process is alkaline waste containing emulsified oils and greases. The free oils and greases are removed before mixing with pickling wastewater. The major contaminants of wastewater from the degreaser process are organics, and oil and grease emulsions.

pH adjustment model. The pH of a solution is defined as:[11]

$$pH = -\log[H^+] \tag{1}$$

Equation 2 predicts the pH change of a specified solution, depending on the dosage of H^+ ions. The concentration of acid/alkali added can be represented as the H^+ dosage and the new pH is thus determined as:[11]

$$\frac{[H^+]_2}{[H^+]_1} = 10^{-[pH_2 - pH_1]} \tag{2}$$

In a wastewater treatment plant, the incoming pH values of the acid and degreaser rinses are known within a range of operation. Thus, the change in hydrogen ion concentration can be determined. The neutralization reaction mechanism is used to quantify the amount of acid or alkaline reagent to be added once the two rinse waters are mixed. Usually, for acidic waste from an acid pickling process, the acid in the waste is hydrochloric acid. For alkaline waste from an alkali degreaser process, the alkali is typically sodium hydroxide.

The required amount of alkali is equal to the change in the hydrogen ion concentration. If sodium hydroxide is used to neutralize hydrochloric acid, the reaction mechanism is:[12,13]

$$HCl + NaOH \rightarrow NaCl + H_2O \tag{3}$$

Typical applicability of the pH adjustment model. Consider the schematic diagram of the pH adjustment model shown in Fig. 1. Assuming that 2000 L/hr of acid pickling waste has 500 mg/L of hydrogen ions, which indicates a very low pH (pH < 1), the required pH for the downstream treatment process of metal ions is 8.5. The pH is adjusted by adding a 10 wt% solution of sodium hydroxide. The reaction proceeds as shown in the reaction mechanism in Equation 3 above.

The change in hydrogen ions from 500 mg/L to concentrations corresponding to a pH of 8.5 is brought about by the reaction of hydrogen ions and hydroxyl ions. The moles of hydroxyl ions required are equal to the moles of hydrogen ions to be reacted.

Input data to the model:

Concentration of hydrogen ions = 500 mg/L

$pH_{outlet} = 8.5$

Model solution:

$$a)\quad [H^+]_{inlet} = (500/RMM_{H^+})/1000 = 0.496 \text{ mol/L}$$

$$b)\quad pH_{inlet} = -\log[H^+]_{inlet} = -\log(0.496) = 0.3045 \quad \Leftrightarrow \quad [H^+]_{inlet} = 10^{-0.3045} \times 1.008 \times 1000 = 499.9891\ mg/L$$

Calculating the hydrogen ion concentration in the outlet from the tank, if the targeted pH is 8.5:

$$c)\quad [H^+]_{outlet} = (10^{-pH_{outlet}}) \times RMM_{H^+} \times 1000 = 10^{-8.5} \times 1.008 \times 1000 = 3.19 \times 10^{-6} \text{ mg/L}$$

$$d)\quad \Delta[H^+] = [H^+]_{inlet} - [H^+]_{outlet} = 499.9891 - 3.19 \times 10^{-6} \sim 499.9891 \text{ mg/L}$$

$$e)\quad Conversion\ of\ [H^+] = \Delta[H^+]/[H^+]_{inlet} = \frac{499.9891}{499.9891} = 1$$

$$f)\quad Mass\,[H^+]\,reacted = X \times [H^+] \times (Q_{tot}/3600) = 1 \times 499.9891 \times (2000/3600) = 277.7717 \text{ mg/sec}$$

From the neutralization reaction (Equation 3), 36 g of hydrochloric acid requires 40 g of sodium hydroxide.

$$g)\quad Mass\ NaOH\ required = (40/36) \times Mass\ [H^+]reacted = 1.1111 \times 277.7717 = 308.6321 \text{ mg/sec}$$

$$h)\quad Total\ mass\ NaOH\ stream = Mass\ NaOH\ required/(10\%) = 3086.321 \text{ mg/sec}$$

The pH adjustment depends on the requirements of the process, *i.e.*, sodium hydroxide or hydrochloric acid can be used interchangeably. Hydrochloric acid is used to decrease the pH, while sodium hydroxide is used to increase it.

Chromium treatment

The chromium plating bath consists of chromium trioxide (CrO_3) and sulfate. Sulfate is used as a catalyst. The typical concentration of chromium trioxide in the plating process is 240 g/L.[10] It reacts with water to form chromic acid. Trivalent chromium (8.0 mg/L) is used to stabilize the bath. Normally, the resultant concentration of chromium in the rinse tank is usually in the range of 70 to 80 mg/L.[1,14]

The hexavalent chromium (Cr^{+6}) contained in the waste rinse water is considered toxic and cannot be treated by direct precipitation with sodium hydroxide. Cr (VI) is reduced by sodium metabisulfite to trivalent chromium. A common industrial practice is to add five times more metabisulfite than Cr (VI) in the feed waste.[10]

The reaction is favored by acidic conditions. Sulfuric acid is used to decrease the pH to 2.5.[10,15]

Trivalent chromium is less toxic than hexavalent chromium and can be precipitated by pH adjustment. Normally, sodium hydroxide is used to adjust the pH to the lowest Cr (III) solubility point. At the lowest solubility point, Cr (III) precipitates out of solution as Cr (III) hydroxide.[13]

Chromium removal model

Hexavalent chromium reduction. The reduction of hexavalent chromium by sulfite has been reported by many authors to be first order with respect to hexavalent chromium and sulfite concentration.[10,15] The reaction is also reported to be highly pH dependent,[10,15] showing an inverse proportionality to pH. The reaction mechanism of hexavalent chromium with sulfite is as follows:[10,14,15,16]

$$2CrO_3 + Na_2SO_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Na_2SO_4 + 3H_2O \tag{4}$$

The reaction rate law for hexavalent chromium with sulfite is:[10,15,16]

$$\frac{d[Cr^{+6}]}{dt} = K[Cr^{+6}][S^{+4}] \tag{5}$$

where $-r_{Cr^{+6}}$ = reaction rate.
K = lumped reaction rate constant (L/mg·sec)
$[Cr^{+6}]$ = concentration of hexavalent chromium ions (mg/L)
$[S^{+4}]$ = concentration of sulfite ions (in terms of sulfur) (mg/L)

In the literature, the pH dependency of the reaction rate of Cr (VI) reduction by sulfite has not been shown. In this study, a mathematical representation of this dependency is incorporated into the rate law expression. This has been accomplished by using experimental data from Martins, *et al.*[16] Martins' work developed a number of experiments to show the effects of pH, temperature and Cr (VI) on the reaction rate constant. This data showed that the pH had a significant effect on the rate constant. Hence, the pH effect has been incorporated into the Arrhenius expression giving a lumped rate constant, as in Equation 6, developed below.

The relationship between reaction rate constant and pH has been determined using the linear regression method. In order to determine the pH dependence of the reaction rate, a reference data point was chosen based on the data given by Martins, *et al.*[16] The reference point was chosen at pH 2.0 and at a temperature of 25°C. The ratio of the rate constant values, $(k_i/k_{reference})$, is plotted versus pH. From this plot, a relationship between pH and the rate constant (K) is deduced. The K factor in the rate law expression (Equation 5) can be approximated by the following expression:[15,16]

$$K = A \exp[-E / RT] \times 84.794\, pH^{-4.368} \tag{6}$$

where E = Activation energy.
A = Frequency factor.
R = Universal gas constant.
T = Temperature of water.

The data showing the relationship between the rate constant and temperature has been used to determine the constant for the Arrhenius law. The magnitude of the activation energy (E) and the frequency factor (A) were determined from the plot of $-Lnk$ and $1/T$. This relationship is determined from the linear regression of the Arrhenius expression.[16]

$A = 5.692 \times 10^{10}$ L/mg·sec

$E = 74.630054$ kJ/mol

Cr (VI) reduction reaction takes place in a continuous stirred tank (CSTR).[17] Using the CSTR design equation for the Cr (VI) reaction tank gives us the following expression:[18]

$$V = \frac{F_{Cr^{+6}} X_{Cr^{+6}}}{-r_{Cr^{+6}}} \tag{7}$$

where V = Volume of the tank in m^3
$F_{Cr^{+6}}$ = Input flow rate of Cr (VI)
$X_{Cr^{+6}}$ = Conversion of species of concern
$-r_{Cr^{+6}}$ = Consumption rate of species of concern

Substituting the rate expression (Equation 5) into the design Equation 7 (*i.e.*, the term $-r_{Cr^{6+}}$ in the design equation is replaced by Equation 5):

$$V = \frac{F_{C^{+6}} X}{K[Cr^{+6}][S^{+4}]} \tag{8}$$

Now setting the initial conditions and using stoichiometry (Referring to Table 1 in the Appendix):

$$V = \frac{F_{Cr^{+6},init}\, X}{K\,[Cr^{+6}]^2_{init}\,(1 - X)\,(\Theta_{S^{+4}/Cr^{+6}} - 3X/2)} \tag{9}$$

where $\Theta_{S^{+4}/Cr^{+6}}$ is the ratio of initial sulfite to initial hexavalent chromium.

Rearranging Equation 9 by making a quadratic expression:

$$\frac{3VK\left[Cr^{+6}\right]^2_{init}}{2} X^2 - \left(\frac{3VK\left[Cr^{+6}\right]^2_{init}}{2} + \Theta_{S^{+4}/Cr^{+6}} VK\left[Cr^{+6}\right]^2_{init} + F_{Cr^{+6}init}\right) X + \Theta_{S^{+4}/Cr^{+6}} VK\left[Cr^{+6}\right]^2_{init} = 0 \tag{10}$$

Equation 10 is then rearranged to solve for X.

The boundaries of the root that represent the conversion of Cr (VI) are:

X: $0 \leq X \geq 1$.

The above quadratic expression can then be solved for the root. The root that satisfies the boundaries of X represents the conversion of hexavalent chromium to trivalent chromium. This conversion can be used to predict the composition of the output stream and the residence time.[18]

Applying the model - an example

Wastewater from chromium single-stage rinse water has a pH of 4.0 and a temperature of 20°C. The pH is adjusted to 2.6 by adding sulfuric acid. The wastewater feed flow rate to the treatment process is 1000 L/hr with 45 mg/L of Cr (VI) and negligible Cr (III) concentration. It is a standard industrial practice to use a 5:1 ratio of metabisulfite to hexavalent chromium for the effective reduction of chromium.

The model requires the following input variables to predict the conversion of chromium, residence time and output composition:

Feed flow rate, Q = 1000 L/hr
Cr (VI) concentration, $[Cr^{+6}]_{init}$ = 45 mg/L
Volume of tank, V_T = 365 L

Ratio of metabisulfite to Cr (VI), $\Theta_{S^{+4}/Cr^{+6}}$ = 5
pH = 2.6
Activation energy, E = 7.46×10^4 J/mol
Universal gas constant, R = 74,600 J/mol
Frequency factor, A = 5.69×10^{10} L/mg·sec
Temperature of the reaction tank = 20°C = 288 K

Model solution

Parameters determined from the input conditions:

$K = 0.0036 \text{ sec}^{-1}$

Equation 10 is used to solve for the conversion of Cr (VI) to Cr (III). Equation 10 is a quadratic expression, and the solution has two roots. The root that represents conversion falls within the boundary conditions cited earlier ($0 \leq X \geq 1$). The following are the coefficients of the quadratic Equation 10:

$$a = \frac{3VK[Cr^{+6}]^2_{init}}{2} = 3986.435 \text{ mg/sec.}$$

$$b = \left(\frac{3VK[Cr^{+6}]^2_{init}}{2} + \Theta_{S^{+4}/Cr^{+6}} VK[Cr^{+6}]^2_{init} + F_{Cr^{+6}init} \right) = -17287.1 \text{ mg/sec}$$

$$c = \Theta_{S^{+4}/Cr^{+6}} VK[Cr^{+6}]^2_{init} = 13288.12 \text{ mg/sec}$$

From these parameters, Equation 10 can be solved to determine the reduction of Cr (VI) to Cr (III).

Using the general quadratic expression:

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$3986.435X^2 - 17287.1X + 13288.12 = 0$$

$X = 0.999$ or 3.340 (the two solutions)

The second root is greater than one. Hence, it does not represent the conversion, since it falls outside the boundaries of conversion.

From the conversion, it can be seen that 99.8% of the Cr (VI) input is converted to Cr (III). This conversion can be used to determine the required time for such conversion and the output concentration.

In order to determine residence time, the above conversion value is substituted into Equation 9.

$$\frac{V}{Q} = \tau = \frac{0.998}{0.0036(20)\ (1-0.998)(5-3\times 0.998/2)}$$

$\tau = 33$ min.

This means that in order to achieve 99.9% conversion of 45 mg/L of Cr (VI), the wastewater must be inside the tank for about 33 min. The residence time depends on the input flow rate and the size of the reaction tank. The influence of the multiple variables is shown in the Mat-Lab program in the results and discussion section.

Results and discussion

This section illustrates the response of the mathematical models to multiple variable inputs. The change of more than one variable at a time simulates the practical experiences in metal finishing wastewater treatment. The models predict the treatment efficiencies, time required for optimum treatment (*i.e.*, residence time) and the amounts of treatment reagents required.

pH adjustment

Figure 2 shows the relationship between the weight of caustic required and the hydrogen ion concentration in the feed waste. From this plot it is evident that the amount of caustic required increases linearly with increasing hydrogen ion content.

Figure 3 shows the relationship between the total mass flow rate of caustic required and the hydrogen ion concentration in the feed waste, for different concentrations of caustic solutions. This relationship shows that the flow rate of the caustic is high for 10 wt% NaOH and at a minimum for 50 wt% NaOH. The discrepancy in the amount of caustic required at different solution concentrations decreases between 30 and 50 wt% NaOH.

The pH adjustment model is shown to respond with variation of input. Hence the model can be used to predict the required amounts of caustic or acid, based on the condition of input waste.

The following can be deduced from Figs. 2 and 3:

- The amount of caustic required is directly proportional to the pH of the wastewater and the target pH.
- Low concentrations of caustic solution result in high pumping costs, due to the enormous amounts to be pumped in case of neutralizing strong acid streams.

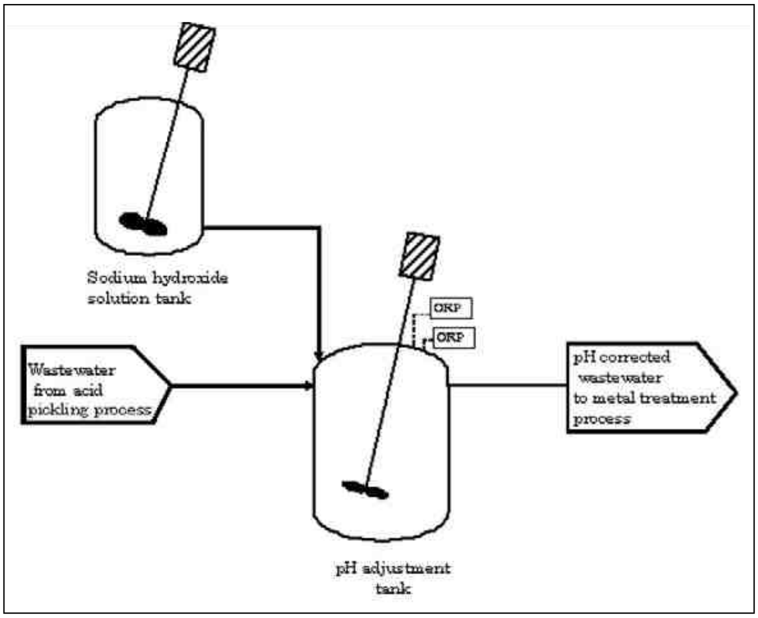

Figure 1—*pH adjustment of wastewater from the acid pickling process.*[17]

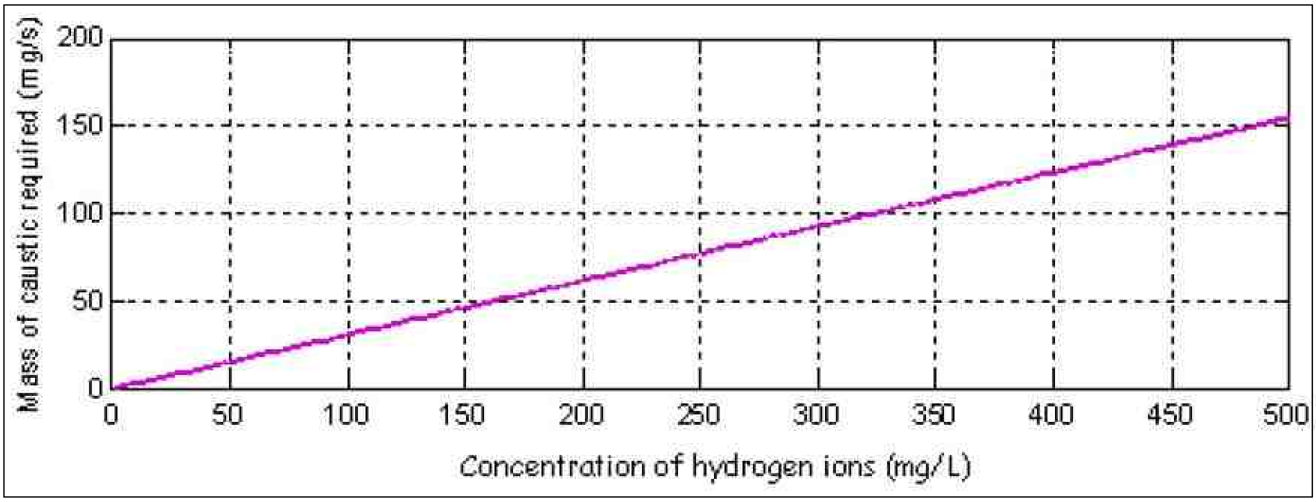

Figure 2—*Variation of caustic required by changing the hydrogen ion concentration in the wastewater.*

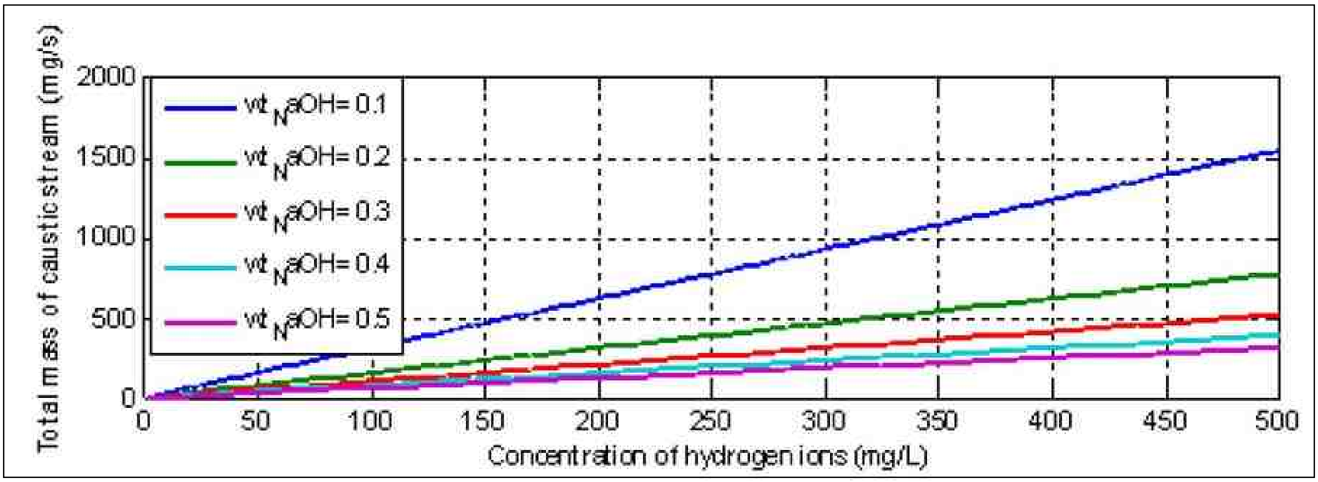

Figure 3—*Variation of the total mass of the caustic stream required by changing the hydrogen ion concentration in the wastewater at different caustic solution concentrations (wt%).*

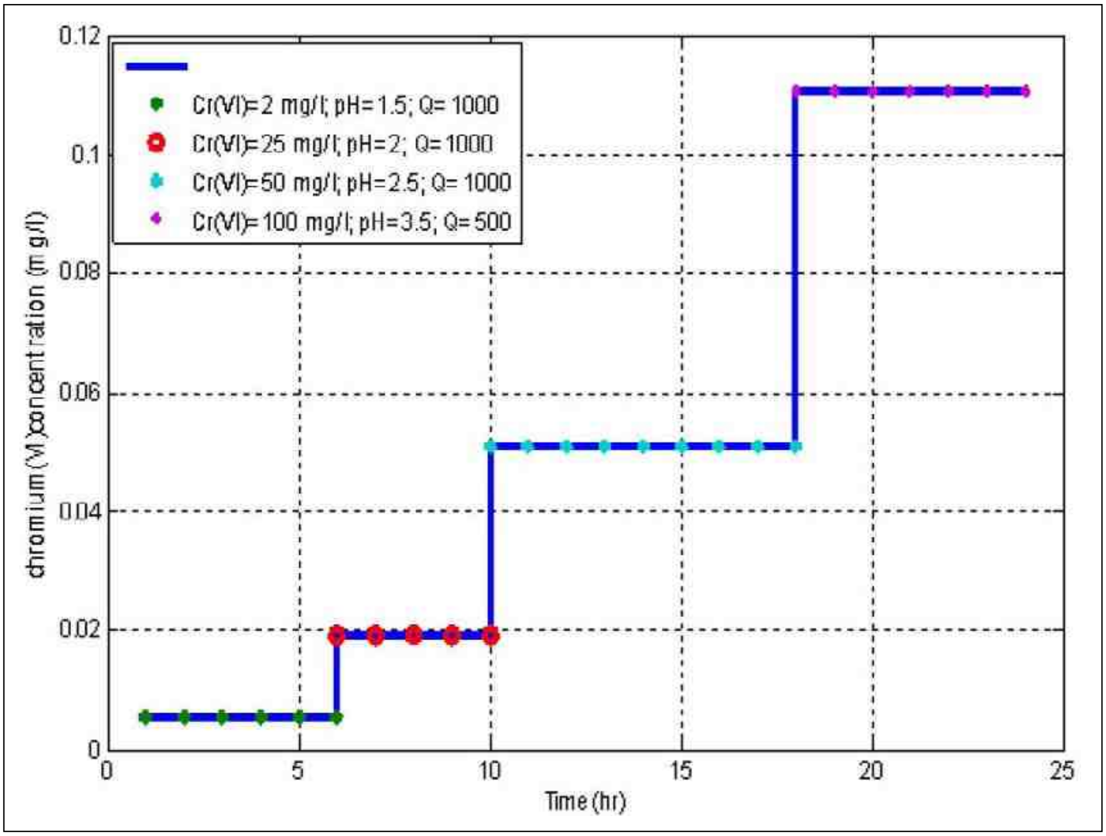

Figure 4—*Variation of Cr (VI) conversion output with time.*

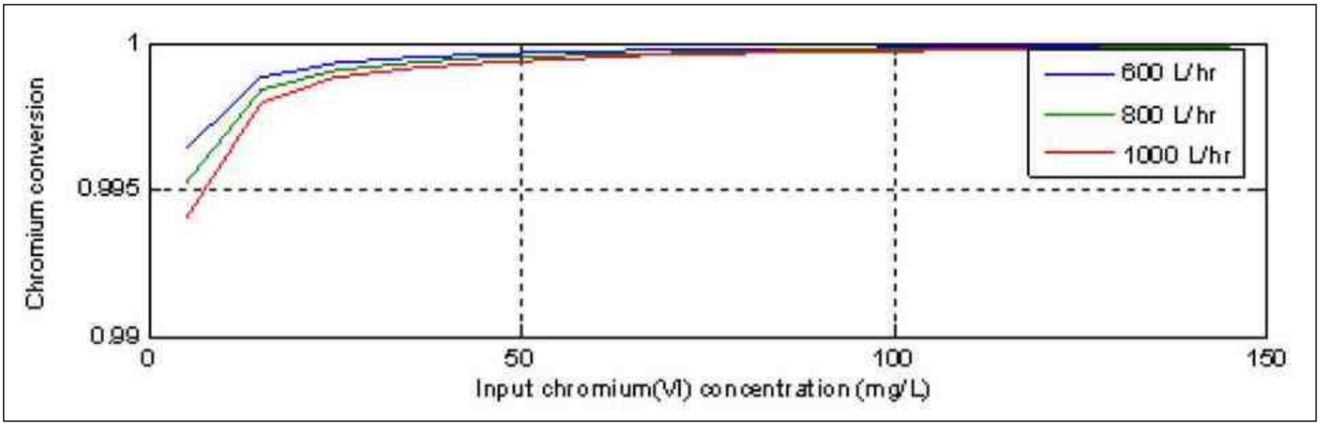

Figure 5—*Variation of Cr (VI) conversion with changing input Cr (VI) at S (IV):Cr (VI) = 5, reaction pH = 2.5 and temperature = 20°C.*

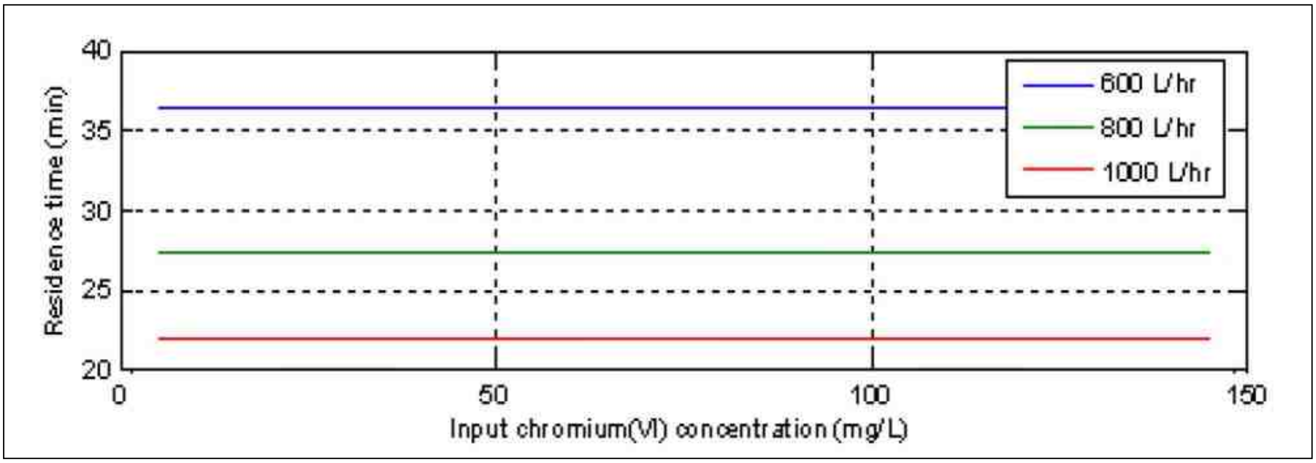

Figure 6—*Variation of wastewater residence time at different flow rates and varying input Cr (VI) concentration, S (IV):Cr (VI) = 5, reaction pH = 2.5 and temperature = 20°C.*

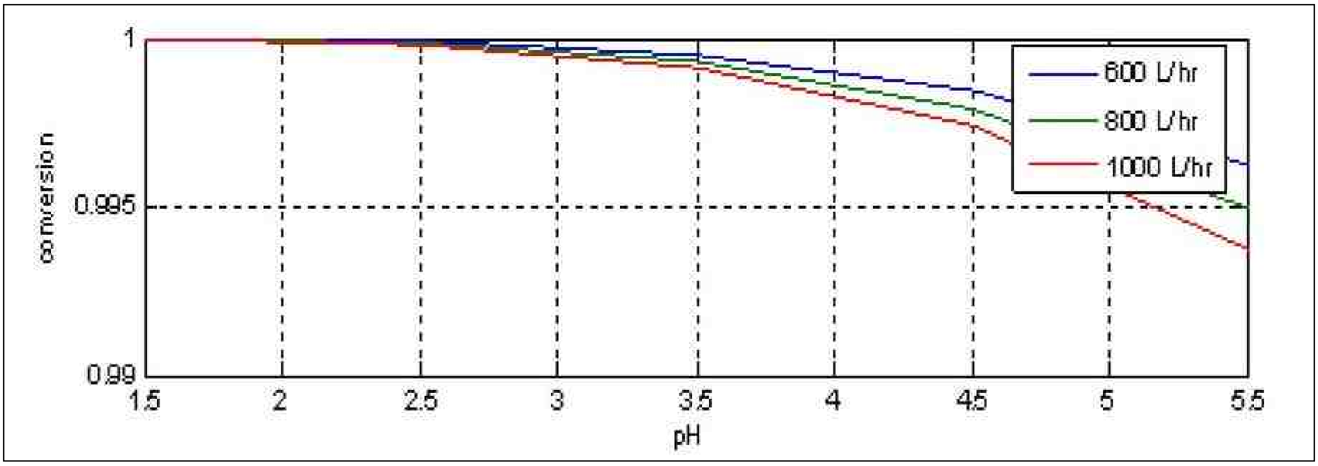

Figure 7—*Variation of Cr (VI) with changing pH at different wastewater flow rates; S (IV):Cr (VI) = 5, temperature = 20°C and input Cr (VI) = 150 mg/L.*

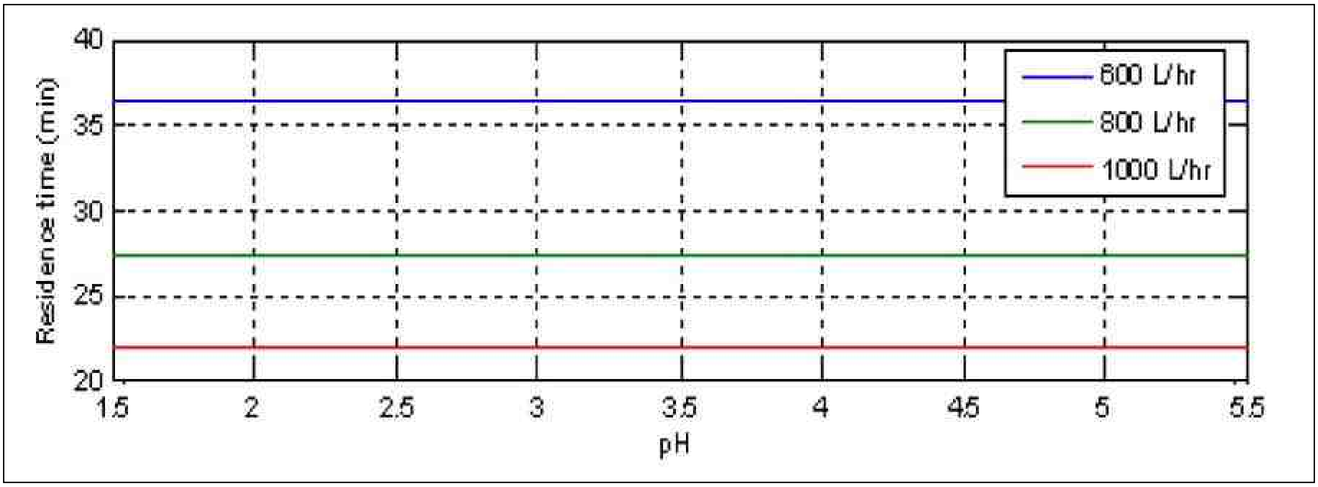

Figure 8—*Variation of wastewater residence time with changing pH for different flow rates, S (IV):Cr (VI) = 5, temperature = 20°C and input Cr (VI) = 150 mg/L.*

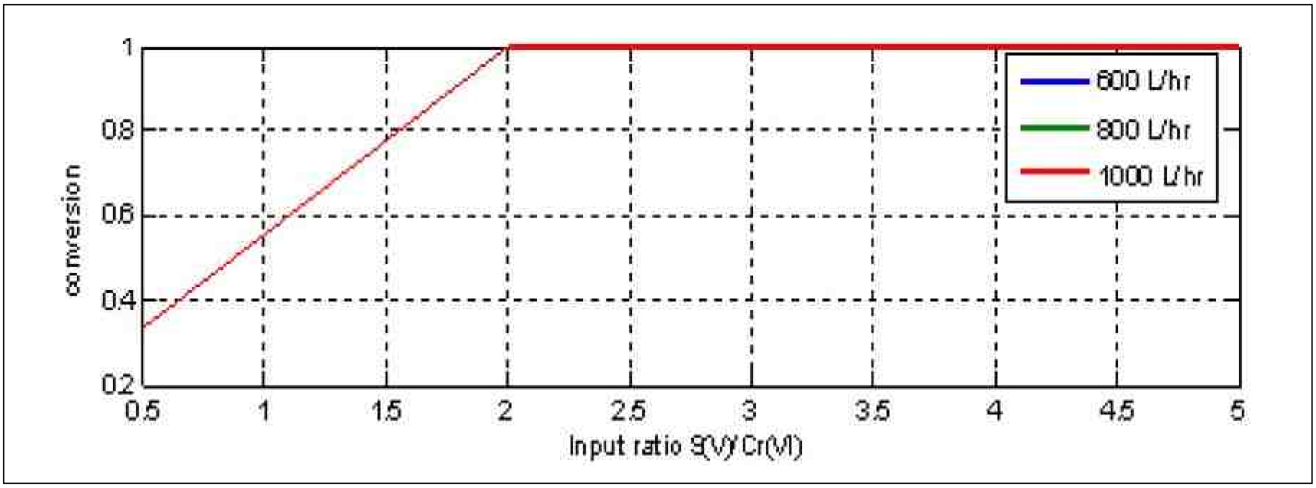

Figure 9—*Variation of Cr (VI) conversion with changing input ratio of S (IV):Cr (VI) at different flow rates; pH = 2.5, temperature = 20°C and input Cr (VI) = 150 mg/L.*

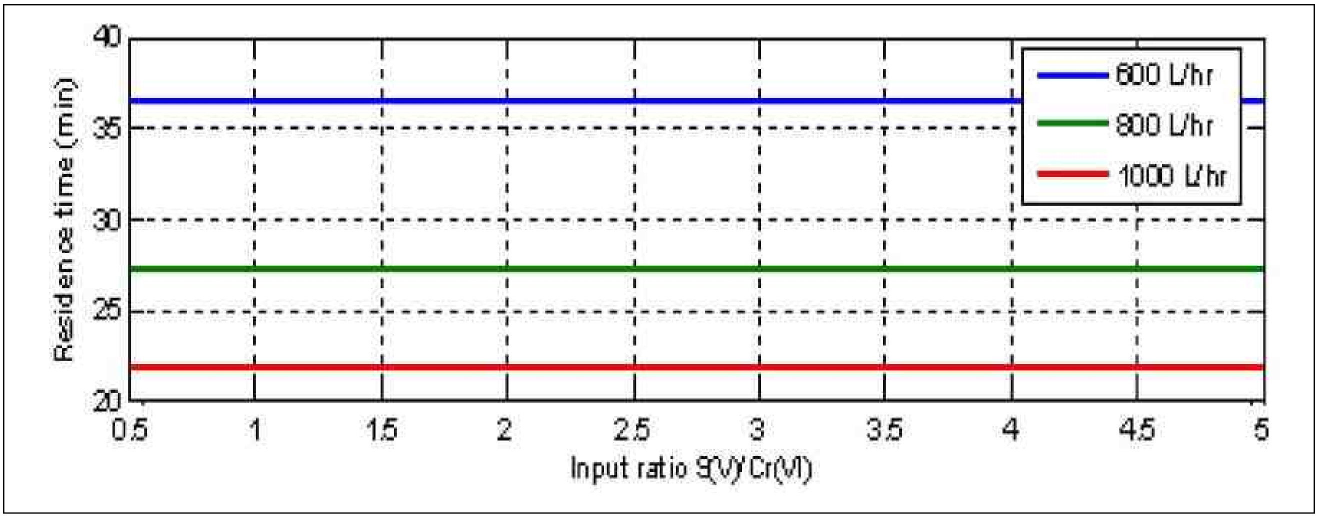

Figure 10—*Variation of wastewater residence time for different flow rates at varying ratios of S (IV):Cr (VI), pH = 2.5, temperature = 20°C, input Cr (VI) = 150 mg/L.*

Cr (VI) reduction

Figure 4 shows the Cr (VI) conversion model response to varying input conditions. A typical series of changes that may take place in the treatment plant is illustrated. Low concentration represents a situation where there is no flow of waste from the plating process. High concentrations represent the situation where there are spills of plating solution into waste. The concentration of Cr (VI) varies from 2.0 to 100 mg/L, while the pH varies from 1.5 to 3.5. The model accordingly responds to changing input conditions. This model can predict the treatment efficiencies, residence time and the amount of reagent required.

Figure 5 shows the relationship of Cr (VI) conversion with changing input of Cr (VI) concentrations at different waste flow rates. Cr (VI) varies from 5.0 to 150 mg/L. The conversion of chromium increases with increasing concentration of Cr (VI) in the feed waste.

Figure 6 shows the wastewater residence time at different flow rates. The flow rate is varied from 600 to 1000 L/hr. The residence time decreases with increasing feed flow rate of waste, showing an inverse proportionality.

The following can be deduced from Figs. 5 and 6:

- At a low residence time, the conversion is low.
- Wastewaters with low concentrations require longer residence time, while high concentrations require short residence times.

Figure 7 shows the relationship of Cr (VI) conversion with varying pH at different waste feed flow rates. The pH is varied from 1.5 to 5.5. The flow rate is varied from 600 to 1000 L/hr. Chromium conversion decreases with increasing pH and flow rate. A significant decrease in Cr (VI) conversion is observed from a pH of 4.5 to 5.5.

Figure 8 shows the wastewater residence time at different flow rates and at varying reaction pH values. The residence time decreases with increasing flow rate.

The following can be deduced from Figs. 7 and 8:

- High pH reduces the conversion.
- The optimum pH is 2.5

Figure 9 shows the response of the model to varying input ratios of metabisulfite to Cr (VI) at different waste flow rates. The metabisulfite to Cr (VI) ratio is varied from 0.5 to 5.0. The chromium conversion increases with increasing ratio for all flow rates. The Cr (VI) conversion reaches 1.0 at a metabisulfite to Cr (VI) ratio of 2.0. If the ratio increases beyond 2.0, this results in excess metabisulfite.

Figure 10 shows the wastewater residence time for different flow rates with varying ratios of metabisulfite to Cr (VI). The residence time decreases with increasing flow rate. The residence time is independent of the ratio of metabisulfite to Cr (VI).

The following can be deduced from Figs. 9 and 10

- The optimum feed metabisulfite to Cr (VI) ratio is 2.0.

Conclusion

From the results of multiple variable inputs, it can be concluded that the models respond in a logical manner and in accordance with literature postulations. The models only depend on the waste input composition and hardware. It is applicable to any conventional treatment hardware arrangement.

The limitations of this model may include the influence of other parameters which may be present in metal finishing waste. These parameters include carbonate, dissolved oxygen, conductivity and the oxidation reduction potential of water. Such parameters can alter the rate of metal oxidation and reduction.

The model can predict the size and type of hardware required, treatment efficiencies and time required for treatment. A schematic diagram of a typical treatment system is shown in Fig. 11.

The following are the conclusions that are drawn from the models:

- At low residence times, the conversion is low.
- Wastewaters with low concentrations require longer residence times, while high concentrations require short residence times.
- High pH reduces the conversion. The optimum pH is 2.5
- The optimum feed metabisulfite to Cr (VI) ratio is 2.0.
- The amount of caustic required is directly proportional to the wastewater pH and the target pH.
- Low concentrations of caustic solution result in high pumping costs, due to the enormous amounts of liquid to be pumped in the case of neutralizing strong acid streams.

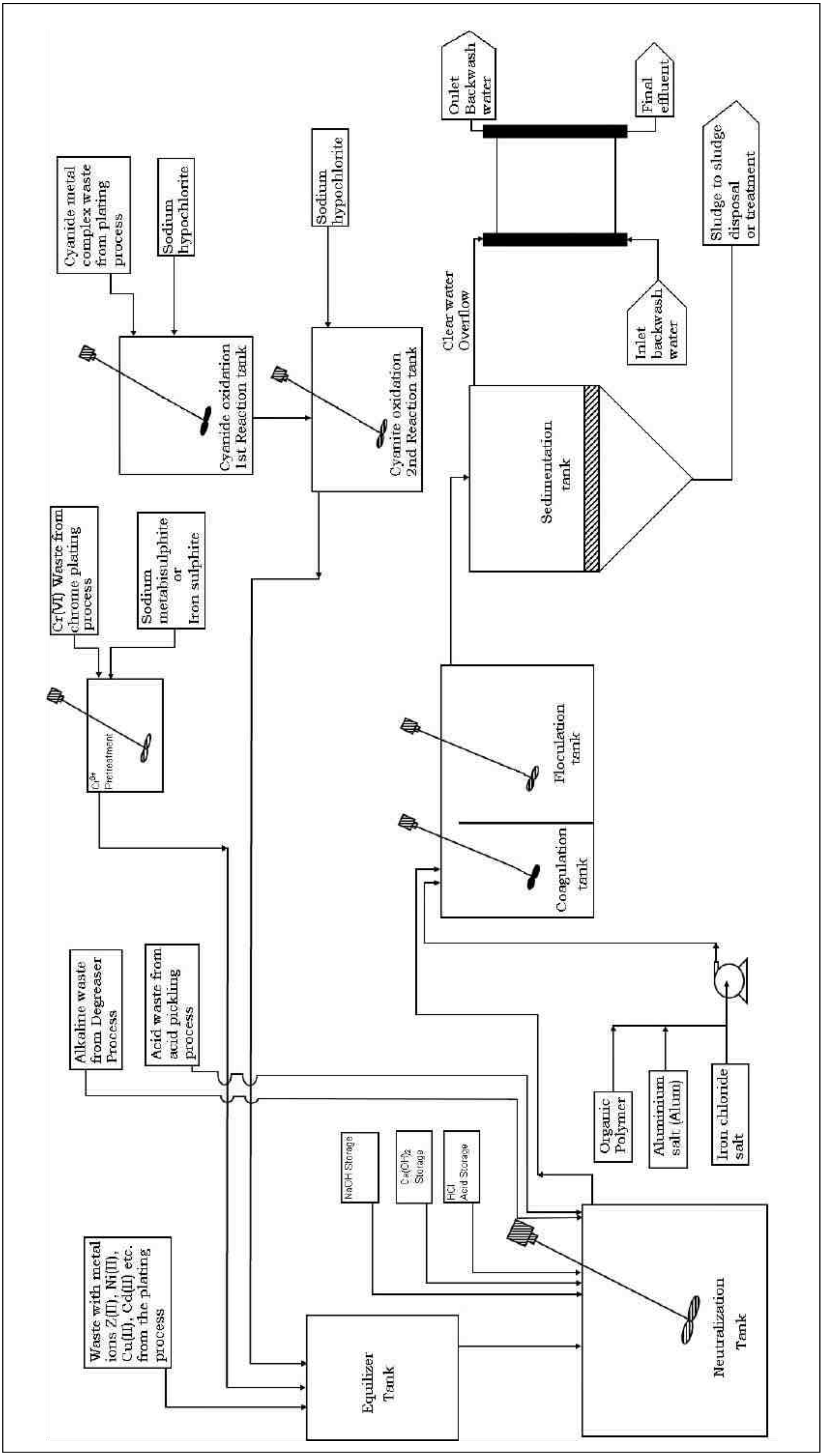

Figure 11—*Conventional method for treating electroplating wastewater treatment.*[19]

Appendix

Stoichiometric table for reaction

In the reaction mechanism below, chromic acid is chosen as a basis reactant. From the balance reaction, a stoichiometric table is developed.

$$2CrO_3 + 3Na_2SO_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Na_2SO_4 + 3H_2O$$

$$aCrO_3 + bNa_2SO_3 + cH_2SO_4 \rightarrow dCr_2(SO_4)_3 + eNa_2SO_4 + fH_2O$$

Table 1

Stoichiometric table for a reaction

Species	*Output concentration, mg/L*
A	$[CrO_3] = [Cr^{+6}] = [Cr^{+6}]_{init}(1 - X)$
B	$[Na_2SO_3] = [S^{+4}] = [Cr^{+6}]_{init}(\Theta_{S^{+4}/Cr^{+6}} - b/a\,X)$
C	$[H_2SO_4] = [H^{+}] = [Cr^{+6}]_{init}(\Theta_{H^{+}/Cr^{+6}} - c/a\,X)$
D	$[Cr_2(SO_4)_3 = [Cr^{+3}] = [Cr^{+6}]_{init}(\Theta_{Cr^{+3}/Cr^{+6}} + d/a\,X)$
E	$[Na_2SO_4] = [Cr^{+6}]_{init}(\Theta_{Na_2SO_4/Cr^{+6}} + e/a\,X)$

Development of design equations

Chromium reduction is carried out in a continuous stirred tank. This tank is considered a continuous stirred tank reactor (CSTR) since there is a reaction and mixing. The mixing is achieved by mechanical stirring. The design equation is developed based on these assumptions:

- The feed and outlet are at steady state.
- The tank content is perfectly mixed
- There is no accumulation inside the reaction tank.
- There are no dead zones in the reaction tank.

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