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# Model Based Process Analysis And Tool Development For Sustainable Electroplating Operations

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**MODEL BASED PROCESS ANALYSIS AND TOOL DEVELOPMENT FOR  
SUSTAINABLE ELECTROPLATING OPERATIONS**

**by**

**NAVDEEP BHADBHADE**

**THESIS**

Submitted to the Graduate School

of Wayne State University,

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in partial fulfillment of the requirements

for the degree of

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Approved By:

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Advisor

Date

## DEDICATION

*To My family, Mother and Father.*

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## CHAPTER 1

### INTRODUCTION

Since electroplating is one of the most polluted industries in United States, waste management is of outmost importance. Virtually manufacturing of all precious metal products involve electroplating. According to data provided by United States census bureau, there are over 3,000 electroplating establishments across the United States. These electroplating plants generate more than 100 chemicals, metals, non-metals contaminants that are regulated by EPA. The waste generation in electroplating facility should be significantly reduced in order to prevent pollution and reduce end of the pipe costs. According to EPA waste management hierarchy, source reduction recycle/reuse and source pretreatment are amongst most desirable options (Rittmeyer, 1991).

Source reduction can be considered as most profitable way of waste minimization since, it also aims at reducing the use of raw materials and utilities (e.g. cleaning chemicals, rinse water). Source reduction can be realized through (i) Process Equipment modification, (ii) Change in technology, (iii) Material substitution and (iv) Process control and optimization. In previous years, a variety of source reduction strategies has been developed. These strategies can be classified into the categories of drag out minimization, bath life extension, rinse water reuse, cyanide free solution substitution, material change and good operating practice (Gong *et al.*, 1991). Due to process complexity and lack of sensors, a successful implementation of source reduction strategies must rely on extensive knowledge, experience, expertise and sufficient process information. Unfortunately, the knowledge and expertise are not always available locally and information is often incomplete and imprecise (Gong *et al.*, 1997). To help electroplaters

implement source reduction strategies a simulation tool is developed based on dynamic models developed of unit operations involved in electroplating. This simulation tool is expected to aid electroplaters in quantitative decision support in cleaning, rinsing and plating operations.

## 1.1 Electroplating System

Electroplating is an electro deposition process for producing dense uniform and adherent coating, usually for of metal or alloys, upon a surface by act of electric current (Lou and Huang, 2006). Electroplating occurs on the surface when metal work piece is placed in solution containing dissolved metal ions. The metal work piece acts as cathode in an electrochemical cell, attracting metal ions from solution. Ferrous and non-ferrous metal work pieces are typically electroplated with aluminum, brass, bronze, cadmium, chromium, copper, iron, lead, nickel, tin and zinc.

Before electroplating takes place, work piece must be cleaned of any dirt or previous plating. Cleaning operation involves removal of grease, oil, soil and oxide films in numerous steps. This ensures good electroplating adhesion. A rinsing step follows every cleaning and plating operation. More than one rinse may be required. Rinsing will remove any residual process solution left on the surface of the work piece.

Electroplating facilities are mainly job shops. They receive parts manufactured by others and apply electroplating process to coat them with one or combination of different metallic coatings. According to United States census bureau, a job shop is usually a small business with average number of employees less than 50 and annual sales less than \$5 million. Most of the job

shops are located in areas such as Chicago, Detroit, and Cleveland and in areas like New York, California.

Other type of electroplating facility is captive shops. Here electroplating operations are performed for in house manufactured parts. Captive shops can be found throughout the nation in number of large manufacturing corporations including major airline manufacturers, computer and electronic manufacturers, hardware and automobile manufactures.

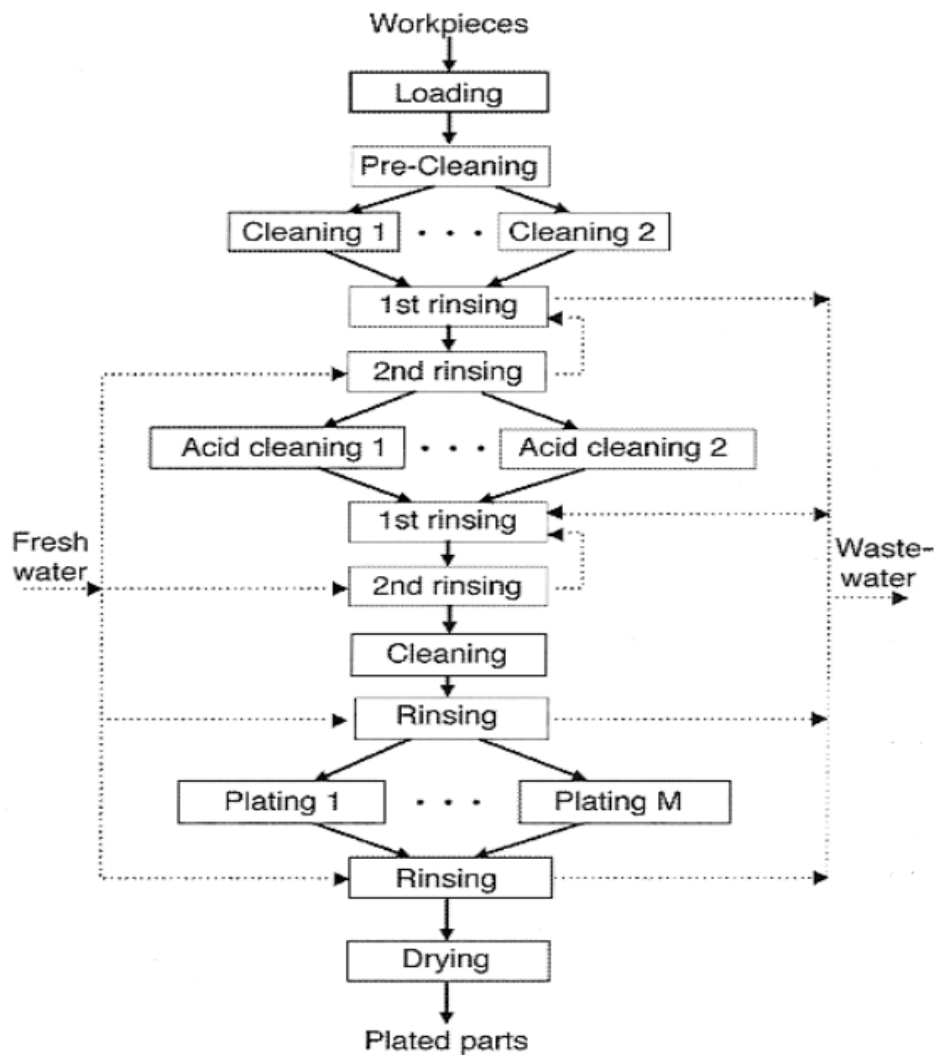


Figure 1.1. Typical electroplating process.

### 1.1.1 Waste streams

An electroplating facility generally contains number of cleaning units, rinsing units and plating units. These unit operations on electroplating facility give rise to several types of waste streams. Most of job shops rely on wastewater pretreatment facilities to comply with federal regulations.

Waste streams generated in an electroplating plant can be classified as wastewater, spent cleaning solvent, spent plating solutions, wastewater treatment sludge and miscellaneous solid waste. Table 1.1 indicates waste generated in electroplating industry. A major portion of wastewater comes from rinsing steps. Wastewater also comes from leakages, spillage, cleaning and dumping process solution. A plant may generate 80 to 200 m<sup>3</sup> of wastewater per day. Various solvents are used for removing oils and grease from surface of the metal. Thus, large quantities of spent solvents are generated. All process bath solutions are removed from process bath after exceeding their useful life. Oil, grease, dirt removed from the surface of the work piece along with chemical used to clean the surface forms base sludge in cleaning tank and rinsing tank. Treatment residue from wastewater treatment also generates sludge. Data from American electroplaters and surface finishers, National Association of surface finishers and EPA shows that daily discharge of wastewater from electroplating facility can be as large as 420,000 gallons with an average of 340,600 gallons. Annual water utility and treatment costs average \$100,000 cumulatively costing \$670 million for complete industry. Major concerns for industry are availability of landfills and cost of disposal. Average annual sludge generation is 158,272 lbs. at a cost of \$80,000.

Table 1.1. Process Wastes generated in electroplating (Palmer *et al.*, 1988).

Waste Category	Waste description	Process origin	Composition
Waste water	Waste rinse water	<ul style="list-style-type: none"> <li>• Drag out</li> <li>• Cleaning</li> <li>• Spills</li> </ul>	Same as the composition in relevant process solutions
Spent Solvent	Spent alkaline cleaning solution	Aqueous cleaning	NaOH, Na <sub>2</sub> CO <sub>3</sub> , Cyanide, soils, saponified and emulsified soils
Spent solution	Spent plating solution	Electroplating	Same as composition relevant to plating bath
Treatment residue	Degrease sludge	Solvent recycling	kerosene, naphtha, toluene, ketones, alcohols, ethers, halogenated hydrocarbons, oils
	Filter sludge	<ul style="list-style-type: none"> <li>• Electroplating</li> <li>• Waste treatment</li> </ul>	Same as above along with HCl from solvents Methyl hydroxide, Sulfur carbonates
	<ul style="list-style-type: none"> <li>• Wastewater treatment sludge</li> <li>• Ion exchange resin reagents</li> </ul>	Demineralization of process water	Brine, HCl, NaOH

### 1.1.2 Existing methods for source reduction

As per EPA's WM hierarchy, source reduction is of highest importance since, it minimizes the waste generation in the first place. Cleaning tanks used in electroplating lines contain sludge formed by dirt that is removed from surface of work pieces. These tanks are replenished periodically to maintain operational quality. Chemicals they contain are lost through evaporation, spills, and drag out. Wastewater from rinsing tank contains cleaning solutions from

surface of work pieces. Spent solution from plating tank contains toxic compounds such as heavy metal ions and cyanides. It is beneficial for electroplaters to curb this waste generation at its very source and reduce end of the process waste. Numerous WM strategies have been developed for source reduction. These approaches can be classified as follows (Freeman, 1988).

- Drag-out minimization
- Bath life extension
- Rinse water minimization
- Use of cyanide free solution
- Alteration of plating metals
- Operational improvement

**Drag out minimization.** Drag out is the volume of solution that is carried over the edge along with the parts. Consequently, this solution enters in following rinsing tanks and becomes a major constituent in waste stream generated from rinse tank.

Some strategies to minimize drag out are,

- Reduce the speed of withdrawal of work piece/ barrel from cleaning tank
- Minimize concentration of process bath
- Increase solution temperature to lower the surface tension
- Use surfactants to lower surface tension
- Install drainage boards between process tanks
- Enlarge hole size on barrels
- Rotate barrel above the tank

**Bath life extension.** Protecting process bath from contamination can extend bath life.

This involves improving rinse efficiency.



Bath life extension strategies are:

- Install filtration
- Adopt proper replenishment strategies
- Use de-ionized water
- Install electrolytic dummyming
- Remove solids by precipitation

**Rinse water minimization.** Most hazardous waste in electroplating plant results from rinsing which follows every cleaning and plating operation. Reducing rinse water consumption will result in reducing the amount of sludge formed.

Strategies for reducing rinse water consumption are,

- Use longer contact time
- Adopt counter current rinse
- Implement multistage static rinse system
- Install flow restrictors
- Install conductivity/pH meters

**Use of cyanide-free solution.** Cyanide is highly toxic substance. It exists in water as HCN, a weak acid. Volatile HCN is highly toxic and indicative of serious pollution problem. It is highly desirable to therefore, find alternatives to use of cyanide in plating solution.

**Alternative plating metals.** A replacement of plating material is feasible in many cases e.g. cadmium plating can be replaced by material such as zinc, titanium etc. however, replacement judgment should be based on quality satisfaction and other economic and environmental criteria.

**Operational improvement.** System optimization can always lead to improved operation, reduced chemical and rinse water consumption and reduced waste. Simple improvements such as effective fluid control, preventing accidental spills, frequent inspection for leaks and proper maintenance scheduling can contribute to source reduction in considerable amount. Usually improving waste management is cheaper than many other approaches for WM

## 1.2 Literature Survey

United States has over 3,000 electroplating facilities that generate large amount of waste that is categorized as hazardous. Due to amount of waste generated, electroplating is considered one of the dirtiest industries in United States. Amongst all the ways to reduce this waste, source reduction has the highest priority according to EPA WM hierarchy. Source reduction aims to prevent the generation of waste in first place.

Huang *et al.* (1991) presented an expert system called Min-Cyanide for waste minimization in electroplating plant. Min-Cyanide evaluates options such as drag out minimization, bath life extension, rinse water reduction, non-cyanide solution and alternative for plating material. System helps user to identify most effective way of achieving source reduction. Huang *et al.* (1997) presented dynamic models for cleaning and rinsing operations in electroplating industry. Cleaning and rinsing are two key unit operations in electroplating. However, these two operations are major source of wastes generated during electroplating. To reduce the generation of waste, thorough understanding of dynamic behavior of the system is required. Dynamic response of the system can be studied with help of first principal based dynamic models. Waste streams can be significantly reduced by operational improvement and

process modification. This requires rigorous multidisciplinary knowledge. Expertise required for this is usually not available. Moreover, process data available is often imprecise. Huang and Luo (1997) developed an intelligent decision support system namely WMEP advisor for waste management. The system is based on first principal based mathematical models for cleaning and rinsing systems. Sludge generated in electroplating plant is one of the major reasons of concern for environmentalist. Effective reduction of sludge requires deep understanding of sludge generation mechanisms. Luo *et al.* (1998) presented a study in which they discussed models developed to predict the sludge generation from different sources. Industrial pollution prevention is a national strategic goal for environmental protection. Over past years, numerous pollution prevention (P2) technologies have been implemented in electroplating industry. These technologies have been greatly successful at reducing toxicity of end of the pipe waste. Lou and Huang (2000) presented new generation of P2 technologies that can also make profit for the plant viz. profitable pollution prevention P3. Basic feature of these technologies is both environmental and economic benefits.

In electroplating lines chemical losses occur from cleaning and plating units to rinsing units through drag out causes dramatic increase in operating cost as well as increase in waste treatment cost. Xu and Huang (2005) presented an optimal reverse drag out system. This method provides comprehensive design and operational information so that designers can identify most desirable design for chemical recovery system. Aiming at P3 technologies, design and operational technologies can be developed to enhance manufacturing sustainability by increasing energy and material efficiency, achieving source reduction and safety assurance. Xiao and Huang (2012) presented opportunities for an effective integration of P3 technologies. They showed that integrated P3 technology can be identified through a technology implementation approach based

on process fundamentals and engineering practicability needed for process design modification and operational strategy development. A successful application of IP3 was demonstrated in electroplating industry.

### **1.3 Sustainability Concerns in Electroplating**

Sustainable manufacturing is the creation of manufactured products through economically sound processes that minimize negative environmental impacts while conserving energy and natural resources. Electroplating industry in United States has nearly 3,000 facilities scattered across the nation. According to Metal Finishing Overview published by EPA, these facilities produce products worth \$5.1 Billion. According to toxic release inventory report in 2013, these facilities released approx. 41 million tons of chemicals in waste. Out of this waste, 72 % waste was managed and 28 % was disposed and released to environment. This indicates a total of approximately 29.5 million tons of waste generated is treated in a year. Cost of treating such a large amount of waste is huge. Most of the waste generated in electroplating plants is end of line waste that can be minimized or even be eliminated.

Excessive use of chemicals in cleaning and plating tanks poses serious threat to economic and social sustainability. Excessive chemical use directly causes loss of chemicals through spills and drag out, which eventually results in economic loss. Moreover, this causes excessive sludge generation and increase in the volume of the waste to be treated which eventually results in increased cost for waste treatment. Emissions resulting from excessive use of chemicals in plating tank seriously jeopardizes social sustainability by making environment unsafe for people working in electroplating facility. Hence, these emissions are highly regulated under National

Emission Standards for Hazardous Air Pollutants by EPA. Emission control techniques such as mist eliminators, fume suppressants and wet scrubbers are typically used in order to comply with these regulations.

Minimization of end of line waste generation is foundation for sustainable electroplating. To achieve waste minimization of reducible waste, in depth understanding of process and knowledge of how production and waste management are correlated is necessary. To gain in depth understanding of process and knowledge of correlation between production and waste management, detailed information about things like maximum permissible dirt residue on the parts before cleaning, optimal setting of chemical solvent concentration during cleaning stages, Minimum water flow rate for each rinsing step, Minimum processing time needed and optimum rinsing system configuration should be available. Simulation tool presented in this work is expected to help user to analyze the process and obtain above-mentioned information. This information in turn is useful in taking decisions for waste minimization and achieve sustainability in electroplating.

#### **1.4 Thesis Organization**

In this work, a simulation tool developed to help minimize the waste generated in cleaning and rinsing operation is presented. In first part of thesis, general electroplating process is described. Sources of waste generation in electroplating facility are identified and source reduction concept and methods to achieve it are explained. In chapter 2 mathematical models developed for cleaning and rinsing system are explained along with detailed explanation of process. Numerical methods are at the heart of simulation tool. These numerical methods are

explained in chapter 2. Chapter 3 includes description of interface of software tool. Internal structure of simulation tool and functions of all the parts of software are also explained in chapter 3. Chapter 4 explains application of software tool to achieve source reduction through case studies.

## CHAPTER 2

### MATHEMATICAL MODELS

The goal of these mathematical models is to predict the dynamics of chemical concentration, dirt residue and contaminant concentration in cleaning and rinsing tank respectively.

#### 2.1 Cleaning Model

In a cleaning tank, dirt (oil, soil, and solid particles) on the surface of parts is removed by applying certain types of energy, such as mechanical, chemical, thermal, electrical, and/or radiation energy. The loose dirt on parts sinks to the bottom of the tank as sludge; the dirt remaining on the surface is carried to succeeding tanks together with the drag-out solution. The model characterizing dirt removal and chemical consumption is as follows (Gong, *et al.*, 1997).

$$A_p \frac{dw_{pc}(t)}{dt} = -r_{pc}(t) \quad (2.1)$$

$$r_{pc}(t) = \gamma_c(t)C_a(t)w_{pc}(t) \quad (2.2)$$

$$\gamma_c(t) = \gamma_0 \left( 1 - e^{-\alpha(t-t_0)} \right) \quad (2.3)$$

$$V_c \frac{dC_a(t)}{dt} = -\frac{r_{pc}(t)}{\mu} + w_c(t) \quad (2.4)$$

where  $A_p$  is the total surface area of parts ( $\text{cm}^2$ ),  $r_{pc}(t)$  is the dirt removal rate ( $\text{g/min}$ ),  $\gamma_c(t)$  is the looseness coefficient ( $\text{cm}^2 \cdot \text{gal}/\text{gal} \cdot \text{min}$ ),  $\gamma_0$  is the kinetic constant ( $\text{cm}^2 \cdot \text{gal}/\text{gal} \cdot \text{min}$ ),  $w_{pc}(t)$  is the amount of dirt on parts ( $\text{g}/\text{cm}^2$ ),  $C_a(t)$  is the chemical concentration ( $\text{gal}/\text{gal}$ ),  $V_c$  is the capacity of

the cleaning tank (gal),  $\alpha$  and  $\mu$  are model parameters and  $w_c(t)$  is the rate of chemical addition (gal./min).

## 2.2 Rinsing Model

After cleaning, the loose dirt on the parts and drag-in should be washed out in the rinsing step. The efficiency of the dirt removal is largely dependent on the gradient between the cleanness of the rinse water, the dirtiness of the parts, and the uniformity of the rinse water in the tanks. On the other hand, the configuration of a rinsing process and the water flow rates are directly related to the wastewater minimization and parts rinsing quality. To derive an optimal configuration and water flow rates, we need to know the cleanness of barrels of parts after rinsing. This requires the models for parts and water of each rinsing tank (Gong, *et al.*, 1997).

$$A_p \frac{dw_{pr}(t)}{dt} = -r_{pr}(t) \quad (2.5)$$

$$r_{pr}(t) = k_r \gamma_c(t_e) (\theta (w_{pr}(t) - w_{pc}(t_e)) - x_r(t)) \quad (2.6)$$

$$V_r \frac{dx_r(t)}{dt} = r_{pr}(t) + F_r(t)(x_r(t_{in}) - x_r(t)) \quad (2.7)$$

where  $w_{pr}(t)$  is the dirt on parts ( $\text{g}/\text{cm}^2$ ),  $w_{pc}(t_e)$  is the dirt on parts when leaving the cleaning tank ( $\text{g}/\text{cm}^2$ ),  $r_{pr}(t)$  is the dirt removal rate ( $\text{g}/\text{min}$ ),  $x_r(t)$  is the pollutant composition ( $\text{g}/\text{gal-water}$ ),  $\gamma_c(t_e)$  is the looseness of dirt when leaving the cleaning tank ( $\text{cm}^2 \cdot \text{gal}/\text{gal-min}$ ),  $\theta$  and  $k_r$  are model parameters,  $F_r(t)$  is the rinse water flow rate ( $\text{gal}/\text{min}$ ),  $V_r$  is the rinsing tank capacity (gal), and  $x_r(t_{in})$  is the pollutant concentration in influent rinse at time  $t$  ( $\text{g}/\text{gal-water}$ ).

The parameters of these models are determined according to the chemicals used, process equipment, and experimental data under specific operating conditions.



When a barrel of parts is withdrawn from a rising tank, rinse water still flows through the tank. The contaminant concentration in the tank is reduced it can be derived by the following equation

$$V_r \frac{dx_r(t)}{dt} = F_r(t)(x_r(t_{in}) - x_r(t)) \quad (2.8)$$

### 2.3 Plating Model

Electroplating is the key step for plating quality. It is of both environmental and economic importance to determine optimal operating conditions and plating processing time. In a plating tank, it is always expected that metal and chemical concentrations are reduced while the plating quality and production rate are guaranteed. This results in the following model (Gong, *et al.*, 1997).

$$\frac{dm_p(t)}{dt} = r_p \quad (2.9)$$

$$r_p = f_p(C_s, \mu_p)g_p(h_p, \gamma_p) \quad (2.10)$$

$$\rho V \frac{dC_s(t)}{dt} = -r_p \alpha_p \quad (2.11)$$

$$\alpha_p = \psi_p(C_s, \mu_p) \quad (2.12)$$

where  $m_p$  is the amount of metal plated on parts (g),  $C_s$  is the concentration of solution in the plating tank (g/gal-water),  $r_p$  is the reaction rate of plating process (g/min),  $\mu_p$  is the efficiency of the solution,  $\gamma_p$  is the factor of effective of the shape of parts,  $h_p$  is the thickness of the plating metal on parts (cm),  $V$  is the volume of plating tank (gal),  $\rho$  is the density of the solution (g/gal), and  $\alpha_p$  is the model coefficient.

## 2.4 Sludge Model

In cleaning and rinsing tanks, most of the dirt on the surface of the parts can be removed by chemicals into chemical solutions and rinse water. The mixture of chemical and dirt will eventually form a sludge. Normally sludge can be identified as either wet or dry. Dry sludge is usually net quantity of waste by weight. Wet sludge is quantified by its volume. In this model, only dry sludge is quantified. According to sludge sources, the base sludge can be found in cleaning and rinsing tanks. The base sludge ( $S_T$ ) in cleaning tank includes dirt removed from parts ( $S_D$ ) and chemical used ( $S_C$ ) to clean the surface of the parts. In rinsing tank sludge includes contaminates in makeup water ( $S_W$ ) used for ring and sludge carried through drag ( $S_G$ ) out from cleaning tank. Total sludge is sum of all sludge (Luo *et al.*, 1998).

$$S_T = S_D + S_C + S_W + S_G \quad (2.13)$$

$$S_D = \sum_{i=1}^N (A_i \sum_{j=1}^n w_{i,j}) \quad (2.14)$$

$$S_C = \sum_{i=1}^N (A_i \sum_{j=1}^n (w_{i,j} k_j / \mu_j)) \quad (2.15)$$

where  $A_i$  is total surface area of  $i$ th barrel of parts (cm<sup>2</sup>),  $K_j$  is precipitation constant for  $j$ th cleaner,  $N$  is number of barrels processed per day,  $n$  is number of kinds of dirt on the surface of the parts,  $W$  is the amount of  $j$ th kind of dirt removed from  $i$ th barrel,  $\mu$  dirt removal capacity of cleaner.

## 2.5 Numerical Method

Numerical methods for solving ODEs are based on formulae that are essentially a polynomial representation of the solution based on current and/or past solution values and derivatives at those values. Mathematical models developed for cleaning and rinsing represent a system of differential equations. This system can be treated as initial value problem with values of chemical concentration, pollutant concentration in rinsing tank and dirt residue known at time  $t=0$ . The task of generating a dynamic response includes finding values of dependent variables at specific intervals of time. This can be achieved with help of Runge-Kutta 4<sup>th</sup> order methods.

Runge-Kutta 4<sup>th</sup> order method, an algorithm for explicit Runge-Kutta 4th order method is developed in Matlab to develop the dynamics of cleaning and rinsing processes. Cleaning and rinsing systems are represented by coupled ordinary differential equations. If initial value problem is presented as

$$\frac{dc}{dt} = f(c, w, t) \quad (2.13)$$

$$\frac{dw}{dt} = g(c, w, t) \quad (2.14)$$

With  $c(t_0)=c_0$  and  $w(t_0)=w_0$ , then RK4 method can be used to find the values of  $c$  and  $w$  at time  $t_{n+1}$ .

$$c_{n+1} = c_n + \frac{h}{6}(k_1 + 2k_2 + 2k_3 + k_4) \quad (2.15)$$

$$w_{n+1} = w_n + \frac{h}{6}(l_1 + 2l_2 + 2l_3 + l_4) \quad (2.16)$$

$$t_{n+1} = t_n + h \quad (2.17)$$

Thus, the RK4 method generates an approximate value of dependent variable at every subsequent time value.

$$k_1 = f(t_n, c_n, w_n) \quad (2.18)$$

$$l_1 = g(t_n, c_n, w_n) \quad (2.19)$$

$$k_2 = f(t_n + \frac{h}{2}, c_n + \frac{k_1}{2}, w_n + l_1/2) \quad (2.20)$$

$$l_2 = g(t_n + \frac{h}{2}, c_n + \frac{k_1}{2}, w_n + l_1/2) \quad (2.21)$$

$$k_3 = f(t_n + \frac{h}{2}, c_n + \frac{k_2}{2}, w_n + l_2/2) \quad (2.22)$$

$$l_3 = g(t_n + \frac{h}{2}, c_n + \frac{k_2}{2}, w_n + l_2/2) \quad (2.23)$$

$$k_4 = f(t_n + h, c_n + k_3, w_n + l_3) \quad (2.24)$$

$$l_4 = g(t_n + h, c_n + k_3, w_n + l_3) \quad (2.25)$$

Thus, the next value of dependent variable is determined from present value plus the product of time interval and estimated slope. The slope is weighted average of four slopes.

$K_1$  or  $l_1$ : Slope at the beginning of the interval,

$K_2$  or  $l_2$ : slope at the mid-point of interval. Using slope  $k_1$  (or  $l_1$ ) to determine the value of dependent variables (C & W) at point  $t_n+h/2$ ,

$K_3$  or  $l_3$ : is also slope at mid-point but calculated using  $K_2$  (or  $l_2$ ),

$K_4$  or  $l_4$ : is the slope at the end of the interval,

Weighted average of the slope is given by

$$\text{Slope} = \frac{1}{6}(l_1 + 2l_2 + 2l_3 + l_4) \quad (2.26)$$

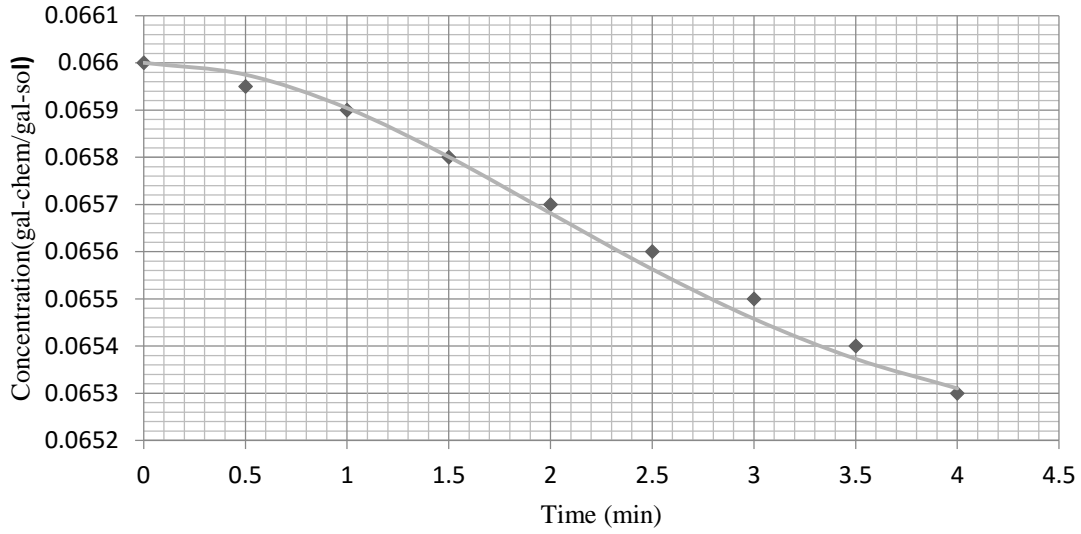
## 2.6 Parameter Fitting

Equations (2.3), (2.4), (2.6) and (2.7) contain certain physical parameters. These parameters depend upon type of cleaner used, type of material to be cleaned and type of soil (oil,

grease) to be removed. Values of these parameters are estimated by fitting the data generated in mathematical models proposed in earlier sections.

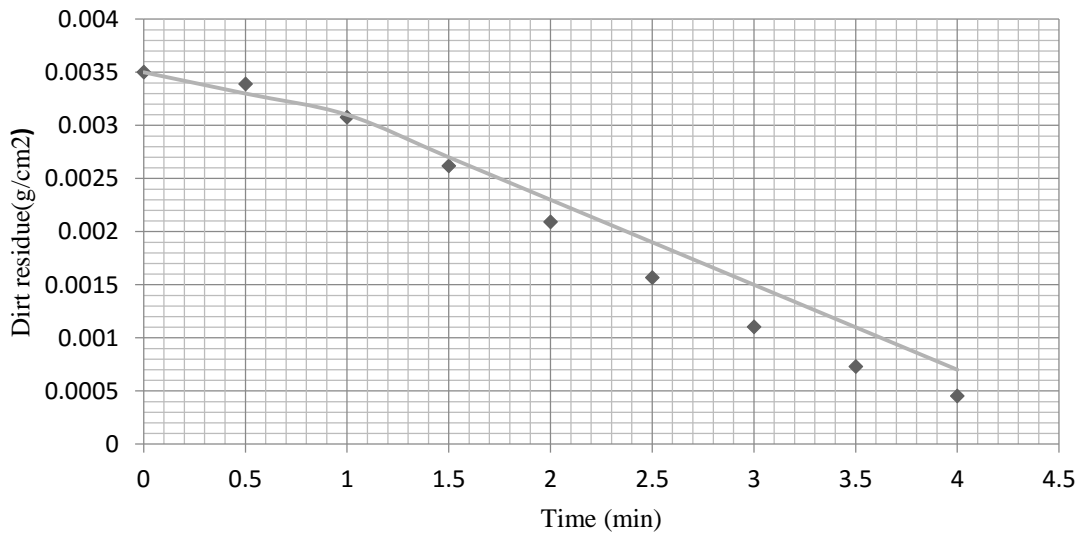
General approach in model fitting is to select an objective function which is measure of agreement between modeled and measured data and which is directly or indirectly related to adjustable parameters of model. Best-fit parameters are obtained by minimizing the objective function.

In present case, parameters  $\alpha$ ,  $\mu$  and looseness coefficient for cleaning system and  $\theta$  and mass transfer coefficient  $k_r$  are to be fitted in proposed model. Optimization framework is used to find the best-fit parameters. Excel spread sheet is used to find these parameters. The sum of the squares of difference between model values and actual data is selected as an objective function. Model values are calculated by solving proposed models using numerical methods. These values are then compared with measured values and sum of squares of residuals is calculated. The sum is set as a target cell for excel solver to minimize  $\alpha$ ,  $\mu$ ,  $\theta$ , looseness factor and mass transfer coefficient etc. are selected as adjustable cells. Excel solver then uses non-linear optimization algorithm to find optimum values of parameters that will minimize sum of squares of residuals.



Key: \_\_\_Model concentration ...Measured concentration

Figure. 2.1. Parameter fitting curve for cleaner concentration.



Key: \_\_\_Model concentration ...Measured concentration

Figure 2.2. Parameter fitting curve for dirt residue.

## CHAPTER 3

### SIMULATION SOFTWARE STRUCTURE

Mathematical modeling of transient processes give rise to a system of ordinary differential equations (principally from mass and energy conservation laws) that must be solved during the execution of dynamic process simulator.

#### 3.1 Simulation Software Architecture

Architecture of any simulation software depend upon computational strategy implemented in that software package. Three fundamental approaches are commonly used to solve system of differential algebraic systems.

##### 3.1.1 Sequential modular

In sequential modular approach, computations are performed unit by unit following a calculation sequence. This approach is more commonly implemented for steady state simulation. Incoming streams are either specified as inputs or initialized as tear streams. Using this information final steady state is obtained by iterative calculations. Iterations are continued until the convergence is achieved. Sequential modular simulator usually has four principal parts 1) Unit model subroutines that contain model equations for associated process equipment, 2) Physical property subsystem, 3) Numerical integrator and 4) A supervisory routine (Fagley and Carnahan, 1990). Sequential-Modular approach can also be implemented for dynamic

simulation. Solution has to be initialized in order to carry out dynamic simulation. This initialization process is carried out using sequential modular approach (Aspen plus guide, 2011).

### 3.1.2 Equation oriented

In equation-oriented approach, all modeling equations are assembled in a large system producing a system of differential algebraic equations for dynamic simulation. Solution is achieved by simultaneously solving all the equations. This approach provides better handling of recycles and flexible environment but at the expense of increased computational efforts. This approach is more suitable for dynamic simulation and real time optimization.

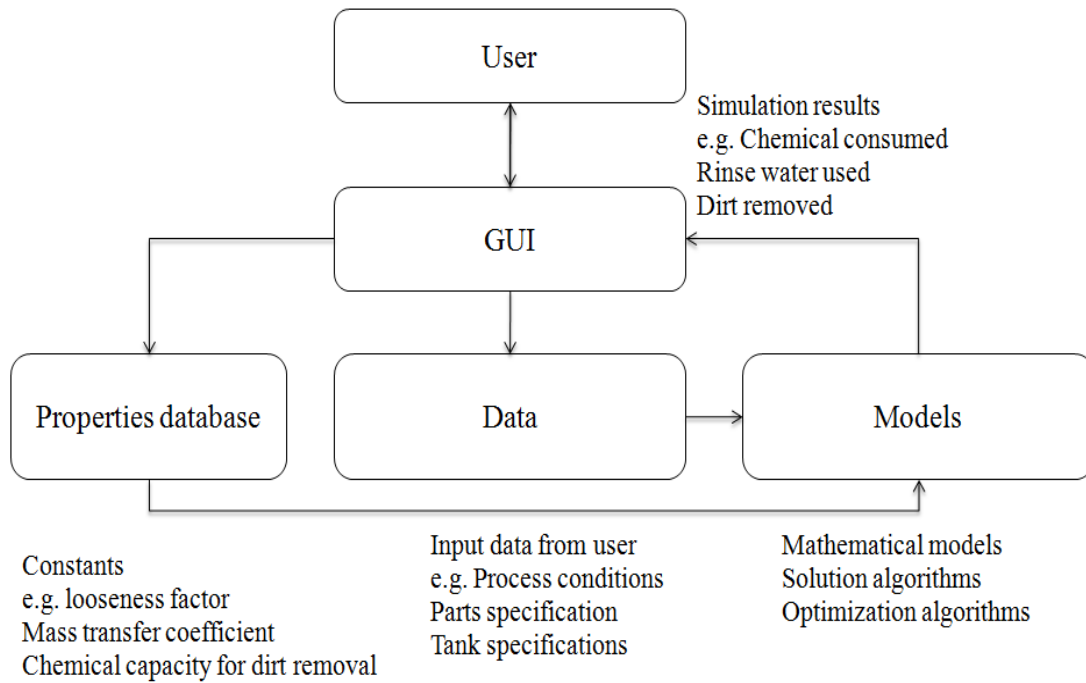


Figure 3.1. Simulation tool structure.



### 3.1.3 Simultaneous modular

This approach is combination of both approaches. Rigorous models are used at unit levels that are solved sequentially, while linear models, used at flow sheet level are solved globally.

## 3.2 Simulation Tool Structure

This simulation tool is developed to aid users to achieve source reduction. This tool is developed using MATLAB as platform. The approach relies on simulation of first principal dynamic models developed for processes involved in electroplating. Computational strategy used for this simulation tool is sequential modular approach. Each unit operation is represented by a set of ordinary differential equations that are solved by implementing Runge-Kutta 4th order and each unit is solved sequentially.

### 3.2.1 Property database

At the core of every simulation software, there are mathematical equations describing the physical or chemical phenomenon occurring in particular unit. These mathematical equations contain some physical constants. Every time when simulation run takes place, solver needs an access to these physical constants. Property database serves as storage for these constants. In present case, while simulating the process solver needs information like looseness factor of dirt, Mass transfer coefficient for rinsing process or the capacity of chemical to remove dirt. This information is stored in property database.

Electroplaters have to deal with number of types of metals that have various types of oxides, oils, greases deposited on their surface. Thus, aforementioned physical constants change with every pair of metal and dirt. Chemical capacity of removing dirt also changes with type of cleaner used. In present software, property database includes information about most commonly plated metals like Nickel, Steel, Stainless Steel, Copper, Titanium, Zirconium, Lead, Brass etc. and alkaline and acidic cleaner. User also has an option of manual input for physical constants.

### **3.2.2 Input data**

Present simulation tool is based on system of ordinary differential equations. This system of equations is simulated with aid of numerical methods. These numerical methods treat the problem as initial value problem. These initial values are the input from users. In this particular case these values include Process specifications like Initial Chemical concentration, Initial dirt residue, Number of barrels, Tank specification like tank volume rinse water flow rate, Parts specifications like radius, length ,weight of the barrel, shape of the part to be treated etc.

### **3.2.3 Solver**

This block of the software tool contains the algorithms used to dynamically simulate the system of odes. These algorithms utilize information from property database and user input to generate solutions. In present simulation tool, Runge-Kutta 4th order algorithm is developed to solve the system of equations. This algorithm uses user input as initial starting point for calculations and returns solution in discrete time steps. The solution is reported in numerical as well as graphical form. All the algorithms are developed as MATLAB codes.

### 3.2.4 Graphical user interface (GUI)

For present simulation tool GUI is divided in 3 primary parts viz. Process specifications which is the part where user has to input the values, Process performance, in this part numerical solutions are displayed and Graphical solution part which displays time plots of dependent variables of equations. This software tool has GUI with several windows. First window is home window where user has to select the operation to be evaluated. All other windows has a unit operation in each i.e. cleaning, rinsing and cleaning-rinsing.

### 3.3 Software Tool: Implementation and Functionality

The home screen of simulation tool contains push buttons to select the system to be analyzed (Fig. 1). This window also provides user with basic information about software tool that can be accessed by clicking on push button *help*.

This software tool offers analysis of cleaning, rinsing and cleaning-rinsing integrated system. These systems can be accessed by clicking on respective buttons on home screen. After selecting the system to be cleaned a window for that particular system pops up.

#### 3.3.1 Cleaning system analyzer

Before plating process can take place, it is essential that the surface of the metal piece to be plated should be cleaned. This cleaning process assures certain quality of plating layer adhesion. Generally, during the cleaning process for barrel plating, certain amount of cleaner is added either manually or automatically to a cleaning tank and then barrel full of parts to be

cleaned is dipped in it for specific time. Cleaner in solution absorbs dirt (i.e. oil, grease) from the surface. This dirt removed from the surface then forms a sludge and settles down in tank.

Cleaning system analyzer will help user to identify amount of cleaner consumed, amount of dirt removed from the surface and sludge generated at any given time. This window has input buttons on left side of the window. Inputs are separated in three different categories viz. part specification, process specification and tank specification (Fig. 3.3).

The menu bar of this window contains an option of operational mode in which cleaning system can be operated (Periodic addition, Single addition, and constant concentration) and an option to select type of cleaner and metal to be cleaned.

Parts specification takes input information about parts to be cleaned. This window has buttons such as shape of part, radius and length and weight of the barrel. Process specification parts takes input regarding initial conditions of unit operation. This window has input buttons such as approx. initial dirt, initial concentration, processing time, number of barrels and cleaning requirement. Tank specification takes input about physical specification of tank such as volume of tank and number of tanks.

System performance is separated in two different categories viz. parts cleanliness and chemical consumption (Fig. 3.4). Parts cleanliness displays values of percentage dirt removed and amount of dirt residue on the part after given time of cleaning. Chemical consumption displays amount of chemical consumed, concentration of cleaner after given period of cleaning and sludge generated during the process. Graphical results display dynamics of chemical consumption and dirt residue.

### 3.3.2 Rinsing system analyzer

After cleaning barrel of parts to be plated is rinsed before going in plating tank. Drag out from cleaning tank and dirt left on the surface are rinsed away in rinsing tank. Similar to cleaning module rinsing system analyzer has input buttons that ask for initial conditions of process and tank specifications (Fig. 3.5). At the bottom of the window, user can chose the way of operation of rinsing system in case of multistage rinsing i.e. co current or counter current. The output part of the window (Fig. 3.6) displays information about dirt removed from the parts in rinsing tank, rinse water consumption and pollutant concentration in rinsing tank. Graphical result window displays the dynamics of pollutant concentration in rinsing tank and dirt residue on the surface of metal in rinsing tank.

### 3.3.3 Cleaning rinsing analyzer

Cleaning rinsing analyzer is an integrated system. Which will help user to evaluate the performance of system under various operational modes when both cleaning and rinsing tanks are connected. This window is divided in three separate sections viz. parts specification, cleaning system and rinsing system. Similar to cleaning and rinsing modules, parts specification takes input information about parts to be cleaned. Cleaning system and rinsing system sections have both input and result section that displays all specifications of system as well as result values and dynamic response of the system. On top of the window, an option is provided for user to select operational mode.

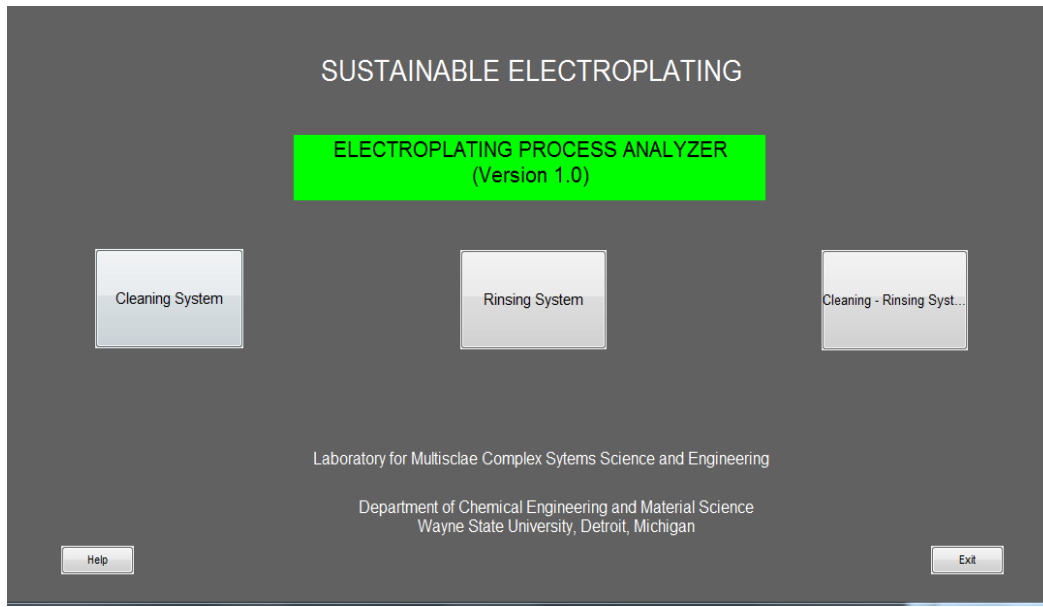


Figure 3.2. Home page.

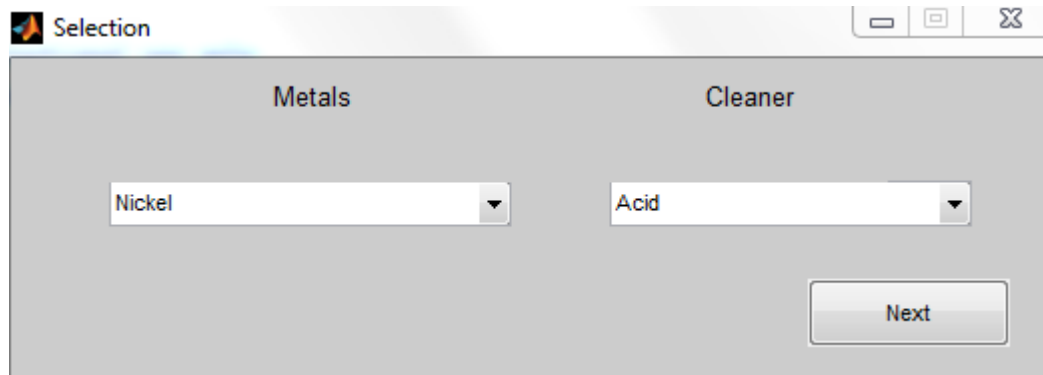


Figure 3.3. Window for metal and cleaner selection.

**System information**

**Parts specification**

Shape	Radius	<input type="text" value="0"/>	Cm
<input type="text" value="Screw"/>	Length	<input type="text" value="0"/>	Cm
	Weight of barrel	<input type="text" value="0"/>	Kg

**Process Specification**

Initial Dirt on parts	<input type="text" value="0"/>	g/cm <sup>2</sup>
Initial Concentration (from 0 to 1)	<input type="text" value="0"/>	gal-chem/ gal of sol
Processing time	<input type="text" value="0"/>	min
Cleaning requirement	<input type="text" value="0"/>	%
Number of barrels	<input type="text" value="0"/>	

**Tank Specification**

Volume of tank (gal)	<input type="text" value="0"/>
----------------------	--------------------------------

Figure 3.4. System information window for cleaning.

**System Performance**

**Parts cleanliness**

<i>Final dirt residue</i>	<input type="text" value="0"/>	g/cm <sup>2</sup>
<i>Percentage dirt removed</i>	<input type="text" value="0"/>	%

**Chemical consumption**

<i>Final concentration</i>	<input type="text" value="0"/>	gal-chem/ gal-sol.
<i>Total chemical consumed</i>	<input type="text" value="0"/>	gal.
<i>Sludge generated</i>	<input type="text" value="0"/>	kg

**Graphical results**

Process Dynamics       Parts Dynamics

Figure 3.5. System performance window for cleaning.



**Parts specification**

Shape:

Radius:  Cm

Length:  Cm

Weight of barrel:  Kg

---

**Process Specification**

Initial pollutant concentration:  g/gal-water

Initial Dirt residue:  g/cm<sup>2</sup>

Rinsing time:  min.

Idle Time:  min.

Number of barrels:

Rinse water flow rate:  gal/min

---

**Tank Specification**

Tank volume:  Gal.

Number of tanks:

Figure 3.6. System information window for rinsing.

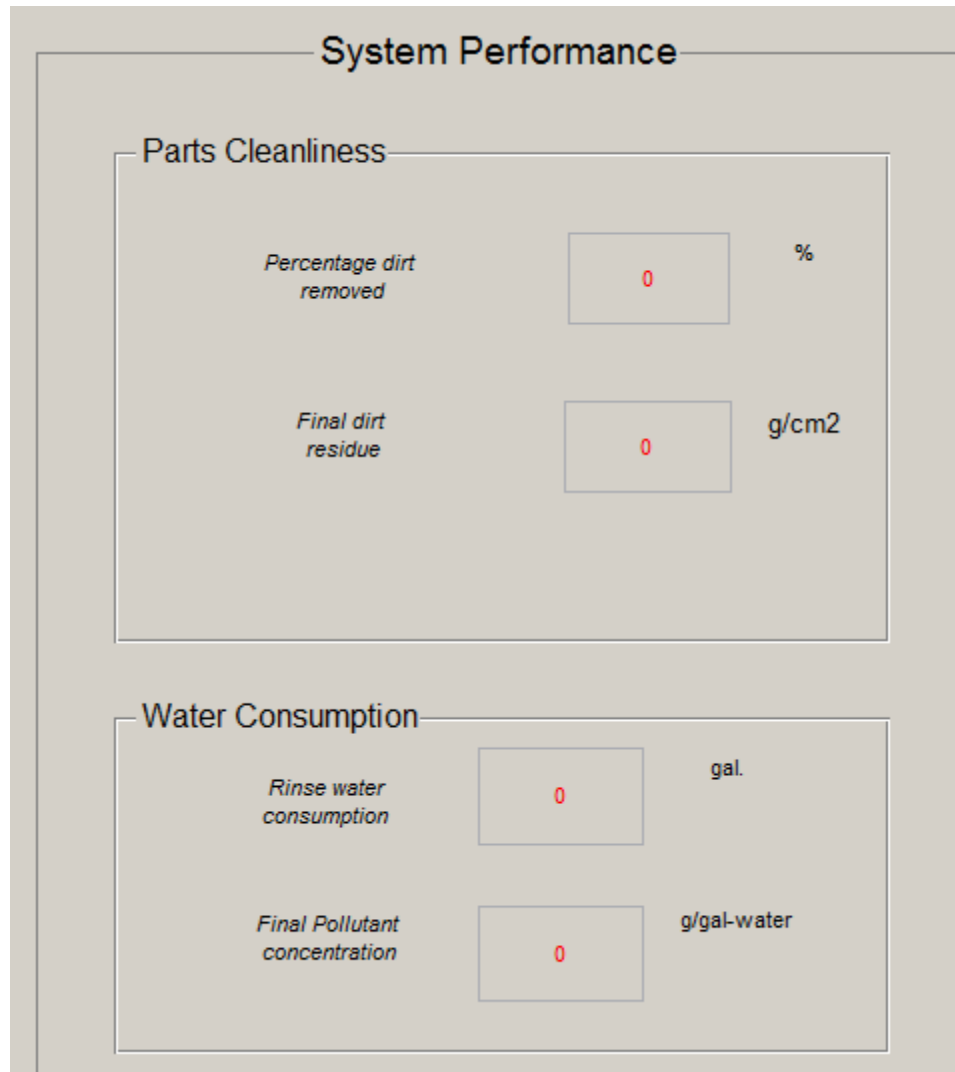


Figure 3.7. System performance window for rinsing.

## CHAPTER 4

### ANALYSIS OF ENVIRONMENTAL AND ECONOMIC IMPACT ON ELECTROPLATING OPERATIONS - A CASE STUDY

Mathematical models presented in earlier in chapter 2 are used to investigate individual operations as well as cleaning/rinsing combined system. Simulation of the model will provide results of dynamics of dirt residue and chemical consumption. These results will help to identify waste management opportunities. The system simulated has two cleaning and two rinsing tanks.

#### 4.1 Cleaning Process

Cleaning simulations are performed based on single barrel and multiple barrel with single step or two-step cleaning. Waste minimization strategies are then identified and operational changes are demonstrated in order to make operation more environmentally benign.

##### 4.1.1 Single barrel single tank cleaning

Simulation is carried out for a single barrel with weight of 200kg. Parts to be plated are assumed as screws. The estimated initial dirt on the parts is assumed  $0.0090 \text{ gm/cm}^2$ . Requirements of subsequent plating process dictate that 80% of cleaning should be achieved. This is equivalent to  $0.0018 \text{ gm/cm}^2$  of dirt residue on the parts after cleaning. Initial chemical (cleaner) concentration is set as 6.0% and no chemical is added during the process. Processing time for cleaning operation is assumed 4 minutes. The results of this simulation (Fig 4.1) run show that dirt removal is 87 %. Chemical consumption is 0.4 gal. , and sludge generated is 1.2

kg. If initial concentration is increased to 8% required cleaning can be achieved in less amount of time (3 min). However, amount of sludge generated is higher than that of in first case (1.27 kg).

**Environmental Impact.** This simulation suggests that excessive use of cleaner is potentially harmful to environment since it increases the amount of sludge generated. This shows an opportunity for waste minimization through source reduction. To achieve source reduction in this case initial amount of chemical added to tank should be optimized in such a way that chemical consumption should be minimized without compromising the quality of cleaning. This simulation tool has a module to calculate this optimized initial chemical requirement for given time, initial dirt and cleaning required. Optimized value of initial chemical concentration comes out to be 4.9%. After running simulation with this value of initial chemical concentration, chemical consumption comes out to be 0.36 gal. , and sludge generated is 1.1 kg. Which is equivalent to 10% reduction in chemical consumption and 14% reduction in sludge generated (Fig. 4.2).

#### 4.1.2 Multi-barrel cleaning

For this simulation, it is assumed that 20 barrels (screws; weight 200kg) are cleaned sequentially. Each barrels is assumed to spend 4 minutes in cleaning tank. Initial dirt on each barrel is assumed  $0.0090 \text{ g/cm}^2$ . Simulation results show that dirt removed from last barrel is 71%. Chemical consumption is 7.2 gal. , and sludge generated is 23 kg. Dynamic response of this simulation (Fig. 4.3) shows that barrels up to barrel 9 are over cleaned which means increase in amount of sludge generated. On the other hand, barrels after barrel 13 are under cleaned. When initial chemical concentration in increased to 8 % all barrels are clean but chemical

consumption and sludge generation increases by considerable amount. Dirt removed from last barrel is 84 %. 8 gallons of chemical is consumed and 26 kg of sludge is generated (Fig. 4.4).

**Environmental Impact.** Dynamic response of this simulation suggests there are some barrels that are over cleaned. Over cleaning implies significant increase in amount of sludge generated and pollutant in effluent streams. Moreover, over cleaning consumes an extra amount of cleaner, which is unnecessary. Waste minimization can be achieved through optimizing the operation. To make the operation more environmentally benign following strategies can be implemented:

1. Addition of particular amount of cleaner after a fixed time interval.
2. Maintaining constant cleaner concentration of cleaner in cleaning tank.

Figure 4.5 shows simulation result of strategy 1. During this simulation, 1 gallon of cleaner is added to tank after every 3 barrels. This strategy allows process to start with lower initial concentration of chemical. Initial concentration for this simulation is 5%. For this case, dirt removal achieved for last barrel is 81%. Chemical consumption is brought down to 6.8 gal, and sludge generation is reduced to 22 kg. Which is equivalent to 10 % reduction in chemical consumption and 12% reduction in sludge generation.

Figure 4.6 shows implementation strategy 2. For this simulation, initial concentration is set to 4.5%. Dirt removal achieved is 81% for all barrels. Chemical consumption is 6.2 gallons and sludge generated is 22 kg, which is equivalent to 14% reduction in chemical consumption and 5% reduction in sludge generation than previous case.

Table 4.1. Comparison 3 cases for single barrel, single stage cleaning

Initial Concentration	Cleaning achieved	Consumption (gal.)	Sludge generated(Kg)
6%	87%	0.4	1.20
11%*	87%	0.4	1.27
<b>4.9%</b>	<b>81%</b>	<b>0.36</b>	<b>1.1</b>

Chemical consumption reduction 10%. Sludge generation reduction 14%.

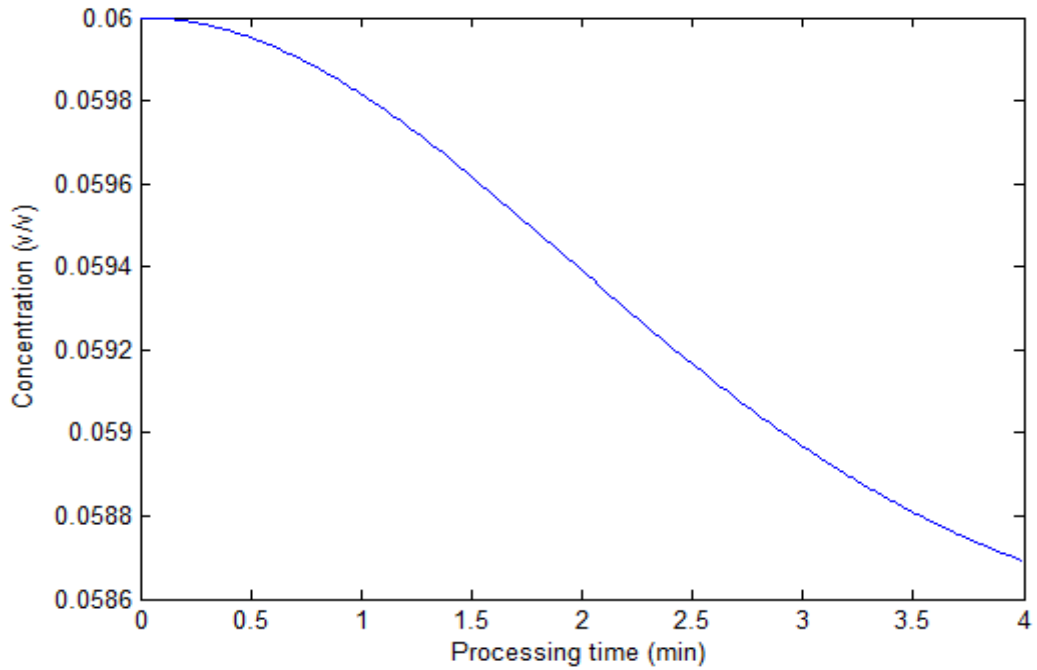
\*processing time 3 min.

Table 4.2. Comparison of 4 cases of multi barrel single stage cleaning

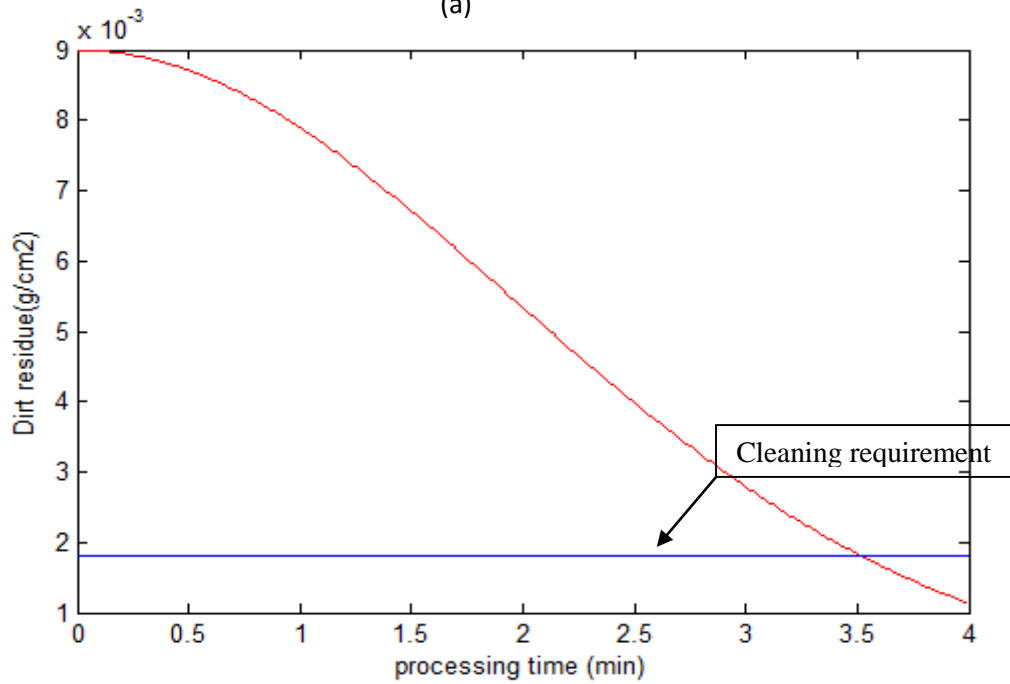
Cleaner addition mode	Initial concentration	Cleaning achieved	Consumption(gal)	Sludge generated(kg)
Single addition	6%	71%	7.2	23
Single addition	8%	84%	8	26
Periodic addition*	5%	81%	6.8	22
<b>Constant concentration**</b>	<b>4.5%</b>	<b>81%</b>	<b>6.2</b>	<b>22</b>

\* Chemical consumption reduction archived 10%. Sludge reduction achieved 5%.

\*\*Chemical consumption reduction 4%. Sludge reduction achieved 5%.



(a)



(b)

Figure 4.1. One time cleaner addition for 1 barrel with initial concentration 6 %:  
 (a) Concentration dynamics and (b) Dirt residue dynamics.

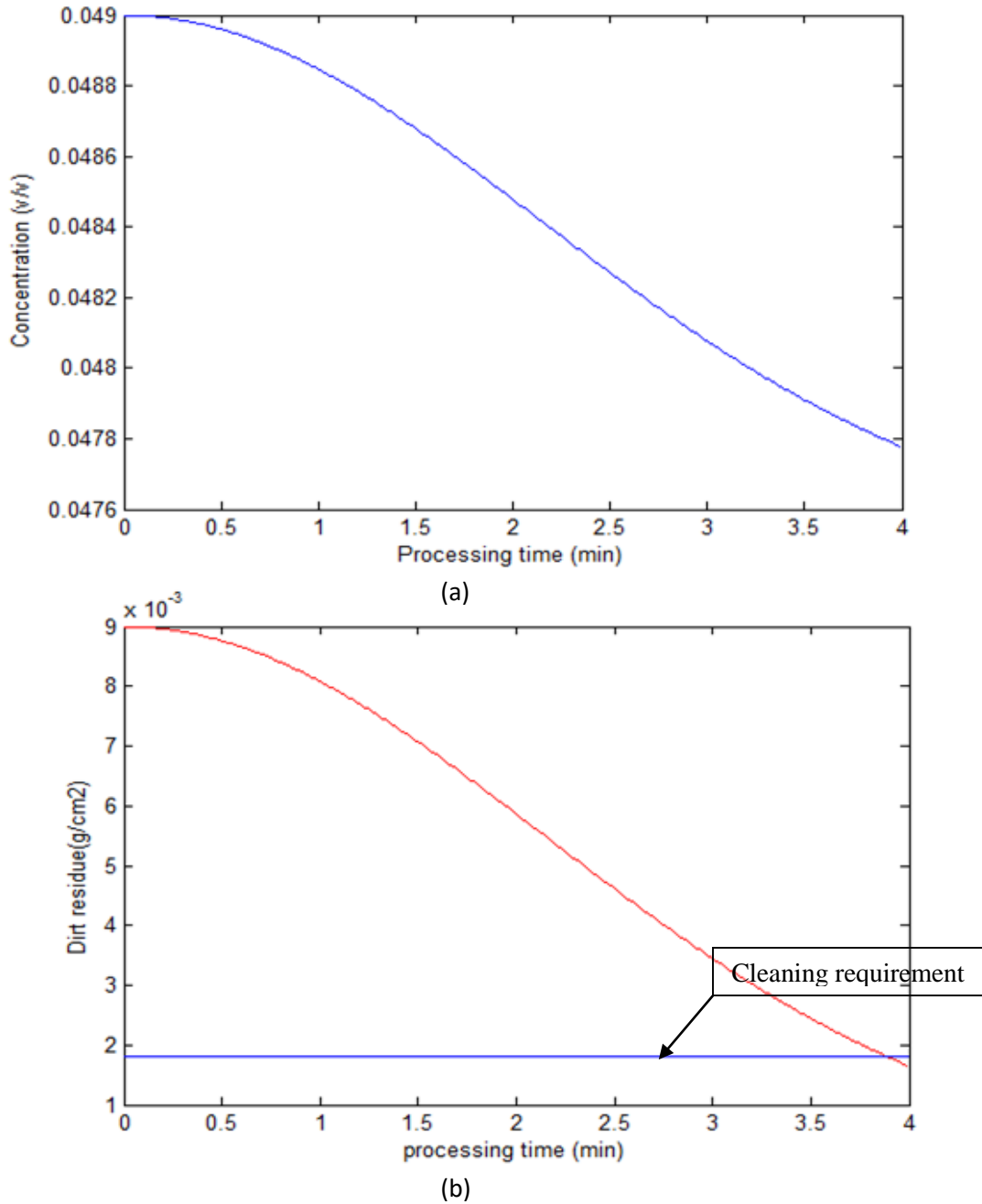


Figure 4.2. One time cleaner addition for 1 barrel with initial concentration 5 %:  
 (a) Concentration dynamics and (b) Dirt residue dynamics.



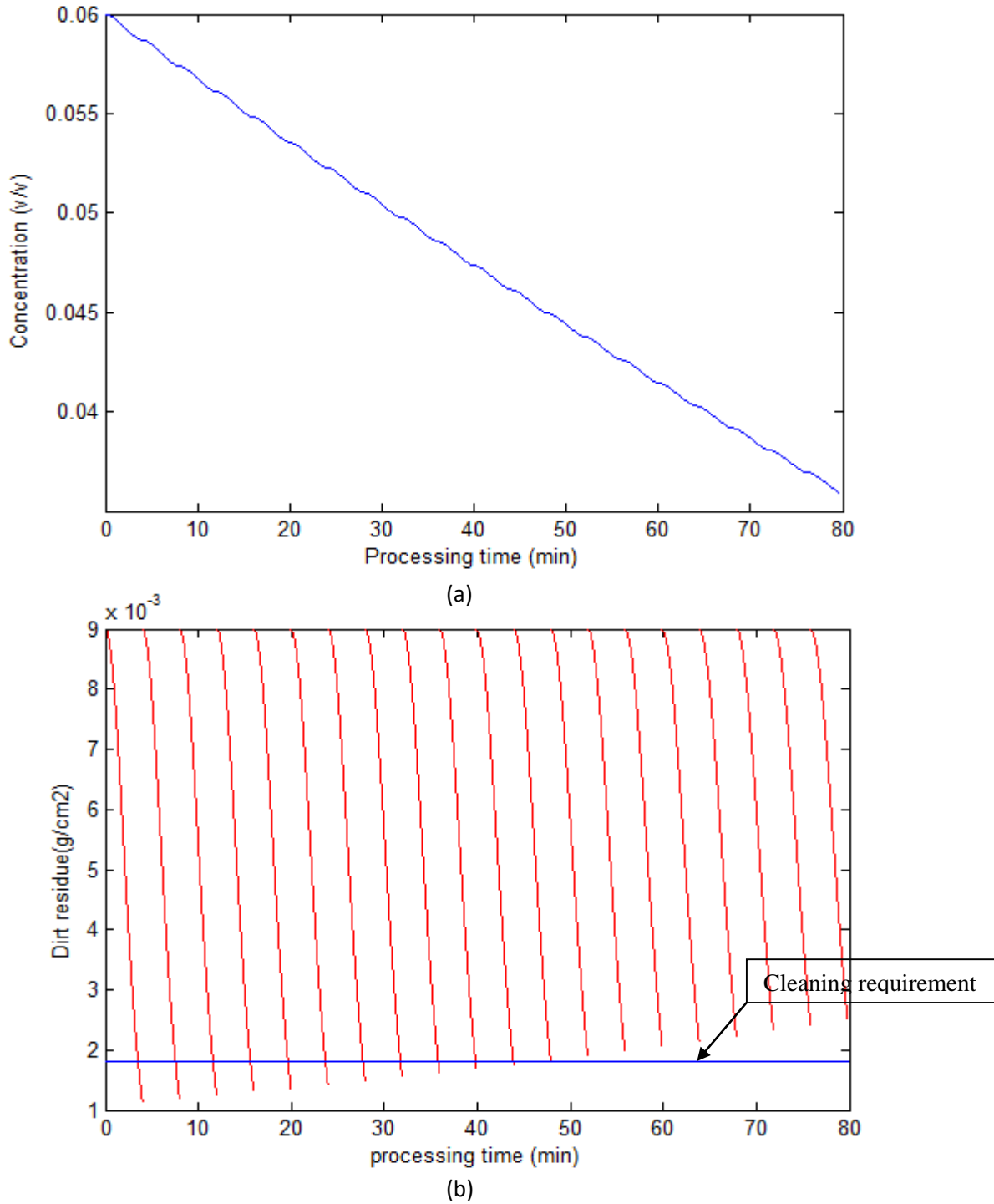


Figure 4. 3. One time cleaner addition for 20 barrels with initial concentration 6 % :  
 (a) Concentration dynamics and (b) Dirt residue dynamics.

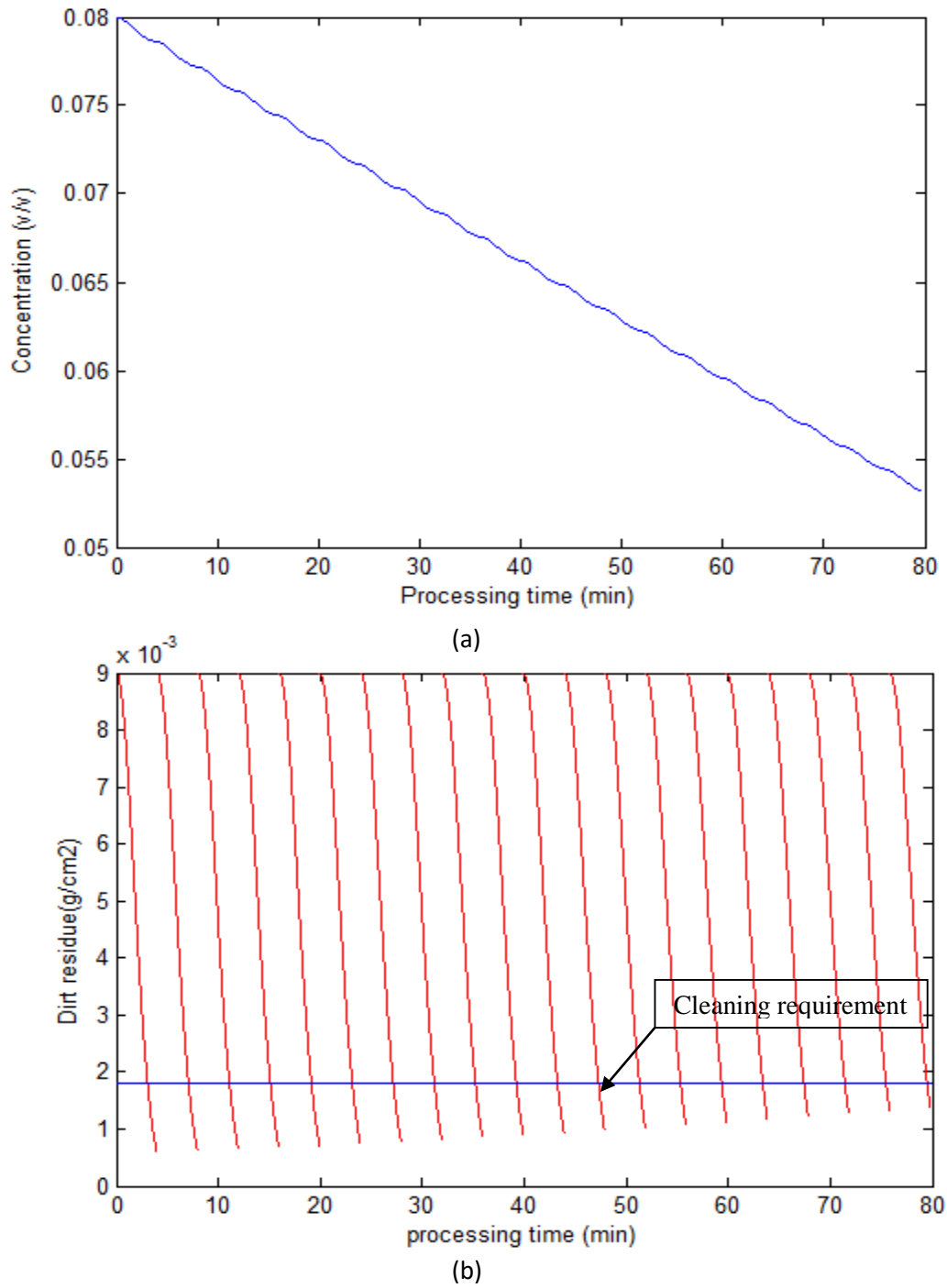
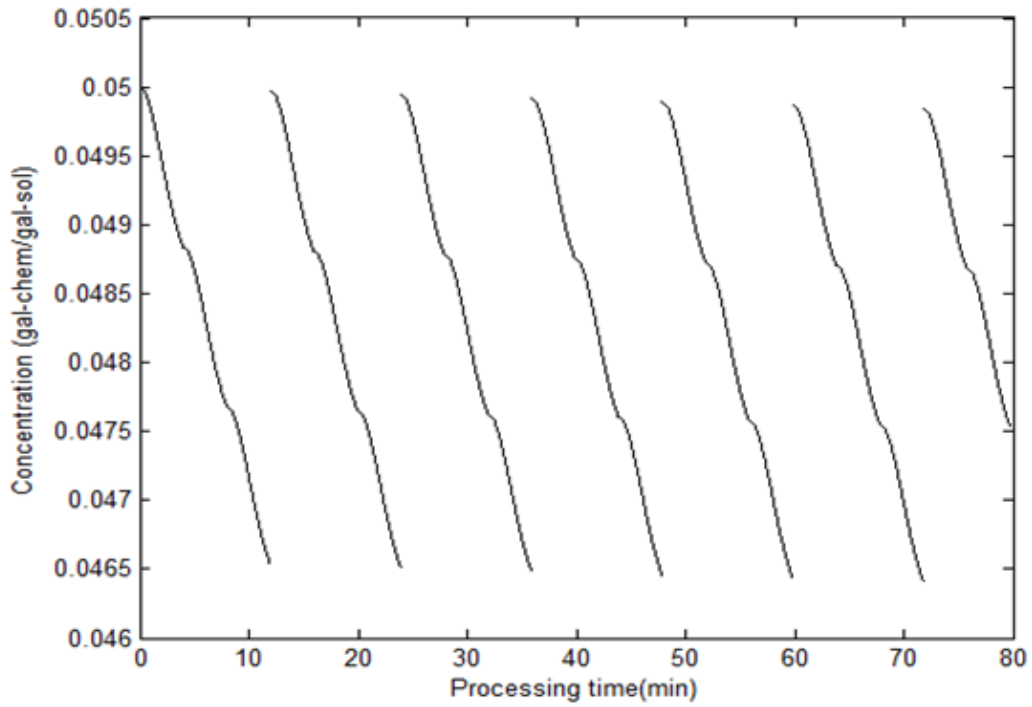
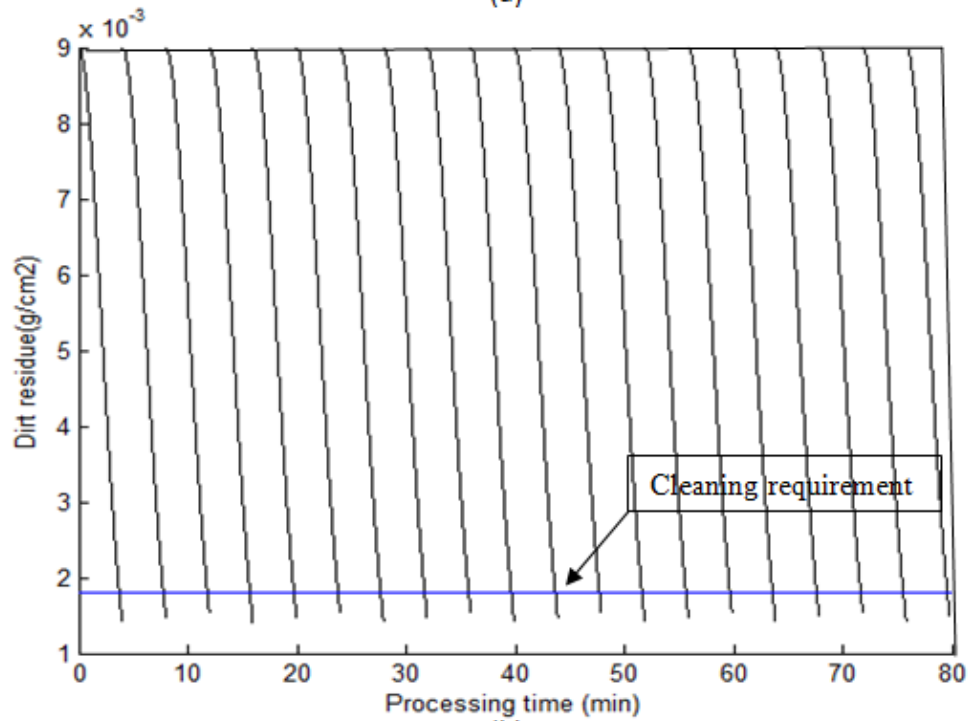


Figure 4.4. One time cleaner addition for 20 barrels with initial concentration 8 %:  
 (a) Concentration dynamics and (b) Dirt residue dynamics.



(a)



(b)

Figure 4.5. Periodic cleaner addition for 20 barrels after every 3 barrels:  
 (a) Concentration dynamics and (b) Dirt residue dynamics.

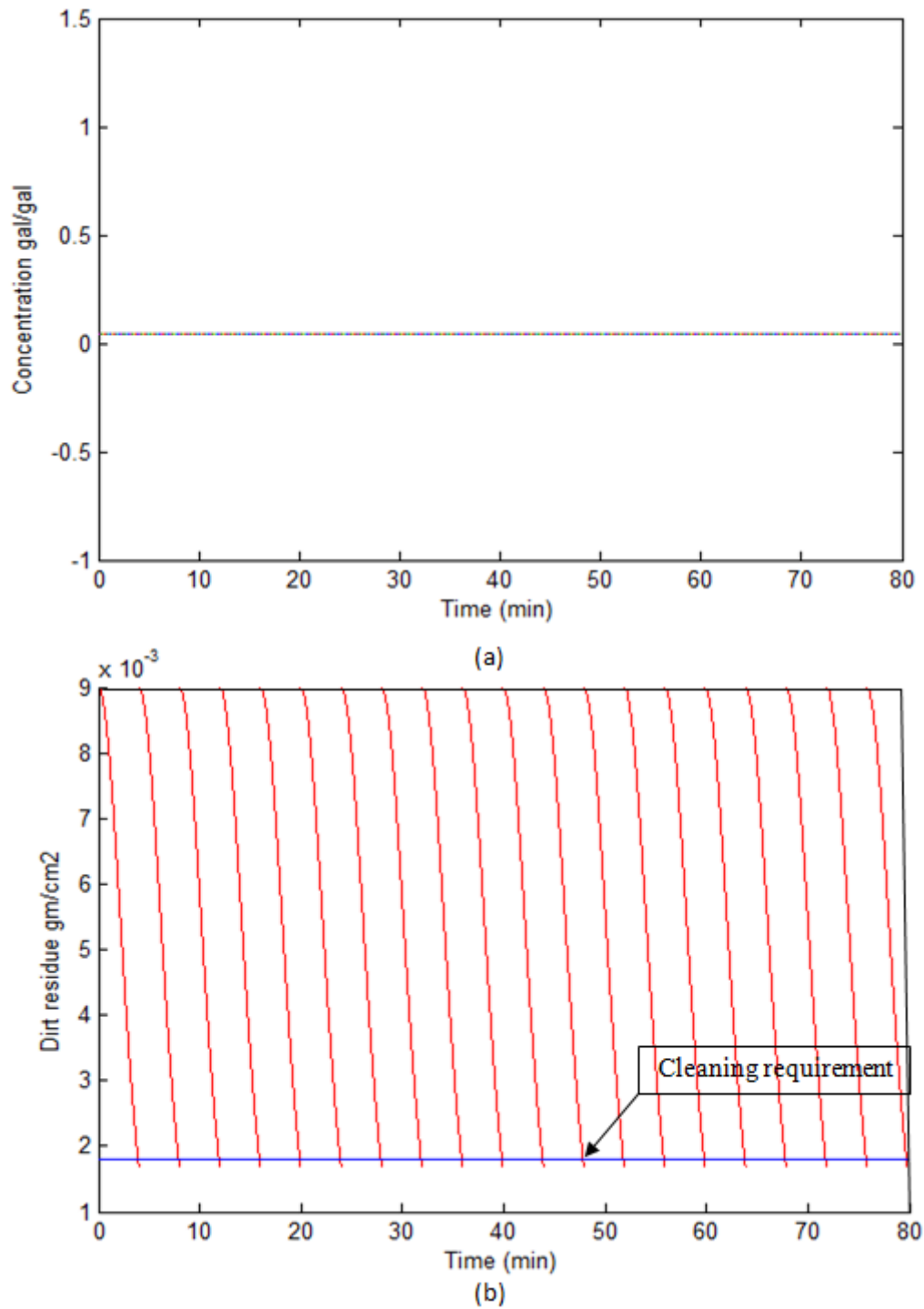


Figure 4.6. Constant cleaner feed for 20 barrels with initial cleaner concentration 4.5%:  
 (a) Concentration dynamics and (b) Dirt residue dynamics.

### 4.1.3 Multi barrel two-step cleaning

For this simulation, two cleaning tanks are arranged in series. Every barrels spends equal amount of time in both cleaning tanks. This simulation is done for 20 barrels. Every barrel is assumed to weigh 200kg and contains screws. It is assumed that approximate dirt residue on each barrel is 0.0090 gm/cm<sup>2</sup>. The dirt should be removed by 80% for subsequent plating operation. For Case 1 both tanks have initial chemical concentration 5%. Chemical consumption in tank 2 is 1.6 gal, and first tank consumes 6.3 gal of chemical. Total chemical consumption is 7.9 gal, and 93 % of dirt is removed from the parts.

**Environmental Impact.** Dirt removal requirement is assumed 80 %. In case 1 dirt removal achieved is 93 % which clearly indicates over cleaning. Chemical consumption can be reduced by changing initial concentration in both tanks.

For Case 2 initial concentration in tank 1 is lowered to 3 % and initial concentration in second tank is kept at 5%. Simulation results of this case show that chemical consumption in first tank is 4.5 gal, and chemical consumption in second tank is 3 gal. Total consumption is reduced to 7.5 gallons, which is equivalent to 6% reduction in consumption. Dirt removal achieved in this case is 87%.

In Case 3 initial concentration of first tank is set at 4% and initial concentration of second tank is set at 3 %. Chemical consumption in first tank is 5.5 gal, and in second tank 1.7 gal. Total chemical consumption is lowered to 7.2 gal. This is equivalent to 9 % reduction in chemical concentration as compared to base case. Cleaning achieved in this case is 82%.

Table 4-3: Comparison of three cases for multi barrel two-step cleaning.

	Initial concentration in tank 1	Initial Concentration in tank 2	Chemical Consumption	Percentage cleaning achieved
Case 1	5%	5%	7.9	93
Case 2*	3%	5%	7.5	87
Case 3**	4%	3%	7.2	82%

\* Chemical Consumption is reduced by 6%

\*\*Chemical Consumption is reduced by 9%

## 4.2 Rinsing Process

Rinsing simulations are performed for single and multi-barrel with single, two stage rinsing and co and counter current rinsing. Waste minimization strategies are then identified and operational changes are demonstrated.

### 4.2.1 Single barrel rinsing

Rinsing usually follows cleaning and plating operations. Rinsing process can be characterized by dirt removal in rinsing tank, final pollutant concentration in rinsing tank and rinse water consumed. This simulation is carried out for single barrel of weight 200 kg and single stage rinsing. Initial dirt on part is assumed 0.0033 gm/cm<sup>2</sup>. Parts to be plated are assumed screws. Rinse water flow rate is set to 3 gal/min. Rinse mode is operated for 1 minute and idle mode for 3 minutes. Results of this simulation (Fig. 4.7) show that dirt residue on the parts is reduced to 0.0016 gm/cm<sup>2</sup> which is equivalent to 83 % removal. Rinse water consumption is 12 gal, and pollutant concentration in rinse tank after operation is 84 ppm. For second case rinse water flow rate is increased to 5 gal/min keeping other parameters unchanged (Fig. 4.8). Simulation results for this process settings show that rinse water consumption is 20 gal. Dirt

removal from the parts is 83 % and pollutant concentration in rinse tank is 49 ppm. These simulation results show that increase in rinse water flow rate decreases the pollutant concentration in rinsing tank but it results in increase in consumption of rinse water. If rinse water flow rate is increased to 6.5 gal/min, dirt removal remains same but pollutant concentration in 31 ppm. Rinse water consumption for this case is 26 gal. Changing contact time affects the dirt removal. In case 3 Rinse time (Contact time) is changed to 0.5 min. Simulation results for this case show that dirt removal is 78 % but final pollutant concentration is 55 ppm which is equivalent to 39% reduction in final pollutant concentration than in case 1. For case 4, rinse time is further reduced to 0.4 min. and rinse water flow rate is increased to 5 gal/min. Simulation results show further decrease in pollutant concentration. Final pollutant concentration in this case is 29 ppm, which is equivalent to 68 % reduction in final pollutant concentration than in Case 1. These results show that as rinsing time is decreased and idle time or rinse water flow rate is increased, dirt removal decreases but final pollutant concentration in rinsing tank also decreases, which in turn guarantees the cleaning quality of subsequent barrel.

Table 4.4. Comparison of four cases for single barrel single stage rinsing.

	Case 1	Case 2	Case 3	Case 4
Tank capacity(gal)	300	300	300	300
Rinse time (min)	1	1	0.5	0.4
Flow rate(gal/ min)	3	5	3	5
Initial dirt(g/cm <sup>2</sup> )	0.0033	0.0033	0.0033	0.0033
Initial pollutant concentration(g/gal)	0.06	0.06	0.06	0.06
Dirt remaining after rinsing (%)	83	83	78	78
Rinse water consumption(gal)	12	20	12	20
Final pollutant concentration(ppm)	89	49	55	29

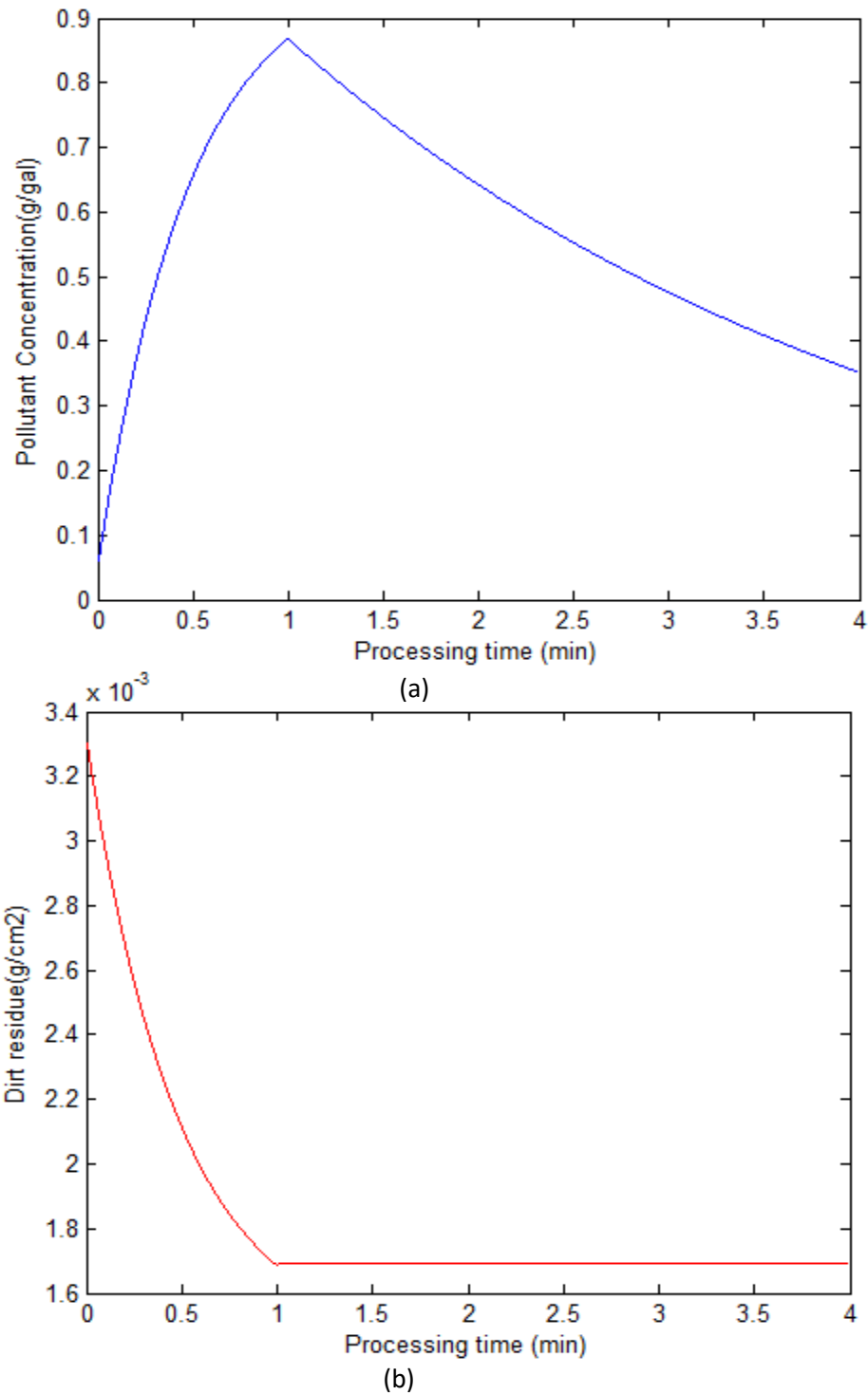


Figure 4.7. Dynamic response for simulation if single barrel single stage rinsing: (a) Pollutant concentration dynamics and (b) Dirt residue dynamics.



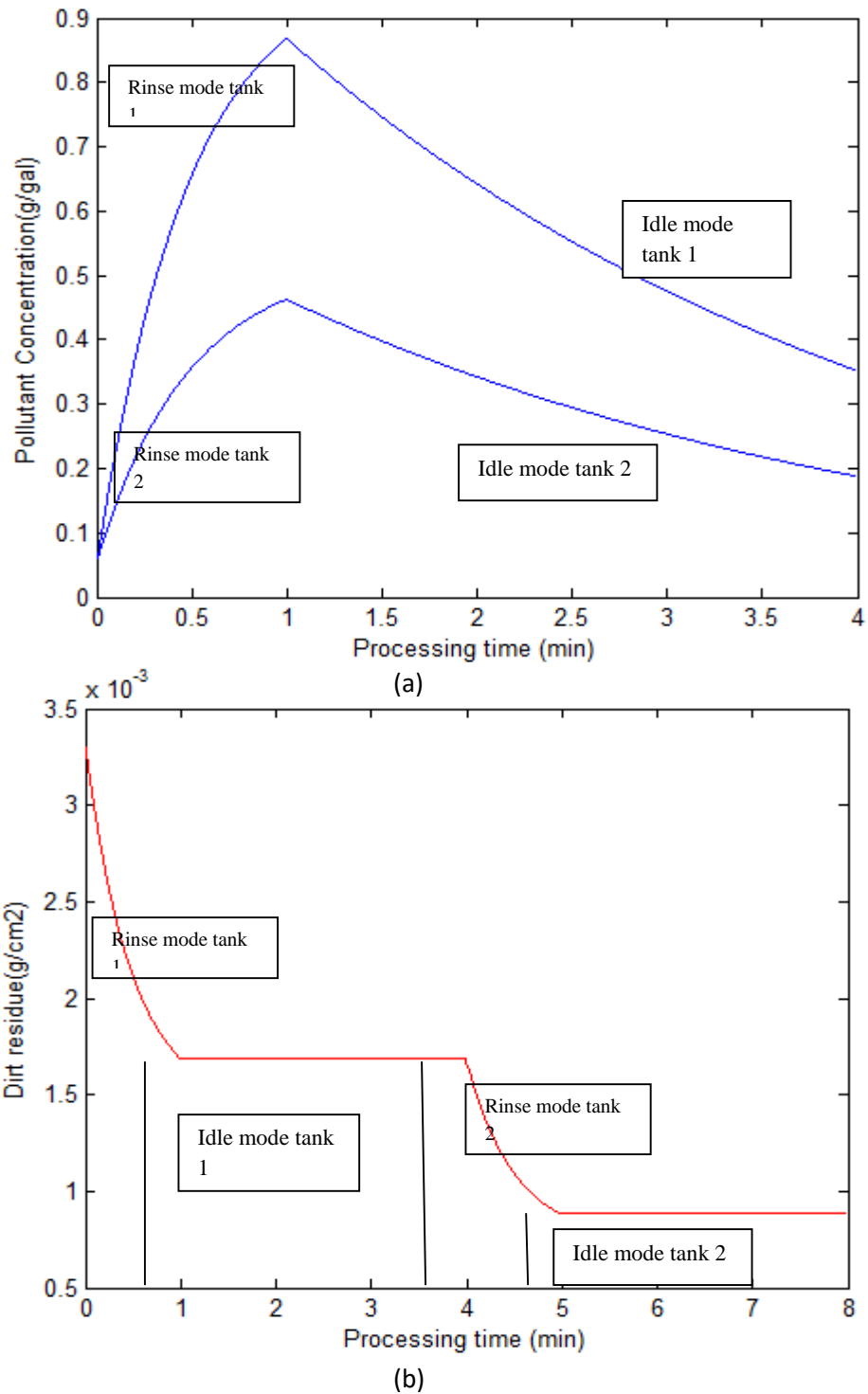


Figure 4.8. Dynamic response for simulation if single barrel two-stage rinsing: (a) Pollutant concentration dynamics and (b) Dirt residue dynamics.

#### 4.2.2 Multi barrel rinsing

Effectiveness of rinsing operation in terms of dirt removal depends on pollutant concentration in rinse tank. Lower the concentration of pollutant in rinse tank higher will be the cleaning achieved. This case is simulated for 20 barrels (Fig. 4.9) with assumption that each barrel has dirt residue of  $0.0033 \text{ g/cm}^2$  after cleaning. Rinse water flow rate is set to 3 gal/min. Initial pollutant concentration in rinse tank is assumed to be 0.06 gm/gal. Rinse time/contact time for each barrel is 0.4 min and idle time is 3 minutes Simulation results for this case show that dirt removed from last barrel is 84%. Rinse water consumption is 180 gal. Final pollutant concentration in rinsing tank at the end of rinsing of 20th barrel is 61 ppm.

**Environmental Impact.** Rinsing process is characterized by dirt removal and final pollutant concentration in rinse tank. Minimization of rinse water in rinse tank depends on rinse water consumption. Rinse water consumption depends on initial flow rate and total processing time for rinsing operation. To make rinsing operation more environmentally sustainable i.e. to reduce rinse water consumption without affecting the quality of cleaning following strategies can be implemented. The amount of sludge generated is directly proportional to organics, bath constituents and metals in rinse water. Thus, any strategy reducing rinse water consumption will help reduce waste generation from rinsing tank.

1. Use multiple step rinsing process.
2. Use counter flow of rinse water.

Dynamic response of strategy 1 is represented in Fig. 4.10. Initial rinse water flow rate is set to 3 gal/min. Results of this simulation show that 88 % of dirt is removed. Rinse water consumed is 120 gal, and final pollutant concentration in second rinse tank is 29ppm. and first

tank has 63 ppm of pollutant concentration. This is equivalent to 44% reduction in rinse water consumption.

For strategy 2, effluent from tank 2 is fed to tank one while barrels are rinsed in tank 1 followed by tank 2. Dynamic response of strategy 2 is represented in figure 4.11. Simulation results of this case show that cleaning achieved is 87%. Rinse water consumption is 80 gal, and final pollutant concentration is 34 ppm. This is equivalent to 66% rinse water reduction for approximately similar amount of cleaning.

In both figures, 10 and 11 first graph depicts dynamics of pollutant concentration in rinsing tanks and second graph shows dynamics of dirt residue on the parts in rinsing tank. In both the cases, initial pollutant concentration is assumed 0.06 g/gal which is equivalent to 15 ppm.

Results of four cases of counter current and co current rinsing operations are tabulated in table 4.5 and 4.6 respectively. Every case is simulated with same process specification for both co current and counter current operational mode. Comparison of each case of co current rinsing with that of counter current rinsing shows that counter current rinsing is more efficient in maintaining low pollutant concentration during rinsing process. For Case 1 pollutant concentration is reduced by 32% for counter current. For Case 2 pollutant concentration is reduced by 36%. For cases, 3 and 4 pollutant concentration goes down by 17% and 42 % respectively for counter current rinsing operation.

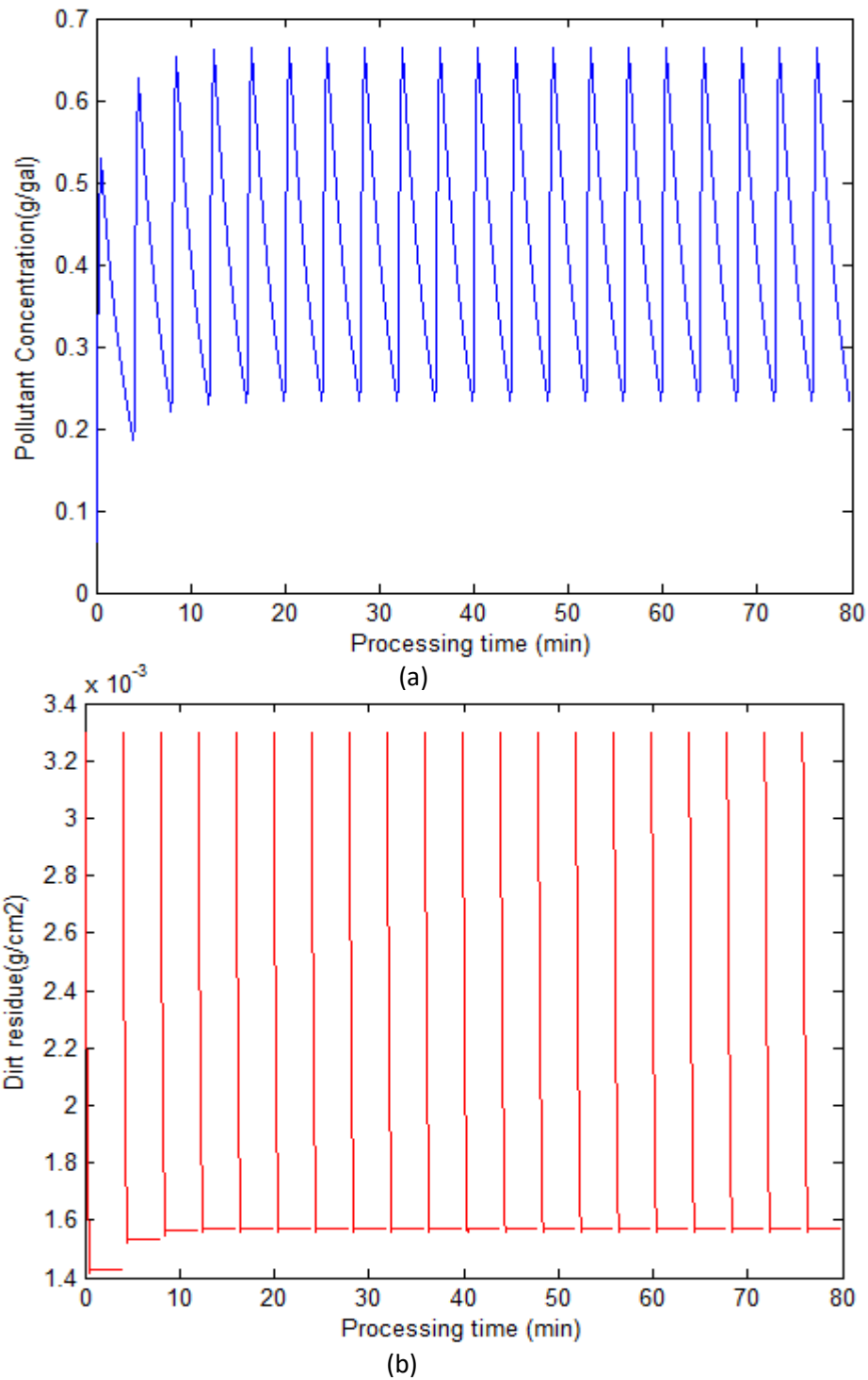


Figure 4.9. Dynamic response for simulation of multi-barrel single-stage rinsing:  
(a) Pollutant concentration dynamics and (b) Dirt residue dynamics.

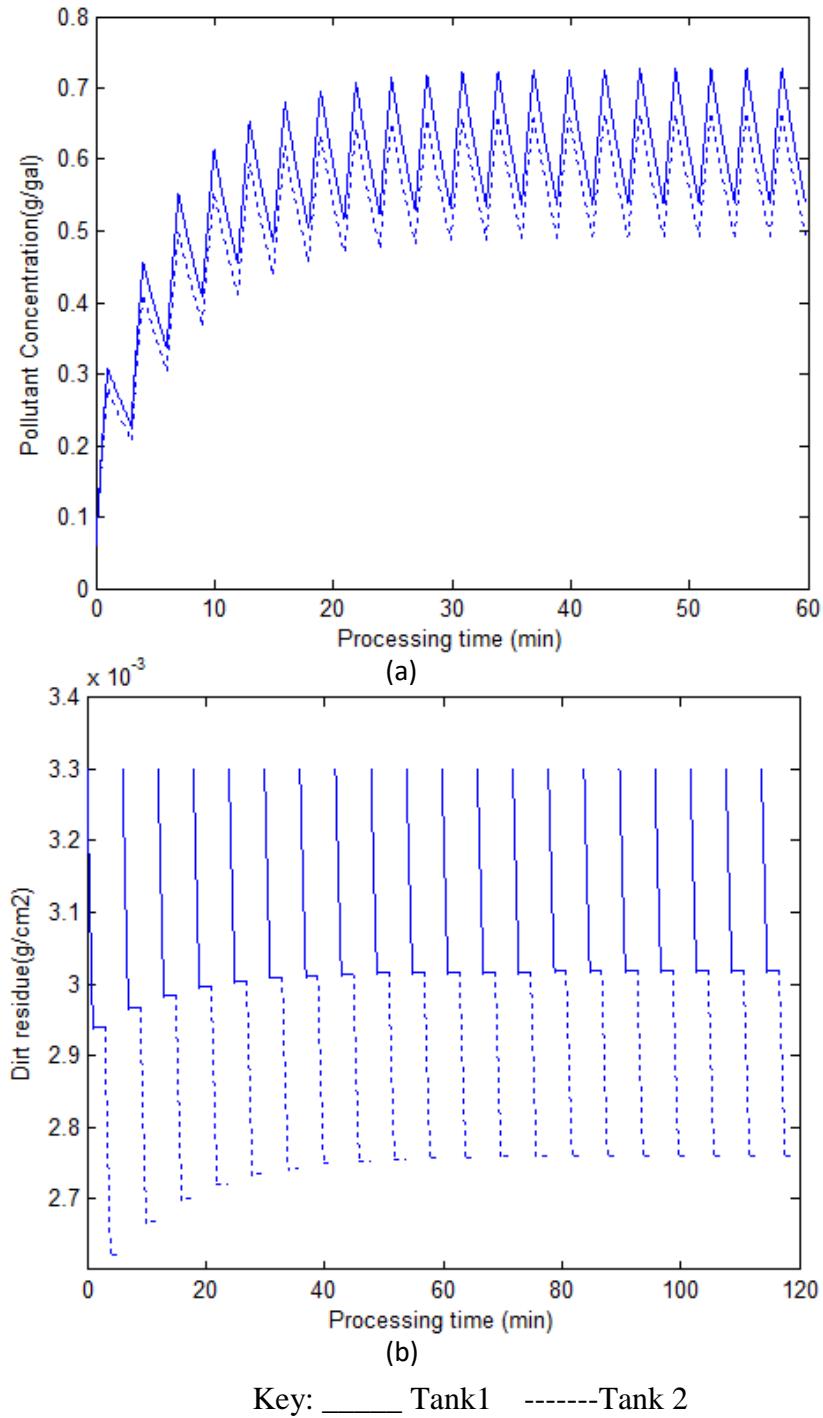


Figure 4.10. Dynamic response for simulation of multi barrel two-stage co current rinsing: (a) Pollutant concentration dynamics and (b) Dirt residue dynamics.

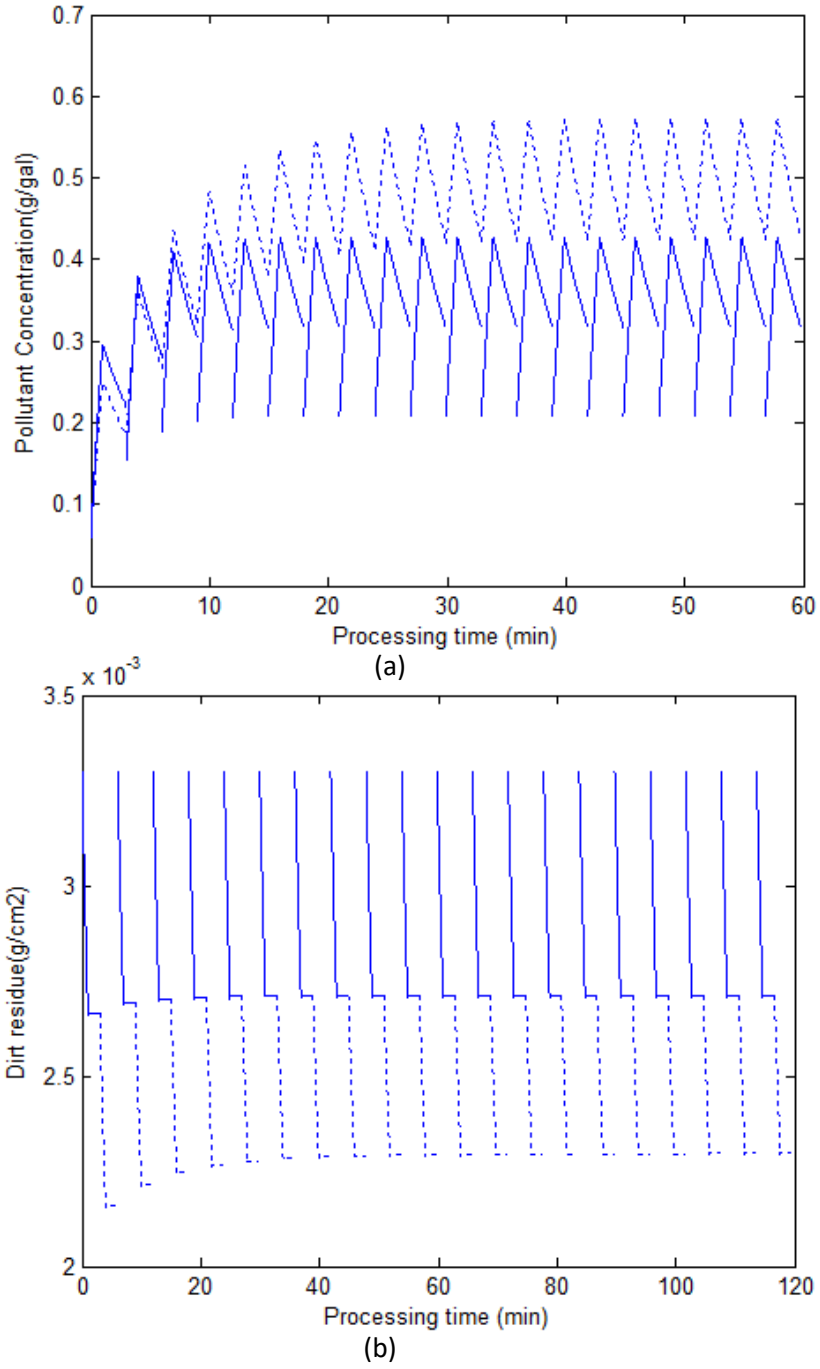


Figure 4.11. Dynamic response for simulation of multi barrel two stage counter current rinsing :  
 (a) Pollutant concentration dynamics and (b) Dirt residue dynamics.

Table 4.5. Comparison of four cases for multi barrel two-step counter current rinsing.

Counter current rinse	Case 1	Case 2	Case 3	Case 4
Initial Dirt residue(g/cm <sup>2</sup> )	0.0033	0.0033	0.0033	0.0033
Rinse water flow rate(gal/min)	2	2	3	5
Tank volume (gal)	300	300	300	300
Rinse time(min)	0.5	1	1	0.4
Idle time (min)	3	3	3	3
Rinse water consumption(gal)	160	160	240	400
Dirt removal achieved (%)	89	93	95	92
Final pollutant concentration (ppm)	50	63	35	10

Table 4.6. Comparison of four cases for multi barrel two-step co-current rinsing.

Co current rinse	Case 1	Case 2	Case 3	Case 4
Initial Dirt residue(g/cm <sup>2</sup> )	0.0033	0.0033	0.0033	0.0033
Rinse water flow rate(gal/min)	2	2	3	5
Tank volume (gal)	300	300	300	300
Rinse time(min)	0.5	1	1	0.4
Idle time (min)	3	3	3	3
Rinse water consumption(gal)	160	160	240	400
Dirt removal achieved	83	88	84	85
Final pollutant concentration (ppm)	73	97	42	17

### 4.3 Cleaning-Rinsing System Characterization

To characterize the complete cleaning-rinsing system, simulation is carried out with 20 barrels of load 200 kg. Initial dirt on the parts is assumed 0.0090 g/cm<sup>2</sup>. Cleaning operation takes place for 4 minutes then barrels are transferred to rinsing process. Rinsing tank operates with rinsing mode for 1 minute and with idle mode for 3 minutes. Initial pollutant concentration in each rinse tank is assumed 0.06 g/gal (15 ppm). Initial chemical concentration in cleaning tank is assumed 6%. It is assumed that at least 80 % of dirt should be removed from the parts. Rinse water flow rate is set to 3 gal/min.

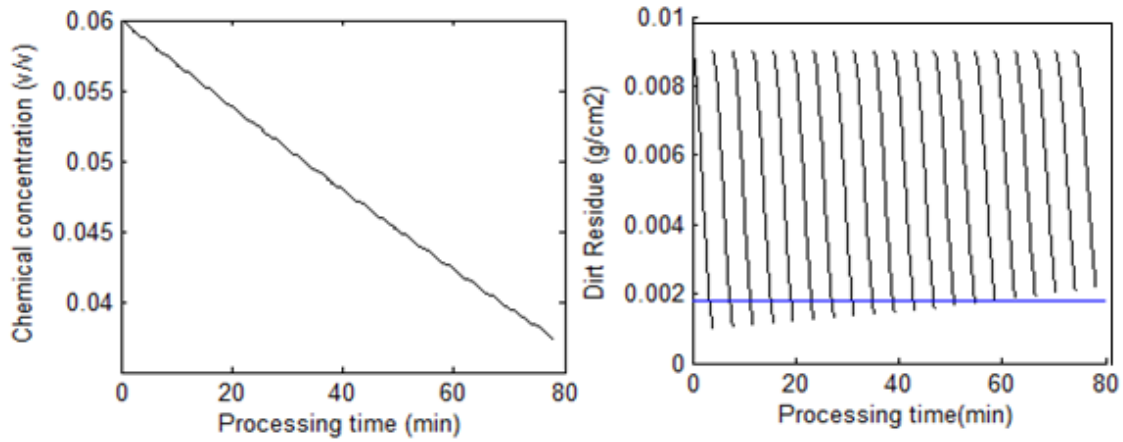
Simulation results (Fig. 4.12) show chemical consumption to achieve 82 % cleaning is 6.7 gal. Rinse water consumption is 240 gal. Sludge generated in cleaning tank is 20 kg and final pollutant concentration in rinsing tank is 75 ppm.

**Environmental Impact.** As represented by dynamics of the process some of the barrels were over cleaned. Over cleaning implies unnecessary consumption of cleaner chemical and excessive sludge generation. Waste minimization can be achieved in this case by implementing various source reduction technologies. Periodic addition of chemical cleaner will allow operator to start with lower initial concentration, which will avoid unnecessary consumption of chemical and minimize the sludge generation. Simultaneously, rinse water consumption can be minimized by using appropriate operational mode (co-current/counter current).

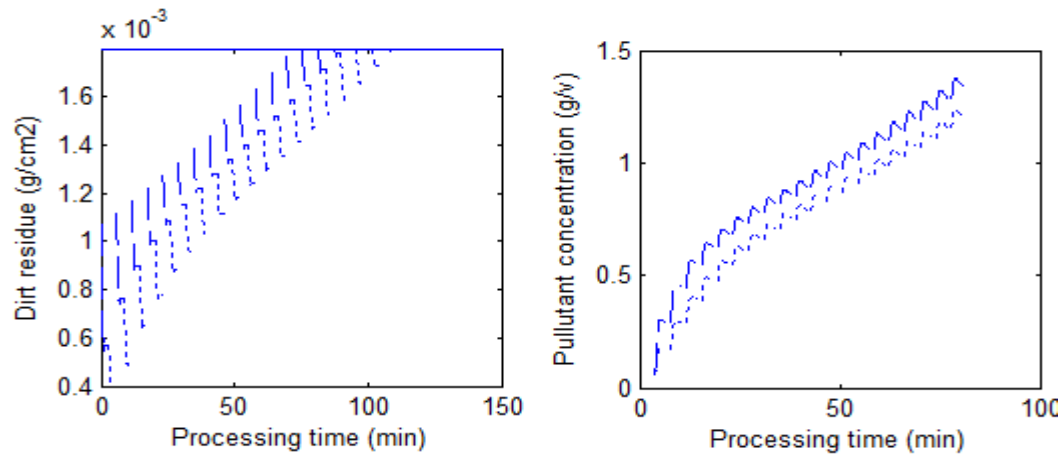
For second case, periodic addition operational mode is selected and rinsing mode is kept at two-step co current rinse. Results of this simulation (Fig. 4.13) show that for same amount of cleaning chemical consumed is 6.2 gal. Rinse water consumption is 240 gal. , and final pollutant concentration is 18 ppm.

For Case 3 (Fig. 4.14) system is operated with periodic addition for cleaning mode and counter current mode for rinsing. Chemical consumption is 6.2 gal, and rinse water consumption is 240 gal but pollutant concentration is reduced to 12 ppm. This is equivalent to 32 % reduction in pollutant concentration in rinsing tank.





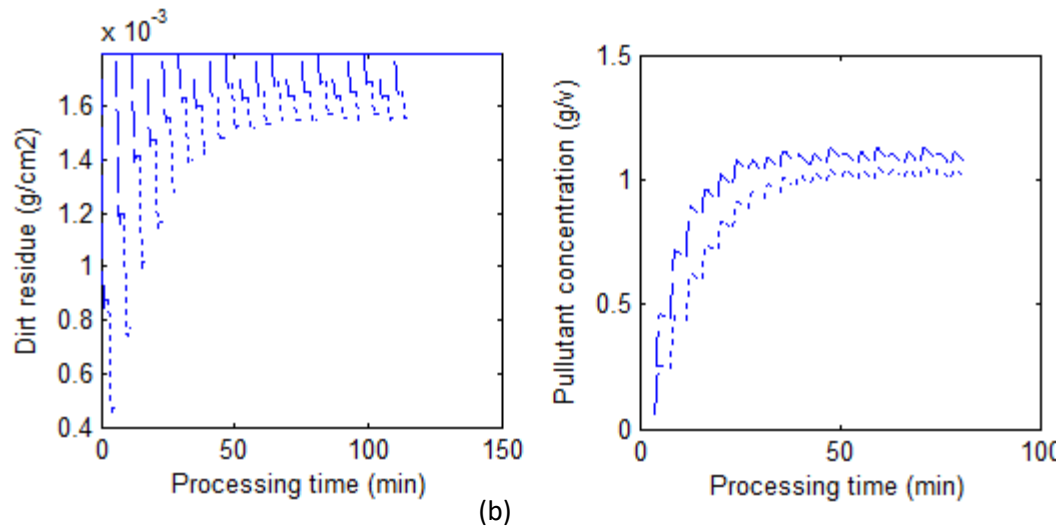
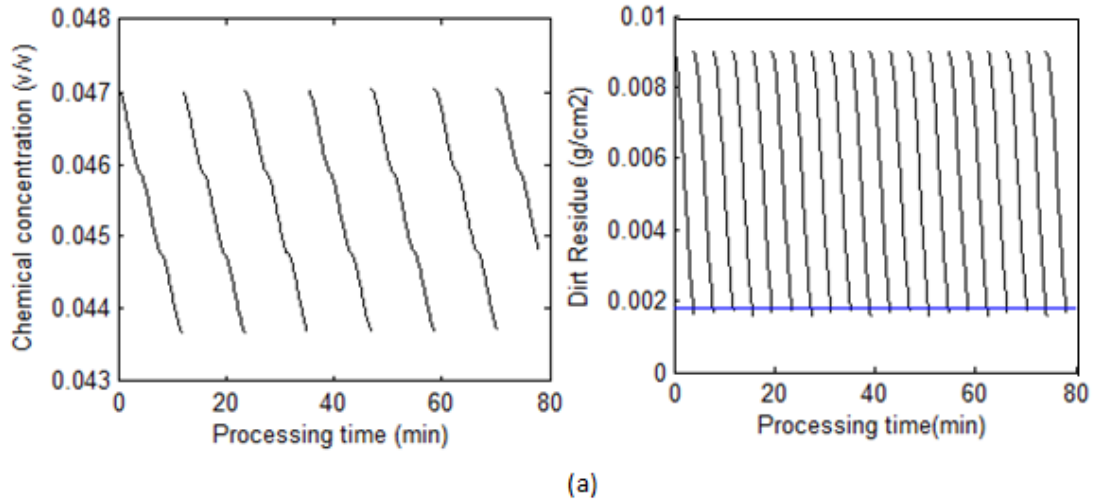
(a)



(b)

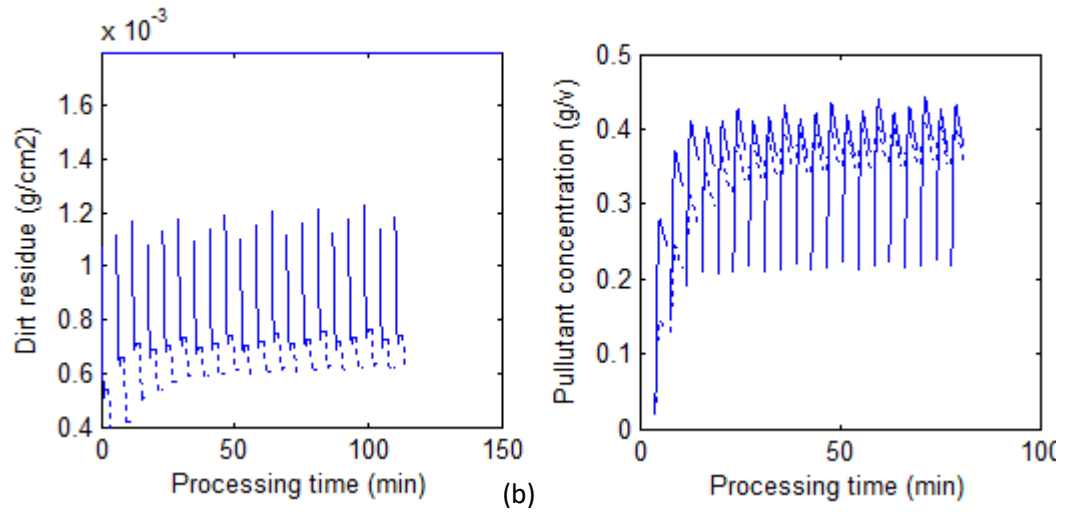
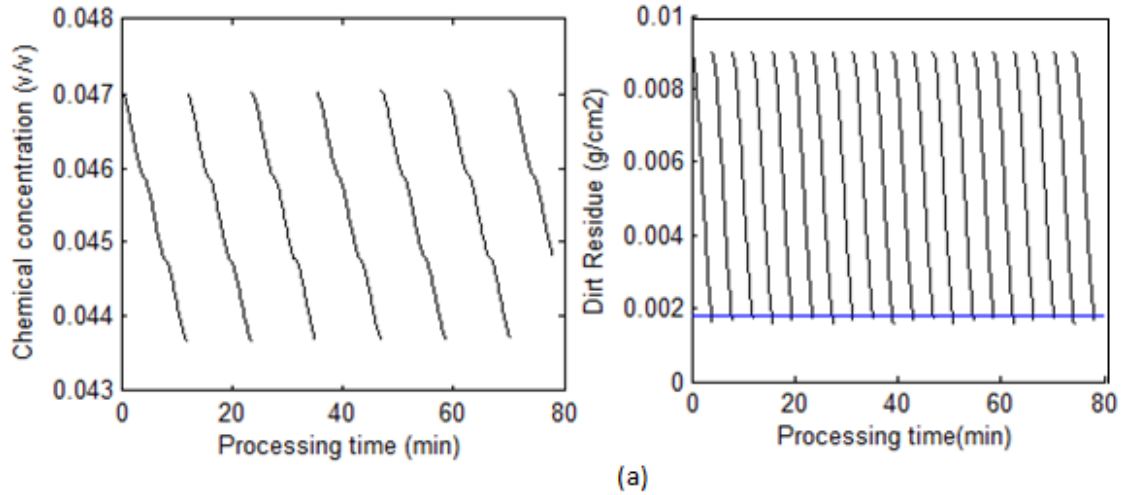
Key: \_\_\_\_\_ Tank1    - - - - - Tank 2

Figure 4.12. Dynamics of multi-barrel cleaning-rinsing system with single chemical addition and co current two stage rinsing: (a) Cleaning tank and (b) Rinsing tank.



Key: \_\_\_\_\_ Tank1    - - - - - Tank 2

Figure 4.13. Dynamics of multi barrel cleaning-rinsing with periodic addition of cleaner and co current two stage rinsing: (a) Cleaning tank and (b) Rinsing tank.



Key: \_\_\_\_\_ Tank1    - - - - - Tank 2

Figure 4.14. Dynamics of multi barrel cleaning-rinsing system with periodic addition of cleaner and two stage counter current rinse: (a) Cleaning tank and (b) Rinsing tank.

## 4.4 Economic Impact

Sustainable manufacturing implies that products should be produced in most economical way while achieving waste and energy minimization.

### 4.4.1 Cleaning operation

Waste minimization techniques demonstrated for cleaning operation achieve waste minimization by changing process of addition of chemical cleaner in cleaning tank (viz. Periodic addition, constant concentration).

Simulation results have demonstrated that these operational changes can successfully help to minimize chemical consumption and sludge formation. Reduced chemical consumption provides an opportunity for economic benefit by reducing utility consumption. Reduction in sludge generation reduces the volume of waste, which results in reduced cost of waste management. Reduction in use of chemicals also results in reduction in emissions caused by fumes generating from cleaning tank that in turn, can also results in cost saving for equipment and energy used for emission control. These waste minimization techniques do not interfere with operational time or hoist scheduling which may cost any economic loss. Thus, waste minimization techniques demonstrated for cleaning operation are environmentally as well as economically beneficial.

Results of cases simulated for cleaning demonstrate about 14 % reduction in chemical consumption. To perform economic analysis, barrels processed per day is selected as basis for calculation. Approximately 30 barrels are processed in an average electroplating facility per day. As per simulation, chemical consumed for 30 barrels is 10.8 gallons. System under consideration

in this case is an acid cleaner. Price of Acid cleaner is obtained to be 12 \$/gallon. Acid cleaner worth \$120 per day is consumed for cleaning. Yearly cost of cleaner comes out to be \$36,000 assuming 300 days of continuous production. After finding optimum mode of operation, this cost comes down to \$31,248. This results in \$4,752 annual savings from one cleaning tank.

#### **4.4.2 Rinsing operation**

Waste minimization techniques for rinsing operation are aimed at reducing rinse water consumption. Rinsing process is characterized by contaminant concentration in rinsing tank and amount of dirt removed during the process. Waste minimization for rinsing is achieved by changing operational modes (viz. co-current and counter current). Simulation results of this process show significant reduction in concentration of contaminant in rinsing tank while complying with cleaning requirement specified for downstream plating process. Reduction in contaminant concentration in rinsing tank guarantees specified dirt removal for subsequent barrel for same amount of rinse water flow rate, which ultimately results in minimizing rinse water consumption. Reduction in rinse water consumption provides an opportunity for economic benefit by minimizing utility consumption. Moreover, minimized contaminant concentration results in reduced volume of waste, which in turn, results in economic benefits via reducing the cost of waste treatment. These operational changes rely on changing the direction of flow of rinse water in order to achieve waste minimization, which does not interfere with operational time or hoist scheduling. Waste minimization techniques demonstrated in this section can be environmentally as well as economically beneficial.

Results for simulation of rinsing process shows 33% reduction in rinse water consumption. Price of fresh water purchased by an industry from municipality is 0.015 \$/gallon.

With basis of 30 barrels / day, cost of rinse water consumed per day comes out to be \$3.6 per day. Yearly cost of rinse water comes out to be \$1,080. After finding optimum operating conditions, yearly cost of rinse water comes down to \$720 that shows \$360 annual savings for two rinsing tanks.

#### **4.4.3 Cleaning-rinsing operation**

Sludge generation is a serious environmental and economic problem in electroplating facilities. More sludge generation causes increase in volume of waste to be treated which results in increased cost and energy for waste treatment. Simulation results from cleaning-rinsing system demonstrate cleaning operation is responsible for majority of sludge generation. Minimization of chemical consumption in cleaning tank results in reduction in sludge generated in cleaning tank as well as reduction in sludge generated through drag out. Thus, minimization of sludge generation results in minimizing the volume of waste and eventually it will result in economic benefit for electroplating facility in terms of cost, utilities and energy saving for waste treatment.

Sludge generation in this simulation is reduced by 5% for cleaning operation. Cost of treating this sludge is 1.5 \$/lbs., which is obtained from national metal finishing resource center. For present case, sludge generation is 2.64 lbs./barrel. Based on 30 barrels per day production rate and assumption of 300 days of production, yearly sludge generation comes out to be 22,000 lbs. Cost of treating this sludge comes out to be \$34,760. After optimization, this amount comes down to \$ 31,000. This indicates annual saving of \$4,760. All three case studies collectively demonstrate potential opportunity of saving nearly \$9,872 annually without significant capital investment.

Operation	Annual savings (in USD)
Cleaning operation	4,752
Rinsing operation	360
Cleaning-Rinsing operation	4,760
<b>Total</b>	<b>9,872</b>

Table 4.7. Annual savings.

\*Results presented in above table are based on simulation carried out for one cleaning tank and two rinsing tanks.

## CHAPTER 5

### CONCLUSIONS

#### 5.1 Conclusions

Waste minimization is one of the major tasks for pollution prevention in electroplating. The effectiveness of waste minimization relies on complete characterization of electroplating process, deep understanding of the process and expertise. This work demonstrates the application of computer aided simulation tool to achieve source reduction through various operational and process changes. Simulation tool implements first principles based mathematical models developed for cleaning and rinsing systems. The simulation tool is developed on MATLAB platform and is deployed as standalone windows application. This application is compatible with windows 7 and later operating systems.

This simulation tool provides an accurate quantitative analysis of major unit operations to reveal opportunities of waste minimization. Dynamic process models are developed for all unit operations viz. cleaning, rinsing and plating. These dynamic process models provide quantitative information about chemical consumption, dirt removal, sludge generation and rinse water consumption. Various operational modes are provided in order to achieve source reduction. Simulations presented in chapter case studies demonstrate up to what extent use of chemical and water can be minimize in order to reduce chemical and rinse water consumption while maintaining the product quality. To achieve minimization in chemical consumption, cleaning system can be simulated with various operational models such as periodic cleaner addition and constant cleaner concentration. With the help of quantitative analysis provided by



the simulation tool optimum operating conditions for given load of parts and specified amount of cleaning can be decided. Rinsing operation can be evaluated with co current or counter current rinse and results obtained can be used to decide optimum operating condition for rinsing tank.

## 5.2 Future Work

Data base enhancement, present simulation tool is based on dynamic mathematical models of cleaning and rinsing system. These models have certain physical constants that are stored in property database part of simulation tool. Physical constants depend upon type of cleaner used, type of metal to be cleaned and type of dirt to be removed. Current version of simulation tool has a limited database of physical constants. In future using experimental data and methods explained in chapter 2, information regarding physical constants for various type of cleaners, metals and soils can be generated.

Model development for plating operation, plating model presented in chapter 2 is more of methodological. Detail models for plating should be studied in order to characterize source reduction in plating tank. Model developed should be able to characterize plating thickness and uniformity on the surface with chemical concentration dynamics in plating tank.

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**ABSTRACT****MODEL BASED PROCESS ANALYSIS AND TOOL DEVELOPMENT FOR  
SUSTAINABLE ELECTROPLATING OPERATIONS**

by

**NAVDEEP BHADBHADE****December 2015****Advisor:** Dr. Yinlun Huang**Major:** Chemical Engineering**Degree:** Master of Science

The electroplating industry has faced tremendous challenges in maintaining its economic competitiveness as well as improving its environmental performance in the global economy. In electroplating systems, waste generation from manufacturing lines has been always a serious concern, as waste emitted in different forms contains various hazardous and toxic chemicals. It is recognized that much of the generated waste is avoidable, and reduction of such avoidable waste could significantly reduce the consumption of chemicals, energy, and water. Proactive source reduction can improve not only environmental quality, but also economic performance. This type of source reduction, which could be called Proactive Pollution Prevention, can be achieved through applying advanced sustainability-bearing process systems engineering techniques, i.e., the fundamental system modeling and simulation techniques.

In this thesis, the process models developed for electroplating systems are reviewed and selectively adopted. These models are embedded in a computer aided simulation tool, which is MATLAB based platform. The tool has been used to conduct comprehensive simulation of

electroplating systems. It can characterize the dynamic operations of cleaning and rinsing operations, where chemicals, energy and water are consumed. This software tool helps users to analyze the process under given conditions and predict the consumption of chemicals in cleaning tanks, and rinse water consumption in rinsing tanks. The simulation facilitates identification of superior operating conditions in the electroplating systems, and it provides comparison between conventional and suggested operational strategies. This model-based simulation methodology as well as the tool should be valuable for the electroplating industry to improve their system's sustainability performance.

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- Developed Simulation tool for sustainable electroplating process.
- Developed software tool using MATLAB.
- Developed dynamic simulation algorithms for various unit operations involved in electroplating process.
- Developed algorithms for optimizing chemical consumption and rinse water in electroplating process.

### SELECTED PUBLICATIONS

Song, H., N. Bhadbhade, and Y. Huang, "Sustainability Assessment and Performance Improvement of Electroplating Process Systems," in *Sustainability in the Analysis, Synthesis, and Design of Chemical Engineering Processes* (H. Cabezas and G. Ruiz-Mercado, eds.), Elsevier, 2015.

Song, H., N. Bhadbhade, and Y. Huang, "Sustainability assessment and performance improvement of electroplating systems" presented at the *AICHE Annual Meeting*, Atlanta, GA. Nov. 16-21, 2014.