Development chemical oxygen demand sensor

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Development of Chemical Oxygen Demand Sensor

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Summary

Chemical Oxygen Demand (COD) is one of the most important parameters in wastewater measurement standard and treatment process. COD measures the oxygen demand of biodegradable pollutants plus the oxygen demand of non-biodegradable oxidizable pollutants. The standard COD measurement method relies heavily on human operation, which is prone to error and also very time consuming. Therefore, fully automated COD sensor is highly desired by the industry and the government body. In past few decades, great amount of researches have been conducted to develop a suitable COD sensor, among which, seven methods have the potential to be automated. These methods can be further categorized into either chemical or physical methods. Each method has its own advantages and limitations. In general, chemical methods are accurate and have wide application range, but take a long time to complete the measurement. On the contrary, most of the physical methods are fast but require a large data base and have limited application range.

After careful study of all existing methods, a new COD sensor is proposed. This new COD sensor relies largely on the properties of ozone. Ozone is well known for its active chemical property, and it has been widely used in wastewater treatment process and infection processes (especially in food industry). The concentration of ozone can be reflected by Oxidation & Reduction Potential (ORP) sensor. This is the most important tool that provides a means to electrically monitor the change in concentration of ozone in the proposed system. Some of other ozone properties, such as temperature dependent pH, solubility, and heat factor are also carefully considered to ensure the reliability of this new COD sensor.

The development of new COD sensor is divided into several parts: mechanical system, electronic system, embedded controller and control theories. All these systems are developed in parallel. Detailed design of the system is presented in this thesis. A 16 bits 96MHz RISK micro-controller is the key component in the embedded controller. The development environment is C/C++. The scheduler implemented is based on clock driven.

The measurement of COD value for the new COD sensor is designed to be performed in three steps: generation of ozone solution, rough estimation of COD value and lastly accurate measurement of COD value. The focus of the author is on the last step.

The accurate measurement of the COD value is a flow analysis problem. Each portion of the stream flowing in the pipeline can be viewed as a batch reactor (BR) since nothing is entering or leaving the system during chemical reaction. Many researches have shown that in BR system, the changes in concentration of reactants presented a fixed pattern with time. For an unknown water sample, if one could find out the time-dependent concentration change of one known reactant (i.e. ozone), the initial concentration of the other reactant under test (i.e. pollutants) or conventionally termed COD value can be determined. Therefore, the measurement of COD is equivalent to identify how the concentration of ozone varies with time. In our system, ORP sensor is used to monitor the concentration change of ozone. ORP voltage reading against time is plotted to identify the pattern and thus we could estimate the initial concentration of the sample under test. To obtain the plot, many sampling points are required at different time slot. The challenge here is how to design the sampling algorithm so that we can obtain maximum sampling points within a short time frame. After careful study of system constraints and requirements, two methods are proposed. One follows strictly the rules and requirements,

and a tricky way is proposed to shorten the overall sampling time. The other method is based on the assumption that the reaction rate is slow for COD removal. The average of ORP values during the sampling period is treated as one sampling entry to the system.

Computer simulation is done for both methods. The results show that on average the COD measurement can be completed within less than 10 mins. This is a great improvement compare to the average sampling time of 2.5 hours in standard method.

Chapter 1 Introduction

1.1 Wastewater Facts

With the increasing human activities, there is more and more wastewater discharged from domestic residences, commercial properties, industry, and agriculture which might lead to encompass a wide range of potential contaminants at all levels. For instance, chemical industries in Europe generated 5.8 million tons of hazardous wastewater composed by aromatic compounds. Within these quantities, 23% are phenol-like wastewater. Given these large quantities of contaminated water, effective wastewater treatment processes are becoming mandatory [1] and are directly related with economic profit. In recent years, considerable efforts have been expended to change or modify the traditional wastewater treatment processes, which mainly relied on tight pH and temperature control alternatives. This trend has changed because new requirements have been imposed when oxygen demand comes into the picture. [2]

Any oxidizable material present in natural waterway or in industrial wastewater will be oxidized during both biochemical (bacterial) and chemical processes. The result is that the oxygen content of the water will decrease. Left over or partially treated, discharged water contains high concentration of oxidizable material will compete with downstream organisms for oxygen, which will kill or inhibit life downstream of the discharge area and cause serious consequences to ecosystem.

The reaction for biochemical oxidation may be written as:

During which, oxygen consumption by reducing chemicals such as sulfides and nitrites are typified as:

Oxygen demand is the quantitative measure of the amount of oxidizable material in wastewater. It has wide application in measuring waste loadings of waste treatment plants and in evaluating treatment efficiency. There are three types of oxygen demand measurements namely Total Organic Carbon (TOC), Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). All of them are definitive indicators of required treatment in wastewater, and the estimation is a key part of wastewater treatment process control. High influent TOC/BOD/COD requires extensive treatment to provide the oxygen necessary to break down the water's organic contents.

1.2 *Oxygen Demand Indicators*

In recent years, total organic carbon (TOC) has been of great interest in different environmental and industrial settings because some modern, automated TOC analyzers can offer interesting characteristics, especially at the lower concentration range. [3] [4] However, the data obtained are sum parameters, which are not enough to explain all the results and show a poor correlation with the actual oxygen demand of aqueous samples.[5] [6] Moreover, determination of TOC relies on specific instruments, which are rather expensive. All these pose the need of an independent method to measure/control the

organic compound concentration.

With the increasing concern of the environmental issues, the importance of BOD/COD measurement has been recognized by most of the industrials as well as government bodies. For instance, the U.S. Environmental Protection Agency (USEPA) requires wastewater treatment plants to bring BOD/COD within limits before discharging treated wastewater, and accurate test results must be recorded for regulatory reporting. Failure to do so is a violation of federal law that can lead to extensive fines. Switzerland is another example that maximum oxygen demand between 200 and 1000 mg/L must be reached before wastewater or industrial water can be discharged to the environment. [7] Actually, most developed countries have strict rules on BOD/COD value of discharging waste water.

In addition, to comply with the law, BOD/COD measurement plays an important role in commercial businesses. Plants that treat wastewater from commercial operations measure the oxygen demand of wastewater as it becomes a factor to determine how much the commercial customer must pay in order to have its waste treated. [8]

BOD and COD

Both BOD and COD tests are measures of the relative oxygen-depletion effect of a waste contaminant. The main difference is the targeted particles. BOD test measures only the oxygen demand of biodegradable pollutants whereas COD test measures the oxygen demand of biodegradable pollutants plus the oxygen demand of non-biodegradable oxidizable pollutants.

The limitation of COD is that it cannot differentiate between levels of biologically active organic substances and those that are biologically inactive. One main advantage of COD

over BOD is that it can be measured within a small fraction of the time compared to the measuring time required by BOD. The standard BOD measurement takes 5-7 days to complete. On the other hand, COD measurement only requires 2.5 hours. Because of this, COD is now the most important parameter in wastewater monitoring. Many governments impose strict regulations regarding the maximum COD allowed in wastewater before they can be returned to the environment. For example, in Singapore, the maximum allowable COD limits for trade effluent discharge is 600mg/L for Sewer, 100mg/L for watercourse and 60 to controlled watercourse.[9]

COD Measurement

The first COD determination can be traced back to year 1949. It is defined as the quantity of a specified oxidant that reacts with a sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. COD is expressed in mg/L [10]

COD is measured in both municipal and industrial wastewater treatment plants. It not only is a reflection of the level of organic pollution, but it also gives an indication of the efficiency of the treatment process. In which case, COD is measured in both influent and effluent water. The efficiency of the treatment process is normally expressed as COD removal, measured as a percentage of the organic matter purified during the cycle [10].

1.3 Objectives

The increasing importance of COD measurement to environment monitoring and wastewater treatment processes poses many new challenges to COD sensor development. Measurements should be able to be carried out at any time, anywhere. It means that

measurements should not be constrained to laboratory environment only. For the sake of faster wastewater treatment process, having a response/delay time of only a few minutes is desired. This requires the result should be obtained as fast as possible.

Taking account of the advantages and disadvantages of existing COD sensors, a new portable COD sensor has been proposed. The objective of this new COD sensor is to provide a fast and accurate measure of COD parameter with minimum manual operation time and minimum pollution to the environment. The key features of the new COD sensor are:

1. Portability: it is becoming increasingly important that measurements can be taken at any place any time. This requires the COD sensor to be portable. It should have its own power source
2. High Accuracy: using chemical method combined with advanced measurement and prediction methods
3. Wide Application Range: can be applied to all kinds of wastewater with minimum changes
4. Automatic: the COD sensors will automatically operate throughout sampling, digestion and measuring without stop. It prevents redundant operations and errors caused by human mistake. One button solution should be provided. Self examination functions are provided for the purpose of easy maintenance.
5. Environment Friendly: standard chemical test method uses KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ as the reagent, which is likely to cause secondary heavy metal contamination if it is not well managed.

In this project, the ultimate goal is to develop a COD sensor which meets the key design

features listed above. From project management point of view, the COD sensor development is achieved in the following stages.

1. System Analysis:

- Background study of wastewater, wastewater measurement methods, current technologies in COD sensor development
- Identify the requirements of the new COD sensor
- Identify key design components
- Review the key design concepts/components, analyze system feasibility

2. System Design

- Based on the key components of the design, design the new COD sensor which fulfills the requirements

3. System Development

- Mechanical system development
- Electronic system development
- Embedded system development
- Control algorithm development

4. Tests and Validations

The author's key roles in this project are analysis, design, and development of COD sensor. During design stage, the focus is on two areas. One area is embedded system development which involves both the platform and the software. The other area is the

optimization of sampling algorithm during accurate COD measurement. In this thesis, the detailed development work is presented; the focus will be on the tasks performed by the author.

1.4 Outline of thesis

The organization of the thesis will be as follows: firstly, an introduction to COD measurement is given, followed by explanations of the significant of this project. In the following chapter, a detailed background study of the various directions on COD sensor development is presented. By comparing the pros and cons of the various methods, one method is chosen as the base version of our COD sensor development. In chapter 3, requirements, system key concepts are analyzed and developed. The actual design/development of the system is given in chapter 4. The focus is on system architecture and embedded system development. In chapter 5, the focus will be on the process optimization of the data capturing process. Simulation results and conclusions are given in the last chapter.

Chapter 2 COD Measurement Method Literature Review

Unlike pH or temperature, there is no simple electronic sensor that could measure/reflect COD value directly. COD is always calculated indirectly by measuring the amount of oxidation agent consumption during chemical reaction with unit amount of wastewater sample. Many researches have been conducted aiming at a cost effective way of COD measurement. Many new methods or improvements have been proposed. In this chapter, the following methods will be discussed.

1. Standard chemical method
2. Automated standard chemical method with suitable detector
3. Electrochemical method
4. UV spectroanalysis method
5. Drop analysis method
6. Catalytic method with Ultraviolet
7. Oxidation & Reduction Potential (ORP) method

2.1 Standard Chemical Method:

Different countries have different regulations on standard COD measurement methods. In literature, the standard method for COD measurement is normally referred as either the standard method by American Public Health Association [11] or the standard COD measurement method by Japan Industrial Standard Committee [12].

In measurement process, COD is identified as the mass concentration of oxygen equivalent to the amount of dichromate consumed by dissolved and suspended matter

when a water sample is treated with that oxidant under defined conditions. It has a unit of mg/L.

An example of standard measurement procedure would be: a test portion of wastewater is refluxed in the presence of mercury (II) sulphate with a known amount of potassium dichromate and silver catalyst in strong sulphuric acid for two hours, during which part of the dichromate is reduced by the oxidizable material present. The remainder of the dichromate is titrated with ammonium iron (II) sulphate. The COD value is calculated from the amount of dichromate reduced. According to chemical reaction formula, 1 mol of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) is equivalent to 1.5 mol of oxygen (O_2).

2.2 Automated Standard Method with Suitable Detector

HANNA Instruments has developed a series of fully automated COD sensor following Standard Chemical Method. [13] 120 minutes of sample treatment time is required for accurate measurement. Closed reflux colorimetric method is applied to the after-treatment sample. A special tungsten lamp which would give 4 wavelengths and narrow band filter has been used to enable the accurate detection. The whole measurement system comprises several major components as shown in Figure 2.1. There is one particular component for heating and one for spectrum analyzing. The sensor is still time consuming and involves a lot of operations.

Figure 2.1 HANNA Instrument COD Measurement Sets

A fully automated detection COD sensor based on Potassium dichromate had been reported by Korenaga and Ikatsu from Japan. [14] In their design, a spectrophotometer has been used to detect the absorbance of Cr (VI) after a series of chemical reaction at high temperature with aqueous glucose solution under acid environment. They have also concluded that for their sensor COD value is proportional to the peak height of the spectrophotometer result for low COD condition. As a result, they have achieved a maximum measurement speed of 15 samples per hour with precision of 0.4% for the prepared target solution. However, the accuracy can be as low as 30% compared to standard method (Mn). This difference was introduced by the concentration of Cr (VI) in wastewater. Similar methods can also be found in [15] and [16]. An illustration of their system design is shown in Figure 2.2.

Figure 2.2 Block Diagram of Automated COD System by Korenaga [14]

A new generation of Glass electrodes had been developed by Beliustin and Pisarevsky. [17] Potentiometric determination of COD was carried out in a simple experimental setup. Chemical reaction is carried out in acid environment. Result shows that error is no more than 2% in low COD range.

2.3 *Electrochemical Method*

In year 1993, Comninellis proposed a new wastewater treatment method based on electrochemical conversion/combustion. [18] Based on the oxidation principle, electrochemical methods can be further categorized into two groups, namely electrocatalytic and photocatalytic.

For electrocatalytic method, Lee and Ishikawa from Japan have their COD Sensor developed based on coulometric determination of Electrochemical Oxygen Demand (EOD) using surface oxidized copper electrode. [19] They have then improved their system by introducing a stopped flow thin layer electrochemical cell. [20]

Figure 2.3 Surface Oxidized Copper Electrode EOD Determination [20]

EOD is equivalent to COD. The total electrons consumed during chemical reaction in the system were used to calculate the COD value. A large electrode area to sample volume ratio was used to guarantee the fast electrolytic reaction. They have achieved an average measurement time of 5 minutes per sample.

However, the accuracy was greatly influenced by chemical composition of wastewater sample. Many sets of measurements were performed with different chemical compositions. The results are stored as references to the actual measurements. For unknown samples, chemical composition must be identified before measurement to ensure the accuracy. In their test cases, linear sweep voltammetry have been performed on samples to identify the chemical composition prior to the COD measurement. This again, raises the cost of the method.

Beside the systems based on electrocatalytic method, Lee and Kim have also developed several models of COD sensor based on photocatalytic method. [21] [22] Their models are then improved by Zhao et. al. [23]. The working principle is illustrated in Figure 2.4.

Figure 2.4 Analytical Signal Generation During Photocatalytic Process [23]

The strong oxidation power of illuminated TiO_2 particles is the key in photocatalytic method. The reaction rate is greatly increased compared to the electrocatalytic degradation method. A similar measurement mechanism is adopted. Overall charge consumed throughout the measurement is proportional to COD value. They have achieved a sampling rate of 1-5 mins per assay. However, the application is only applicable to low COD range of 0 to 200 mg L^{-1}

Shanghai Precision & Scientific instrument Co. Ltd has developed their online COD measurement device COD-580 based on electrochemical method with measurement range 10-1000mg/L and accuracy of $\pm 15\%$. [24]

2.4 UV Spectroanalysis Method

Ultraviolet was used during wastewater treatment process. [25] In recent years, there is also report that UV is used in COD measurement. Automatic W-control system for relative evaluation of organic water pollution, [26] Fang and Dai had developed their online COD sensor solely depending on UV spectrums [27] as shown in Figure 2.5.

Figure 2.5 UV Spectrum Measurement Process [27]

An online adaptive algorithm based on LS-SVM has been developed. Unknown sample was modeled with the most relevant training samples based on the assumption that similar spectra lead to similar COD values. Results have shown that their sensor has an accurate prediction on the trend of COD change. However, the difference per sample can not be neglected.

2.5 Drop Analysis Method

Qiu et al. have developed their COD sensor solely based on physical method. [28] The detection mechanism adopted in their sensor is called drop analysis technology. Earlier research has shown that liquid forms its drop in unique way based on its chemical, physical and mechanical characteristics. This is known as the fingerprint of the liquid. In this method, liquid characteristics are monitored by its drop forming process under certain condition and environment. COD value is then predicted by database mapping. The system setup is shown in Figure 2.6.

Figure 2.6 Scheme Connection Graph of Integrated Drop Sensor [28]

In order to have accurate estimation of all COD ranges, it will definitely require a large database and excessive experiments are required to create the database. There is no way they could do COD prediction on unknown samples. In addition, there is no actual data on the accuracy of the method presented in their paper. A lot of efforts are needed in order for this method to be practical.

2.6 Catalytic method with Ultraviolet

Chai et al. have developed their system based on photocatalytic oxidation using nano- $\text{TiO}_2\text{-Ce}(\text{SO}_4)_2$ as the catalyst. [29] The method has been proposed to improve the inefficient degradation process in standard measurement method for low COD condition. The system setup is shown in Figure 2.7.

Figure 2.7 Schematic of Photocatalytic Reactor [29]

Ce (IV) has absorption spectra at 320nm while Ce (III) is having its absorption peak at 250nm. The consumption of Ce (IV) during degradation is monitored by differentiating the UV absorption at 320nm. From their experiment results, absorbance of Ce (IV) was found to have a linear relationship with COD value. This is a very good method for COD determination, results has shown very good agreement with standard method. However, it is still a manual method with limited application range on low COD condition.

2.7 *Oxidation Reduction Potential (ORP) Method*

Holman and Wareham have developed their on-line Dissolved Oxygen (DO) Monitoring System based on ORP measurements. [30] The system was developed to work under low DO condition. Experiments have been setup to monitor the ORP change during the entire wastewater treatment process. dORP/dt against time profile has been studied. In the result figures, two jumps have been identified as common to all wastewater treatments.

Figure 2.8 Typical ORP Profile Plot [30]

Figure 2.8 elaborates the findings from Holman's experiments. According to their observation, the first jump corresponds to the time where COD is essentially depleted. They have suggested using this jump point as wastewater treatment control point. It is the point of time to turn off the inflow oxidant. Depending on the initial COD concentration and the speed of the flow string, it might take around 25 minutes to reach this point. From control point of view, this is not a very good skim. The signal feedback is too slow, large overshoot might take place.

Zipper, Fleischmann and Haberl have conducted a series of experiments to simulate the environment of small wastewater treatment plant. [31] Nitrate, ammonia concentration and ORP have been measured. In their experiments, they showed clearly a linear relationship between ORP voltage reading and nitrate concentration.

Both of the studies indicate the possibility to use ORP probe to do COD measurement.

2.8 Conclusion of Existing Methods

All the above methods can be further categorized into physical methods and chemical methods. In general, physical methods are faster, need less man power, easy to be automated, but most of them rely on large sample base for result prediction and have limited application range, only targeting at particular types of wastewater

Compared to physical methods, chemical methods are more accurate and adaptive with a wide range of wastewater samples. However, traditional chemical methods require a long measuring time, large amount of water and electric power. KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ used in standard methods and various catalysts like HgSO_4 involved in other improved methods are difficult to dispose. Left over chemicals are toxic and likely to cause secondary pollution. In addition, the dilution and titration required in chemistry process are to be done by testers. This increases the operation and maintenance cost greatly. The accuracy of test results greatly depends on the skill level of tester.

Considering the fact that the application range is very narrow for physical method, and testing data is only accurate for specific type of wastewater. We would prefer the chemical method which basically can be performed on any type of wastewater. Since standard method is time consuming and can only be carried out in laboratories, many researches and improvement have been done on existing methods such as modification of heating process [32][33][34], change of oxidant[35][36][37] etc. However, the overall performance is still not very satisfactory. Therefore, there is an urgent need to have a novel COD measurement device which is accurate and less time consuming. This project is proposed to develop such a COD sensor based on chemical method.

Chapter 3 Analysis of New COD Sensor

3.1 Basic Measuring Principle

As discussed in previous chapter, compared to physical methods, COD measurement has the advantages of accuracy and wide application range. However, most chemical methods are suffered from long measurement time and troubles in dealing with reaction agent before and after measurement. Considering the requirement that a general purpose COD sensor should be applicable to all kinds of wastewater COD measurements, chemical methods will be adopted.

COD value reflects the oxygen demand of biodegradable pollutants plus the oxygen demand of non-biodegradable oxidizable pollutants. The whole idea of standard method which uses KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ is because they are strong oxidants, and their presence in water can be identified by color through titration. Through the chemical reaction formulas such as:

the mass concentration of oxygen equivalent can be calculated. With the same idea in mind, a new COD sensor based on chemical method is proposed. In addition, several technologies have been employed in the new sensor design to compensate the disadvantages involved in normal chemical methods. For design efforts, attentions are concentrated on modifying the following factors to improve the overall performance of

COD sensor in terms of speed, accuracy, and application range.

- Choice of oxidation agent to achieve faster reaction rate and avoid secondary contamination
- Oxidant concentration detection device/method to avoid the potential inaccuracies introduced by human. (spectrometer/titration etc)
- Process optimization to shorten the over all sampling time per serve.

3.2 Choice of Oxidant

KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ are the standard oxidant for COD chemical measurement. However, the disadvantages such as heavy metal contamination, requirements on tester skill level etc have proven that either KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ is not an ideal oxidant. Moreover, the amount of these two chemicals is examined through titration and relies on human eyes, which cannot be automatic. A new oxidant shall be chosen.

Consider the fact that ozone is also a very strong oxidant, and it has been used intensively in wastewater treatment and in low COD wastewater treatment especially in food industry. It is becoming a classic oxidizing agent for advanced treatment of wastewater [37]. Many studies have reflected that ozone has a very efficient COD removal rate [38] [39] [40] [41] [42].

3.2.1 Reasons of Choosing Ozone

There are three main advantages for ozone to be chosen:

- Ozone is a very strong oxidation agent, it has active chemical property.

Oxidation by ozone is more effective than that by potassium permanganate. [43]

Table 3.1 shows clearly that ozone has higher oxidation reduction potential than most of the other oxidants. It directly proves that ozone can be used to replace the chemicals used in standard method with no question in its oxidation ability.

Table 3.1 Oxidation-Reduction Potential (Volts) of Different Chemical Oxidants [44]

Agent Molecular	Chemical Formula	Oxidation Reduction Potential
Fluorine	F_2	2.87
Ozone	O_3	2.07
Hydrogen Peroxide	H_2O_2	1.78
Potassium Permanganate	$KMnO_4$	1.70
Iodine	I_2	0.54

In addition, ozone is such a strong oxidant that it can theoretically provide sufficient energy in aqueous solution to degrade the strong chemical bonds in reducer. During oxidizing process, ozone may react directly with chemical molecules in aqueous solution. It may also generate hydroxyl radicals to oxidize chemical molecules. [45]

- Ozone can be obtained easily.

Ozone can be generated directly from air or oxygen by applying high voltage through bipolar material. There is no need of preparing testing chemical.

- The concentration of ozone in water can be monitored by electronic means.

COD removal process is basically the oxidation process. It is caused by transfer of electrons from oxidant to the substances being oxidized. The voltage reading of ORP has a constant relation with ozone concentration in solution under controlled environment. This can be used to reflect the ozone concentration. By comparing the initial ozone concentration before reaction and the one after chemical reaction, ozone consumption can be calculated. The ORP properties and its correlation with pH, temperature and COD will be discussed in more details in section 3.3.

3.2.2 Drawbacks of Ozone and Compensation Method

Despite the promising properties of ozone in automated COD measurement methods, there are several drawbacks that must be carefully considered before implementation.

3.2.2.1 Nature Decomposition

One of the major draw backs for ozone is its stability. Ozone will undergo decomposition in natural environment. The decomposition formula is shown below:

Ozone will decompose to oxygen with time. Table 3.2 demonstrates the relationship between ozone lifetime and temperature. From the table, it is clear that ozone has a longer lifetime under lower temperature.

Table 3.2 Ozone Lifetime [46]

Gaseous		Dissolved in water	
Temp(°C)	Half-life	Temp(°C)	Half-life

-50	3-months	15	30-minutes
-35	18-days	20	20-minutes
-25	8-days	25	15-minutes
30	3-days	30	12-minutes
120	1.5-hours	35	8-minutes
250	1.5-seconds		

Reading from Table 3.2, under room temperature, the half-life time of ozone is still too short as compared to the chemical reaction time required. A complete oxidation reaction between ozone and organic compound is very time consuming, it may take hours or even days to fully react. In which case, due to the decomposition of ozone, the actual amount that is consumed is not known. Ways to reduce the decomposition rate and methods of compensation are needed.

Not only temperature, the decomposition rate is indeed affected by other parameters as well. In gaseous phase, decomposition is also affected by humidity and concentration. However, in solution, it is a function of pH, concentration of various additives, and temperature [47]. Many studies have been carried out to study ozone decomposition properties. Many mathematical models have been proposed. [48] [49].

Figure 3.1 demonstrates the decomposition rate of ozone in solutions with different pH values at temperature of 25°C. The vertical axis is the ozone decomposition rate given by current ozone concentration over initial ozone concentration. From the figure, we can clearly tell that the lower the pH value, the slower the decomposition rate. Moreover, the decomposition rate is almost constant at low pH range.

Figure 3.1 Effect of pH on Ozone Decomposition [50]

This very important property reminds us that the chemical reaction should be carried out in acid environment. At constant temperature, the amount of ozone lost due to nature decomposition can be easily calculated by the constant decomposition rate at low pH condition.

3.2.2.2 Ozone Solubility

Since chemical reactions for COD measurement are carried out in water solution, ozone solubility in water must be taken into consideration. Ozone concentration in water is recorded as mg/L or PPM. The relation between them is shown below:

$$1 \text{ mg/L} = 1 \text{ PPM O}_3 = 1 \text{ g O}_3/\text{m}^3 \text{ water}$$

Ozone solubility is affected by several factors. The most important parameter affecting the solubility of ozone is probably water temperature. Based on Henry-Dalton constants, the solubility of ozone in water is higher at lower temperatures. In addition, the original

concentration of ozone in its gas phase will definitely influence the resulting ozone concentration in water. Figure 3.2 and Table 3.3 elaborate the actual influences by these two factors.

Figure 3.2 Ozone Solubility [46]

Table 3.3 Ozone Solubility[46]

%O ₃ Gas	5°C	10°C	15°C	20°C
1.5% (w/w)	11.09	9.75	8.40	6.43
2% (w/w)	14.79	13.00	11.19	8.57
3% (w/w)	22.18	19.50	16.79	12.86

pH value not only affects the decomposition rate, but also the ozone concentration as well. Figure 3.3 demonstrates well on this point. In general, with fixed initial concentration (IC) of ozone, the lower the pH value, the higher the ozone concentration. This again,

emphasizes the importance of placing the COD measurement process in acid environment.

Figure 3.3 Effect of pH on ozone concentration [44]

Last but not least, by Henry's law, ozone solubility in liquid is directly proportional to the pressure that the gas exerts on the liquid surface[51]. In order to have ozone solution with consistent concentration, pressure should be carefully maintained.

3.2.2.3 Other Considerations

In addition to above ozone properties, health factor is one more aspect that must be considered. Table 3.4 concludes a series experiment on the lethal concentration of ozone. From this table, it is clear that excess ozone must be destroyed before it is discharged.

Table 3.4 Lethal Concentration for Ozone [52]

Species	LC _{Lo} (ppm)	Time	Adjusted 0.5-hr LC (CF)	Derived value
---------	---------------------------	------	-------------------------------	------------------

Mouse	12.6	3 hr	23 ppm (1.8)	2.3 ppm
Human	50	30 min	50 ppm (1.0)	5.0 ppm
Rabbit	36	3 hr	65 ppm (1.8)	6.5 ppm
Mouse	21	3 hr	38 ppm (1.8)	3.8 ppm
Rat	21.8	3 hr	39 ppm (1.8)	3.9 ppm
G. pig	24.8	3 hr	45 ppm (1.8)	4.5 ppm
Rat	4.8	4 hr	10 ppm (2.0)	1.0 ppm

It is so good that ozone temperature property provided us an easy way of destroy ozone.

3.3 *ORP Working Principle and Properties*

The most basic principle of how Oxidation Reduction Potential (ORP) sensor works is as follow: the strong oxidizers pulls electrons away from platinum or gold probe which will create a small voltage different to the reference probe. The reference electrode is normally a silver electrode in a silver salt solution. A typical ORP probe is shown in Figure 3.4

Figure 3.4 ORP Probe

A strong oxidizer, such as ozone, or a strongly oxidizing condition, such as concentrated hypochlorite or chlorine dioxide, will rapidly steal electrons from the microbial membrane resulting in the loss of its vital functions. The more oxidizer, the greater the comparative voltage generated between the two probes.

The Nernst equation describes the relation of ORP of the system to the concentration ratio of the oxidant and the substance being oxidized. [53]

$$E = E_0 - (RT / nF) \ln[Oxid] / [Red] \quad (1)$$

where R is the gas constant; T is the absolute temperature; n for number of electrons reacting in redox equation; F is Faraday constant; E for ORP of the system, or electrode potential of chemical reactions; E_0 represent standard electrode potential; $[Oxid]$ for molar concentration of oxidant and $[Red]$ is molar concentration of substance being oxidized.

From Eq. (1), in controlled environment, where E_0 , R , T , n and F are all constants, the concentration of reducer $[Red]$ can be calculated from $[Oxid]$, E as:

$$[Red] = [Oxid] \cdot \exp\left[-\frac{nFE_0}{RT} + \frac{nFE}{RT}\right] = \exp\left(-\frac{nFE_0}{RT}\right) \cdot \left(\exp\left(\frac{nFE}{RT}\right) \cdot [Oxid]\right) \quad (2)$$

$[Red]$ is proportional to COD value. This provides a hint on how to estimate COD value.

ORP probe measures the electrode potential E of the chemical reaction. The output of ORP sensor is voltage in mV. Tango and Gagnon have successfully measured residual ozone concentration using ORP measurement as shown in Figure 3.5. [54]

Figure 3.5 ORP Reading against Ozone Concentration

Table 3.5 Measured Field Data for residual ozone using ORP method [54]

Sample	Control module		Ozonated module 1		Ozonated module 2	
location	ORP (mV)	O3 (mg/l)	ORP (mV)	O3 (mg/l)	ORP (mV)	O3 (mg/l)
Biofilter	218.9	<0.1	322.4	0.18	345.1	0.20
Swirl	219.6	<0.1	320.5	0.18	318.7	0.18
Pre-ozone	213.1	<0.1	287.0	0.16	282.6	0.16
Post-ozone	220.5	<0.1	330.4	0.20	364.9	0.22

Over the past twenty years, attempts have been made to utilize ORP as a control parameter for wastewater treatment/monitoring process. Kim and Nam from Korea have developed pigment wastewater treatment system based on ORP measurement using fenton oxidation Process Control. [55] Their system applies the same basic design theory as the one presented in this thesis.

In principle, ORP reading is proportion to ozone concentration. However, studies have shown that there are many factors affecting this relation. pH is one of the example. In general, the lower the pH value, the higher the ORP voltage reading. In addition, ORP reading is also affected by temperature. [56] The presence of certain chemicals like NaOCl will also affect the voltage reading.

Oxidation-reduction potential offers great advantage to real time monitoring of wastewater imperfection. However, the potential disadvantages are largely related to equipment maintenance, calibration and cross-checking sensors. [57] ORP sensors cannot be exposed to air for long time. If it is not in operation, it shall be kept in silver solution. The electrode needs to be cleaned to allow accurate reading.

3.4 COD Measurement Principle

Based on the new COD sensor measurement principle, instead of measuring the amount of KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ consumed in standard method, the problem here becomes how to measure the amount of ozone consumed throughout the process by ORP sensor. ORP voltage readings before and after chemical reaction are used to calculate ozone consumption based on the ozone/ORP relation as shown in Figure 3.5. By definition, COD value, which reflects the concentration of reduction agent in wastewater, is proportional to the overall ozone consumption during the chemical reaction as shown in Figure 3.6.

Figure 3.6 Consumed Ozone vs COD value

However, the amount of consumed ozone cannot be simply calculated by subtracting from the initial dissolved ozone for reasons mentioned in section 3.2.2. Direct subtraction will give the result of change in dissolved ozone which is a combination of consumption plus self-decomposition as illustrated in Figure 3.7.

Figure 3.7 Ozone Deduction [58]

The amount of ozone deduction due to self-decomposition process must be compensated.

As decided, our chemical reactions for COD measurement are to be carried out in acid environment ($\text{pH} = 3$) where a decomposition rate is maintained constant. A simple mathematical model is

$$\text{COD} = k \cdot \text{Ozone Consumption} = a \% \cdot \Delta (\text{Dissolved Ozone}) \quad \text{where } k < 1.$$

Figure 3.8 [59] was captured by Kaulbach during COD removal process. It is plotted under the initial conditions $\text{COD} = 950 \text{ mg/L}$ and $\text{pH} = 7.35$. The contact time in the plot is referring to how long the reactants are in contact, it actually describes the chemical reaction time. It demonstrates a typical wastewater treatment/ COD removal process. COD value drops as the ozone contact time increases.

Figure 3.8 COD Value vs Ozone Contact Time

Chapter 4 Design and Implementation of New COD Sensor

4.1 *Sensor Design*

Based on the theoretical analysis of new COD sensor, the new COD sensor is designed.

There are totally three steps designed to achieve the ultimate purpose of COD measurement.

4.1.1 *Preparation of Ozone Solution*

First of all, there must be a consistent source of ozone and it must be able to be generated on site. In general, there are three ozone generation techniques [61]:

- UV – similar to UV radiation from sun (low ozone production)
- Cold Plasma – visually similar to neon tube (medium ozone production)
- Corona Discharge – similar to lighting (high ozone production)

Since the amount of ozone required in this project is relatively large, the corona discharge method with high production rate is preferred.

Furthermore, COD measurement is done indirectly by calculating the ozone consumption.

This poses a strict requirement on the quality of input ozone solution. The input concentration of ozone solution should be maintained unchanged through out the measurement. Recall in 3.2.2.2, ozone maximum solubility is affected by input ozone concentration in its gas phase, temperature and pressure/air flow rate. A good ozone generator with consistent production rate/pressure is required. Temperature of water solution needs to be carefully maintained at a fixed level. In addition, due to the

decomposition of ozone, pH needs to be controlled as well. All the above requirements are fulfilled in the very first control system of the COD sensor. The control system is identified as below:

Figure 4.1 Control System Identification

There are totally 4 control variables in the system and 6 manipulation variables are available for control purpose. pH, temperature and ozone solution concentration should be kept constant before chemical reaction, water flow rate is used to control the reaction time of chemicals in lateral system since to total volume is fixed. Each of the control variables can be controlled by manipulating several manipulation variables. pH value is affected by pH buffer injection rate, pH value and water flow rate. Heater, ozone gas flow rate and water flow rate are the greatest influence factors on temperature. Ozone solution concentration is directly controlled by the voltage level, voltage frequency and air flow rate in ozone generator. In addition, air pressure and inlet water temperature, buffer pH value are identified as the disturbance to the system. However, there is too much freedom from control point of view. To simplify the control, a simpler control system is proposed.

Figure 4.2 Ozone Solution Preparation Control Model

In this new design, ozone generator frequency, air pump speed should be kept constant. Only voltage is used to directly control the ozone generator production rate. And the new system now has equal number of manipulation variables and control variables. The relative gain array matrix is square.

4.1.2 Define Flow ratio (Rough Estimation)

After ozone solution is produced, the next step is to commence chemical reaction and record ORP reading according to contact time. However, sample COD value can range from 0 to 1 g/L or even more. Since ozone solubility is fixed, for fixed amount of solution, amount of dissolved ozone is fixed. If sample COD is too high, it is possible that the ozone is fully consumed before measurement. In such a case, test sample must be diluted to a suitable level so that the change in ozone concentration can be monitored.

To achieve a dynamic control of the mixing ratio of sample inlet and ozone solution inlet, flow injection method is adopted. Flow injection had been successfully used in other COD measurement methods as reported in [14] [15] and [43]. The basic design is that inlet streams are driven by two independent pumps with adjustable speeds. Sample

dilution ratio is controlled by different speed combinations of each pump. Ideally, we can achieve arbitrary ratio up to the pump limitation.

It is not an easy task to identify the dilution ratio. A fuzzy control system is implemented here. As a result of this part, the speed ratio of ozone solution pump and sample pump has been determined as one of the following:

Ratio: 8:1 7:1 6:1 5:1 4:1 3:1 2:1 1:1 1:2

4.1.3 Accurate Measurement

Once the optimized flow ratio of the inlet streams had been defined, the last step is to obtain the accurate ORP reading. The whole idea is to do curve fitting of captured data. This is where the optimization plays.

The standard ORP uptake rate curve can be described by a second order exponential decay equation:

$$ORP = a_0 + a_1 \exp(-t/t_1) + a_2 \exp(-t/t_2) \quad (3)$$

where t refers to reaction time. As chemical reaction goes on, ORP value will drop gradually. As illustrated in Figure 4.3, after time t_s , ORP reading reaches a steady state at where the imperfections in test sample are fully neutralized. The clean curve labeled with oxidization is corresponding to the level of oxidation reduction reaction. Reaction starts immediately after the mixing of reagents. Due to the high concentration of reagents, reaction is very fast initially. As reaction goes on, the concentration drops with time, thus, reaction slows down, until t_s where one of the reagents is fully consumed. At the same time, since concentration of oxidant drops, ORP voltage drops as well. Line marked

with dots represents ORP change. In order to measure the COD value, the fully consumed reagent must be wastewater sample. To ensure this, excess ozone is a must and it is ensured through fuzzy control.

Figure 4.3 Plot of ORP Reading against Contact time

Few ORP data were captured in the first few minutes of the process; those data will be used to estimate t_s value by curve fitting using least square method. After t_s is found, COD value can be calculated using the relation below:

$$COD \propto 1/t_s \text{ or } COD = C_1(S_o, k)/t_s \quad (4)$$

where $C_1(S_o, k)$ is constant and k is also constant and represents temperature and pH. A more detailed description of the problems in accurate estimation of COD value and the solution will be elaborated more in next chapter.

4.2 Hardware Implementation of Sensor System

Based on the COD measurement method that is proposed, the system is designed as

shown in Figure 4.4:

Figure 4.4 Mechanical Design of Proposed COD Sensor

1. O₃ generator, 2. water inlet, 3. pH doser, 4. heater, 5. pH probe, 6. ventilation, 7,12. pumps, 8. ORP probes, 9. thermistors, 10. sample inject port, 11. sample inlet, 13. bio-reaction chamber, 14. mixer, 15. embedded controller, 16. data bus, 17. ozone mixing chamber.

The main components can be grouped into four parts according to their location and respective functions:

- Ozone Generator (1)

There already exist some COD sensors based on ozone. However, their ozone generators are taking pure oxygen as the source. Pure oxygen can ensure a high ozone production rate, but it limits the use of the COD sensor by additional oxygen

tank. In this project, an ozone generator which can generate ozone from air is designed. High production rate and consistent output are the two most important criteria to measure the success of the ozone generator. Section 4.1.1 had already discussed the 3 methods to generate ozone. Among which, corona discharge method is the best choice because of its highest production rate. The proposed ozone generator is shown in Figure 4.5. The air pump is essential to run at a high speed. Because by enriching the process air, depending on the design parameters, the production rate of given ozone generator can be increased by a factor ranging from 1.7 to 2.5 versus the production capacity with steady air. [62]

Figure 4.5 Ozone Generator

- Ozone Mixing Chamber (17)

This is the place where ozone is dissolved into water to produce ozone solution. Air with ozone and fresh water are pumped through aspirator to get well mixed ozone solution. In order to have consistent ozone concentration, excess ozone is pumped to ensure a maximum solubility. In addition, pH and temperature are maintained at

Chapter 4 Design and Implementation of New COD Sensor

constant value by manipulating dozer pump (2) and heater (4) respectively. Two pH probes (5) and two thermistors (9) are feedback sensors.

One ORP probe (8) is placed in this chamber to measure the initial ORP reading which will be used as a reference value for future calculation.

- Bio-reaction Chamber(13)

This is the most important part. Chemical reactions and monitoring are carried out in this chamber. The flow rates of test sample and ozone solution are controlled by two servo-pumps (7 & 12). Three ORP probes (8) are placed in equal distances from each other in this chamber. By comparing the voltage differences in reference to the pre-mentioned ORP probe in ozone mixing chamber, the change in ozone concentration is therefore identified, so does amount of ozone consumption.

In this chamber, how well the two streams are mixed will directly affect the reaction speed and thus the measurement accuracy. The U shape design of the chamber will create disturbances to the chamber. In addition, humps (14) were introduced to create additional chaos to the flow.

- Embedded Controller(15)

The embedded controller is the brain of the whole system. This is where all the control algorithms and automation were realized. The behaviors of all the electronic devices such as pumps and valves etc are to be controlled through this unit.

All the sensor readings are to be captured and stored onto the resident memory.

After data collection, calculations are done in micro processor. The whole

controller is represented as one unit in Figure 4.4 as embedded controller.

Figure 4.6 shows system schematic drawing from data/signal view. To achieve the system requirements, many types of electronic devices are used in this system. The signal is passed by various ways as shown.

Figure 4.6 Electrical Design of Proposed COD Sensor

The embedded controller has 4 ways of communication channels. There are two RS232 COM ports. One port is connected to remote computer for development and data retrieve purpose. One is connected to 8051 micro controller. The controller is developed as the DIO and AO device. Valves and some water pumps are controlled with DO signal for digital and analog outputs. There is also one RS485 COM port available, this port is used to control the servo pumps. The SISA port is connected to 12 bit AD converter which can provide up to 16 analog to digital conversion channels.

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Figure 4.7 Network Connection of COD Sensor

Currently, those physical layout and the software structures are built. Here is a checklist for sensors and devices used in this system.

- 5 ORP Probes: Shanghai Precision & Scientific Instrument Co. Ltd, YXLG133
- 2 pH Probes: Shanghai Precision & Scientific Instrument Co. Ltd, 231
- 4 Thermesters: Renewable Alternatives, 7B
- Sample Pump and Water Pump: KNF Flodos AG, FEM1.03 TTRC and FEM1.08 TTRC
- 4 Solenoid 2 Way Valves: ASCO Scientific Valves ,
- 1 unit 3 Way Valve: Cole-parmer instrument, 01367-72

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- Proximity Sensor: Omron E2k-c25
- Air Pump & Liquid Pump: PAD, 19.002, 12.012
- Embedded Controller and Peripherals: Emtronix, ETR232 Controller, ETA101 Data Collection module, 320 X 240 Dot Matrix LCD.

A snap shoot of the developed system is shown below:

Figure 4.8 Developed COD Sensor

4.3 Embedded Software Implementation for COD Sensor

The software system development follows an OO approach. The software system has been developed into the following parts

4.3.1 Main Function

Starting from the boot up of the system, two sub systems were implemented. One is for COD measurement and the other is implemented for sensor maintenance purpose.

For COD measurement, each test comprises of three steps, warm-up, testing and warm-down as shown in Figure 4.9.

Figure 4.9 State Diagram of System Operation

During the warm-up stage, the system checks the status of all devices, initializes the system parameters, starts preparing ozone solution and cleans up the chamber. This step will normally last 5 to 7 minutes. After warm-up, the system enters testing stage. There are two modes being set, online monitoring and single sampling. Online monitoring is

effectively a recursive loop of the single sampling. The last step is warm down. The chamber is flushed with ozone solution alone to wash away the undesired particles to keep the chamber clean. At any point of time, if the user halts the system, it shall be able to resume the operation. More detailed state diagrams for each step is shown in Appendix A.

Each of the steps involves the operation of several devices. Proper scheduling algorithm is a must. The new COD sensor is a hard real-time system, single processor is used, and only one task can operate at a time. Clock driven is used throughout the system since it is the most stable and reliable algorithm and used most widely in control applications. All tasks are guaranteed a priori in all anticipated execution scenarios. Scheduling decisions are made off-line and generates a static schedule (table listing jobs) that contains decision times for all jobs. A typical clock drive cycle used in the system is shown in Figure 4.10:

Figure 4.10 Typical Clock Cycle Used in the Project

For the maintenance function, calibrations of pump, probes were provided as well as some debug programs for the whole system. History option is also implemented to recall the past test results. A full function list is shown in Figure 4.11.

Figure 4.11 System Maintenance Functions

4.3.2 Application Programming Interface (API)

Drivers are implemented for pumps, heater, OG, pH doser as independent APIs in software system. Data sampling and storing mechanisms for analog sensors are also implemented as API.

4.3.3 User Interface

The user interface of the system is developed to provide the user interaction with the sensor. A 5x4 keypad and 320 x 240 dot matrix LCD provide the main interface, some LED are also present to indicate to user the system status.

Based on the functions provided by the system, the user interface is developed, a detailed description is attached in Appendix C.

Besides the major components stated above, there are also some data structures been implemented for storing purpose, Table 4.1 illustrate the data structure defined for system setting. Each cell is one byte. Beside password, all the rest are calibration parameters used to adjust sensor data output.

Table 4.1 Typical Data Structure Used in the Project

	1st Column	2nd Column	3rd Column
Row 1	Password	Status, Time Int	Reference COD
Row 2	K1	B1	DDMMYYYY
Row 3	K1	B1	DDMMYYYY

Legend:		
	Each Bits Assignment	
Password	PPPPPP00	

(P=integer)

Chapter 5 Accurate COD Estimation

5.1 Formulation of Problem

As mentioned earlier, accurate COD Estimation is the last step of COD measurement. It is basically a flow analysis problem based on slow reaction. It consists of two stages, data collection and curve fitting.

Since ORP reading is proportional to ozone concentration, and inversely proportional to COD level, the relationship is similar to the one in Figure 4.3. The ORP/time relation is modeled by mathematical formula in the form Eq.(4). For simplicity, in this chapter, we consider that ORP sensor result is converted to ozone concentration automatically.

Therefore, the ORP sensor output is ozone concentration.

The overall flow rate in Bio-Reaction chamber is the summation of ozone solution pump and sample pump speed. Once the flow ratio of the two pumps is fixed from control step two, the two pumps will change their speed together while keeping the ratio consistent. From here onwards, if it is not specified, flow rate refers to the combined flow rate of two streams.

The curve we want to extract is ORP reading against contact time as Figure 5.1. Normally, it takes hours for ORP to reach steady state (fully react). To optimize the overall performance of COD sensor, it is desired that we could predict the curve within a small time frame. Least square method can achieve a very accurate curve fitting if enough data were collected. Therefore, the goal of system design is to collect as many data points as possible with minimum time.

Figure 5.1 ORP vs Contact Time

Figure 5.2 ORP at Fixed Flow Rate

Due to the physical design of the chamber, if flow speeds of two pumps are fixed, the sampled ORP will have a fixed contact time for all probes as shown in Figure 5.2.

However, if there is a step change happens, then ORP reading against time plot becomes Figure 5.3 in next page.

To describe it mathematically, consider one ORP probe and the flow rate changes only once, total volume from stream mixing point to ORP probe location is assumed to be V , initial flow rate is v , the flow rate changes to v' ($v > v'$) at time t_0 by which the initial stream has already flowed through the ORP measuring point. Then, at time $(t_0 + t)$ the measured signal is having a contact time of

$$\begin{cases} \frac{V}{v} + \left(1 - \frac{v'}{v}\right)t & \text{for } t < \frac{V}{v'} \\ \frac{V}{v'} & \text{for } t \geq \frac{V}{v'} \end{cases} \quad (5)$$

Figure 5.3 Effect of Step Change

Steady state is achieved after time $\frac{V}{v'}$. In Bio-Reaction chamber, there are totally three ORP probes. Assume the volumes from stream mixing point to probes are V_1 , V_2 and V_3 respectively, with $V_1 < V_2 < V_3$ and probe 3 is the last sampling point as shown in Figure 5.4.

Figure 5.4 Placement of ORP Probes

The problem is how to obtain as many sampling points as possible with different contact time by changing flow speed within limited time. The challenges in this problem are:

How to obtain maximum data within smallest time

- How to place ORP1 and ORP2
- Samples can only be captured during steady state. It means that after the speed had changed, the measurement can only start until the contact time is greater than V/v'
As shown in Figure 5.3, samples are taken during the time while the plot of Contact Time against Process Time is horizontal
- Sample contact time should have a wide span over the curve
- Samples shall be taken within least time possible

In addition, for the purpose of optimization, samples are only taken during the first few minutes. For example, if the objective is to complete the task within 10 minutes for the accurate measurement. Therefore, the last sampling time of ORP3 must be smaller than 10 minutes. The other constraints of the problems are:

- Stream flow rate is slower than 120 ml/min and greater than 10 ml/min (a more accurate calculation of the speed is presented in the later part of this chapter)
- V_3 is 200ml
- ORP probe reading is not so stable. It requires few seconds to take stable reading by averaging adjacent sampling data. The data reading process of three probes can be simultaneous
- Flow speed is changed by sending command to respective pumps through RS485 serial port. The maximum frequency that the speed can be changed is 5 times per

minutes per pump

Moreover, there are few assumptions made before the derivation is carried out.

- The overall flow rate is one of the outputs of MIMO system. If the MIMO system is well designed, the flow rate shall be very close to ideal case. In chapter 5, the pumps are assumed to be ideal. The speed changes are in step manner with no delay.
- Reagents are well mixed. Reaction is unique throughout the Bio-reaction chamber.

The most challenging work is how to get a stable reading for all probes within limited time.

5.2 *Solution to Problem*

The problem has been formulated in previous part. It is a matter of how to control the flow speed so that more horizontal sections can be obtained in Contact Time against Process Time plot. From here onwards, the discussion will be concentrated on the optimization. Since ORP values are probe readings. In this part, the contact time of sampling time is considered

To obtain a wide span of data point, flow rate must start from maximum value. This allows the stream to reach first sampling point with minimum sampling time. After that, flow rate changes in a deduction manner.

Due to hardware constraint, there is a maximum initial combined flow speed and a minimum value of final combined flow speed v_n .

In order to have a maximum combined initial speed, one of the pump shall be operating at

its upper speed limit. Suppose the speed ratio is determined to be ozone solution pump:

sample pump = a : b, the operation speed of each pump is calculated as follow:

$$\text{multiplier} = \min\left(\frac{80}{a}, \frac{30}{b}\right)$$

$$v_{\text{ozone}0} = a \times \text{multiplier}$$

$$v_{\text{sample}0} = b \times \text{multiplier}$$

$$v_0 = v_{\text{overall}} = (a + b) \times \text{multiplier}$$

Similarly, the minimum overall speed is calculated as follow:

$$\text{multiplier}' = \max\left(\frac{5}{a}, \frac{5}{b}\right)$$

$$v_{\text{ozone}n} = a \times \text{multiplier}'$$

$$v_{\text{sample}n} = b \times \text{multiplier}'$$

$$v_n = v_{\text{overall}}' = (a + b) \times \text{multiplier}'$$

The speed checkup table for each speed ratio in fuzzy part is shown below in Table 5.1

Table 5.1 Flow Rate Checkup Table

Ratio	$v_{\text{ozone}0}$ mL/min	$v_{\text{sample}0}$ mL/min	$v_{\text{ozone}min}$ mL/min	$v_{\text{sample}min}$ mL/min	$v_{\text{overall}0}$ mL/min	$v_{\text{overall}min}$ mL/min
8:1	80	10	40	5	90	45
7:1	80	11.429	35	5	91.429	40
6:1	80	13.333	30	5	93.333	35
5:1	80	16	25	5	96	30
4:1	80	20	20	5	100	25
3:1	80	26.667	15	5	106.667	20

2:1	60	30	10	5	90	40
1:1	30	30	5	5	60	35
1:2	15	30	5	10	45	15

In the above table, the minimum speed is the bottom line where the speed shall not go below.

With the speed constraints in mind, two approaches have been studied. One follows strictly the sampling rule. Samples are only taken when a stabilized contact time is obtained for particular probe. This approach is named precise control approach. The other approach assumes that the ORP reading does not change during measuring period, It is called approximation approach.

The symbols used in the derivation are defined as follows:

- N : total number of samples taken, $N \in \mathbb{N}$
- v_i : flow rate, with initial speed. v_i decreases as i increases $i \in \{0, N\}$
- t_i : process time/sampling time, i increases with the number of speed changes.
 $i \in \{0, N\}$
- T_{ij} : contact time. i is the probe number, j is the number of changes, $i \in \{1, 2, 3\}$
 $j \in \{0, N\}$
- V_1, V_2, V_3 : Volume from mixing point to respective ORP
- ΔT : sampling time, normally it is 5 seconds. It includes the time required to take one sample. This includes waiting time for each sample to stabilize and the time for the controller to take multiple surveys. The actual ORP reading for one sample will be the average of the survey results.

Precise Control Approach

Data sampling only happens while the contact time of the combined stream which passes by the ORP probe is having a constant value. From Figure 5.3 and Eq.(5), it is easy to conclude that contact time will only be constant when the whole volume has been replaced by the stream with new speed.

In order to have as many sampling points as possible, the first measurement is taken immediately after the flow head reaches the first ORP probe (ORP1) as shown in Figure 5.5 A and B, and the corresponding contact time is

$$T_{10} = \frac{V_1}{v_0}$$

At this moment, ORP2 and ORP3 do not have reading yet, T_{20} and T_{30} are not available.

Figure 5.5 First Step of ORP Sampling

After time ΔT , flow rate is changed to v_1 ($v_1 < v_0$), system will keep speed v_1 until the whole volume of V_1 is replaced with new flow speed. The new data captured at ORP1 will be

$$T_{11} = \frac{V_1}{v_1}$$

ORP2 is placed at V_2 , by the time the flow head arrives at the ORP probe, the speed property of the stream is having a combination as shown in Figure 5.6

Figure 5.6 Speed Profile of Stream from ORP1 to ORP2

According to the initial discussion, the contact time of the stream that just arrives at ORP2 is described as:

$$T_2' = \frac{V_2 - V_1 - \Delta T \cdot v_0}{v_1} + \frac{V_1}{v_0} + \Delta T$$

After time $\frac{V_1}{v_1} + \Delta T$, the solution in V_1 is fully replaced by the stream with new flow

speed v_1 and the second sample of ORP1 is taken. The stream with initial speed had been pushed further. Flow head locates at $2V_1 + \Delta T \cdot v_0 + \Delta T \cdot v_1$. If flow speed v_1 remains unchanged, the measured sample at V_2 will have a contact time of

$$T'_{21} = \frac{V_2}{v_0} + \left(1 - \frac{v_1}{v_0}\right)(t - T_{10} - \Delta T) \quad (6)$$

It is clear that T'_{21} increases with process time t . No stable value can be obtained. Flow will only stabilize when the stream property within V_2 , is unique, that is $t - T_{10} - \Delta T = \frac{V_2}{v_1}$ after the speed changes. This is very time consuming. We are not affordable to wait for that long. A tricky method is used here to ensure ORP2 reads a stable value.

Figure 5.7 Second Step of Sampling

The stream that arrives at ORP2 is having an original flow rate of v_0 . From Eq. (6), we can see the change is proportional to $1 - \frac{v_1}{v_0}$, if the speed changes back to v_0 , then the contact time is a fixed value. Figure 5.7 illustrates the behavior of the flow rate and the influence on contact time of probes. After ORP1 reading is obtained, flow rate changes back to v_0 , by which ORP2 starts to take readings. Voltage taken by ORP2 at this moment

is having a contact time of:

$$T_{21} = T_{11} + 2\Delta T + \frac{V_2 - V_1 - \Delta T \cdot (v_1 + v_0)}{v_0} \quad (7)$$

To ensure that the relation holds, the following condition must be satisfied:

$$V_1 + \Delta T(v_0 + v_1) \leq V_2 \leq 2V_1 + \Delta T(v_0 + v_1)$$

The inequality is to ensure the sampling will only happen when the contact time of that stream arriving at ORP2 is constant under the new control scheme. During measurement time ΔT , the stream that is passing through ORP sensor shall not have any transient part of speed profile. This is elaborated by the upper drawing of Figure 5.7 B. ORP2 shall be placed in between flow head and P_0 .

However, since the proposed control scheme requires a step back to the previous flow speed for ORP2 to take reading, the result of such action is that flow head is pushed forward by another $\Delta T \cdot v_0$. This will affect the ORP2 placement as elaborated by point P in the lower drawing of Figure 5.7 B.

At this moment, since stream has not arrived at ORP3, T_{31} is not available yet.

The same analysis and sampling strategy is applied to third ORP probe as illustrated in Figure 5.8.

Figure 5.8 Third Step of Sampling

The measured sampling times are:

$$\begin{cases} T_{12} = \frac{V_1}{v_2} \\ T_{22} = T_{12} + 3\Delta T + \frac{V_2 - V_1 - \Delta T(v_2 + v_1 + v_0)}{v_1} \\ T_{32} = T_{11} + T_{12} + 6\Delta T + \frac{V_3 - 2V_1 - \Delta T(3v_0 + 2v_1 + v_2)}{v_0} \end{cases} \quad (8)$$

Now, consider the location of the last ORP probe, in order for above derivation to hold true:

$$2V_1 + \Delta T(3v_0 + 2v_1 + v_2) \leq V_3 \leq 3V_1 + \Delta T(3v_0 + 2v_1 + v_2)$$

The constraints for volume V_2 is generalized as

$$V_1 + \Delta T \sum_{i=3}^i v_j \leq V_2 \leq 2V_1 + \Delta T \sum_{i=3}^i v_j \quad (10)$$

Similarly, the generalized constraint equation for volume V_3 is

$$\begin{aligned} 2V_1 + \Delta T \left(\sum_{i=4}^{i-2} v_j + \sum_{i=3}^{i-1} v_j + \sum_{i=2}^i v_j \right) \\ \leq V_3 \leq \\ 3V_1 + \Delta T \left(\sum_{i=4}^{i-2} v_j + \sum_{i=3}^{i-1} v_j + \sum_{i=2}^i v_j \right) \end{aligned} \quad (11)$$

In above two inequalities, if $i-n < 0$, $v_{i-n} = 0$

The optimization is to minimize the overall processing time t_{total} , and the number of samples needed is N . Then the total steps required is

$$\begin{aligned} n &= \frac{N}{3} - 1 && \text{for } N > 3 \\ t_{\text{total}} &= \left(\frac{V_1}{v_0} + \Delta T \right) + \left(\frac{V_1}{v_1} + 2\Delta T \right) + \left(\frac{V_1}{v_2} + 3\Delta T \right) + \left(\frac{V_1}{v_3} + 3\Delta T \right) + \dots + \left(\frac{V_1}{v_n} + 3\Delta T \right) \\ \Rightarrow t_{\text{total}} &= \sum_{i=0}^n \frac{V_1}{v_i} + 3n\Delta T \end{aligned}$$

In the above equation, ΔT is a small customized value which equals to 5 seconds maximum, v_i is subject to hardware constraints. n is to be defined by customer depending on the samples required. The problem is simplified to a non-linear optimization problem with:

$$\text{Minimize: } z = \sum_{i=0}^n \frac{V_1}{v_i} \quad \text{for } n > 2$$

Subject to: $v_n \geq c$

Where c is subject to system constraints. It refers to the minimum overall speed the system can have. To minimize z , V_1 shall be as small as possible. Eqs. (10) and (11) are guidelines for set the positions of ORP1 and ORP2. From Eq. (11):

$$\begin{cases} V_1 \geq \frac{V_3}{3} - \frac{1}{3} \Delta T \left(\sum_{j=4}^{i-2} v_j + \sum_{j=3}^{i-1} v_j + \sum_{j=2}^i v_j \right) \\ V_1 \leq \frac{1V_3}{2} - \frac{1}{2} \Delta T \left(\sum_{j=4}^{i-2} v_j + \sum_{j=3}^{i-1} v_j + \sum_{j=2}^i v_j \right) \end{cases} \quad (12)$$

Once V_1 is obtained, the possible range of V_2 is calculated from Eq. (10).

In Eq. (12), to obtain V_1 , it is equivalent to finding the minimum value of

$A = \sum_{j=4}^{i-2} v_j + \sum_{j=3}^{i-1} v_j + \sum_{j=2}^i v_j$. From Table 5.1, we can easily tell the minimum A is obtained

when pump ratio is 1:2 and $i = 2$, with $v_0 = 45$ mL/min, $v_2 < v_1 < v_0$, and 15 mL/min $< v_2 < v_1$. The minimum $A > 180$ mL/min. Thus:

$$V_1 = \frac{V_3}{3} - 5mL$$

To simplify the mechanical structure and design, V_1 and V_2 are designed to be equal to $1/3 V_3$ and $2/3 V_3$ respectively. All the equations for calculating contact time still hold.

To limit our solution to one, we define that the speed change follows the trend below:

$$v_i = a^i v_0 \quad \text{where } 0 < a < 1$$

The problem is to find the feasible solution of a . A new transform of the problem is:

$$\text{Minimize: } z' = \frac{V_1}{v_0} \cdot \frac{1 - a^{-(n+1)}}{1 - a^{-1}}$$

$$\text{Subject to: } a^n v_0 \geq c$$

where v_0 and c can be read out from Table 5.1, since the flow ratio has been defined.

z' always decreases with increasing a , therefore, the minimum value is obtained when a is maximum. The constraint is described as eq(13)

$$a \geq \left(\frac{c}{v_0} \right)^{1/n} \quad (13)$$

However, the other requirement of the system states that samples shall have a wide span.

It is not only referring to the initial or end point of the samples. It is also referring to the contact time difference among samples. It is meaningless to have the contact times of

samples differ by only a few seconds. To avoid such situation, a is chosen to be $\left(\frac{c}{v_0} \right)^{1/n}$,

and the overall flow rate and the speed change instance for each control step are

calculated as follow:

$$\begin{aligned} v_i &= a^i v_0 \\ t_i &= \sum_{j=0}^i \frac{V_1}{v_j} + 3i\Delta T \quad \text{for } i > 2 \end{aligned} \quad (14)$$

This method can be extended to application when more probes are involved in the system; the difference is just that the change of speed involved in each step will increase to a number that is equal to the number of probes. However, there is an additional problem: while probe number increases to M , the condition will not hold if:

$$\Delta T(v_i + v_{i+1} + \dots + v_{i+M}) > \frac{1}{M} V_M$$

Above in-equality basically means that in between last two probes, the stream is filled with all flow types during data sampling. And there is no way that the last probe could get a stable ORP reading.

Approximation Approach

The basic idea of the approximation approach comparing to the precise control approach is by assuming that the ORP reading change during the sampling period is negligible. A justification of the above assumption is shown below:

Figure 5.10 Impact of Flow Rate Change on Contact Time

In Figure 5.10, solution firstly flows through volume V with speed v , then, at time t_0 , its

speed is changed to v' . After time t , the original solution before speed change has been pushed to section B and section A is filled with new solution of speed v' . Suppose an ORP probe is placed at the end of the volume V , then the measured contact time of the solution after time t of the speed change is expressed as:

$$T = \frac{V}{v} + \left(1 - \frac{v'}{v}\right)t$$

For a small difference from t , say Δt , sample is having a contact time T' :

$$T' = \frac{V}{v} + \left(1 - \frac{v'}{v}\right)(t + \Delta t)$$

Therefore:

$$\Delta T = T' - T = \left(1 - \frac{v'}{v}\right)\Delta t < \Delta t$$

Δt is the time difference from the very first sampling instance. It has a value of less than 5 seconds. Moreover, COD removal reaction is a very slow process which can last up to few days. ORP change within 5 seconds is very small and can be approximated by a linear relationship. The actual ORP reading is then calculated as the average ORP reading during $\pm \Delta t$ of the desired contact time.

With this assumption, there is no need to wait for the sample to be stabilized, and process design has more freedom. The sample can be taken at any instant that is desired.

Therefore, it is possible that the last sample can have a contact time which is equal to the process time which is not achievable in the first case.

The discussion is carried out by assuming that there are totally 3 ORP probes placed in equal distances in the system. In order to fully utilize all probes, the process is designed in such a way that ORP probes only take readings after the solution has flowed through the whole chamber, and subsequently, by each speed change, we are able to take three readings. Similar to the previous approach, solution has an initial speed of v_0 , and it will reduce step by step in lateral processes.

For discussion, it is assumed that each probe will sample 4 times. Moreover, the volume between starting point and each probe is $V_1 = 1/2 V_2 = 1/3 V_3 = 1/3 V_0$ shown in Figure 5.11

Figure 5.11 Placement of ORP Probes

The sampling design is shown in Figure 5.12, whereby, each sample has a contact time that is T_c apart.

Figure 5.12 Sampling Design

Figure 5.13 illustrates the designed control process.

Figure 5.13 Speed Change and Contact Time against Process Time

1st sample: taken immediately after solution reaches last ORP probe. The sampled data is for solution with contact time, sampling instance $t_0 - \Delta T$:

$$\begin{aligned} T_{10} &= V_1 / v_0 = \frac{1}{3} V_0 / v_0 \\ T_{20} &= V_2 / v_0 = \frac{2}{3} V_0 / v_0 \\ T_{30} &= V_3 / v_0 = V_0 / v_0 \end{aligned}$$

2nd sample: change the flow speed to v_1 at time t_0 , 2nd sample is taken ΔT before 2nd change of speed at time t_1 , the sampled data is for stream with contact time below:

$$\begin{aligned}
T_{11} &= \frac{V_1 - v_1 \times \left(t_1 - t_0 - \frac{1}{2} \Delta T \right)}{v_0} + \left(t_1 - \frac{1}{2} \Delta T - t_0 \right) \\
&= T_{10} + (t_1 - t_0) \left(1 - \frac{v_1}{v_0} \right) - \frac{1}{2} \Delta T \left(1 - \frac{v_1}{v_0} \right) \\
T_{21} &= T_{20} + (t_1 - t_0) \left(1 - \frac{v_1}{v_0} \right) - \frac{1}{2} \Delta T \left(1 - \frac{v_1}{v_0} \right) \\
T_{31} &= T_{30} + (t_1 - t_0) \left(1 - \frac{v_1}{v_0} \right) - \frac{1}{2} \Delta T \left(1 - \frac{v_1}{v_0} \right)
\end{aligned}$$

3rd sample: taken at ΔT before 3rd change of speed. New speed is v_2 , 3rd change happens at t_2 . The sampled data is for stream with contact time:

$$\begin{aligned}
T_{12} &= \frac{V_1 - v_1(t_1 - t_0) - v_2(t_2 - t_1 - \frac{1}{2} \Delta T)}{v_0} + (t_2 - t_0 - \frac{1}{2} \Delta T) \\
&= T_{10} + (t_1 - t_0) \left(1 - \frac{v_1}{v_0} \right) + (t_2 - t_1) \left(1 - \frac{v_2}{v_0} \right) - \frac{1}{2} \Delta T \left(1 - \frac{v_2}{v_0} \right) \\
T_{22} &= T_{20} + (t_1 - t_0) \left(1 - \frac{v_1}{v_0} \right) + (t_2 - t_1) \left(1 - \frac{v_2}{v_0} \right) - \frac{1}{2} \Delta T \left(1 - \frac{v_2}{v_0} \right) \\
T_{32} &= T_{30} + (t_1 - t_0) \left(1 - \frac{v_1}{v_0} \right) + (t_2 - t_1) \left(1 - \frac{v_2}{v_0} \right) - \frac{1}{2} \Delta T \left(1 - \frac{v_2}{v_0} \right)
\end{aligned}$$

4th sample: taken at ΔT before 4th change of speed. New speed is v_3 , 4th change is happening at t_3 . The sampled data is for stream with contact time:

$$\begin{aligned}
T_{13} &= T_{10} + (t_1 - t_0) \left(1 - \frac{v_1}{v_0} \right) + (t_2 - t_1) \left(1 - \frac{v_2}{v_0} \right) + (t_3 - t_2) \left(1 - \frac{v_3}{v_0} \right) - \frac{1}{2} \Delta T \left(1 - \frac{v_3}{v_0} \right) \\
T_{23} &= T_{20} + (t_1 - t_0) \left(1 - \frac{v_1}{v_0} \right) + (t_2 - t_1) \left(1 - \frac{v_2}{v_0} \right) + (t_3 - t_2) \left(1 - \frac{v_3}{v_0} \right) - \frac{1}{2} \Delta T \left(1 - \frac{v_3}{v_0} \right) \\
T_{33} &= T_{30} + (t_1 - t_0) \left(1 - \frac{v_1}{v_0} \right) + (t_2 - t_1) \left(1 - \frac{v_2}{v_0} \right) + (t_3 - t_2) \left(1 - \frac{v_3}{v_0} \right) - \frac{1}{2} \Delta T \left(1 - \frac{v_3}{v_0} \right)
\end{aligned}$$

In conclusion:

$$T_{ij} = T_{tempj} - \frac{1}{2} \Delta T \times \left(1 - \frac{v_j}{v_0}\right) + T_{i0} \quad (15)$$

$$T_{tempj} = T_{temp(j-1)} + (t_j - t_{j-1}) \left(1 - \frac{v_j}{v_0}\right) \text{ where } T_{temp0} = 0 \quad (16)$$

Eqs. (15) and (16) provide an iterative way to estimate sample contact time, which can be easily implemented in software. Furthermore, if contact time has equal distance from one another, we only need to let

$$T_{ij} - T_{i(j-1)} = T_{tempj} - T_{temp(j-1)} + \frac{1}{2} \Delta T \left(\frac{v_j}{v_0} - \frac{v_{j-1}}{v_0}\right) = (t_j - t_{j-1}) \left(1 - \frac{v_j}{v_0}\right) = \text{constant} = T_c$$

Since ΔT is small compare to overall reaction time, and the speed is always deducing, the above equation can be approximated by:

$$(t_j - t_{j-1})(v_0 - v_j) = v_0 T_c = \text{constant} \quad (17)$$

$$\begin{aligned} (t_i - t_{i-1})v_0 - (t_i - t_{i-1})v_i &= v_0 T_c = \text{constant} \\ (t_i - t_{i-1})v_i &= (t_i - t_{i-1})v_0 - v_0 T_c \end{aligned} \quad (18)$$

For ease of control, periodic process is preferred, since v_j is changing always, we shall let

$$\begin{aligned} t_j &= 2^{j-1} \times \text{constant} = 2^{j-1} \Delta t & t_0 = 0, t_1 = \Delta t \\ t_j - t_{j-1} &= 2^{j-2} \times \text{constant} = 2^{j-2} \Delta t & \text{for } (j \geq 2), \text{ and } t_0 = 0, t_1 = \Delta t \end{aligned} \quad (19)$$

For each probe, assume we need to sample n times. In order for above conditions to be true, solution in one section must not flow into the next, which means once solution flow

speed changes for the first time, solution with new speed will not travel more than one third of the total volume. Thus, the two criteria below must be satisfied:

$$T_c \times n = \frac{V_0}{3v_0} \Rightarrow T_c = \frac{V_0}{3nv_0} \quad (20)$$

$$\sum_{j=1}^n (t_j - t_{j-1}) \times v_j \leq \frac{V_0}{3} \quad (21)$$

In the above equations, $n = \text{Total number of samples}/3 - 1$. With rules defined by (20) and (21), Eqs. (15), (16) will hold always. In such a way, the calculation is simplified. In addition, sample contact time is taken at the same instance for all ORP probes with the constant relation as:

$$T_{2j} - T_{1j} = T_{3j} - T_{2j} = \frac{V}{3v_0}$$

From (21):

$$(t_1 - t_0) \times v_1 + (t_2 - t_1) \times v_2 + \dots + (t_n - t_{n-1}) \times v_n \leq \frac{1}{3} V_0$$

$$\sum_{j=1}^n [(t_j - t_{j-1}) \times v_0 - v_0 T_c] \leq \frac{1}{3} V_0$$

$$\sum_{j=1}^n (t_j - t_{j-1}) \times v_0 \leq \frac{1}{3} V_0 + nv_0 T_c$$

$$\sum_{j=1}^n (t_j - t_{j-1}) \leq \frac{V_0}{3v_0} + nT_c$$

$$t_n - t_0 \leq \frac{V_0}{3v_0} + nT_c$$

Since $t_n - t_0$ is $2^{n-1} \Delta t$, then we have:

$$t_n - t_0 = 2^{n-1} \Delta t \leq \frac{V_0}{3v_0} + nT_c \quad (22)$$

From (21)

$$\begin{aligned} T_c &= \frac{V_0}{3v_0 \cdot n} \\ t_n - t_0 &= 2^{n-1} \Delta t \leq \frac{2V_0}{3v_0} \end{aligned} \quad (23)$$

If the job is to be completed within time t_{total} , then $t_n = t_{\text{total}}$. Taking the extreme, Δt is calculated as

$$\Delta t = \frac{2^{2-n} V_0}{3v_0}$$

From (18), (19) and (23), the speed at every stage is calculated as:

$$v_j = v_0 - \frac{V_0}{3n \times 2^{j-2} \times \Delta t} \quad j \geq 2 \quad \text{and} \quad v_1 = v_0 - \frac{V_0}{3n \times \Delta t} \quad (24)$$

5.3 Determination of COD

After the sample data are collected, least square method is applied to retrieve the parameters in Eq. (3). Those coefficients are then used to determine the actual COD value by comparing with COD-ORP database. The database is constructed from experimental results. Standard COD solution having COD value range from 100 to 1000 mg/L is tested with step size 100 mg/L per sample.

When an unknown sample is tested, its coefficients are then compared to the standard value to find the most adjacent curve, by which, the COD value of the mixed stream is obtained.

After the COD value in the system is determined using the above process. The actual COD value is calculated. Recall that the overall flow speed within the system is the combination of ozone solution flow rate and sample solution flow rate. When ozone solution is mixed with sample solution, because the overall volume is increased, it is equivalent to dilute the sample solution. The final sample concentration is related to the original sample concentration by dilution rate:

$$C_{\text{sample_new}} = C_{\text{sample_origin}} \times \frac{v_{\text{sample}}}{v_{\text{sample}} + v_{\text{water}}}$$

Together with the drop of the sample concentration, ozone solution is diluted as well. It can be transformed to a similar form.

$$C_{\text{ozone_new}} = C_{\text{ozone_origin}} \times \frac{v_{\text{water}}}{v_{\text{sample}} + v_{\text{water}}}$$

It is easy to find out the relation below:

$$\frac{C_{\text{sample_new}}}{C_{\text{ozone_new}}} = \frac{C_{\text{sample_origin}}}{C_{\text{ozone_origin}}} \times \frac{v_{\text{sample}}}{v_{\text{water}}}$$

The same relation holds true to the COD value. C_{sample} can be replaced by COD since COD is proportional to sample concentration. Since the flow ratio between the two streams is known from fuzzy logic and maintained throughout the accurate measurement.

$$\frac{COD_{new}}{COD_{origin}} = \frac{C_{ozone_new}}{C_{ozone_old}} \times \frac{v_{sample}}{v_{water}}$$

$$\Rightarrow COD_{origin} = \frac{C_{ozone_origin}}{C_{ozone_new}} \times \frac{v_{water}}{v_{sample}} \times COD_{new}$$

$$COD_{origin} = \left(1 + \frac{v_{water}}{v_{sample}}\right) \times \frac{v_{water}}{v_{sample}} \times COD_{new} \quad (25)$$

With Eq. (25), the actual COD value is estimated.

Chapter 6 Simulation, Results and Conclusions

6.1 *Simulation and Results*

Due to some issues during hardware development, the designed COD sensor is not ready for full operation yet. Therefore, simulations were done to verify the proposed data sampling algorithm. The simulation work is mainly for precise control case since the approximation control is just a back up strategy when the actual implementation for precise control fails.

In order to have the simulation more close to reality, constraints of the system is discussed. The two precise pumps used in the system are having their own physical constraints. For ozone solution pump, the operation range is 5mL/min to 80mL/min, while the sample pump can only operate from 5mL/min to 30mL/min. Therefore, v_i is having a maximum of 120mL/min and a minimum of 10mL/min. However, the only scenario that v_i can go as high as 120mL/min is when the sample pump and water pump ratio is set to be 3:8. In order for v_i to reach a minimum value of 10mL/min, sample pump and water pump speed ratio is 1:1.

In addition, the system is set to act in such a way that the speed of pumps is always reducing. Therefore the initial speed of any pump shall be much greater than 5mL/min. Similarly, the final overall speed should be greater than 10mL/min based on the speed ratio. COD value differs a lot depending on the wastewater type; the COD value can range from 0 to 10000ppm.

The total volume of the bio-reaction chamber is approximate 200mL. Above information

was used to simulate the data sampling system.

Suppose the speed ratio from fuzzy control is determined as 5:1, and totally 12 samples are required. The initial overall speed is 96mL/min. From Eq. (13),

$$a \geq \left(\frac{30}{96} \right)^{1/4} = 0.7477$$

From Eq. (14), the actual control input and time are calculated as shown in Table 6.1

Table 6.1 Flow Speed Control for Precise Control Approach

	Step 1	Step 2	Step 3	Step 4	Step 5
Flow Rate(mL/min)	96	71.7792	53.6693	40.1285	30
Ozone Pump(mL/min)	80	59.816	44.7244	33.4405	25
Sample Pump(mL/min)	16	11.9632	8.9449	6.6881	5
System Time (min)	0	0.7777	1.8732	3.532	5.2767

To verify the correctness of the sampling algorithm, the full control process is simulated.

The control actions were exactly as shown in Figure 5.9. The input flow speed and corresponding system time is taken from Table 6.1

The contact time vs process time profile is drawn in Figure 6.1. The diamond is referring to ORP1 data, square is referring to ORP2 data and triangle is referring to ORP3 data.

Data sampling only happens at when the event is triggered, therefore the contact time during data sampling period is studied.

Figure 6.1 ORP Probe Reading During Sampling Period

From Figure 6.1 we could tell that the contact time during sampling period is constant.

In order to analyze the sampling mechanism, the experiment data in Shimabukuro's experiment are used in the simulation [62]. The sample contact time is calculated by the optimization algorithm mentioned above, the original data plot and the curve fitting is shown in Figure 6.2

In Figure 6.2, the diamond dotted line represents the data from Shimabukuro's experiment, solid line is the fitted curve with Eq. (3). It proved that Eq (3) describes the actual experiment data very well.

Figure 6.2 ORP Reading During COD Removal

If the sampling algorithm is applied to the above experiment, the sampled data is shown as below. Square represents the data sampling point in new algorithm.

Figure 6.3 Sampling by Proposed method

The actual calculation of COD can not be simulated, because in order to calculate the

actual COD value, extensive experiments data are required. There shall be a database which we could refer to once ORP is obtained.

Based on the simulation, if the MIMO system is developed very well, the precise control algorithm shall be able to work perfectly.

6.2 Conclusions

In this project, the principle of COD measurement and various COD measurement methods have been carefully studied. A new COD sensor has been designed and prototyped. The ozone has been chosen as the oxidant because of its active chemical and electrochemical properties. This new COD sensor greatly reduced the process time required for the COD value measurement in wastewater treatment and fully automated the measurement process. The main focus of the author is on embedded software development and data sampling algorithm derivation.

In the embedded software development, Objective-Oriented approach has been adopted. The main infrastructure of the software is constructed according to the measurement process. Drivers have been implemented for all electronic devices. User interface has been designed for external communication between the end-user and the sensor devices. Clock driven scheduler has been developed for each measurement procedure. Many tests and trial runs have been carried out on the prototype, which confirmed that the current developed software fulfilled the initial design expectations of the project.

For the data sampling algorithm, two approaches have been proposed. According to the calculation, the COD value can be obtained within 10 minutes which is a great improvement compared to 2.5 hours in standard COD measurement. Simulations has

been done and results show that the proposed data sampling algorithm have achieved the design requirements as well.

6.3 *Future Work*

There are three things need to be done before this new COD sensor can be deployed to the market. First of all, only the simulation on the sampling algorithm has been carried out in current work; hence further tests on actual system are required to justify the validity of the sampling algorithm. Secondly, software and hardware are developed concurrently.

Therefore the fully system tests need to be carefully performed. Necessary changes may be required to achieve better performance. The criteria for the integration tests include stability, effectiveness and accuracy. Last but not least, the database of the standard COD value, which will be used as reference for future COD value estimation, needs to be created. Excess experiments must be conducted to construct this database.

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Appendix A State Diagrams

In appendix A, the state diagrams for COD test is shown. There are three super-states.

Warm-up, Testing and Warm-Down. Details of all super-states are elaborated.

Appendix B Default Settings for COD Sensor

Mode of operation	: Offline
COD Reference value	: NULL
Maximum Testing Time	: 20 min
Password	: 123456

Quick Start

1. Ensure all connections are connected correctly and press '1'.
2. Put the sample into the sensor and press 'ENT'. Wait while the sample is being treated.
3. After the testing is completed, its COD value is displayed on the LCD.
4. To test for another sample, press 'ENT'. To exit and go back to the main menu, press 'ESC'.
5. If want to test another sample, another screen will be displayed asking if flushing is required. If testing a sample with very different content, press '1'. If testing a sample with similar content, can press '2'. If decided not to test can choose 'ESC' option and this will go back to the main menu.

Calibration

pH Probes Calibration

1. Press '1' at 'Calibration & History' menu. Press '1' for calibration.
2. Select a probe for calibration.
3. Select the type of method for calibration.
4. Remove the selected probe from the sensor. Place it into a known pH value solution and enter its pH value.
5. Repeat step 1-4 for other probe.

ORP Probes Calibration

1. Press '2' at 'Calibration & History' menu. Press '1' for calibration.
2. Select a probe for calibration.
3. Remove the selected probe from the sensor. Place it into a known ORP value solution and enter its ORP value.
4. Repeat step 1-3 for other probes.

COD Calibration

1. Press '3' at 'Calibration & History' menu. Press '1' for calibration.
2. Select the type of known solution used for calibration.
3. Pump the known solution into the sensor through the sample inlet and enter its COD value.
4. Repeat step 1-3 for future calibration.

Appendix C User Interface Description

Main Menu

This is the first page of the user interface.

Main Menu shows the basic functions of the COD sensor: Testing of sample and Settings, Calibration & History of various sensors.

Testing Sample

Online

This page will be shown if the user predefined 'Online' testing as the default-testing mode.

The user will be prompt to ensure all tubes and connections are connected correctly. This is to ensure that all components are ready for testing.

Cancel will bring the user back to Main Menu.

This page shows the real-time graph of COD vs Time. It serves as a monitoring tool for the whole testing process. So if there is any drastic change in the COD value, the user will be able to notice it easily.

When ESC is pressed, a pop-up screen displaying the message “Attention! Flushing in progress”. It will return to Main Menu after flushing is done.

Offline

Please put the sample into
The COD sensor

ENT Continue
ESC To Cancel

This page prompts the user to put the sample to be tested into the sensor.

ESC will bring the user back to Main Menu.

Please wait while the sample is being
treated.

[*****]

The sensor is processing the sample and various readings are taken and recorded by the microcontroller. These readings will be processed and used in determining the COD value of the sample.

The status bar at the bottom left indicates that the testing is in progress.

Measurement is completed
The COD value of the
sample is :
ENT Test another sample
ESC Main Menu

After the completion of the test on the sample, the COD value of the sample will be displayed.

ENT allows the user to test another sample. ESC will bring the user back to Main Menu.

Actions to be taken before
next measurement

1. Continue With Flush
2. Continue Without Flush

ESC Stop

If the user pressed ENT to test another sample, the user will be asked if he wants to flush the chamber or not before moving on to test another sample.

ESC will bring the user back to Main Menu.

Settings, Calibration & History

Please key in password.

Password:

ESC Back to Main Menu

Before entering Settings, Calibration & History page, the user will be prompt to key in a 6-digit password. This is to ensure that only authorized personnel is allowed to change any setting of the sensor.

Wrong Password

ENT To key in password again

ESC Exit

If the user entered a wrong password, this page will be displayed.

ENT will allow the user to key in the password again. ESC will bring the user back to Main Menu.

SETTINGS, CALIBRATION & HISTORY

1. Mode of Operation
2. COD Reference
3. Maximum Testing Time
4. Calibration & History
5. Change Password
6. Maintenance

If the user entered a correct password, this page will be displayed. He can then select one of the five options available on this page.

Mode of Operation

Select the mode of operation

Online

Offline

ESC Settings, Calibration & History

The user is able to predefine the default-testing mode.

‘Online’ testing is to perform testing on a sample continuously with an interval time that is to be defined later. The sample is extracted from a continuous flow of sample.

‘Offline’ testing is to perform one testing on a sample each time. The user puts the sample into the sensor manually.

ESC will bring the user back to Settings, Calibration & History menu.

If the user selects ‘Offline’ testing as the default-testing mode, it will bring the user back to Settings, Calibration & History menu.

Enter interval time of Online sampling
(min 0; max 60)

Time: MM min

ESC Mode of Operation

If the user selects ‘Online’ testing as the default-testing mode, the user will be asked to set the time interval between each testing.

ESC will bring the user to the previous page, Mode of Operation menu.

COD Reference

Key in the reference COD value

COD Value: NNNNN ppm

ESC Setting, Calibration & History

If the user is a profession of this field, he will have certain knowledge of the COD value of the sample. He can set COD reference value for easy computation in determining the actual COD of the sample.

It is not necessary to fill up this section.

Maximum Testing Time

Key in the maximum
testing time for each sample
(min 20; max 50)

Time: MM min

ESC Setting, Calibration & History

The ideal time taken for each testing is 20mins. However, there may have situations when the sensor is unable to determine the COD value of a sample at all. Hence this maximum testing time is used to terminate the testing if the time taken exceeds this maximum testing time.

Calibration & History

Calibration & History

1. pH Probes
2. ORP Probes
3. COD

ESC Setting, Calibration & History

The sensor requires some calibrations. This page allows the user to select and view information of various calibrations.

pH Probes

pH Probes

1. Calibration
2. History

This page allows the user to select whether he wants to calibrate the probes or view the last calibration date that is available in History.

ESC will bring the user to Calibration & History menu.

Select pH Probes

1. Probe 1
2. Probe 2

The sensor consists of two pH probes that have to be calibrated before usage. If the user selects Calibration, he will be asked to select which probe to calibrate.

ESC will bring the user to pH Probe menu.

Select the number of
point(s) for calibration

1. 1 point
2. 3 points

There are two types of methods of calibrating pH probes. They are 1-point calibration and 3-points calibration. The user can select one of these types of methods.

ESC will bring the user to the previous page ('Select pH Probes' menu).

pH probe #

point #

pH: NN.NN

Place the probe into Cal-solution
and enter the pH of Cal-solution

ESC Back to pH probes

After the user has selected which probe to calibrate and which method to use for calibration, this page will prompt the user to place the probe into calibration-solution and enter its pH value.

ESC will bring the user back to pH Probes menu.

Probe No.	Last Calibration Date
PH 1	
PH 2	
PH 3	

ESC pH Probes

If the user selects History in pH Probes menu, dates of last calibrations of all probes will be displayed.

ESC will bring the user back to pH Probes menu.

ORP Probes

ORP Probes

1. Calibration
2. History

ESC Calibration & History

This page allows the user to select whether he want to calibrate the probes or view the last calibration date that is available in History.

ESC will bring the user to Calibration & History menu.

Select ORP Probes

1. Probe 1
2. Probe 2
3. Probe 3
4. Probe 4
5. Probe 5
6. Probe 6
7. ESC Previous

The sensor consists of six ORP probes that have to be calibrated before usage. If the user selects Calibration, he will be asked to select which probe to calibrate.

ESC will bring the user to ORP Probe menu.

ORP Probe

ORP: NNNNN mV

Place the probe into Cal-solution and enter the ORP value of Cal-solution

ESC Previous

After the user has selected which probe to calibrate, this page will prompt the user to place the probe into calibration-solution and enter its ORP value.

ESC will bring the user back to previous page ('Select ORP Probes' menu).

Probe No.	Last Calibration Date
ORP 1	
ORP 2	
ORP 3	
ORP 4	
ORP 5	
ORP 6	

ESC ORP Probes

If the user selects History in ORP Probes menu, dates of last calibrations of all probes will be displayed.

ESC will bring the user back to ORP Probes menu.

COD

COD

1. Calibration
2. History

This page allows the user to select whether he want to calibrate the probes or view the last calibration date that is available in History.

ESC will bring the user to Calibration & History menu.

Select the type of Cal-solution

1. Standard Solution
2. Real Sample

There are two types of methods of calibrating COD. They are the calibration using standard solution or real sample. The user can select one of these types of methods.

ESC will bring the user back to COD menu.

COD

COD: NNNNN.NN

Place the probe into Cal-solution and enter the COD value of Cal-solution

ESC Previous

After the user has selected the type of calibration method, this page will prompt the user to place the probe into calibration-solution and enter its COD value.

ESC will bring the user back to previous page ('Select the type of Cal-solution' menu).

Date	Time	COD	Remark

Scroll Up 1

Scroll Down 2

Back To Main Menu 3

If the user selects History in COD menu, dates of last calibrations of COD will be displayed.

ESC will bring the user back to COD menu.

Change Password

Please key in new 6-digit password

New Password: *****

New Password: *****

ESC Exit

The user is able to change the password to ensure security. He will have to enter the new password twice to ensure consistency.

ESC will bring the user back to Settings, Calibration & History menu.

Wrong Password

ENT To key in password again
ESC Exit

If the two passwords are not the same, this page will be displayed, telling the user that the two passwords are not the same. The user can choose to enter again or ESC to go back to Settings, Calibration & History menu.

Maintenance

Maintenance

1. Pumps
2. Valves
3. ORP probes
4. pH probes
5. Temperature probes

ESC Settings, Calibration & History

This page is to allow easy maintenance of the sensor. There are various components that can be checked if they are still in working condition or not.

ESC will bring the user back to Settings, Calibration & History menu.

Pumps

Select Pump Device Number

1. Water Pump
2. Sample Pump
3. Doser Pump

ESC Maintenance

If the user selects Pumps, this page will be displayed. As there are various pumps used in different control in the sensor, the user can choose which pump to check.

ESC will bring the user back to Maintenance menu.

Key in Water Pump rate
(min 0; max 80000)

Rate: NNNNN µl/min

ESC PUMP TESTING

After the user selects Water Pump, this page will display and ask the user to enter the rate of the water pump.

ESC will bring the user back to previous page ('Select Pump Device Number' menu).

Key in Sample Pump rate
(min 0; max 30000)

Rate: NNNNN μ l/min

ESC PUMP TESTING

After the user selects Sample Pump, this page will display and ask the user to enter the rate of the sample pump.

ESC will bring the user back to previous page ('Select Pump Device Number' menu).

Key in Doser Pump rate
(min 0; max 256)

Rate: NNN μ l/min

ESC PUMP TESTING

After the user selects Doser Pump, this page will be display and ask the user to enter the rate of the doser pump.

ESC will bring the user back to previous page ('Select Pump Device Number' menu).

Valves

Select Valve Device Number

1. Valve 1 – ON/OFF
2. Valve 2 – ON/OFF
3. Valve 3 – ON/OFF
4. Valve 4 – ON/OFF

ESC Maintenance

After the user selects Valves, this page will be displayed. The user can switch on or off each valve by pressing its corresponding number. This can check if the valve is still in working condition or not.

ESC will bring the user back to Maintenance menu.

ORP Probes

Select Device Number

1. ORP probe 1 – NNNNN.NN
2. ORP probe 2 – NNNNN.NN
3. ORP probe 3 – NNNNN.NN
4. ORP probe 4 – NNNNN.NN
5. ORP probe 5 – NNNNN.NN
6. ORP probe 6 – NNNNN.NN

ESC Maintenance

After the user selects ORP Probes, this page will be displayed. The value beside each ORP probe is the reading read by the probe. If any of the values is found to be incorrect, the user can know which probe is not working well and change it.

ESC will bring the user to Maintenance menu.

pH Probes

Select Device Number
1. pH probe 1 – NN.NN
2. pH probe 2 – NN.NN
ESC Maintenance

After the user selects pH Probes, this page will be displayed. The value beside each pH probe is the reading read by the probe. If any of the values is found to be incorrect, the user can know which probe is not working well and change it.

ESC will bring the user to Maintenance menu.

Temperature Probes

Select Device Number
1. Temperature probe 1 – NN.NN
2. Temperature probe 2 – NN.NN
3. Temperature probe 3 – NN.NN
4. Temperature probe 4 – NN.NN
ESC Maintenance

After the user selects Temperature Probes, this page will be displayed. The value beside each temperature probe is the reading read by the probe. If any of the values is found to be incorrect, the user can know which probe is not working well and change it.

ESC will bring the user to Maintenance menu.

Appendix D Mechanical Design of COD Sensor

PCB Board 1

PCB Board 2