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Assessment and optimization of environmental systems using data analysis and simulation.

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ASSESSMENT AND OPTIMIZATION OF
ENVIRONMENTAL SYSTEMS USING DATA
ANALYSIS AND SIMULATION

By

Milad Ebrahimi

A Dissertation

Submitted to the Faculty of the

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University of Louisville

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ASSESSMENT AND OPTIMIZATION OF ENVIRONMENTAL
SYSTEMS USING DATA ANALYSIS AND SIMULATION

By
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A Dissertation Approved on
April 12, 2018
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This dissertation is dedicated to my beloved Mother,

Mrs. Mahnaz Shahmoradibalsin

for her invaluable and unconditional love and support throughout my life

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ABSTRACT

ASSESSMENT AND OPTIMIZATION OF ENVIRONMENTAL SYSTEMS USING DATA ANALYSIS AND SIMULATION

Milad Ebrahimi

April 12, 2018

For most environmental systems, specifically wastewater treatment plants and aquifers, a significant number of performance data variables are attained on a time series basis. Due to the interconnectedness of the variables, it is often difficult to assess over-arching trends and quantify temporal operational performance. The objective of this research study was to provide an effective means for comprehensive temporal evaluation of environmental systems. The proposed methodology used several multivariate data analyses and statistical techniques to present an assessment framework for the water quality monitoring programs as well as optimization of treatment plants and aquifer systems.

The developed procedure considered the combination of statistical and data analysis algorithms including correlation techniques, factor analysis and principal component analysis, and multivariate stepwise regression analysis. Those methodologies were used to develop a series of independent indexes to quantify the composition of wastewater and groundwater.

Also, by developing a stepwise data analysis approach, a baseline was introduced to discover the key operational parameters which significantly affect the performance of environmental systems. Moreover, a comprehensive approach was introduced to develop numerical models for forecasting key operational and quality parameters which can be used for future simulation and scenario analysis practices. The developed methodology and frameworks were successfully applied to four case studies which include three wastewater treatment plants and an aquifer system.

In the first case study, the aforementioned approach was applied to the Floyds Fork water quality treatment center in Louisville, KY. The objective of this case study was to establish simple and reliable predictive models to correlate target variables with specific measured parameters. The study presented a multivariate statistical and data analyses of the wastewater physicochemical parameters to provide a baseline for temporal assessment of the treatment plant. Fifteen quality and quantity parameters were analyzed using data recorded from 2010 to 2016. To determine the overall quality condition of raw and treated wastewater, a Wastewater Quality Index (WWQI) was developed. To identify treatment process performance, the interdependencies between the variables were determined by using Principal Component Analysis (PCA). The five extracted components adequately represented the organic, nutrient, oxygen demanding, and ion activity loadings of influent and effluent streams. The study also utilized the model to predict quality parameters such as Biological Oxygen Demand (BOD), Total Phosphorus (TP), and WWQI. High accuracies ranging from 71% to 97% were achieved for fitting the models with the training dataset and relative prediction percentage errors less than 9% were achieved for the testing dataset. The presented techniques and procedures in this

case study provide an assessment framework for the wastewater treatment monitoring programs.

The second case study focused on assessing methane production of a novel combined system for treatment of high strength organic wastewater. The studied pilot plant comprised Rotating Biological Contactor (RBC) process under anaerobic condition, in conjunction with Moving Bed Biofilm Reactor (MBBR) as the combining aerobic process. Various operational parameters were tested to maximize the Chemical Oxygen Demand (COD) removal performance and methane gas production from treating high strength synthetic wastewater. The identified optimal parameters included hydraulic retention time, organic loading rate, and disk rotational speed; equal to 5 days, 7 rpm, and 2 kg COD/m³/d, respectively. Under these conditions, the combined system achieved high removal efficiency (98% from influent COD of 10,000 mg/L) with additional benefit of methane production (116.60 L/d from a 46-liter AnRBC reactor). The obtained results from conducting this case study confirmed the effectiveness of integrated hybrid system in achieving both high removal efficiency and methane production. Thus, this system was recommended for treating high strength organic wastewater.

The third case study focused on assessing the feasibility of using a contact stabilization process for secondary treatment of refinery wastewater through a step by step analysis. the studied pilot plant comprised contact-stabilization activated sludge process in conjunction with clarification reactor. Various operational parameters were tested to minimize excessive sludge production and maximize system removal performance from treating petroleum refinery wastewater. The mixed liquor dissolved oxygen (DO) and the rate of activated return sludge (RS) were selected as key operational parameters. The

results indicated that the system had an optimum performance under applied aeration of 3.7 mg oxygen per liter of mixed liquor and 46% return sludge. This operational combination resulted in COD removal efficiency of 78% with daily biomass production of 1.42 kg/day. Considering the results from this case study, the contact stabilization activated sludge process was suggested as an effective alternative for secondary treatment of wastewater from petroleum refineries.

The last case study combined probabilistic and deterministic approaches for assessing aquifer's water quality. The probabilistic approach used multivariate statistical analysis to classify the groundwater's physiochemical characteristics. Building upon the obtained results, the deterministic approach used hydrochemistry analyses for a more comprehensive assessment of groundwater suitability for different applications. For this purpose, a large geologic basin, under arid weather conditions, was evaluated. The ultimate objective was to identify: 1) groundwater classification scheme, 2) processes governing the groundwater chemistry, 3) hydrochemical characteristics of groundwater, and 4) suitability of the groundwater for drinking and agricultural purposes.

Considering the results from multivariate statistical analysis, chloride salts dissolution was identified within the aquifer. Further application of the deterministic approach revealed degradation of groundwater quality throughout the basin, possibly due to the saltwater intrusion. By developing the water quality index and a multi-hazard risk assessment methodology, the suitability of groundwater for human consumption and irrigation purposes were assessed. The combined consideration of deterministic and probabilistic approaches provided an effective means for comprehensive evaluation of groundwater quality across different aquifers or within one.

The presented procedures and methodologies in this research study provide environmental analysts and governmental decision makers with a comprehensive tool to evaluate current and future quality conditions within any given wastewater treatment plants and/or aquifer systems.

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CHAPTER ONE. INTRODUCTION

1.1. Statement of the Issue

As populations expand and urbanization increases, the associated water demands from both domestic and industrial applications put significant pressures on natural water resources. This sustained water demand and associated release of municipal and industrial sewage can negatively affect aquifers and other receive waterbodies. Wastewater, however, is not static in quality, and its characteristics change with respect to time of day, season, operation, and other factors. As a result, understanding the temporal qualitative and quantitative dynamics of both wastewater and groundwater systems is critical for protecting the natural water resources as well as establishing sustainable management practices.

1.2. Importance of the Issue

Each year, wastewater treatment plants process billions of gallons of sanitary and/or combined stormwater flow. In this case, identifying the dynamics of wastewater's constituents and their range are critical for establishing cost-effective treatment systems. Understanding the temporal performance and optimization of wastewater treatment plants is also crucial considering the ever-increasing energy costs and strict pollutant removal

regulations. Aquifer systems are also subjected to tremendous quality deterioration due to overexploitation. Understanding the long-term temporal fluctuations of groundwater quality within the basins is vital. In this case, comprehensive interpreting of the groundwater chemistry processes and integrated methodologies for temporal investigating the groundwater suitability for drinking and agriculture purposes are crucial. As a result, providing an effective means for comprehensive temporal evaluation and optimization of wastewater and aquifer systems is essential.

1.3. Current Practices and Challenges

Optimization and performance assessment of wastewater and groundwater systems have always been a challenge. In both cases, the main challenge is to develop appropriate indexing variables to better describe and evaluate the effectiveness of systems. However, due to the regional characteristics of both systems and the natural temporal variation, it is difficult to establish standardized one-to-one relationships that can characterize flows throughout all anticipated conditions.

Conducting routine water quality monitoring programs, experimental sampling campaigns, and geo-physicochemical analysis of the samples by using the traditional graphical methods, diagrams, and pre-established standard guidelines are the general approaches for evaluating the overall performance of environmental systems. However, appropriate temporal assessment of wastewater and aquifer systems is difficult due to the abundant chemical, physical, and microbiological parameters that should be considered. In both cases, the system's characteristics not only have a unique composition, but the

organic, inorganic and nutrient loadings, and also the operational parameters vary in terms of time, place and source. Even if all necessary data are collected, it is still challenging and often difficult to assess over-arching trends, quantify operational performance, and make the optimal decision due to the complex interrelationships of the parameters. Thus, there is a need to develop a series of multidisciplinary approaches that can be used to effectively manage water quality monitoring programs while reducing the number of quality parameters which must be routinely measured.

1.4. Objective of the Research

The objective of this research study is to provide a scientific basis for a robust control system on the performance of wastewater and aquifer systems and also to recommend a more accurate method of environmental management. Multivariate data analysis and simulation techniques could be used for better understanding of the processes and also for quality evaluating and optimizing the systems. Thus, the intent of this research is to develop a robust overarching methodology based on data analysis, statistical techniques, and simulation that will provide for a comprehensive assessment and optimization of environmental infrastructure systems, specifically, wastewater treatment plants and aquifer systems.

The intent of applying the multivariate data analysis and statistical algorithms is to 1) identify the temporal characteristics of each monitored water quality parameter, 2) define the statistical interrelationships between different parameters, 3) develop wastewater and/or groundwater quality indexes to quantitatively define the water quality, and 4)

develop multivariate statistical forecasting techniques to numerically express the significant quality parameters based on the measured historical process data base. Also, stepwise procedures were developed to better identify and optimize the key operational parameters for sustainable management of environmental systems.

1.5. Research Approach

Multivariate data analysis techniques provide a mechanism to better quantify environmental systems by establishing relationships between interrelated data. This strategy has been widely applied in the water field, like sewage management, surface and ground water quality, and wastewater treatment management during recent years.

In the field of wastewater systems, this research study focused on quality evaluation and optimization of the treatment plants. The intent is to transform the laboratory results into practical information for decision makers, assess the wastewater's make-up, performance assessment, and finally optimization of the treatment plants. Multivariate statistical techniques were used for comprehensive identification of the dynamics of wastewater's constituents to establish the preferred treatment processes. The most appropriate operating configurations resulting in a sustainable setup for the full-scale plants were identified using step-by-step data analysis. Various empirical models were developed to numerically express and estimate the significant properties of the influent and effluent of the treatment plants. Finally, the treatment processes were optimized by considering higher pollutant removal efficiency, lower operational costs, and less negative environmental impacts. The aforementioned methodology was successfully applied to

three different municipal and industrial wastewater treatment systems. For all cases, achieving higher removal efficiency, lower sludge production, and increased bio-gas generation was the main objective.

In the field of aquifer systems, this research study focused on evaluating the groundwater quality deterioration due to over-withdrawal rates and saltwater intrusion. The intent was to control the recharge and discharge cycles for basins located in arid climate conditions. A robust methodology, based on multivariate statistical techniques, was developed for assessing the aquifer's quality condition. The proposed method combined the probabilistic and deterministic approaches. Application of GIS based and graphical methods in conjunction with the multivariate statistical algorithms provided a classification scheme for comparing the overall groundwater quality conditions across the basins. Also, the suitability of groundwater for drinking and agriculture was determined and categorized by developing a step-by-step data analysis algorithm. The aforementioned methodology was successfully applied to two basins located in arid regions. For all cases, the initial intent was to provide a groundwater classification scheme based on human consumption and/or irrigation purposes, identify the processes governing the groundwater chemistry, detect the hydro-geochemical characteristics of groundwater, score the combined influences of individual quality variables on the overall groundwater quality for drinking purposes, and complete a multi-hazard risk assessment of the groundwater quality for agricultural activities.

The ultimate objective of conducting those case studies was to provide a rigorous procedure to draw meaningful results of the overall performance of wastewater and groundwater systems by inclusive consideration of the obtained voluminous data from

the routine monitoring programs. The described methodologies in this research study enable environmental analysts and governmental decision makers to accurately identify the quality of different current and/or future wastewater and or groundwater systems.

1.6. Structure of the Dissertation

The remainder of this research study has seven chapters. Chapter 2 represents the proposed methodology based on multivariate data analysis and statistical techniques for assessing the performance of environmental systems considering the results from the routine water quality monitoring programs. Chapters 3, 4, and 5 present applications of data analysis techniques for the assessment and optimization of three municipal and industrial wastewater treatment systems. Chapter 6 presents application of multivariate data analysis for long-term qualitative and quantitative appraisal of an aquifer located within arid climate conditions. Finally, chapter 7 provides a summary of all conducted case studies and presents some recommendations regarding further research potentials in the field of environmental system assessment.

Chapter 2 introduces the developed methodology for temporal performance assessment of environmental systems. The introduced multidisciplinary approach comprised combined consideration of data analysis, statistical algorithms, and numerical techniques. By using the multivariate data analyses and statistical techniques, a robust overarching methodology was developed for:

- Evaluating water quality composition

- Transforming the laboratory results into practical information
- Performance assessment of system process
- Identification of preferred process

The proposed methodology in this chapter attempted to discover appropriate indexing variables to better describe temporal characteristics of environmental systems. Those indexing variables provide practical information for Development, Upgrading, and Optimization of wastewater treatment plants and aquifer systems. The resultant information assists governmental decision makers and environmental analysts for:

- Assessing over-arching trends of routinely measured quality parameters
- Quantifying operational performance of current and future systems
- Sustainable system development

By combined considerations of Descriptive statistics, Pearson Product Moment Correlation Analysis, Principal Component analysis, Cluster Analysis, and Multivariate Regression Analysis this chapter produced a procedure for comprehensive assessment of any given wastewater treatment plant and aquifer system in order to:

- Identify temporal characteristics of each monitored parameter,
- Define statistical interrelationships between different parameters,
- Monitor the performance of environmental systems,
- Asses the temporal and spatial changes of water quality by introducing water quality index,

- Determine the important relationships among the monitored parameters through descriptive data analysis,
- Discovering a finite set of uncorrelated factors by using Principal Component Analysis technique to effectively describe the characteristics of influent loads and system's performance,
- Establishing the numerical expressions, using multivariate statistical models, for predicting the significant properties of the influent and effluent loads

Chapter 3 presents wastewater quality evaluation procedures, based on multivariate statistical techniques, for providing an assessment framework for the wastewater treatment monitoring programs. To develop the procedures, the study objectively evaluated the performance of the Floyds Fork wastewater treatment plant near Louisville Kentucky during 2010 and 2016.

This chapter focused on evaluating the wastewater's make-up, and temporal performance assessment of the systems. By using the multivariate data analyses and statistical techniques, a robust overarching methodology was developed for monitoring the performance of full-scale wastewater treatment plants, assessing the temporal and spatial changes of water quality by introducing wastewater quality index, discovering the important relationships among the monitored parameters through descriptive data analysis, and establishing the numerical expressions for predicting the significant properties of the influent and effluent of the treatment plants.

Performing the descriptive statistical analysis on 9200 measured quality and quantity samples for 2010 to 2016 discovered interesting understandings for the wastewater load and the treatment effectiveness. Those can be summarized as following:

- Trends for influent BOD, TSS, N and P concentrations moved similarly for the entire period of study
- While, DO concentration moved in the opposite direction for similar period
- It can be inferred that while the availability of free oxygen within the influent load increased, contaminants level of incoming wastewater dropped
- This process was identified to be directly related to variation of inflow rate
- As a result: As inflow rate increased, availability of dissolved oxygen improved, and pollutants concentration decreased
- Regarding the treatment effectiveness: Variation of RAS affects effluent TSS and BOD concentrations
- Increase of RAS caused a raise of effluent TSS and decrease of effluent BOD for the entire period of study
- As a result, it can be inferred that availability of active microorganisms throughout the system significantly affects process performance

Analyzing monitoring program data comprised a complex matrix of physicochemical parameters which individually could not provide reliable temporal evaluation of whole system. Thus, Wastewater Quality Index (WWQI) was developed to summarize large amounts of monitored parameters into a simple term. As a result, it was concluded that:

- Influent WWQI changed between 45 and 60, which indicated Water quality would be threatening to a receiving water
- Effluent WWQI changed between between 96 and 100 which indicated Stream could be released to receiving waters with little threat of impairment

- Finally, it was concluded that treatment process improved wastewater quality by more than 51 percent

To more comprehensively describe the overall characteristics of influent and effluent wastewater, the Principal Component Analysis (PCA) was applied. That technique converted a large number of original variables into a set of uncorrelated components. Derived components represented information of the whole dataset with minimal loss of original information. As a result, five components were extracted from fifteen parameters. The derived components include:

- PC1 which represented the Influent organic load
- PC2 which represented the Flow and Recycled rates
- PC3 which represented the Ion activity
- PC4 which represented the Effluent oxygen demand
- PC5 which represented the Nutrient removal efficiency

Investigating the fluctuation of derived components within the study period indicated that:

- Positive scores for PC1 were observed for samples with negative scores on PC2 that means: More polluted incoming wastewater during seasons with lower flow rates
- Peak PC1 positive scores observed from 2013 that means: Overall increase of influent pollutant level from 2013
- PC5 fluctuations were considerably higher that means: Non-uniform nutrient removal performance over the study period

- Combined consideration of PC1 and PC5 indicated that more polluted influent led to less nutrient removal performance of the system
- Overall positive scores for PC4 for recent years indicated Less oxygen content and high oxygen demand of effluent wastewater

To provide a comprehensive data-basis for future studies on simulation and optimization of environmental systems, the multivariate statistical modeling was applied. As a result, six numerical forecasting models were developed for influent and effluent phosphorus, BOD, and WWQI, considering training dataset of 2010 - 2015 and validating dataset of 2016. The model preparation involved three steps including:

Step 1: Pearson product moment correlation analysis:

- Identifying predictor variables for each model
- Variables with correlation significance level of 0.01 were considered as predictors

Step 2: Stepwise Multivariate Regression Analysis:

- Multiple complex-terms of predictors and their interactions were considered
- Stepwise backward model generation were used with threshold p-value of 0.05
- Least statistically significant predictors with largest p-value were iteratively removed in each step

Step 3: ANOVA Test:

- To confirm and detect the optimum model from various developed models for each target parameter
- Admit/reject the null hypothesis of the p-values $< \alpha = 0.05$

Chapter 4 presents performance assessment of a novel combined system for treatment of high strength organic industrial wastewater. The proposed system comprised Rotating Biological Contactor (RBC) process under anaerobic condition, in conjunction with Moving Bed Biofilm Reactor (MBBR) as the combining aerobic process. The objective of this chapter is to identify the specific operational parameters which affect the performance of the proposed combined system. A robust systematic data analysis was developed to optimize the performance of treatment plant by considering achieved maximum bio-gas removal production and pollutant removal efficiency.

Various operational parameters were tested to maximize the Chemical Oxygen Demand (COD) removal performance and methane gas production from treating high strength synthetic wastewater. The identified optimal parameters included hydraulic retention time, organic loading rate, and disk rotational speed; equal to 5 days, 7 rpm, and 2 kg COD/m³/d, respectively. Under these conditions the combined system achieved high removal efficiency (98% from influent COD of 10,000 mg/L) with additional benefit of methane production (116.60 L/d from a 46-liter AnRBC reactor). Also, analysis of kinetic models on experimental results from AnRBC stage indicated the suitability of Stover Kincannon model with prediction accuracy of 93%. The results confirmed the effectiveness of integrated AnRBC system in achieving both high removal efficiency and methane production. Thus, this system was recommended for treating high strength organic wastewater.

Chapter 5 presents feasibility assessment of using a biological treatment approach for treatment of refinery wastewater through a step by step data analysis. Excessive sludge production is cost prohibitive and a major concern in biological treatment of petroleum refinery wastewater. Thus, the intent of this chapter is to identify operational conditions for treatment systems that result in low sludge production of the system, while maintaining its high removal performance. The mixed liquor dissolved oxygen (DO) and the rate of activated return sludge (RS) were selected as operational parameters governing the optimum performance of the system. A total number of 32 individual experiments were conducted on a pilot plant under four different aeration phases (DO) and eight RS percentages. The analyses investigated the biokinetic coefficients, observed removal efficiencies, and the amount of produced sludge to identify suitable operational conditions. The results indicated that the system had an optimum performance under applied aeration of 3.7 mg oxygen per liter of mixed liquor and 46% return sludge. This operational combination resulted in COD removal efficiency of 78% with daily biomass production of 1.42 kg/day.

Chapter 6 explores using deterministic and probabilistic approaches for evaluating the quality of groundwater resources. To present this multidisciplinary approach, the study objectively investigated the groundwater quality condition of a basin, called Shiraz, located in an arid region, and subjected to quality deterioration due to saltwater intrusion. The incorporated method combined the multivariate statistical analysis and hydrochemistry analyses for classifying the groundwater's physiochemical characteristics and also for comprehensive evaluating of groundwater quality based on different

applications. Considering the results from correlation and principal component analyses, along with hierarchical Q-mode cluster analysis, chloride salts dissolution was identified within the aquifer. Further application of the deterministic approach revealed degradation of groundwater quality throughout the basin, possibly due to the saltwater intrusion. By developing the water quality index and a multi-hazard risk assessment methodology, the suitability of groundwater for human consumption and irrigation purposes were assessed. The obtained results were compared with two other studies, conducted on aquifers under similar arid climate conditions. This comparison indicated that quality of groundwater resources within arid regions are prone to degradation from salinization. The combined consideration of deterministic and probabilistic approaches provided an effective means for comprehensive evaluation of groundwater quality across different aquifers or within one.

Chapter 7 provides a comprehensive summary of applying the proposed methodology for optimization and temporal performance assessment of four case studies, described in previous chapters. Also, some recommendations for conducting similar studies for optimization and performance assessment of other environmental infrastructures are proposed.

CHAPTER TWO. METHODOLOGY

2.1. Introduction

To protect natural water resources and establish sustainable management practices, it is essential to have an accurate understanding of temporal performance of environmental systems. Thus, wastewater treatment plants and aquifer systems are consistently under development, upgrading, and optimization. However, optimization and temporal performance assessment of these systems have been always a challenge for the governmental decision makers as well as environmental analysts.

For each environmental system, the physicochemical properties of the influent streams are unique and dependent on factors such as the origin of discharge, type of sewer system infrastructure (combined or separate), development level of the area, climate condition, and groundwater levels. Thus, in all cases, the influent load not only has a unique composition, but the organic, inorganic and nutrient loadings vary in terms of time, place and source (Ebrahimi et al. 2017). As a result, appropriately characterizing influent load is difficult due to the abundant chemical, physical, and microbiological parameters that should be considered (Bryant 1995). The significant challenge here is to develop appropriate indexing variables to better describe temporal characteristics of system.

Developing indexing variables for existing wastewater treatment plants provides practical information of temporal characteristics of key operational parameters. These understandings serve as a baseline for performing temporal optimization. Indexing variables can also deliver a comprehensive understanding of the dynamic nature of wastewater composition, which is significantly valuable for future treatment plant's planning and design practices. Moreover, in the case of aquifer systems, the aforementioned indexing variables provide meticulous information of groundwater chemistry processes which facilitate identification of groundwater suitability for different purposes.

The general approach for providing the aforementioned fundamental information is conducting routine water quality monitoring programs, and analyzing sampling results using traditional graphical methods, diagrams, and standard guidelines. However, even if all necessary data are collected, it is still challenging for the operators to make decision due to the complex interrelationships of the parameters. Also, due to the regional characteristics of the influent loads and the natural temporal variation, it is difficult to:

- Establish standardized one-to-one relationships that can characterize flows throughout all anticipated conditions,
- Assess over-arching trends
- Quantify operational performance
- Make the optimal decision

As a result, there is a need to utilize a series of multidisciplinary methods to effectively manage monitoring programs in order to:

- Reduce number of routinely measured parameters
- Control quality of sampling efforts and measurements
- Optimize temporal performance of systems

The objective of this research study is to apply multivariate data analysis techniques and statistical algorithms to calculate improved spatial and temporal relationships to better understand the process. Multivariate statistical techniques provide a mechanism to quantify water quality and system processes by establishing relationships between interrelated data (Aguado and Rosen 2008). This strategy has been widely applied in the water field during recent years (Avella et al. 2011; Bayo and López-Castellanos 2016; Costa et al. 2009; Durmusoglu and Yilmaz 2006; Goode et al. 2007; Platikanov et al. 2014; Sun et al. 2016; Tomita et al. 2002). In the field of Sewage management, Singh et al. (2005) applied the principal component analysis (PCA) and partial least analysis (PLS) to derive information on seasonal influence and compositional differences in sewage generated by domestic and industrial waste. In the field of surface water quality, Zhang et al. (2010) performed the PCA method for determining the contribution level of nutrients, heavy metals, natural and organic compounds on the spatial and temporal quality variation of a local river. Regarding the wastewater treatment management, Ouali et al. (2009) applied the correlation and PCA methods for designing a network for monitoring the performance level of a treatment plant. Also, there are some recent studies on developing models for estimating the concentration of major effluent quality parameters of treatment plants using the statistical methods (Platikanov et al. 2014; Wallace et al. 2016).

Most of the aforementioned studies used one specific algorithm or technique to provide useful understandings of the system. However, there is limited study concentrating on combined consideration of multivariate statistical, simulation, and data analyses for temporal performance assessment and optimization of environmental systems. Thus, this research study focuses on developing a series of multidisciplinary procedures by using Multivariate Data Analysis, Statistical Algorithms, and Simulation Techniques to perform the following specific tasks:

- Evaluate the water quality make-up
- Transform the laboratory results into practical information
- Performance assessment of treatment process
- Identify of preferred treatment process

The proposed methodology considered to be a comprehensive combination of statistical techniques and data analysis algorithms including:

- Descriptive data analysis of monitored parameters in terms of central tendency, dispersion, and distribution
- Identification of temporal characteristics of each monitored parameter
- Developing Water Quality Index to quantitatively define influent and effluent quality and categorize flow conditions over the time
- Defining statistical interrelationships between different parameters by developing Pearson product moment correlation analysis

- Developing principal component analysis for historical dataset to introduce a finite set of uncorrelated variables to represent overall characteristic of system
- Evaluate temporal variation of influent and effluent organic loading, ion activities, oxygen demanding, and nutrient loading
- Determining interrelationship level between measured data using Correlation Analysis
- Developing numerical predictive models to numerically forecast significant operational and quality parameters using multivariate statistical and complex regression analyses

The above procedures are applied to three wastewater treatment systems and an aquifer to evaluate and optimize the temporal performance of systems. The established framework and methodologies provide environmental analysts and governmental decision makers with a comprehensive tool to evaluate and optimize current and future quality conditions within any given environmental systems.

2.2. Descriptive Data Analysis of Monitored Parameters

Studying the temporal fluctuation of the routine monitored quality and quantity parameters can provide interesting insights. In this research study, descriptive statistics were used to identify the characteristics of each measured parameter in terms of central tendency, dispersion, and distribution. Central tendency provides the location of the distribution for each parameter including the mean, median and mode. Dispersion measures the spread in the data set including the standard deviation, coefficient of

variation, range, minimum and maximum. Distribution estimates using skewness and kurtosis to describe time series distribution's symmetry and shape.

Investigating the quality parameter's fluctuations can provide fundamental information regarding the characteristics of influent and effluent loads as well as system's effectiveness in treating the pollutants. However, there is a complex interrelationship within the water quality variables. Thus, it is difficult to utilize one parameter or one set of parameters to appropriately characterize the overall system's performance. Moreover, interpreting the variable's variation without a clear understanding of the processes would not lead to a comprehensive assessment of the system efficiency. As a result, this research study attempted to develop a series of uncorrelated indexes and components to effectively investigate and describe the composition of the system's influent and effluent loads as well as temporal performance of the processes.

2.3. Water Quality Index Development

Analyzing monitoring program data comprise a complex matrix of physicochemical parameters which individually cannot provide reliable temporal evaluation. Thus, it is difficult to use a single parameter to characterize water quality and comprehensively assess system efficiency. Hence, Water Quality Index (WQI) is an efficient mechanism to express the overall condition of water by cumulative consideration of all monitored quality indices. In other words, WQI is a dimensionless number that cumulatively describes the quality of an aggregated set of measured chemicals, physicals, and

microbiological parameters (Bordalo et al. 2006). In this research study, WQI was developed separately for wastewater and groundwater streams.

2.3.1. Wastewater Quality Index

To assess the quality of wastewater, Wastewater Quality Index (WWQI) was developed to enable interpretation of monitoring data by ranking the wastewater quality on a rating scale from zero to 100 based on the measured parameters and established water quality standards (Bharti and Katyal 2011). The higher values tend to indicate that wastewater effluents are meeting design objectives and the plant is operating efficiently. As such, influent streams to wastewater treatment plants generally have low WWQI values as they would be harmful to surrounding waterbodies if released untreated. After treatment, the wastewater streams should have relatively high WWQI values indicating they can be released to surrounding water bodies. Using the WWQI as an indicator variable is beneficial for decision makers as it enables them to rapidly identify the quality of different wastewater streams and also compare different treatment processes (Asadi et al. 2007).

Considering the aforementioned objective, the WWQI was developed using analytics introduced by the Canadian Council of Ministers of Environment, CCME method (CCME 2001; Lumb et al. 2006). The CCME WWQI was calculated based on the combination of three factors, that consider the number, frequency, and amount of variables whose objectives are not met based on the quality limitations, (refer to Equations 1-6) (De Rosemond et al. 2009; Hurley et al. 2012). The water quality was then ranked in different categories as described in Table 2-1 (Khan et al. 2004).

$$F1 = \frac{\text{number of failed parameters}}{\text{total number of parameters}} \times 100 \quad (1)$$

$$F2 = \frac{\text{number of failed tests}}{\text{total number of tests}} \times 100 \quad (2)$$

$$\text{Excursion}_i = \frac{\text{failed test value}_i}{\text{limitation}_i} - 1 \quad (3)$$

$$\text{nes} = \frac{\sum_{i=1}^n \text{excursion}_i}{\text{number of tests}} \quad (4)$$

$$F3 = \frac{\text{nes}}{0.01 \text{ nes} + 0.01} \quad (5)$$

$$\text{WWQI} = 100 - \frac{\sqrt{F1^2 + F2^2 + F3^2}}{1.732} \quad (6)$$

where:

F1 = percentage of measured parameters that do not meet their limit at least once during the time period

F2 = percentage of individual tests that do not meet limitation

F3 = amount by which failed test values do not meet their limitation

Excursion = number of times by which an individual test is greater than the limitation

nes = collective amount by which individual tests are out of compliance

F3 = amount by which failed test values did not meet their objectives

Table 2-1. Wastewater Quality Category based on CCME WWQI

Quality Range	WWQI	Water Category
Excellent	95 – 100	Very close to natural or pristine levels
Good	80 – 94	Rarely depart from natural or desirable levels
Fair	65 – 79	Sometimes depart from natural or desirable levels
Marginal	45 – 64	Often depart from natural or desirable levels
Poor	0 – 44	Quality is almost always threatened or impaired

2.3.2. Groundwater Quality Index

To assess the quality of groundwater, the Groundwater Quality Index (GWQI) was introduced. The GWQI is a dimensionless number that cumulatively expresses the quality of an aggregated set of measured groundwater physiochemical parameters from different samples in a given area (Hallock 2002). The groundwater can be categorized into five classes based on the calculated WQI, as illustrated in Table 2-2 (Sahu and Sikdar 2008). The lesser values indicate that the quality of water is more adapted with the pre-established standards proposed by the WHO. The established GWQI, as a variable indicator, enables decision makers to distinguish different groundwater sources based on their suitability for drinking purposes (Bordalo et al. 2006).

Table 2-2. Classification of Groundwater Quality based on the GWQI

GWQI	Description
<50	Excellent
50-100	Good
100-200	Poor
200-300	Very Poor
>300	Unfit for Drinking

The GWQI was calculated based on the method proposed by Yidana et al. (2010). All parameters (n) were assigned a weight (wi) on a scale of 1 to 5, based on their influence on drinking water quality and human health. The relative weight value (Wi) and the quality rating scale (qi) for each parameter were calculated using equations 7 and 8, in which Ci and Si are the measured concentration and the WHO standard for each parameter, respectively. Finally, the GWQI for an individual well was then expressed as the sum of the sub-index (SIi) of all parameters by using equations 8 and 10.

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (7)$$

$$q_i = \frac{C_i}{S_i} \times 100 \quad (8)$$

$$SI_i = W_i \times q_i \quad (9)$$

$$GWQI = \sum_{i=1}^n SI_i \quad (10)$$

2.4. Pearson Product Moment Correlation Analysis

The Pearson product moment correlation analysis quantifies the linear relationship between two variables (Mackiewicz and Ratajczak 1993). The established correlation coefficient, ranging from negative one to positive one, is the magnitude of the interrelationship in the same direction (positive values) or in the opposite direction (negative values) (Khambete and Christian 2014). A strong positive or negative relationship is identified when the coefficient is closer to the absolute value of one. Coefficients closer to zero indicate a weak or nonexistent relationship between the two variables. The correlation analysis was applied to:

- 1- Define statistical interrelationships between different measured quality and quantity parameters
- 2- Identify variables with correlation significance level of 0.01 as a predictor variable for developing numerical predictive models which forecast significant operational and quality parameters based on historical dataset

2.5. Principal Component Analysis

Although the correlation analysis is a useful method to categorize the correlations between two variables, application results of such an analysis is limited for simultaneously evaluating the correlations among several variables (Rastogi and Sinha 2011). Rather, principal component analysis (PCA) can be applied to investigate the

interrelationships between a large group of variables (Lebart et al. 1979). PCA is a valuable technique to convert a large number of original correlated variables into a finite set of uncorrelated variables. Through this dimension reduction process, the derived components represent the information of the whole dataset with minimal loss of original information (Alberto et al. 2001). Each of the obtained components capture as much of the variation which has not been explained by the former component as possible. This approach has been successfully applied to water and wastewater data in a variety of study areas (Lee et al. 2006; Lee and Vanrolleghem 2004).

The PCA method is usually performed in five steps;

- 1- Preparing the data matrix with original variables X_i
- 2- Transforming matrix X_i into a standardized matrix Y_i by using Eq. 11
- 3- Calculating the covariance matrix R using Eq. 12 and 13
- 4- Identifying the principal components which account for a large portion of the variation in the data set
- 5- Calculating the score (Z_i) of the principle components and the comprehensive score (Z) of each group of data set using Eq. 14 and 15 (Ouyang 2005).

$$Y_i = \frac{X_i - E(X_i)}{\sqrt{D(X_i)}} \quad (11)$$

$$|R - \lambda_i E| = 0 \quad (12)$$

$$L_i = \frac{B_i}{\sqrt{\lambda_i}} \quad (13)$$

$$Z_i = L_i \times Y_i \quad (14)$$

$$Z = \sum_{i=1}^m d_i \times Z_i \quad (15)$$

where,

$E(X_i)$ = average value of the original data

$D(X_i)$ = variance of X_i

E = unit matrix

B_i = component loading matrix value

d_i = variance contribution

λ_i = eigenvalues

L_i = corresponding eigenvector

Using the statistical software, SPSS (Statistical Package for Social Science, version 13.0), PCA was carried out for all measured parameters. To account for the differing parameter scales, all variables were normalized to mean zero and unit variance. As a result, a finite principal factors were extracted based on Kaiser's rule of eigenvalues greater than one (Chong and Jun 2005). Each derived component explained a specific variance percentage of all studied variables, which is referred to component loading. Components with higher loadings can better describe the characteristic of the total dataset (Bayo and López-Castellanos 2016). To maximize the variation of loadings on each component, orthogonal factor rotation was generated using the Varimax method (Reimann et al. 2002). Finally, the component's score was estimated based on the correlated values of the significant

factor loadings. Based upon these procedures, the derived components described significant portion of the total variability of the data set and represented the overall variation in water quality during the period of study. As a result, the dimension of the data set was significantly decreased from high number of measured variables to limited number of factors with a minimal percent loss of information.

2.6. Statistical Modelling Approach

To perform optimization of current systems as well as design of future systems, there is always a need for predicting significant operational and quality parameters. Although there are several theoretical models for predicting the water quality parameters, those are considerably complicated. For applying the theoretical modeling, there is a need for incorporating many bio-kinetic, hydrodynamic, diffusion, and detachment coefficients which are intrinsically dynamic and hard to accurately estimate (Goode et al. 2007). As an alternative, multivariate statistical techniques can be performed to develop predictive models for quality parameters based on the measured historical process data base. Considering the measured quality and quantity parameters as the training data, descriptive numerical models were developed to forecast key influent and effluent parameters. The developed models were then subjected to validation processes.

The modeling approach was carried out by combining three statistical methods including correlation, multivariate regression, and ANOVA analyses. Firstly, the predictor variables for each model were identified based on the results from the established correlation analysis section. Among all variables which were determined to be correlated

with the target parameter, the variables with correlation significance level of 0.01 were considered as the predictor variables.

Following the correlation analysis, the predictive models were developed for each target parameter using the stepwise multivariate regression analysis including multiple complex-terms of variables. Several combination sets of predictor variables in conjunction with their interactions were considered for model generation. By defining the threshold p-value of 0.05 and performing the backward method, all possible predictor variables were firstly considered for developing the model. Subsequently, the least statistically significant predictors with the largest p-value were iteratively removed in a stepwise manner until all the remaining variables in the model contained a significant predefined p-value.

To confirm and detect the optimum model from various developed models for each target parameter, the final step attempted to conduct the ANOVA test to admit/reject the null hypothesis of the p-values $< \alpha = 0.05$.

2.7. Conclusion

The methodologies described above can provide a scientific basis for a robust control system on the performance of environmental systems. Also, the methods presented by this research study can be used to effectively manage water quality monitoring programs, while reducing the number of quality parameters which must be routinely measured and also controlling the quality of sampling efforts and measurements. The presented methodologies in this research study provide the environmental analysts and

governmental decision makers with a comprehensive tool for evaluation of current and future quality conditions within any given environmental system.

The proposed procedure can be summarized in the following steps:

- 1- Calculate WQI for influent and effluent streams
- 2- Categorize flow conditions over the time
- 3- Evaluate systems effectiveness by comparing influent and effluent indexes
- 4- Conduct the PCA for historical dataset
- 5- Evaluate temporal variation of influent and effluent organic loading, ion activities, oxygen demanding, and nutrient loading
- 6- Determine interrelationship level between measured data using Correlation Analysis
- 7- Identify the most highly correlated variables with target parameter
- 8- Develop predictive models for target parameters
- 9- Verify accuracy of models in terms of fitting with training and testing data

The developed multidisciplinary frameworks were applied for the temporal performance assessment and optimization of four different case studies including:

- 1- A full scale municipal wastewater treatment plant located in Louisville, KY
- 2- A laboratory scale pilot plant of a combined anaerobic-aerobic wastewater treatment system receiving high strength organic industrial sewage

3- A laboratory scale pilot plant of a two-stage aerobic wastewater treatment system receiving petroleum refinery sewage

4- An aquifer system located in a semi-arid region and at the vicinity of a Salt Lake

For all case studies, the ultimate objective was to apply the above-mentioned developed methodologies on the results from the conducted water quality monitoring programs in order to:

1- Comprehensively characterize the influent and effluent loads

2- Identify the key operational parameters governing the effectiveness of process

3- Temporal performance assessment of the system

4- Optimization of the process

CHAPTER THREE. TEMPORAL PERFORMANCE ASSESSMENT OF WASTEWATER TREATMENT PLANTS BY USING MULTIVARIATE STATISTICAL ANALYSIS

3.1. Introduction

Each year, wastewater treatment plants process billions of gallons of sanitary and/or combined stormwater flow. For each treatment plant the physicochemical properties of the influent streams are unique and dependent on factors such as the origin of discharge, type of sewer system infrastructure (combined or separate), development level of the area, climate condition, and groundwater levels. Thus, in all cases, the wastewater stream not only has a unique composition, but the organic, inorganic and nutrient loadings vary in terms of time, place and source (Avella et al. 2011; Lefkir et al. 2015).

Identifying the dynamics of wastewater's constituents and their range are critical for establishing the preferred treatment system (Tchobanoglous and Burton 1991). Process designs must be optimized to effectively mitigate contaminants throughout all expected ranges and combinations of flow levels (Ebrahimi et al. 2016). This is especially important when effluent is directed towards a reuse project. Depending on the reuse objective, i.e. discharge to surface or groundwater bodies, irrigation purposes, or industrial reuse, the effluent should meet established quality limitations at all times. Thus, understanding the influent variability and its impact within the treatment process is essential to prevent the adverse health and environmental impacts of reused wastewater.

Appropriately characterizing wastewater streams and assessing wastewater treatment plant efficiencies is difficult due to the abundant chemical, physical, and microbiological parameters that should be considered (Bryant 1995). Even if all necessary wastewater data are collected, it is still challenging for the operators to make decision due to the complex interrelationships of the parameters (Timmerman et al. 2010). Thus, there is a need for developing appropriate indexing variables to better describe wastewater quality and evaluate treatment system's efficiency (Boyacioglu 2007; Rosén and Lennox 2001). However, due to the regional characteristics of the wastewater stream and the natural temporal variation, it is difficult to establish standardized one-to-one relationships that can characterize flows throughout all anticipated conditions (Platikanov et al. 2014). Rather, multivariate statistical techniques could be used to provide better spatial and temporal relationships to facilitate better understanding of the process.

Multivariate statistical techniques provide a mechanism to better quantify wastewater quality and treatment processes by establishing relationships between interrelated data (Aguado and Rosen 2008). This strategy has been widely applied in the water field during recent years (Avella et al. 2011; Bayo and López-Castellanos 2016; Costa et al. 2009; Durmusoglu and Yilmaz 2006; Goode et al. 2007; Platikanov et al. 2014; Sun et al. 2016; Tomita et al. 2002). In the field of Sewage management, Singh et al. (2005) applied the principal component analysis (PCA) and partial least analysis (PLS) to derive information on seasonal influence and compositional differences in sewage generated by domestic and industrial waste. In the field of surface water quality, Zhang et al. (2010) performed the PCA method for determining the contribution level of nutrients, heavy metals, natural and organic compounds on the spatial and temporal quality variation of a

local river. Regarding the wastewater treatment management, Ouali et al. (2009) applied the correlation and PCA methods for designing a network for monitoring the performance level of a treatment plant. Also, there are some recent studies on developing models for estimating the concentration of major effluent quality parameters of treatment plants using the statistical methods (Platikanov et al. 2014; Wallace et al. 2016).

The objective of this study is to develop wastewater quality evaluation procedures for regional treatment facilities. To develop the procedures, the study objectively evaluated the performance of Floyds Fork Water Treatment Plant near Louisville Kentucky during 2010 and 2016. Multivariate statistical methods were applied to 1) identify the temporal characteristics of each monitored parameter, 2) define the statistical interrelationships between different influent and effluent parameters, 3) develop Wastewater Quality Index (WWQI) to quantitatively define the wastewater quality, and 4) develop multivariate statistical forecasting techniques to numerically express the significant quality parameters based on the measured historical process data base. The procedures developed for the Floyd's Fork case study should be applicable to other water/wastewater treatment systems.

3.2. Materials and methods

3.2.1. Description of the Floyds Fork Water Quality Treatment Center

Located at 1100 Blue Heron Drive, Louisville, Kentucky 40225, the Floyds Fork Water Quality Treatment Center (WQTC) has been functional since 2000 and upgraded in 2013. The treatment plant services 15,490 residential connections and is designed to treat the

municipal wastewater with an average daily and maximum peak hour flow capacity of 6.5 mgd and 24 mgd, respectively. The plant consists of preliminary, secondary, and tertiary treatment systems. Screenings and grit removal units were designed for preliminary treatment. For secondary treatment, the oxidation ditch process coupled with clarification units was designed to biologically remove organic and nutrient materials from the wastewater. To meet the established effluent phosphorus concentration limitation, chemical addition with sodium aluminate to the oxidation ditch mixed liquor was performed. Following clarification, the effluent flows to the cloth filters and ultraviolet radiation disinfection units for tertiary treatment. The final effluent is discharged to a stream.

3.2.2. Monitored Parameters and Analytical Methods

To comprehensively analyze the composition of wastewater, a wide range of water quality indices should be taken into account (Nagels et al. 2001; Wanda et al. 2015). In the case of Floyds Fork WQTC, those indices were derived from the routine water quality monitoring program performed by Louisville MSD during 2010 and 2016. Collectively 9180 samples were obtained from nine quality and quantity variables. The measured parameters include biochemical oxygen demand (BOD), total suspended solids (TSS), phosphorus (P), nitrogen (N), dissolved oxygen (DO), pH, mixed liquor volatile suspended solids (MLVSS) content in aeration tank, flow rate and the recycled activated sludge (RAS) rate. All analytical methods applied in the sampling and measurement program were in accordance with the standard methods for examination of water and wastewater (Apha 2012).

3.2.3. Descriptive Analysis of the Parameters

Descriptive statistics were used to identify the characteristics of each measured parameter in terms of central tendency, dispersion, and distribution, see Table 3-1. Central tendency provides the location of the distribution for each parameter including the mean, median and mode. Dispersion measures the spread in the data set including the standard deviation, coefficient of variation, range, minimum and maximum. Distribution estimates using skewness and kurtosis are able to describe a time series distribution's symmetry and shape.

Table 3-1. Descriptive Statistics of the Influent (i) and Effluent (e) Parameters

Variable	Unit	Discharge Limit	Mean	Median	Stan. Error	Stan. Dev.	Var.	Kurtosis	Skewness	Range	Min	Max
Flow Rate	MGD		2.9	2.8	0.1	0.7	0.5	0.2	0.7	3.0	1.7	4.7
Pi	mg/L		5.6	5.6	0.2	1.4	2.1	0.9	0.6	7.8	2.3	10.0
BODi	mg/L		177.2	161.2	9.5	71.9	5174	5.1	1.6	448	40.2	488
TSSi	mg/L		361.2	351.8	15.4	115.9	13441	-0.3	-0.1	495	90	584
Ni	mg/L		18.3	16.9	0.6	4.5	19.9	5.3	1.5	28.5	9.3	37.8
pHi	-		7.4	7.3	0.0	0.2	0.1	0.8	0.8	1.0	7.0	8.0
DOi	mg/L		4.2	4.1	0.1	1.0	1.1	0.0	0.2	5.2	1.6	6.7
Pe	mg/L	0.5	0.3	0.3	0.0	0.1	0.0	-0.3	0.3	0.7	0.1	0.7
BODe	mg/L	6	2.3	2.0	0.1	0.6	0.4	3.1	2.0	2.3	2.0	4.3
TSSe	mg/L	30	2.3	2.1	0.1	0.6	0.4	3.6	1.6	3.5	1.3	4.7
Ne	mg/L	3	0.5	0.4	0.1	0.5	0.2	2.9	1.7	2.0	0.1	2.0
pHe	-	7 - 9	7.9	7.9	0.0	0.2	0.0	1.9	-0.3	1.2	7.2	8.4
DOe	mg/L	7	9.2	9.0	0.1	1.0	0.9	-0.6	0.7	3.4	8.0	11.3
MLVSS	mg/L		2050	1989	32.8	247.5	61271	0.5	0.9	1040	1661	2701
RAS	MGD		1.2	1.1	0.1	0.4	0.1	-0.4	0.5	1.6	0.6	2.2

Studying the temporal fluctuation of the parameters can provide interesting insights. As observed in Figure 3-1, the trends for influent BOD, TSS, nitrogen and phosphorus parameters moved similarly, while DO concentration moved in the opposite direction. This opposing trend indicates that while the available amount of free oxygen increased, the contaminants level of the incoming wastewater dropped. This condition is directly related to the variation of inflow rate. As the stream flow increased, the availability of dissolved oxygen improved, and the pollutants concentration decreased consequently. For the effluent quality parameters, it was observed that the variation of recycled sludge through the treatment process had a considerable impact on the concentration of other quality parameters, especially TSS and BOD. Increasing the amount of RAS caused a raise of effluent TSS concentration and decrease in the amount of BOD level. Although, investigating the quality parameter's fluctuations can provide some basic information, there is a complex interrelationship within the wastewater quality variables. It is thus difficult to utilize one parameter or one set of parameters to appropriately characterize the waste stream. Moreover, interpreting the variable's variation without a clear understanding of the treatment processes would not lead to a comprehensive assessment of the treatment system efficiency.

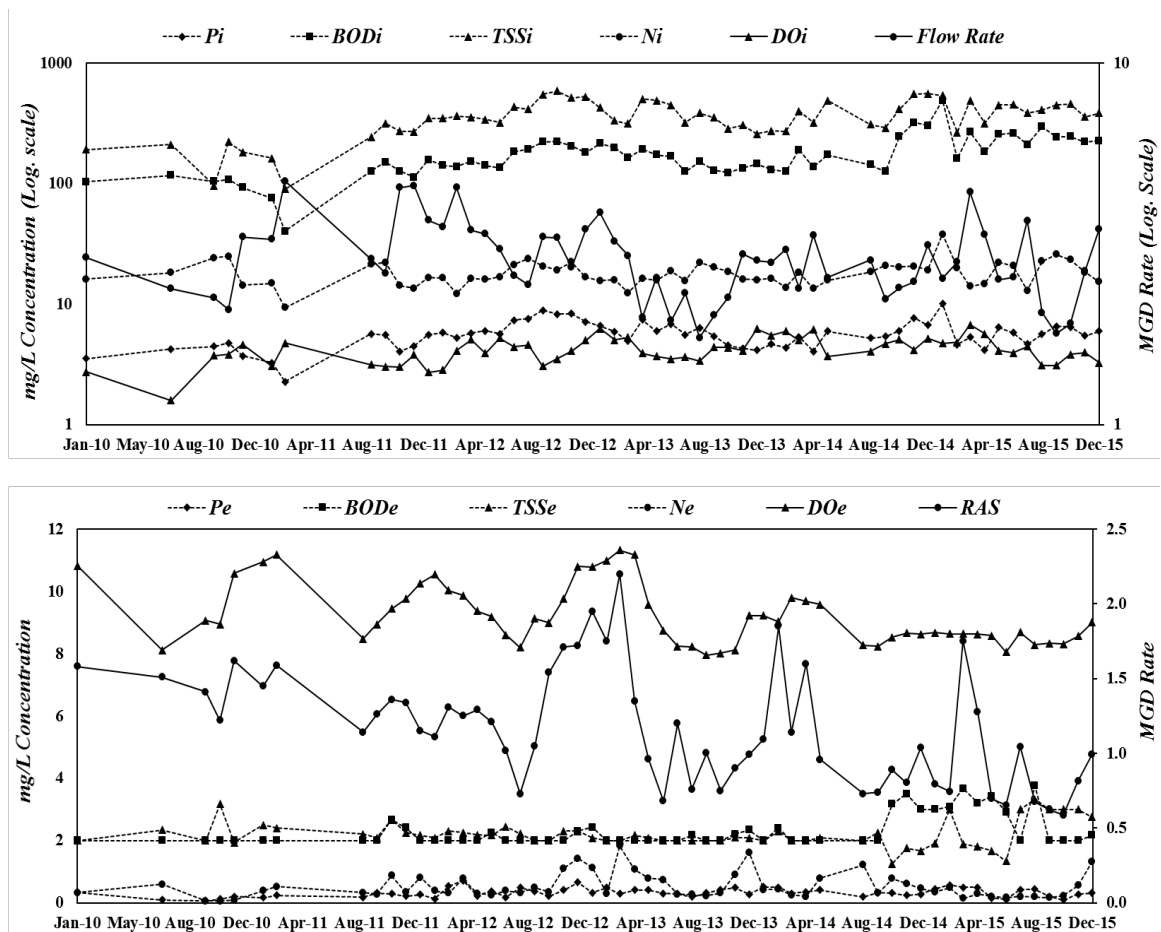


Figure 3-1. Temporal Variation of Average Monthly Influent (top) and Effluent (bottom) Parameters

3.2.4. Temporal Assessment of the Experimental Data

The results of the wastewater monitoring program comprise a complex matrix of physicochemical parameters which individually cannot provide a reliable temporal evaluation of the wastewater quality or assessment of the treatment plant's performance. To overcome this challenging issue, two approaches were implemented; 1) the Wastewater Quality Index (WWQI) was introduced to summarize large amounts of monitored parameters into one simple term, and 2) multivariate statistical analyses and

exploratory data analyses were applied to provide a comprehensive methodology to temporally assess wastewater characteristics.

3.3. Results and Discussion

3.3.1. Wastewater Quality Index (WWQI)

The Wastewater Quality Index (WWQI) is an efficient mechanism to express the overall condition of wastewater by cumulative consideration of all monitored quality indices. In other words, WWQI is a unit-less number that cumulatively describes the quality of an aggregated set of measured chemical, physical, and microbiological parameters (Bordalo et al. 2006). The WWQI tries to easily enable interpretation of monitoring data by ranking the wastewater quality on a rating scale from zero to 100 based on the measured parameters and established water quality standards (Bharti and Katyal 2011). The higher values tend to indicate that wastewater effluents are meeting design objectives and the plant is operating efficiently. As such, influent streams to wastewater treatment plants generally have low WWQI values as they would be harmful to surrounding waterbodies if released untreated. After treatment, the wastewater streams should have relatively high WWQI values indicating they can be released to surrounding water bodies. Using the WWQI as an indicator variable is beneficial for decision makers as it enables them to rapidly identify the quality of different wastewater streams and also compare different treatment processes (Asadi et al. 2007).

Considering the aforementioned objective, the WWQI was developed for the influent and effluent of Floyds Fork WQTC using analytics developed by the Canadian Council of Ministers of Environment, CCME method (CCME 2001; Lumb et al. 2006). The CCME

WWQI was calculated based on the combination of three factors, that consider the number, frequency, and amount of variables whose objectives are not met based on the quality limitations, (Equations 1-6) (De Rosemond et al. 2009; Hurley et al. 2012). The water quality was then ranked in different categories as described in Table 3-2 (Khan et al. 2004).

$$F1 = \frac{\text{number of failed parameters}}{\text{total number of parameters}} \times 100 \quad (1)$$

$$F2 = \frac{\text{number of failed tests}}{\text{total number of tests}} \times 100 \quad (2)$$

$$\text{Excursion}_i = \frac{\text{failed test value}_i}{\text{limitation}_i} - 1 \quad (3)$$

$$\text{nes} = \frac{\sum_{i=1}^n \text{excursion}_i}{\text{number of tests}} \quad (4)$$

$$F3 = \frac{\text{nes}}{0.01 \text{ nes} + 0.01} \quad (5)$$

$$\text{WWQI} = 100 - \frac{\sqrt{F1^2 + F2^2 + F3^2}}{1.732} \quad (6)$$

where:

F1 = percentage of measured parameters that do not meet their limit at least once during the time period

F2 = percentage of individual tests that do not meet limitation

F3 = amount by which failed test values do not meet their limitation

Excursion = number of times by which an individual test is greater than the limitation

nes = collective amount by which individual tests are out of compliance

F3 = amount by which failed test values did not meet their objectives

Table 3-2. Wastewater Quality Category based on CCME WWQI

Quality Range	WWQI	Water Category
Excellent	95 – 100	Very close to natural or pristine levels
Good	80 – 94	Rarely depart from natural or desirable levels
Fair	65 – 79	Sometimes depart from natural or desirable levels
Marginal	45 – 64	Often depart from natural or desirable levels
Poor	0 – 44	Quality is almost always threatened or impaired

For the Floyds Fork analysis, the WWQI was based on the DO, BOD, TSS, N, P, and pH concentrations of the incoming and outgoing wastewater. These parameters are the main organic/inorganic contaminant indicators characterizing the overall quality of wastewater (Tchobanoglous and Burton 1991). The WWQI variation for the influent and effluent wastewater during the study period did not show significant fluctuations, see Figure 3-2. As expected, the influent index quality value was between 45 and 60 indicating the water quality was frequently threatened or impaired and would be threatening or potentially damaging to a receiving water. After treatment, the effluent WWQI was consistently between 96 and 100 indicating that the stream could be released to receiving waters with little threat of impairment. The analysis showed that the treatment process average resulted in a 51 percent improvement of the wastewater quality.

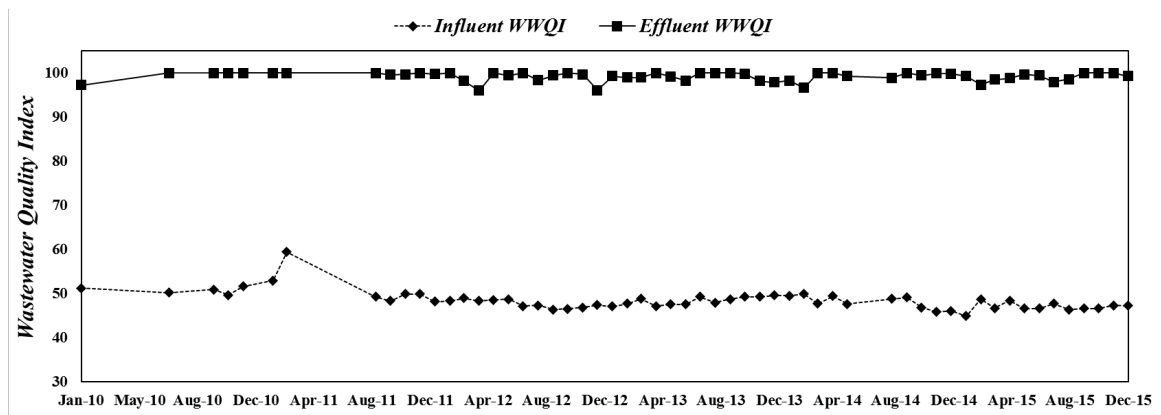


Figure 3-2. Influent and Effluent WWQI Variation

3.3.2. Multivariate Statistical Analysis Approach

Statistical analytics is a powerful mathematical tool that can identify trends and correlations within complex data sets. For the Floyds Fork WQTC, the statistical analysis procedure was used to extract and organize information from the water quality monitoring program. The technique incorporated 1) correlation analyses to determine the extent specific parameters were statistically correlated; 2) principal component analyses (PCA) to analyze interrelationships among the variables and to quantify the significance of different variables in the dataset; and 3) multivariate regression analyses to develop models that can predict important quality parameters based on input conditions.

3.3.2.1 Correlation Analysis

The Pearson product moment correlation analysis quantifies the linear relationship between two variables (Mackiewicz and Ratajczak 1993). The established correlation coefficient, ranging from negative one to positive one, is the magnitude of the interrelationship in the same direction (positive values) or in the opposite direction

(negative values) (Khambete and Christian 2014). A strong positive or negative relationship is identified when the coefficient is closer to the absolute value of one. Coefficients closer to zero indicate a weak or nonexistent relationship between the two variables.

The Pearson product moment correlation analysis was applied to each pair of influent and effluent variables within the Floyds Fork WQTC parameter dataset to identify potential bivariate associations, see Table 3-3. Based on this analysis, the influent WWQI was observed to be negatively correlated with influent phosphorus, BOD, TSS, and nitrogen concentrations. The effluent quality variables, phosphorus, BOD, TSS, and nitrogen were found to be highly correlated with the calculated values for effluent WWQI. Thus, it can be determined that out of six measured quality parameters for influent and effluent wastewater, four parameters were responsible for the variation of influent and effluent indexes. Additionally, influent phosphorus concentration was positively correlated with influent BOD, TSS, and nitrogen. Similarly, the influent BOD concentration was positively correlated with influent phosphorus, TSS, and nitrogen. Also, effluent phosphorus and BOD were positively correlated with the returned activated sludge (RAS) rate, influent BOD, TSS, and DO concentrations. It was concluded that the effluent WWQI is negatively correlated with effluent P, BOD, TSS, and N concentrations with high degree of significance.

Table 3-3. Wastewater Quality Category based on CCME WWQI

	Flow Rate	P _i	BOD _i	TSS _i	N _i	pH _i	DO _i	P _e	BOD _e	TSS _e	N _e	pH _e	DO _e	MLVSS	RAS	WWQI _i	WWQI _e
Flow Rate	1.0																
P _i	-.3*	1.0															
BOD _i	-2	.7**	1.0														
TSS _i	-2	.8**	.8**	1.0													
N _i	-.6**	.6**	.6**	.3*	1.0												
pH _i	.0	.3	-2	-3	-1	1.0											
DO _i	.2	-1	.1	.1	-2	-3	1.0										
P _e	.3	.1	.4*	.5*	-2	-2	.4**	1.0									
BOD _e	.0	.2	.6**	.3*	.2	.1	.3**	.1	1.0								
TSS _e	.0	-2	-2	-.3*	-1	.1	-2	.0	-2	1.0							
N _e	.1	.1	.0	.2	-3	-2	.1	.2	-1	-1	1.0						
pH _e	.0	-2	-1	-3	-1	.8**	-3	-2	.1	.0	-1	1.0					
DO _e	.3	-2	-3	-2	-.5**	.2	.1	.2	-2	.1	.3	.2	1.0				
MLVSS	.0	.1	.1	.0	-1	.2	.2	.1	.1	-1	.3	.1	.2	1.0			
RAS	.5**	-3	-.3*	-2	-.5**	.2	.3*	.5*	.5*	.0	.2	.1	.7**	.5**	1.0		
WWQI _i	.3**	-.8**	-.8**	-.8**	-.5**	-3	.0	-2	-2	.2	-1	.2	.2	-1	.3**	1.0	
WWQI _e	-2	.0	.0	-1	.2	.1	-2	-.7**	-.3**	-.3**	-.4**	.1	-2	-2	-2	.1	1.0

** Correlation is significant at 0.01 level

* Correlation is significant at 0.05 level

3.3.2.2 Principal Component Analysis

Although the correlation analysis is a useful method to categorize the correlations between two variables, application results of such an analysis is limited for simultaneously evaluating the correlations among several variables (Rastogi and Sinha 2011). Rather, principal component analysis (PCA) can be applied to investigate the interrelationships between a large group of variables (Lebart et al. 1979). PCA is a valuable technique to convert a large number of original correlated variables into a finite set of uncorrelated variables. Through this dimension reduction process, the derived components represent the information of the whole dataset with minimal loss of original information (Alberto et al. 2001). Each of the obtained components capture as much of the variation which has not been explained by the former component as possible. This approach has been successfully applied to water and wastewater data in a variety of study areas (Lee et al. 2006; Lee and Vanrolleghem 2004).

The PCA method is usually performed in five steps; 1) Preparing the data matrix with original variables X_i , 2) Transforming matrix X_i into a standardized matrix Y_i by using Eq. 7, 3) Calculating the covariance matrix R using Eq. 8 and 9, 4) Identifying the principal components which account for a large portion of the variation in the data set, and 5) Calculating the score (Z_i) of the principle components and the comprehensive score (Z) of each group of data set using Eq. 10 and 11 (Ouyang 2005).

$$Y_i = \frac{X_i - E(X_i)}{\sqrt{D(X_i)}} \quad (7)$$

$$|R - \lambda_i E| = 0 \quad (8)$$

$$L_i = \frac{B_i}{\sqrt{\lambda_i}} \quad (9)$$

$$Z_i = L_i \times Y_i \quad (10)$$

$$Z = \sum_{i=1}^m d_i \times Z_i \quad (11)$$

where,

$E(X_i)$ = average value of the original data

$D(X_i)$ = variance of X_i

E = unit matrix

B_i = component loading matrix value

d_i = variance contribution

λ_i = eigenvalues

L_i = corresponding eigenvector

Using the statistical software, SPSS (Statistical Package for Social Science, version 13.0), PCA was carried out for all fifteen parameters, which included 612 replications. To account for the differing parameter scales, all variables were normalized to mean zero and unit variance. As a result, five principal factors were extracted based on Kaiser's rule of eigenvalues greater than one (Chong and Jun 2005). Each derived component explained a specific variance percentage of all studied variables, which is referred to component loading. Components with higher loadings can better describe the

characteristic of the total dataset (Bayo and López-Castellanos 2016). To maximize the variation of loadings on each component, orthogonal factor rotation was generated using the Varimax method (Reimann et al. 2002). Finally, the component's score was estimated based on the correlated values of the significant factor loadings. Based upon these procedures, the derived components described approximately 75.25% of the total variability of the data set and represented the overall variation in wastewater quality during the period of study, see Table 3-4. As a result, the dimension of the data set was decreased from 15 variables to five factors with only a minimal 24.75 percent loss of information.

Table 3-4. Rotated Component Matrix with Factor Loadings (>0.4) a

Attribute	Principal Component				
	PC1	PC2	PC3	PC4	PC5
Flow Rate		0.54			
P _i	0.90				
BOD _i	0.89				
TSS _i	0.84				
N _i	0.68				
pH _i			0.91		
DO _i	-0.63				
P _e					0.61
BOD _e				0.69	
TSS _e					0.88
N _e					0.61
pH _e			0.88		
DO _e				-0.84	
MLVSS		0.66			
RAS		0.78			
Eigenvalue	4.12	2.86	1.86	1.43	1.02
Initial Variance (Loading)	27.45	19.08	12.40	9.51	6.80
Cumulative Variance	27.45	46.53	58.93	68.44	75.25

a. Rotation converged in 13 iterations

The highest loading was attributed to PC1 which accounted for 27.45% of total dataset variance. This factor represented influent quality parameters loading and can provide a dominant pattern of the data set for better understanding the characteristics of the influent wastewater. The second component, accounting for 19.08% of initial data variance, contained significant loadings for the quantitative characteristics of wastewater including inflow and recycled rates. The third component could be labeled as the ion activity component because it highly represented the influent and effluent pH values. The fourth component (PC4) was mainly considered for the oxygen demand characteristics of the treated wastewater. The last component (PC5) accounted for the effluent nutrient loadings including phosphorus, nitrogen and TSS. Thus, this factor can be respected as a measure of the treatment plant's performance level.

The component score (Z) of the governing principle components were calculated and analyzed for the entire study period to better understand the wastewater characteristics, see Figure 3-3. High fluctuated trend was observed for PC1, PC2, and PC5, corresponding to seasonal influent and effluent wastewater quality and quantity variation. The PC1 was initially related to the organic loading of the influent wastewater, while PC2 was mainly correlated to the quantity characteristics of wastewater. Positive scores for PC2 were mostly observed for samples collected during the late-autumn to mid-spring, indicating higher inflow rate receiving by the treatment plant during those periods. Also, lower flow rates entered to the treatment plant from late-spring to mid-autumn due to the negative observed scores of this component. Positive scores for PC1, which indicated more polluted influent wastewater, were mainly observed for the samples which have negative scores on PC2. It can be explained that by decreasing the scores for

PC2 the observed scores of PC1 increased, representing more polluted incoming wastewater during seasons with lower flow rates. Also, the overall PC1 negative and positive scores respectively observed during 2010 to 2013 and 2013 to 2015 indicated the overall increase of the influent pollutant level from the year of 2013.

For PC5, which corresponds to the nutrient removal performance of the treatment plant, fluctuations were considerably high, and the effluent wastewater nutrient loading was significantly changed over the study period. This can be attributed to the ununiformed removal performance of the treatment plant. Positive PC5 scores, indicating higher effluent nutrient loadings, were mainly observed for 2013 to 2015 when most of the samples exhibited positive scores for PC1. Considering the opposite trend during the period of 2010 to 2013, it can be interpreted that increasing the influent pollutant levels significantly affected the nutrient removal performance of the treatment system. More positive scores for PC5 were observed during winter and spring seasons indicating lower achieved nutrient removal rates during those months. For PC4 which accounts for the effluent oxygen demand properties, uniform score changing was observed. High oxygen content and less oxygen demand for the effluent wastewater can be concluded due to positive observed scores for this component during the study period.

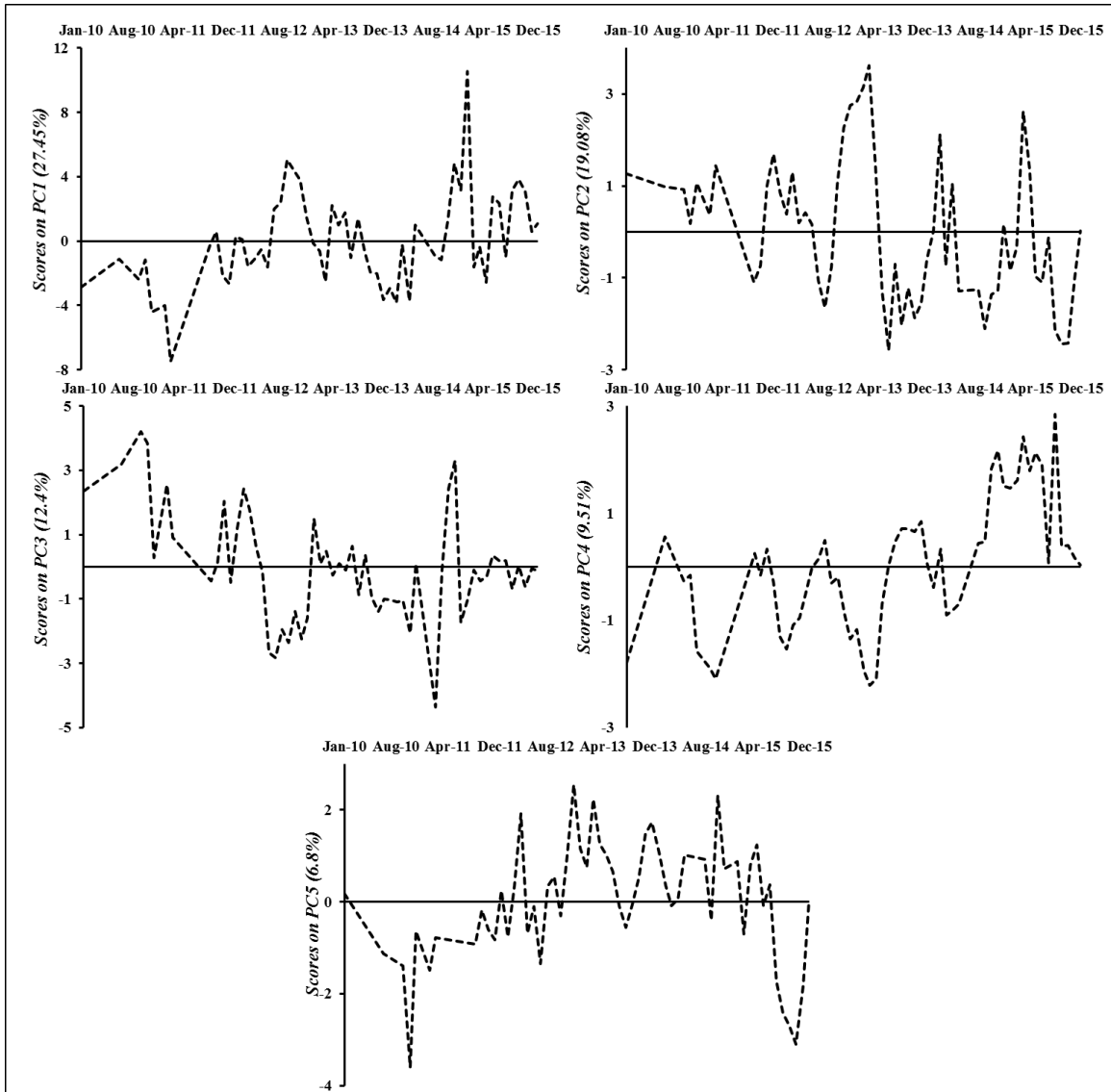


Figure 3-3. Temporal Variation of the Principal Components Scores

3.3.2.3 Statistical Modelling Approach

The purpose of developing forecasting models for the significant quality parameters is to provide comprehensive dataset for performing future studies on simulation and scenario analyses through desktop modeling by using simulator software packages. Although there are several theoretical models for predicting the wastewater quality parameters, those are

considerably complicated. For applying the theoretical modeling, there is a need for incorporating many bio-kinetic, hydrodynamic, diffusion, and detachment coefficients which are intrinsically dynamic and hard to accurately estimate (Goode et al. 2007). As an alternative, multivariate statistical techniques can be performed to develop predictive models for quality parameters based on the measured historical process data base. Considering the measured quality and quantity parameters during 2010 to 2015 as the training data, this section attempts to develop six descriptive numerical models to forecast influent and effluent phosphorus, BOD, and WWQI parameters. The developed models were then subjected to validation processes based on the results from the monitoring program conducted in the first ten months of 2016.

The modeling approach was carried out by combining three statistical methods including correlation, multivariate regression, and ANOVA analyses. Firstly, the predictor variables for each model were identified based on the results from the established correlation analysis section (Table 3). Among all variables which were determined to be correlated with the target parameter, the variables with correlation significance level of 0.05 were considered as the predictor variables. Following the correlation analysis, the predictive models were developed for each target parameter using the stepwise multivariate regression analysis including multiple complex-terms of variables. Several combination sets of predictor variables in conjunction with their interactions were considered for model generation. By defining the threshold p-value of 0.05 and performing the backward method, all possible predictor variables were firstly considered for developing the model. Subsequently, the least statistically significant predictors with the largest p-value were iteratively removed in a stepwise manner until all the remaining

variables in the model contained a significant predefined p-value. To confirm and detect the optimum model from various developed models for each target parameter, the final step attempted to conduct the ANOVA test to admit/reject the null hypothesis of the p-values $< \alpha = 0.05$.

3.3.2.3.1. Predictive Model for Influent Parameters

The numerical expression of influent Phosphorus, BOD, and WWQI was described once the correlations between the parameters were established. It was obtained that the influent phosphorus was significantly correlated with the BOD, TSS, and Nitrogen concentrations of the raw wastewater. Thus, these three variables were considered as the predictors for the influent phosphorus concentration. Also, it was perceived that the influent TSS, nitrogen and phosphorus were strongly correlated with the influent BOD concentration. As a result, those parameters were considered as predictor variables to develop model for influent BOD. Finally, to develop predictive models for the influent WWQI, phosphorus, BOD, nitrogen, and TSS were considered as the predictors due to their significant derived correlation coefficients. Once the predictor variables were established, the stepwise multivariate regression analysis, based on the backward elimination method, was performed to develop numerical forecasting equations for each target parameter. Considering numerous interactions between the established predictor variables, more than a hundred regression equations were constructed for each target parameter. Finally, the models which exhibited the most possible variance accounted for the total dataset were selected, and listed in the following Tables, as the nominees for the optimum model detection.

Considering seven developed models for estimating the influent phosphorus, it was found that the Model 7 was able to account for approximately 86% of the variability using only three predictors, see Table 3-5. The results from conducting the ANOVA test indicated that the achieved model was significant as the derived p-value is far less than 0.05. Also, the high calculated F value of 114.6, which is considerably greater than that from the other models, indicated that the selected model is effectively fitted with the original data set.

Table 3-5. Model Summary for the Influent Phosphorus

Model	R	R ²	Adjusted R ²	Std. Error of Estimate	Sum of Squares	df	Mean Square	F	p-value
1 ^a	.937	.878	.855	.55	101.6	9	11.3	37.6	.000
2 ^b	.937	.878	.858	.54	101.6	8	12.7	43.2	.000
3 ^c	.937	.878	.861	.54	101.6	7	14.5	50.4	.000
4 ^d	.937	.877	.862	.53	101.5	6	16.9	59.5	.000
5 ^e	.936	.875	.863	.53	101.3	5	20.3	71.5	.000
6 ^f	.932	.869	.859	.54	100.6	4	25.1	86.3	.000
7 ^g	.931	.866	.859	.54	100.3	3	33.4	114.6	.000

Predictors: BOD_iTSS_i, N_i, TSS_i, BOD_i, BOD_iN_i, N_iTSS_i, TSS_i², N_i², BOD_i²
Predictors: BOD_iTSS_i, TSS_i, BOD_i, BOD_iN_i, N_iTSS_i, TSS_i², N_i², BOD_i²
Predictors: BOD_iTSS_i, TSS_i, BOD_i, N_iTSS_i, TSS_i², N_i², BOD_i²
Predictors: BOD_iTSS_i, BOD_i, N_iTSS_i, TSS_i², N_i², BOD_i²
Predictors: BOD_iTSS_i, BOD_i, N_iTSS_i, TSS_i², BOD_i²
Predictors: BOD_iTSS_i, N_iTSS_i, TSS_i², BOD_i²
Predictors: BOD_iTSS_i, N_iTSS_i, TSS_i²
Dependent Variable: Phosphorus

Four models were nominated for estimating the influent BOD, see Table 3-6. Containing the least number of predictors, and with an accuracy of 81%, model 4 was considered as the best model based on the results of the ANOVA test. Compared to the other models, the designated model was found to be significant considering the derived p-value is less

than 0.05 and also to be more accurately fitted with the original dataset because of its larger F value of 41.1.

Table 3-6. Model Summary for the Influent BOD

Model	R	R ²	Adjusted R ²	Std. Error of Estimate	Sum of Squares	df	Mean Square	F	p-value
1 ^a	.916	.840	.809	31.44	243315.7	9	27035.1	27.3	.000
2 ^b	.916	.839	.813	31.13	243264.5	8	30408.1	31.4	.000
3 ^c	.913	.833	.809	31.45	241309.2	7	34472.7	34.8	.000
4 ^d	.912	.831	.811	31.26	240916.8	6	40152.8	41.1	.000

Predictors: P_iN_i, TSS_i, N_i, P_i, TSS_i², N_iTSS_i, P_i², N_i², P_iTSS_i
Predictors: P_iN_i, N_i, P_i, TSS_i², N_iTSS_i, P_i², N_i², P_iTSS_i
Predictors: N_i, P_i, TSS_i², N_iTSS_i, P_i², N_i², P_iTSS_i
Predictors: N_i, P_i, TSS_i², N_iTSS_i, N_i², P_iTSS_i
Dependent Variable: BOD

To identify the optimum numerical expression for the influent WWQI, six different models were investigated, see Table 3-7. Model 6, containing eight predictor variables, provided an incredible 97% fit to the dataset. Performing the ANOVA test, it was obtained that this model was highly significant via comparison of the p-value to our threshold (0.05) and also contained the highest F value of 231.4.

Table 3-7. Model Summary for the Influent WWQI

Model	R	R ²	Adjusted R ²	Std. Error of Estimate	Sum of Squares	df	Mean Square	F	p-value
1 ^a	.988	.977	.970	.37	250.6	13	19.3	139.0	.000
2 ^b	.988	.977	.970	.37	250.6	12	20.9	154.1	.000
3 ^c	.988	.977	.971	.36	250.6	11	22.8	171.6	.000
4 ^d	.988	.977	.971	.36	250.5	10	25.1	191.4	.000
5 ^e	.988	.976	.971	.36	250.3	9	27.8	211.5	.000
6 ^f	.987	.975	.971	.37	250.0	8	31.2	231.4	.000

Predictors: P_iBOD_i, N_i, TSS_i, P_i², TSS_i², BOD_i, N_iTSS_i, N_i², P_i, BOD_i², BOD_iN_i, BOD_iTSS_i, P_iTSS_i
Predictors: P_iBOD_i, N_i, TSS_i, P_i², TSS_i², N_iTSS_i, N_i², P_i, BOD_i², BOD_iN_i, BOD_iTSS_i, P_iTSS_i
Predictors: P_iBOD_i, N_i, TSS_i, P_i², TSS_i², N_iTSS_i, N_i², P_i, BOD_i², BOD_iN_i, BOD_iTSS_i
Predictors: P_iBOD_i, N_i, TSS_i, P_i², TSS_i², N_iTSS_i, N_i², P_i, BOD_i², BOD_iN_i

Predictors: $P_iBOD_i, N_i, TSS_i, TSS_i^2, N_iTSS_i, N_i^2, P_i, BOD_i^2, BOD_iN_i$
Predictors: $P_iBOD_i, N_i, TSS_i, TSS_i^2, N_iTSS_i, N_i^2, BOD_i^2, BOD_iN_i$
Dependent Variable: $WWQI_i$

3.3.2.3.2. Predictive Model for Effluent Parameters

Considering the same strategy applied for developing the predictive models for influent target parameters, this section attempts to determine optimum numerical expressions for forecasting the effluent phosphorus, BOD, and WWQI contents. To recognize the predictors participating in model development, those variables which were previously identified as to be correlated with the target parameter with the significance of greater than 95% were selected. To prepare the list of nominee models for the prime model detection, the multiple complex stepwise regression was performed based on the backward elimination method. More than one hundred models were constructed for each list of the nominated models and those which exhibited the highest possible variance with the training dataset were presented in the following tables. Finally, to select the preferred model for each target parameter, the ANOVA test were performed.

The effluent phosphorus was significantly correlated with the influent TSS, BOD, and DO concentrations as well as RAS. Thus, the mentioned variables in conjunction with their interactions were considered for model developments. Out of over hundred developed models, eight models with the accuracy level ranging from 63% to 69% were considered, see Table 3-8. The results of applying the ANOVA test indicated that model 7 exhibited the highest adjusted accuracy level of 69% with the training dataset and provided nearly the best fit to the original data set compared to the other models. Although model 7 contained one more predictor compared to model 8, the selected model

The correlation analysis indicated that effluent BOD was significantly correlated with influent BOD, TSS, and DO content as well as the RAS. Thus, these variables in conjunction with their interactions were considered for numerical expression development. The best predictive model which was achieved from conducting the backward multivariate regression analysis had the accuracy of 77%, see Table 3-9. The selected model has an F value of 15.4 and p-value of less than alpha based on the results of ANOVA test.

Table 3-9. Model Summary for the Effluent BOD

Model	R	R ²	Adjusted R ²	Std. Error of Estimate	Sum of Squares	df	Mean Square	F	p-value
1 ^a	.906	.820	.728	.26	11.3	19	.59	8.9	.000
2 ^b	.906	.820	.735	.25	11.3	18	.63	9.6	.000
3 ^c	.906	.820	.742	.25	11.3	17	.66	10.5	.000
4 ^d	.912	.831	.745	.25	11.4	19	.60	9.6	.000
5 ^e	.912	.831	.751	.25	11.4	18	.63	10.4	.000
6 ^f	.912	.831	.757	.24	11.4	17	.67	11.3	.000
7 ^g	.911	.830	.761	.24	11.4	16	.71	12.2	.000
8 ^h	.910	.829	.766	.24	11.4	15	.76	13.2	.000
9 ⁱ	.909	.827	.769	.24	11.4	14	.81	14.3	.000
10 ^j	.907	.824	.770	.24	11.3	13	.87	15.4	.000

Predictors: DO_i , TSS_i , $BOD_i^3 \times TSS_i^3$, $BOD_i^2 \times DO_i^5$, $RAS \times TSS_i^3$, DO_i^6 , $BOD_i^2 \times RAS$, $BOD_i \times TSS_i$, $DO_i^2 \times TSS_i$, BOD_i^3 , $BOD_i \times DO_i$, $BOD_i^3 \times RAS^2$, DO_i^3 , $TSS_i^2 \times RAS$, $BOD_i^3 \times DO_i^2$, $BOD_i^3 \times DO_i^5$, $BOD_i^4 \times RAS^2$, BOD_i^2 , $BOD_i^2 \times TSS_i^2$

Predictors: DO_i , TSS_i , $BOD_i^3 \times TSS_i^3$, $BOD_i^2 \times DO_i^5$, $RAS \times TSS_i^3$, DO_i^6 , $BOD_i^2 \times RAS$, $BOD_i \times TSS_i$, $DO_i^2 \times TSS_i$, BOD_i^3 , $BOD_i^3 \times RAS^2$, DO_i^3 , $TSS_i^2 \times RAS$, $BOD_i^3 \times DO_i^2$, $BOD_i^3 \times DO_i^5$, $BOD_i^4 \times RAS^2$, BOD_i^2 , $BOD_i^2 \times TSS_i^2$

Predictors: DO_i , TSS_i , $BOD_i^3 \times TSS_i^3$, $BOD_i^2 \times DO_i^5$, DO_i^6 , $BOD_i^2 \times RAS$, $BOD_i \times TSS_i$, $DO_i^2 \times TSS_i$, BOD_i^3 , $BOD_i^3 \times RAS^2$, DO_i^3 , $TSS_i^2 \times RAS$, $BOD_i^3 \times DO_i^2$, $BOD_i^3 \times DO_i^5$, $BOD_i^4 \times RAS^2$, BOD_i^2 , $BOD_i^2 \times TSS_i^2$

Predictors: $BOD_i^4 \times RAS^2$, DO_i , $TSS_i^2 \times RAS$, TSS_i , DO_i^6 , $BOD_i^2 \times DO_i^5$, BOD_i^2 , $BOD_i^3 \times TSS_i^3$, $DO_i^2 \times TSS_i$, $BOD_i^2 \times RAS$, $RAS \times TSS_i^3$, $BOD_i \times DO_i$, DO_i^3 , $BOD_i^3 \times RAS^2$, $BOD_i^2 \times DO_i^2$, $BOD_i \times TSS_i$, $BOD_i^3 \times DO_i^4$, $DO_i^3 \times BOD_i$, $BOD_i^2 \times TSS_i^2$

Predictors: $BOD_i^4 \times RAS^2$, DO_i , $TSS_i^2 \times RAS$, TSS_i , DO_i^6 , $BOD_i^2 \times DO_i^5$, BOD_i^2 , $BOD_i^3 \times TSS_i^3$, $DO_i^2 \times TSS_i$, $BOD_i^2 \times RAS$, $RAS \times TSS_i^3$, $BOD_i \times DO_i$, DO_i^3 , $BOD_i^2 \times DO_i^2$, $BOD_i \times TSS_i$, $BOD_i^3 \times DO_i^4$, $DO_i^3 \times BOD_i$, $BOD_i^2 \times TSS_i^2$

Predictors: $BOD_i^4 \times RAS^2$, DO_i , $TSS_i^2 \times RAS$, TSS_i , DO_i^6 , $BOD_i^2 \times DO_i^5$, BOD_i^2 , $BOD_i^3 \times TSS_i^3$, $DO_i^2 \times TSS_i$, $BOD_i^2 \times RAS$, DO_i^3 , $BOD_i^2 \times DO_i^2$, $BOD_i \times TSS_i$, $BOD_i^3 \times DO_i^4$, $DO_i^3 \times BOD_i$, $BOD_i^2 \times TSS_i^2$

Predictors: $BOD_i^4 \times RAS^2$, $TSS_i^2 \times RAS$, TSS_i , DO_i^6 , $BOD_i^2 \times DO_i^5$, BOD_i^2 , $BOD_i^3 \times TSS_i^3$, $DO_i^2 \times TSS_i$, DO_i^3 , $BOD_i^2 \times DO_i^2$, $BOD_i \times TSS_i$, $BOD_i^3 \times DO_i^4$, $DO_i^3 \times BOD_i$, $BOD_i^2 \times TSS_i^2$

Predictors: $BOD_i^4 \times RAS^2$, $TSS_i^2 \times RAS$, TSS_i , DO_i^6 , $BOD_i^2 \times DO_i^5$, BOD_i^2 , $BOD_i^3 \times TSS_i^3$, $DO_i^2 \times TSS_i$, DO_i^3 , $BOD_i^2 \times DO_i^2$, $BOD_i \times TSS_i$, $BOD_i^3 \times DO_i^4$, $BOD_i^2 \times TSS_i^2$

Predictors: $BOD_i^4 \times RAS^2$, $TSS_i^2 \times RAS$, TSS_i , DO_i^6 , $BOD_i^2 \times DO_i^5$, BOD_i^2 , $BOD_i^3 \times TSS_i^3$, $DO_i^2 \times TSS_i$, DO_i^3 , $BOD_i^2 \times DO_i^2$, $BOD_i \times TSS_i$, $BOD_i^3 \times DO_i^4$, $BOD_i^2 \times TSS_i^2$

Dependent Variable: BOD_e

The effluent phosphorus, nitrogen, and TSS were found to be significantly correlated with effluent WWQI. Conducting the backward regression analysis, considering different combinations of the predictors and their interactions, ten models were nominated for expressing the target parameter, see Table 3-10. Model 10, containing the least number of predictors, provided 69% accuracy. Performing the ANOVA test, it was attained that the model was significant regarding the p-value, using the selected threshold of 0.05, and also contained the highest F value of 25.6.

Table 3-10. Model Summary for the Effluent WWQI

Model	R	R ²	Adjusted R ²	Std. Error of Estimate	Sum of Squares	df	Mean Square	F	p-value
1 ^a	.869	.755	.674	.59	44.9	14	3.2	9.3	.000
2 ^b	.868	.753	.679	.58	44.8	13	3.4	10.1	.000
3 ^c	.867	.751	.683	.58	44.7	12	3.7	11.1	.000
4 ^d	.863	.745	.682	.58	44.3	11	4.0	11.9	.000
5 ^e	.860	.739	.682	.58	43.9	10	4.4	13.0	.000
6 ^f	.857	.734	.683	.58	43.7	9	4.8	14.4	.000
7 ^g	.856	.733	.688	.57	43.6	8	5.4	16.4	.000
8 ^h	.853	.727	.688	.57	43.2	7	6.2	18.6	.000
9 ⁱ	.849	.721	.687	.58	42.9	6	7.1	21.5	.000
10 ^j	.845	.715	.687	.58	42.5	5	8.5	25.6	.000

Predictors: TSS_e²×N_e, P_e³, TSS_e³, N_e²×P_e, P_e, TSS_e²×P_e, N_e, P_e²×N_e, TSS_e², N_e²×TSS_e, P_e×N_e, P_e², N_e×TSS_e, P_e×TSS_e

Predictors: TSS_e²×N_e, P_e³, TSS_e³, P_e, TSS_e²×P_e, N_e, P_e²×N_e, TSS_e², N_e²×TSS_e, P_e×N_e, P_e², N_e×TSS_e, P_e×TSS_e

Predictors: TSS_e²×N_e, TSS_e³, P_e, TSS_e²×P_e, N_e, P_e²×N_e, TSS_e², N_e²×TSS_e, P_e×N_e, P_e², N_e×TSS_e, P_e×TSS_e

Predictors: TSS_e³, P_e, TSS_e²×P_e, N_e, P_e²×N_e, TSS_e², N_e²×TSS_e, P_e×N_e, P_e², N_e×TSS_e, P_e×TSS_e

Predictors: TSS_e³, P_e, TSS_e²×P_e, N_e, TSS_e², N_e²×TSS_e, P_e×N_e, P_e², N_e×TSS_e, P_e×TSS_e

Predictors: P_e, TSS_e²×P_e, N_e, TSS_e², N_e²×TSS_e, P_e×N_e, P_e², N_e×TSS_e, P_e×TSS_e

Predictors: P_e, N_e, TSS_e², N_e²×TSS_e, P_e×N_e, P_e², N_e×TSS_e, P_e×TSS_e

Predictors: P_e, N_e, N_e²×TSS_e, P_e×N_e, P_e², N_e×TSS_e, P_e×TSS_e

Predictors: P_e, N_e, N_e²×TSS_e, P_e², N_e×TSS_e, P_e×TSS_e

Predictors: P_e, N_e, P_e², N_e×TSS_e, P_e×TSS_e

Dependent Variable: WWQI_e

3.3.2.3.3. Model Quality Appraising and Verification

All six derived numerical expressions for the selected influent and effluent quality parameters in previous sections were studied for quality identification see Table 3-11. The approach was performed in two separate steps. The first step, was evaluating the accuracy level of the developed models in term of fitting with the training data for 2010 and 2015 monitoring program years. The next step was to validate the predictive capability of each selected model based on the results from the data monitoring program for 2016. The approach consisted of comparing the predicted values versus the measured values both for training and testing datasets see Figures 3-4 and 3-5. The coefficient of determination (R^2), the root mean squared error (RMSE), and the percentage relative prediction errors of concentrations (%Rel. error) were used for numerically assessing the quality of each model, Eq. 12 and 13. These statistics represented the degree to which the models fit the measured concentrations of training data and how accurately they were able to estimate the testing data.

$$RMSE = \sqrt{\frac{\sum_{i=1}^n Squared\ Residual_i}{n}} \quad (12)$$

$$Relative\ Error\% = \sqrt{\sum_{i=1}^n \frac{Squared\ Residual_i}{y_i^2}} \times 100 \quad (13)$$

where

$$Squared\ Residual = (\bar{y}_i - y_i)^2$$

y_i = values of measured parameter

\bar{y}_i = values of predicted parameter

n = number of samples

Table 3-11. Statistical Predictive Models for the Wastewater Quality Parameters

Numerical Expression	R ² %		RMSE		% Rel. error	
	Train data	Train data	Test data	Train data	Test data	Test data
<p><i>Influent Phosphorus Model</i></p> $= 2.71 + 8.5 \times 10^{-6} TSS_i^2 + 3.9 \times 10^{-4} N_i \times TSS_i - 1.4 \times 10^{-5} BOD_i \times TSS_i$	87	0.52	1.79	0.89	2.88	
<p><i>Influent BOD Model</i></p> $= 126.95 + 45.93 P_i - 20.9 N_i + 0.42 N_i^2 + 0.001 TSS_i^2 - 0.16 P_i \times TSS_i + 0.03 N_i \times TSS_i$	83	29.26	85.36	1.53	3.21	
<p><i>Influent WWQI Model</i></p> $= 68.84 - 0.057 TSS_i - 0.814 N_i + 4.5 \times 10^{-5} BOD_i^2 + 3.5 \times 10^{-5} TSS_i^2 + 0.011 N_i^2 - 0.001 BOD_i \times N_i + 0.002 N_i \times TSS_i - 0.002 P_i \times BOD_i$	97	0.34	1.56	0.07	0.33	
<p><i>Effluent Phosphorus Model</i></p> $= 1.274 - 2.2 RAS + 2.3 \times 10^{-5} BOD_i^2 - 4.3 \times 10^{-5} BOD_i \times TSS_i - 0.134 DO_i^2 - 1.09 RAS^2 + 0.004 BOD_i \times DO_i + 0.002 TSS_i \times RAS + 8.2 \times 10^{-8} BOD_i^3 \times RAS^2 + 4.5 \times 10^{-11} TSS_i^4 + 0.006 DO_i^4 + 0.085 RAS^4 - 2.4 \times 10^{-6} BOD_i^2 \times DO_i^2 + 4.3 \times 10^{-6} TSS_i^2 \times RAS^2 - 3.6 \times 10^{-11} TSS_i^4 \times RAS + 3.5 \times 10^{-9} BOD_i^2 \times DO_i^5 - 9 \times 10^{-5} DO_i^6 - 0.004 BOD_i \times RAS^3$	71	0.32	0.27	9.01	8.34	

Effluent BOD Model

$$\begin{aligned}
 &= -0.174 + 0.023 TSS_i + 1.3 \\
 &\times 10^{-4} BOD_i^2 - 2 \times 10^{-4} BOD_i \\
 &\times TSS_i + 6.8 \times 10^{-10} BOD_i^2 \times TSS_i^2 \\
 &- 1.3 \times 10^{-15} BOD_i^3 \times TSS_i^3 \\
 &+ 0.015 DO_i^3 + 6.2 \times 10^{-6} TSS_i^2 \\
 &\times RAS + 2.1 \times 10^{-6} BOD_i^2 \times DO_i^2 \quad 82 \quad 0.21 \quad 0.86 \quad 0.88 \quad 2.84 \\
 &- 3.5 \times 10^{-4} DO_i^2 \times TSS_i + 1.7 \\
 &\times 10^{-8} BOD_i^2 \times DO_i^5 - 2.7 \\
 &\times 10^{-10} BOD_i^3 \times DO_i^4 - 5.6 \\
 &\times 10^{-5} DO_i^6 - 3.7 \times 10^{-10} BOD_i^4 \\
 &\times RAS^2
 \end{aligned}$$

Effluent WWQI Model

$$\begin{aligned}
 &= 99.7 + 9 P_e - 3.16 N_e - 13.25 P_e^2 \quad 71 \quad 0.55 \quad 0.46 \quad 0.06 \quad 0.05 \\
 &- 2.1 P_e \times TSS_e + 1.23 N_e \times TSS_e
 \end{aligned}$$

The results confirmed strong accuracy, ranging from 71% to 97%, of the developed models in term of fitting with the training dataset. Also, all models showed minimum relative prediction errors for the training and testing dataset. The highest relative error of 8.34% was observed for the effluent phosphorus model in term of fitting with the testing dataset. Considering the residual values of this model ranging from -0.67 to 0.34, the obtained relative error is significantly negligible compared to the similar modeling efforts reported in literature (Kolluri et al. 2015; Platikanov et al. 2014).

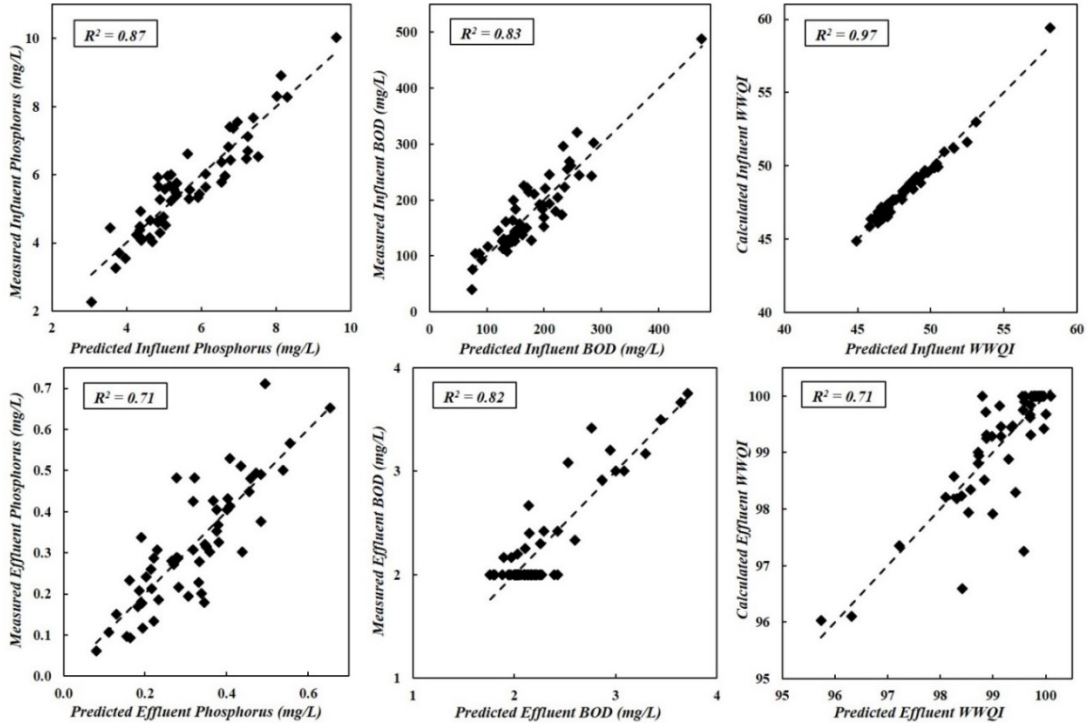


Figure 3-4. Verification of Predictive Models with Training Dataset (2010 – 2015)

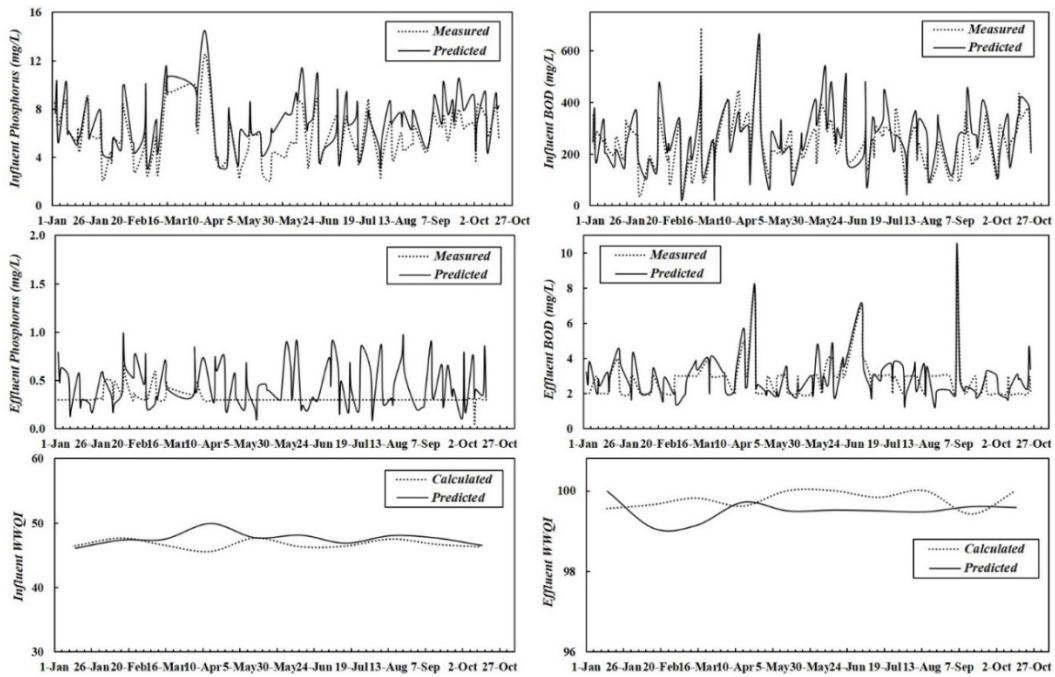


Figure 3-5. Validation of the Predictive Models with Testing Dataset (2016)

3.4. Conclusions

This study used statistical techniques to identify the inherent structure of the wastewater physicochemical characteristics from a treatment plant in Louisville, Kentucky. These multivariate data analysis efforts involved monitoring the performance of a full-scale wastewater treatment plant, assessing the temporal and spatial changes of water quality by introducing wastewater quality index (WWQI), discovering the important relationships among the monitored parameters through descriptive data analysis, and establishing the numerical expressions for predicting some significant quality parameters.

Developing the WWQI it was observed that almost all monitored effluent streams successfully met the established discharge standards, so that the calculated indices were in the range of 96.03 and 100. By the means of PCA, five components were extracted which accounted for 75.25% of the total dataset variance. The first two components, with cumulative loading of 46.53%, explained the raw wastewater quality and quantity circulation within the treatment plant. Also, considering six consecutive years' dataset, six predictive models were developed for the influent and effluent phosphorus, BOD, and WWQI. All the established models showed high levels of statistical significance in addition to admissible accuracy in terms of fitting with the training data parameters, with 81.8% average accuracy, and validating with the testing dataset, with average relative prediction error of 2.9%.

3.5. Recommendation

The methodology described in this paper can provide a scientific basis for a robust control system on the performance of any treatment plant and also provide a more accurate method of environmental management. The methods described in this paper can be used to effectively manage water quality monitoring programs while reducing the number of quality parameters which must be routinely measured and also controlling the quality of sampling efforts and measurements. The proposed procedure can be summarized in the following seven steps:

- Considering the regional discharge standards and the results of the wastewater monitoring program, calculate the WWQI for influent and effluent streams using Eqs. 1 through 6.
- Categorize the overall flow conditions over the time using Table 3-1 and then, evaluate the treatment process effectiveness by comparing the calculated influent and effluent indexes.
- Conduct the principal component analysis for all measured quality and quantity variables using Eqs. 7 through 10.
- Evaluate the overall variation of influent and effluent organic loading, ion activities, oxygen demanding, and nutrient loading characteristics considering the fluctuation of calculated components' scores using Eq. 11.

- Determine the interrelationship level between the measured data by conducting Pearson product correlation analysis. Identify the most highly correlated variables with initial indices like BOD, COD, phosphorus, nitrogen, WWQI, etc.
- Using a multivariate regression technique, develop predictive models for initial parameters considering the highly-correlated variables as the predictors.
- Verify the accuracy of produced models in terms of fitting with the training and testing data by using Eqs. 12 and 13.

CHAPTER FOUR. AN INTEGRATED APPROACH TO TREATMENT OF HIGH STRENGTH ORGANIC WASTEWATER BY USING ANAEROBIC ROTATING BIOLOGICAL CONTACTOR

4.1. Introduction

Each year, a large amount of high strength industrial wastewater is discharged into surface waters, which negatively affects ecosystems and human lives. Controlling these high strength wastewaters and mitigating their adverse environmental impacts have been challenging. Thus, developing innovative and cost-effective treatment systems is essential, especially considering the ever-increasing energy costs and strict pollutant removal regulations (Ebrahimi et al. 2016; Mirbagheri et al. 2014).

Depending on type of the industry, wastewater streams are divided into two major categories; inorganic and organic. The organic industrial wastewaters, which are the subject of this study, are produced by industries such as breweries, cheese production, textile factories, and tanneries. These industries use organic substances for chemical reactions. Organic streams contain high amounts of hydrocarbons, solvents, nutrients, toxins, and other organic compounds (Javadi et al. 2016), and are generally treated through either aerobic or anaerobic biological systems.

Aerobic systems are suitable for treatment of low strength organic wastewaters (COD concentrations less than 1000 mg/L) (Chan et al. 2009). Activated sludge processes are

the common approach for treating this type of effluents. However, sludge settleability is a prevalent problem, which limits the effectiveness of such processes (Zinatizadeh and Ghaytooli 2015). Thus, there is a need to overdesign the aeration and sedimentation units to overcome this issue, which can be cost prohibitive. The moving bed bio reactor (MBBR) process combines the superiorities of both the activated sludge system and biofilm reactor by embodying floating carriers, which provide large surface areas for microorganism's establishment (Zinatizadeh and Ghaytooli 2015). Some significant advantages of MBBR systems include: small reactor volume, high solid retention times for slow growing organisms, and ease of upgrading the existing facilities (Khan et al. 2011). Several studies have assessed using MBBR process for treating low organic wastewater. Martín-Pascual et al. (2012) observed COD reduction efficiencies of 60% under retention time of 15 hours, while Zinatizadeh and Ghaytooli (2015) reported up to 88% COD removal efficiency under retention time of 12 hours. Chu et al. (2011) used synthetic wastewater for a MBBR system and observed (total organic carbon) TOC removal performance ranging from 72% - 90% under retention times of 14 – 40 hours.

For higher organic content wastewaters, the anaerobic systems are usually recommended (Chan et al. 2009). The conventional anaerobic techniques include, fluidized bed reactor, up-flow anaerobic sludge blanket, biofilm reactor, and anaerobic membrane bioreactor (Kheradmand et al. 2010). The anaerobic rotating biological contactor (AnRBC), introduced by Tait and Friedman (1980), can achieve high removal efficiencies and methane production rates. By grouping suspended and attached growth mechanisms of microorganism, the AnRBC offers associated benefits of combining RBC process under anaerobic operational condition.

Previous studies have indicated that AnRBC process leads to satisfactory treatment of high organic content streams (Laquidara et al. 1986; Lu et al. 1995; Lv et al. 2011; Noyola et al. 1988; Patel and Madamwar 1997; Teixeira et al. 2010; Yeh et al. 1997). A comparative lab-scale study (Abubakkar et al. 2015) was performed on a conventional anaerobic digester and a single stage AnRBC. Lower hydrogen partial pressure, greater diversity of hydrogenotrophic methanogens, and less effluent COD concentrations were concluded for the AnRBC system compared to the conventional digester. Various operational parameters such as rotational speed and organic and hydraulic loading rates can affect the overall performance of AnRBC systems (Cortez et al. 2008). Yang et al. (2007) investigated the effect of disks rotational speed on organic carbon removal of a system for treating acetic acid synthetic wastewater. The high removal efficiency of 98% was reached under rotational speed of 30 rpm for an organic loading rate of 2.69 kg/m³/d. Another study performed on a pilot plant, reported up to 80% COD removal efficiencies under volumetric loading rate of 2 kg/m³/d for treating winery wastewater (Arnaud 2009). Additional benefits of AnRBC processes include high biomass concentration, low hydraulic retention time, small energy consumption, reduction in sludge production, and high methane production (Teixeira and Oliveira 2000; Hassard et al. 2015). As an example, implementation of an AnRBC reactor within a small-scale combined heat and power system was found to be economically justified due to revenues from biogas production (Renda et al. 2016).

When dealing with wastewaters containing high degrees of organic carbons, using anaerobic treatment alone may not always result in effluents that comply with common discharge regulations. This shortcoming is generally attributed to insufficient

microorganisms' growth rates and poor settling rates of anaerobic processes (Heijnen et al. 1991). Combining anaerobic systems with post treatment aerobic processes is recommended for improving the overall organic matter removal (Cervantes et al. 2006; Cortez et al. 2011; Hassard et al. 2015). Thus, treatment plants are commonly equipped with hybrid systems, consisting of an anaerobic reactor followed by an aerobic process, for treating high strength organic wastewaters (Moletta 2005).

Various combinations of aerobic and anaerobic systems have been studied for treating high organic wastewaters (Ahn et al. 2007; Abeling and Seyfried 1992; Zhou et al. 2006). However, a few have assessed the feasibility of using AnRBC as the main anaerobic reactor within a combined treatment system. Watanabe et al. (1988) investigated the effect of retention times on performance of AnRBC reactor combined with (dissolved air flotation) DAF unit, for treating alcoholic distillery wastewater. The removal efficiencies up to 90% were achieved under retention time of two hours and influent TOC of 2500 mg/L. Also, Lo and Liao (1986) reported total COD removal efficiency up to 98% by grouping AnRBC with sequencing batch reactor for dairy manure treatment.

A combined system that utilizes AnRBC and MBBR processes is an innovative alternative for treatment of high strength organic wastewater, commonly generated from industries such as chlorophenolic manufacturing, synthetic textile production, and cheese production. Several operational parameters can affect the performance of the proposed combined system. This study investigates specific parameters, including hydraulic retention time (HRT), organic loading rate (OLR), and disk rotational speed, through a robust systematic analysis. Additionally, another objective is to determine biokinetic coefficients for the AnRBC process from common predictive models. The findings from

this research can support selection of operational parameters for large-scale AnRBC systems. Also, the results may be used for designing AnRBC-based combined treatment systems for treating high organic industrial streams.

4.2. Materials and methods

4.2.1. Combined System Design

This study was conducted on a combined anaerobic-aerobic biological pilot plant under continuous flow condition. The experimental studies were conducted at the environmental engineering laboratory of the K.N.Toosi University of Technology, Tehran, Iran. The treatment process involved three distinct zones: AnRBC, MBBR, and settling tank. Initially, by using a peristaltic pump, the wastewater flowed to the AnRBC reactor. During the start-up, the sludge from the anaerobic digester of a municipal wastewater treatment plant was added into the reactor, to develop a biofilm consisting of both acidogenic and methanogenic bacteria. Once equilibrium condition was reached, the effluent of anaerobic reactor was fed into the MBBR bioreactor, where the residual organic compound was degraded through further aeration and contact with the biofilms media. Finally, the effluent from the aerobic reactor passed through the settling tank.

The AnRBC stage consisted of four fully immersed bio-disks and was constructed of Plexiglas acrylic sheets. A layer of polyurethane foam (PUF) was attached to both sides of each bio-disk. Having high porosity and specific surface area, the PUF serves as an appropriate media to facilitate both microorganism's growth and organic matter biodegradation (Yang et al. 2007). The disks were connected through a stainless-steel

shaft, which was supported at both ends and rotated parallel to the direction of flow. The reactor was fully covered by Plexiglas acrylic sheets and sealed to provide anaerobic conditions. The produced biogas samples were collected from the top of the reactor. To ensure appropriate condition for the activity and growth of mesophilic bacteria, the reactor temperature was kept at 34oC. The water level inside the tank was controlled by a dynamic head tube resembling a vented inverted siphon on the effluent line. Detailed dimensions and specifications describing the anaerobic reactor are included in Table 4-1.

Table 4-1. Description of AnRBC Reactor

Component	Value
Effective volume (L)	46.5
Number of discs	4
Thickness of PUF-discs (cm)	4
Diameter of discs (cm)	25
Spacing between discs (cm)	2
Total surface area of discs (m ²)	0.393
Disk submergence (%)	100

The MBBR reactor consisted of a 12-liter tank fabricated from Plexiglas acrylic sheets. The bioreactor was packed with carrier Kaldnes-2 with a volume fraction of 50%. The carrier was made of high density polyethylene which provided a specific biofilm growth area of 370 m²/m³. Air diffusers were installed at the bottom of the reactor for aeration to ensure the movement and circulation of biofilm support carriers. The dissolved oxygen (DO) level inside the reactor was adjusted by using a gas flow meter to control the airflow. The MBBR bioreactor was operated under room temperature of 25 ± 2°C.

The cone-shaped settling tank had a working volume of 10 liters and a surface area of 740 cm². This stage worked to separate the mixture of new cells and old cells (sludge) from the receiving stream. The remaining suspended biomass were settled out and removed subsequently.

4.2.2. Synthetic Wastewater

The synthetic wastewater was prepared from tap water with added glucose (1400 mg/L), meat extract (350 mg/L), di-potassium hydrogen phosphate (470 mg/L), ferric chloride (75 mg/L), ammonium chloride (250 mg/ L), magnesium chloride hexahydrate (100 mg/L), and potassium dihydrogen phosphate (75 mg/L), to simulate the desirable level of organic strength. The concentration of each chemical ingredient was proportionally adjusted to achieve the target COD concentration in the influent. The general characteristics of the influent wastewater are presented in Table 4-2.

Table 4-2. Chemical characteristics of the influent wastewater

Parameter	Value
Chemical Oxygen Demand (COD)	3500 (mg/L) – 20000 (mg/L)
Total Dissolved Solids (TDS)	267 (mg/L) - 1941 (mg/L)
Nitrogen (N)	25 (mg/L) – 100 (mg/L)
Phosphorus (P)	14 (mg/L) – 57 (mg/L)
pH	7.1 – 8.2

4.2.3. Process Description

To investigate and identify the most effective operational conditions for the combined anaerobic-aerobic system, ten different experiments were conducted. The individual experiments used varied operational parameters, including HRT, disks rotational speed, and OLR for the anaerobic reactor. These operational parameters are known to significantly influence the overall removal efficiency and methane production of the reactor. For the aerobic bioreactor, HRT and OLR were used to test the reactor's performance. Table 4-3 presents the applied operational conditions. All the quality parameters were measured in accordance with the analytical procedures in the Standard Methods for the Examination of Water and Wastewater (APHA 2012).

Table 4-3. Applied operational conditions for AnRBC and MBBR reactors

Parameter	AnRBC	MBBR
HRT (day)	1 - 4	0.875 – 3
Disks Rotational Speed (rpm)	5 - 10	-
OLR (kg COD/m ³ /d)	1.17 – 6.67	0.66 – 5.17
SLR (kg COD/m ² /d)	0.14 – 0.83	-
Influent COD Concentration (mg/L)	3500 - 20000	1581 – 10336

During the start-up, the anaerobic reactor was inoculated with acclimatized sludge and operated in batch mode for a week. The mixed liquor was removed after seven days and the reactor was refilled with the synthesized substrate. Then, the combined system continuously operated throughout the study. Steady-state condition was assumed for each

individual experience, once the effluent COD concentrations and methane production rates varied by less than $\pm 5\%$ within period of one week as the mean cell residence time. Following the establishment of steady-state conditions, each individual experiment was conducted for a duration of four days. Sampling was carried out during the total duration of each experiment. The collected samples were tested for COD concentration and methane rate, and their mean values were used in the analysis.

4.2.4. Anaerobic Biokinetic Coefficients

Biokinetic coefficients are usually used in process modeling to control and optimize the performance of the treatment processes. Biokinetic coefficients especially have significant importance in industrial anaerobic reactor designs. Thus, the results of kinetic analyses obtained from experimental studies, can be used for estimating treatment efficiencies of full-scale reactors under the same operational conditions. Additionally, modeling efforts can serve as an optimization tool to accomplish the best design and operation for full-scale AnRBC systems. Different kinetic models have been developed for substrate removal in continuously operated anaerobic bioprocess systems. The modified Stover-Kincannon and Grau second order models are the two most widely used mathematical models for describing the kinetic constants, as well as the organic matter removal. Thus, they were selected for this study.

4.2.4.1. The modified Stover-Kincannon model

Considering the monomolecular kinetics of biodisks, the Stover–Kincannon model estimates the consumption rate of substrate as a function of substrate loading rate at steady state (Padilla-Gasca and López 2010; Stover and Kincannon 1982). This model proposes that the influent organic loading rate highly affects the rate of substrate removal.

The original model for the rotating biological reactor is:

$$\frac{dS}{dt} = \frac{Q(S_0 - S_e)}{V} = \frac{U_{\max} \left(\frac{QS_0}{A} \right)}{K_B + \left(\frac{QS_0}{A} \right)} \quad (1)$$

where:

dS/dt = substrate removal rate [mg/L/d]

Q = flow rate [L/day]

V = reactor liquid volume [L]

S_0 = influent substrate concentrations [mg/L]

S_e = effluent substrate concentrations [mg/L]

A = total disc surface area on which biomass concentration is immobilized [m²]

U_{\max} = maximum substrate removal rate [mg/L/d]

K_B = saturation value constant [mg/L/day]

The suspended biomass concentration is assumed to be negligible compared with that of the attached biomass. A simple modification of the original Stover Kincannon model is

the introduction of total organic loading rate, $Lo = QSo/V$, instead of QSo/A (Yu et al. 1998). Further linearization of Equation (1) gives the following relationship:

$$\frac{dS}{dt} = \frac{HRT}{(S_0 - S_e)} = \frac{K_B}{U_{max}} \times \frac{HRT}{S_0} + \frac{1}{U_{max}} \quad (2)$$

The equation can then be solved for either the effluent substrate concentration or the required volume of the reactor by substituting kinetic constants as follows:

$$S_e = S_0 - \frac{U_{max}S_0}{K_B + \left(\frac{S_0}{HRT}\right)} \quad (3)$$

$$V = \frac{QS_0}{\left[\frac{U_{max}S_0}{S_0 - S_e}\right] - K_B} \quad (4)$$

4.2.4.2. Grau second-order substrate removal model

The general equation of the Grau kinetic model (Grau et al. 1975) is:

$$-\frac{dS}{dt} = K_S \times X \times \left(\frac{S}{S_0}\right)^2 \quad (5)$$

Integration and then linearization of the equation yield to:

$$\frac{S_0 \times HRT}{S_0 - S_e} = HRT - \frac{S_0}{K_S \times X} \quad (6)$$

Since the second term at the right side of equation 6 is a constant, the following equation may be derived:

$$\frac{S_0 \times HRT}{S_0 - S_e} = a + b \times HRT \quad (7)$$

The term $(S_0-S)/S_0$ expresses the substrate removal efficiency and is symbolized as E. The terms “a” and “b” are constant coefficients. Thus, the equation can be written as:

$$\frac{\text{HRT}}{E} = a + b \times \text{HRT} \quad (8)$$

4.3. Result and discussion

4.3.1. Anaerobic Reactor

To investigate the effectiveness of key operational conditions, the experiments were conducted in three different steps: retention time testing, rotational speed testing, and organic load testing. In the first step, different HRTs were applied under fixed rotational speed and OLR. In the next step, considering the established HRT from the previous step, the effect of disk rotational speed on the reactor performance was investigated. The third step evaluated the maximum operating capacity of the AnRBC reactor through a stepwise increase of OLR under established conditions from previous steps. Maximum COD removal efficiency and methane production were considered as main criteria to identify the most appropriate operational conditions in all three steps.

4.3.1.1. Effect of Hydraulic Retention Time (AnRBC)

The effect of four different applied HRTs (1, 2, 3, and 4 days) on the performance of AnRBC reactor was investigated, see Fig. 4-1. For all HRTs, the feeding strength and rotational speed were kept constant at 7000 mg COD/L and 5 rpm, respectively. The applied surface loading rate (SLR) for the conducted experiments was in the range of 0.21 to 0.83 kg COD/m²/d. The COD reduction, which characterized the reactor's

biodegradation efficiency, was found to be approximately 42% at HRT of 1 day. The removal efficiency reached 72% at HRT of 3 days. Increasing the contact time between substrate and microorganism under a suitable HRT can increase the quantity of methanogens immobilized on the polyurethane foam media and subsequently higher removal efficiency (Chan et al. 2009). Further increase of HRT to 4 days resulted in negligible (~2.5%) improvement of removal performance.

The methane production was 27.41 L/d at 1-day HRT and increased with HRT. Maximum methane production, 63.09 L/d, was obtained when the reactor was operated under HRT of 3 days. Further increase of HRT decreased the rate of produced methane. However, an increase in methane gas production was expected due to the increase of removal efficiency. This decline is possibly due to unfavorable laboratory conditions, such as leaks within the gas collection setup.

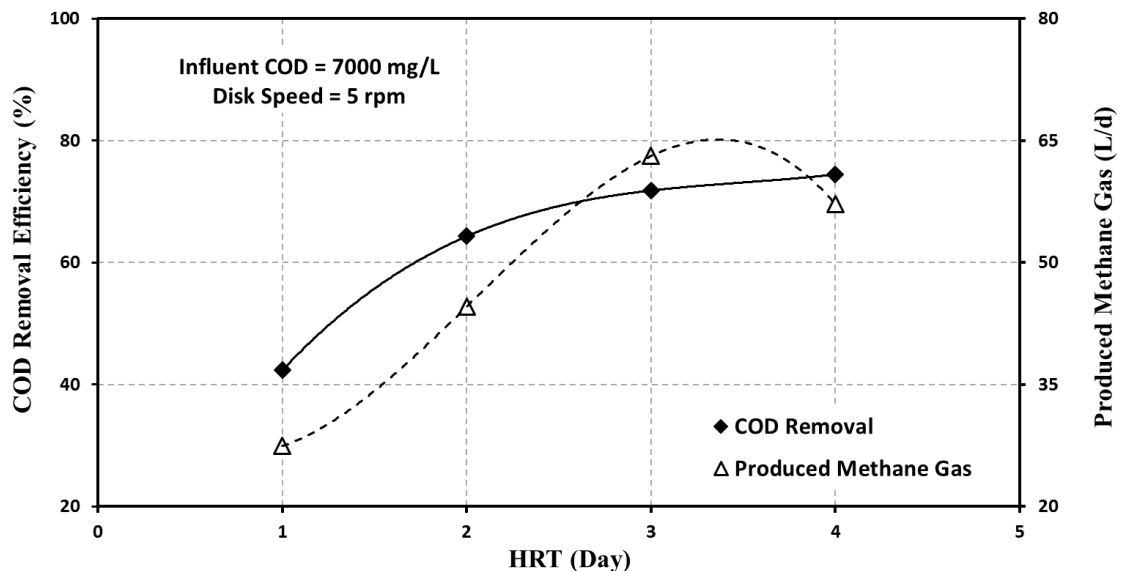


Figure 4-1. The effect of HRT on COD removal efficiency and produced methane in the anaerobic reactor

4.3.1.2. Effect of Disk Rotational Speed (AnRBC)

Following the previous step, the effect of applied rotational speed on reactor's performance was evaluated by fixing HRT and feeding strength at 3 days and 7000 mg COD/L, respectively, which is corresponded to the SLR of 0.28 kg COD/m²/d, see Fig. 4-2. The disk rotational speed, which is a measure for hydraulic conditions, influences the biofilm activity and subsequently, overall performance of the system (Banerjee 1997). Different rotational speeds used in this step included 5, 7, and 10 rpm. Increasing the rotational speed from 5 rpm to 7 rpm resulted in improvement of reactor's efficiency. This can be attributed to better flow mixing and higher contact ratio between substrate and microorganism (Yang et al. 2007). Approximately 76% COD removal was achieved at rotational speed of 7 rpm. However, further increase of rotational speed to 10 rpm decreased the treatment performance, which is attributed to increase of the fluid shear stress over the mass transfer (Yang et al. 2007).

Maximum methane production of 71.28 L/d was observed under rotational speed of 7 rpm. Generally, increasing the rotational speed can improve the mixing quality level. On the other hand, over speeding may lead to desquamation of the biofilm layer from the media (Yang et al. 2007).

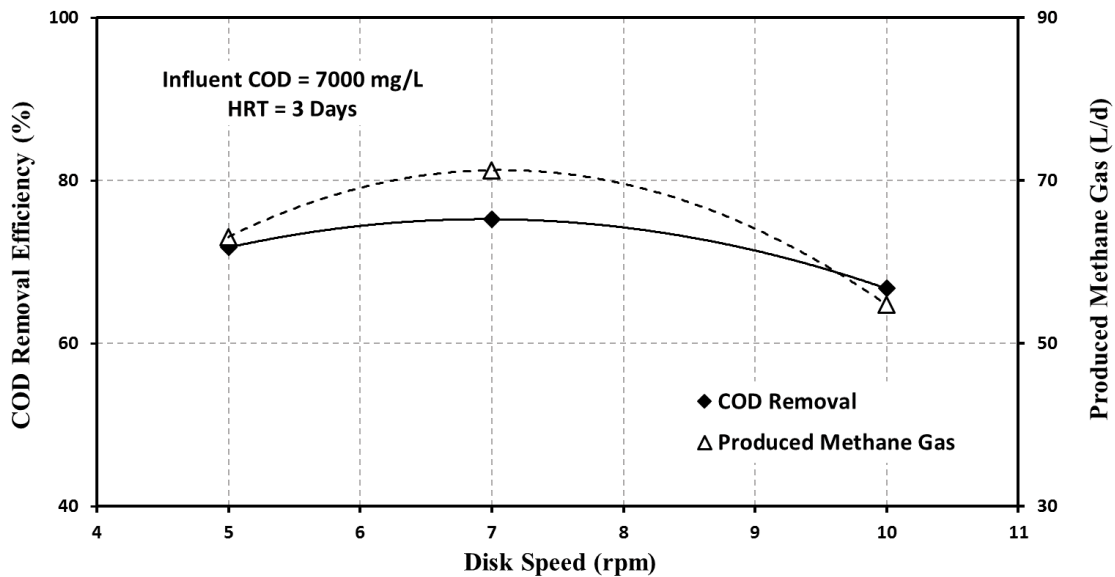


Figure 4-2. The effect of disk rotational speed on COD removal efficiency and produced methane in the anaerobic reactor

4.3.1.3. Effect of Organic Loading Rate (AnRBC)

Subsequent experiments worked to ascertain the effect of OLR on performance capacity of the AnRBC reactor. Five different rates were applied at HRT of 3 days and rotational speed of 7 rpm, see Fig. 4-3. The loading rates included 1.17, 2.33, 3.33, 5, and 6.67 kg COD/m³/d based on 3500, 7000, 10000, 15000, and 20000 mg/L influent COD concentrations, respectively. For all conducted experiments, the SLR fell in the range of 0.14 to 0.79 kg COD/m²/d. Initially, by increasing OLR and subsequently available biodegradable organic matter, the removal efficiency increased and reached its maximum value. Further increase of OLR decreased the removal efficiency. The observed decline may be attributed to organic overloading and unbalanced reactions in the reactor (Metcalf and Eddy 2003). The maximum removal performance of 81% was observed under OLR

of 3.33 kg COD/m³/d, which was the resultant of well-developed bacteria biofilm in the reactor.

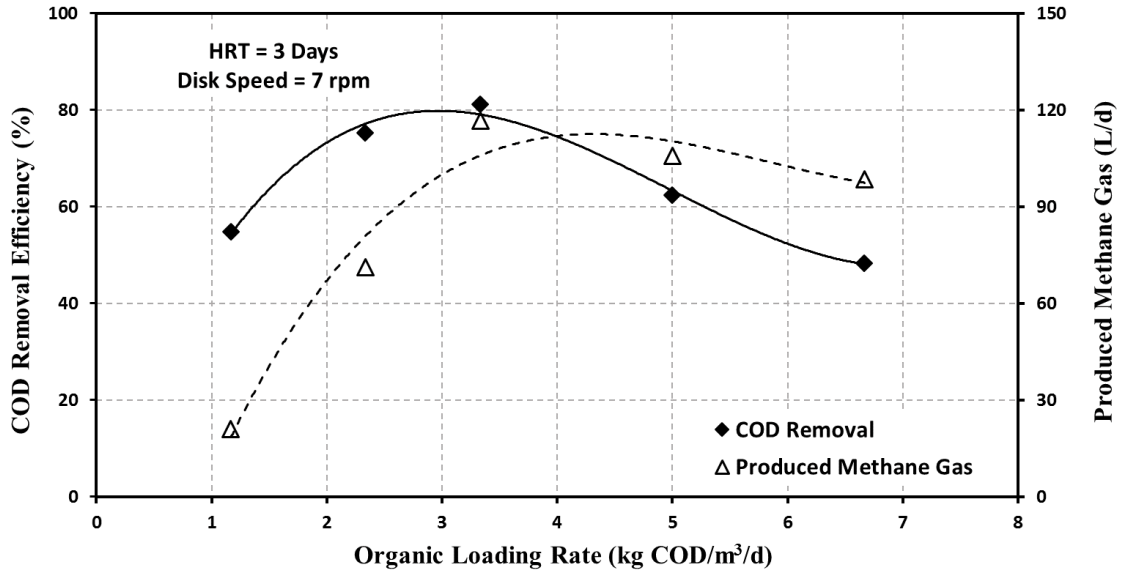


Figure 4-3. The effect of OLR on COD removal efficiency and produced methane in the anaerobic reactor

The rate of produced methane increased from approximately 20.97 L/d to 116.60 L/d by increasing OLR from 1.17 kg COD/m³/d to 3.33 kg COD/m³/d. The methane production declined following the decrease of COD removal rate at higher OLRs. Thus, it can be inferred that under higher loading rates, the methanogenic activity was unable to proceed to completion.

4.3.1.4. Biokinetic Coefficients

The modified Stover–Kincannon model was applied to the experimental results obtained from the AnRBC bioreactor. The maximum utilization rate (U_{max}) and saturation value constant (K_B) were derived from the intercept and slope of the straight line from equation 3, see Fig. 4-4. U_{max} and K_B were determined as 7.77 g/L/d and 8.57 g/L/d with coefficient of determination of 0.93. The model suggested that the higher maximum utilization rates increase the reactor efficiency (Pandian et al. 2011).

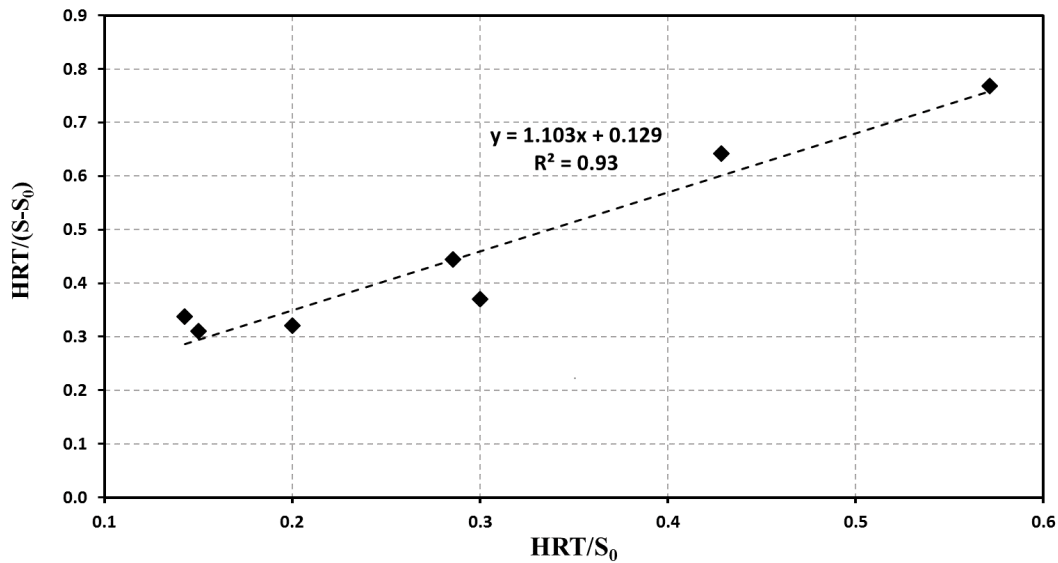


Figure 4-4. Determination of kinetic constants for modified Stover-Kicannon model

As for the Grau second-order substrate removal model, the kinetic coefficient values, a and b , were obtained from the intercept and slope of the straight line from the equation 8, see Fig. 4-5. The calculated values for constants a and b were equal to 1.23 L/d and 1.01, respectively, with coefficient of determination of 0.99.

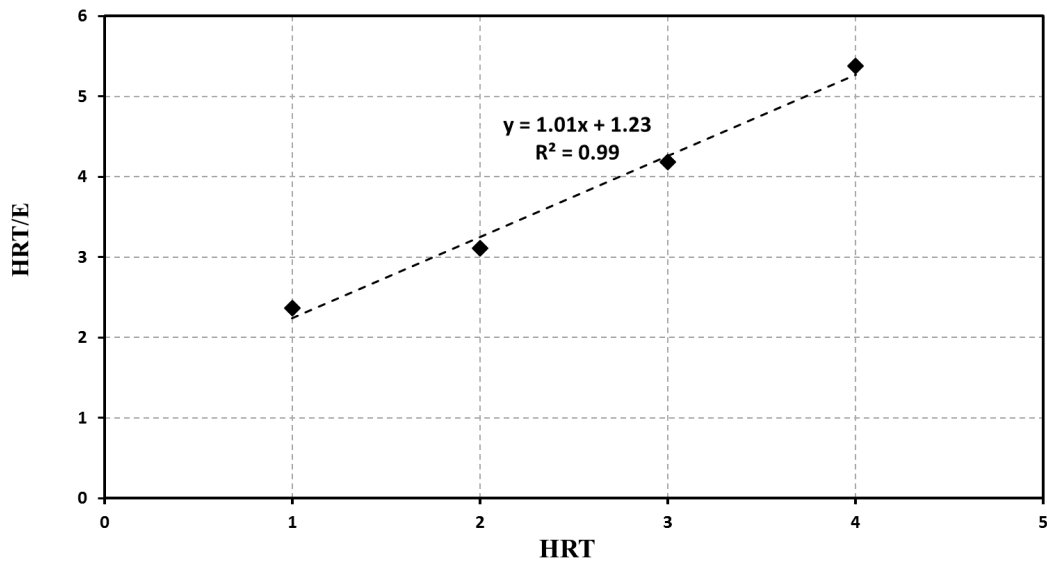


Figure 4-5. Determination of kinetic constants for Grau second-order substrate removal model

4.3.1.4.1. Prediction and validation

To evaluate the validity of biokinetic coefficients, which were obtained from developing the modified Stover–Kincannon and the Grau second-order substrate removal models, the predicting capability of each model was investigated. The approach was performed by comparing the experimental effluent COD values with the predicted values resulted from the two developed models, see Fig. 4-6. The coefficient of determination (R^2), the root mean squared error (RMSE), and the percentage relative prediction error (%Rel. error), were used to assess the quality of each model, see Table 4-4. These statistics represented the fitness of the models and their accuracy for estimation of COD concentrations.

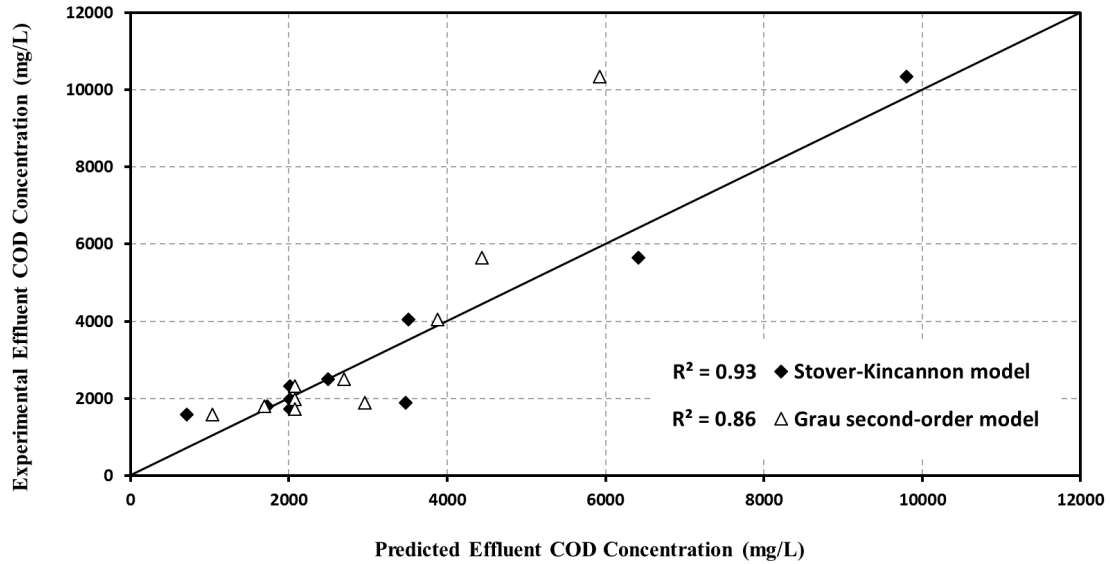


Figure 4-6. The experimental and predicted COD concentrations from Stover-Kincannon and Grau second-order models

Table 4-4. Comparison of Stover-Kincannon and Grau second-order models

Referenced Method	Numerical Expression	Adjusted R ² %	RMSE	% Rel. Error
Stover-Kincannon	$S_e = S_0 - \frac{7.77 \times S_0}{8.57 + \left(\frac{S_0}{\text{HRT}}\right)}$	93	680.5	1.6
Grau second-order	$S_e = S_0 - \frac{S_0 \times \text{HRT}}{1.23 + 1.01 \times \text{HRT}}$	86	1504.6	3.5

The results confirmed higher fitness (Adjusted R² = 93%) of predicted values from the modified Stover–Kincannon model with the testing dataset, compared to those of the Grau second-order model. Also, this model showed lower relative prediction error of 1.6% compared to that from the Grau second-order model. Since the Stover-Kincannon

model exhibited higher predicting capability, the obtained biokinetic coefficients from this model are recommended for design of AnRBC processes.

4.3.2. Aerobic bioreactor

Although high organic removal efficiencies were obtained from the anaerobic reactor, the effluent would still require further treatment before final discharge. Thus, for each individual experiment, the effluent from the anaerobic reactor were fed to the MBBR reactor. The experiments in MBBR stage examined the effects of HRT and OLR to evaluate the maximum performance of the combined system.

4.3.2.1. Effect of Hydraulic Retention Time (MBBR)

To evaluate the effect of HRT, five different rates (0.875, 1, 1.5, 2, and 3 days) were applied to the MBBR reactor, see Fig. 4-7. In all experiments the influent COD concentrations ranged from 1732 to 1975 mg/L. Increasing HRT from 21 hours to 48 hours led to significant raise of removal efficiencies (35% to 88.5%). Further increase of HRT did not result in any further improvements of removal efficiency. Overall, the results indicated that HRT of 2 days is the most suitable retention time for the aerobic reactor and led to highest performance of the combined system.

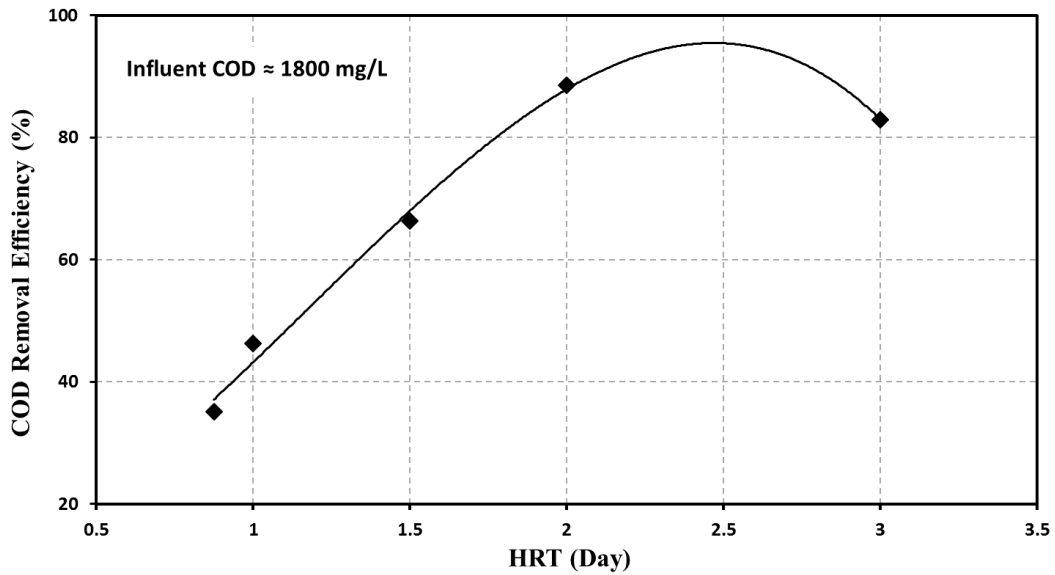


Figure 4-7. The effect of HRT on COD removal efficiency in the aerobic reactor

4.3.2.2. Effect of Organic Loading Rate (MBBR)

The aerobic reactor was tested for five different OLRs under constant HRT of 2 days, see Fig. 4-8. The removal efficiency was improved by increasing OLR from 1.16 kg COD/m³/d to 2.82 kg COD/m³/d, which corresponded to 2328 mg/L and 5650 mg/L influent COD concentrations, respectively. The maximum removal efficiency of 94% was achieved at OLR of 2.82 kg COD/m³/d. Further increase of OLR declined the removal performance.

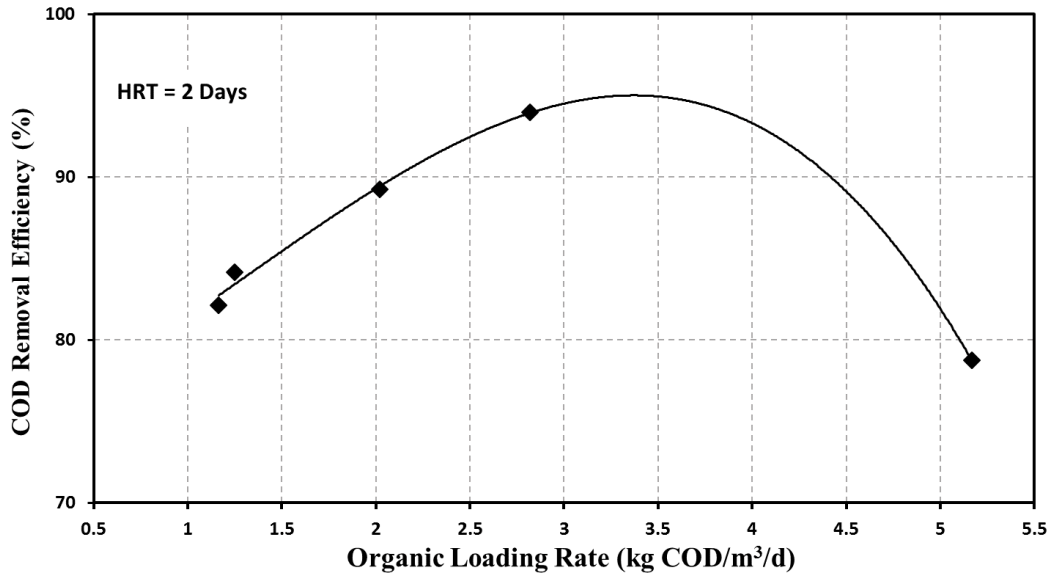


Figure 4-8. The effect of OLR on COD removal efficiency in the aerobic reactor

4.3.3. Combined System

A synopsis of the conducted experiments under different operational conditions for anaerobic reactor, aerobic reactor, and the combined system, is presented in Table 4-5. The highest performance of the combined system was achieved under HRT of 5 days, disk rotational speed of 7 rpm, and OLR of 2 kg COD/m³/d. Under these recommended conditions, the combined system achieved the highest removal efficiency of 97.85%. Additionally, the identified optimized operational conditions led to maximum methane production rate of 116.60 L/d, which corresponds to methane yield of 0.309 L CH₄/g COD.

Table 4-5. Performance of the system under optimal operational conditions

	Operational Condition				Performance	
	HRT (day)	Disks Rotational Speed (rpm)	OLR (kg COD/m ³ /d)	SLR (kg COD/m ² /d)	Removal Efficiency (%)	Produced Methane (L/d)
AnRBC Reactor	3	7	3.33	0.39	81.5	116.60
MBBR Reactor	2	-	2.82	-	94	-
Combined System	5	7	2	0.39	97.85	116.60

Fig. 4-9 presents the boxplots of the observed COD concentrations for all conducted experiments. To investigate if the achieved COD reduction by using the combined system was statistically significant, a paired t-test with a criterion of 95% confidence level was conducted. The results indicated significant difference of COD contents between AnRBC and MBBR effluents ($p\text{-value} = 0.006 < 0.05$). This confirms that under all operational conditions, using the combined system led to higher removal rates compared to individual AnRBC reactor. The proposed conditions (Table 4-5) achieved the lowest level of COD content to approximately 200 mg/L, see Fig. 4-10.

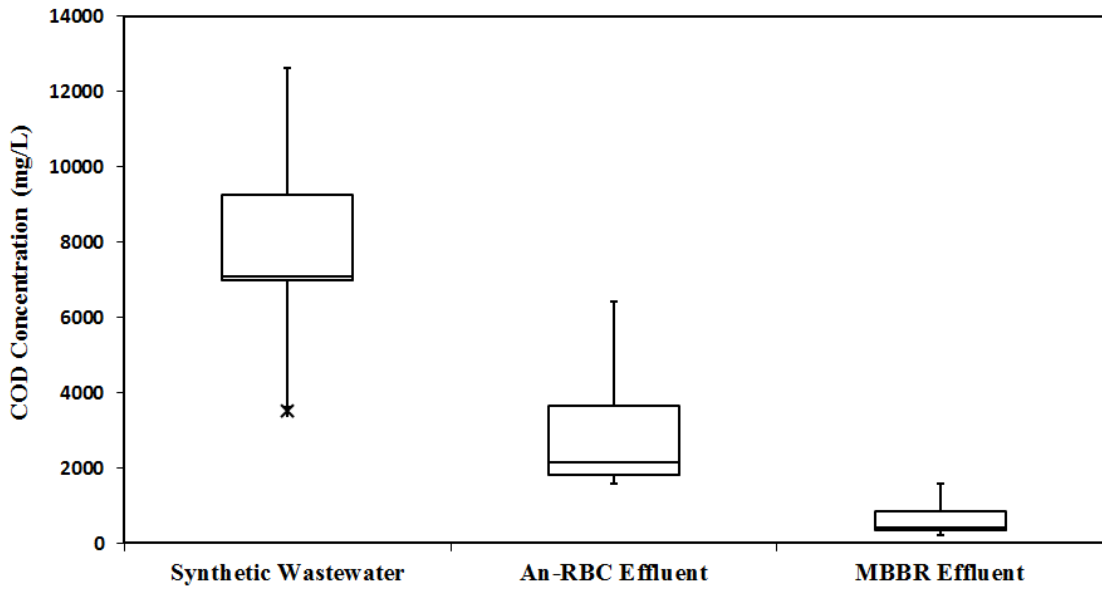


Figure 4-9. COD concentrations from all conducted experiments. The box illustrates the 25th percentile, median, and 75th percentile. The top and bottom whiskers represent the highest and lowest values

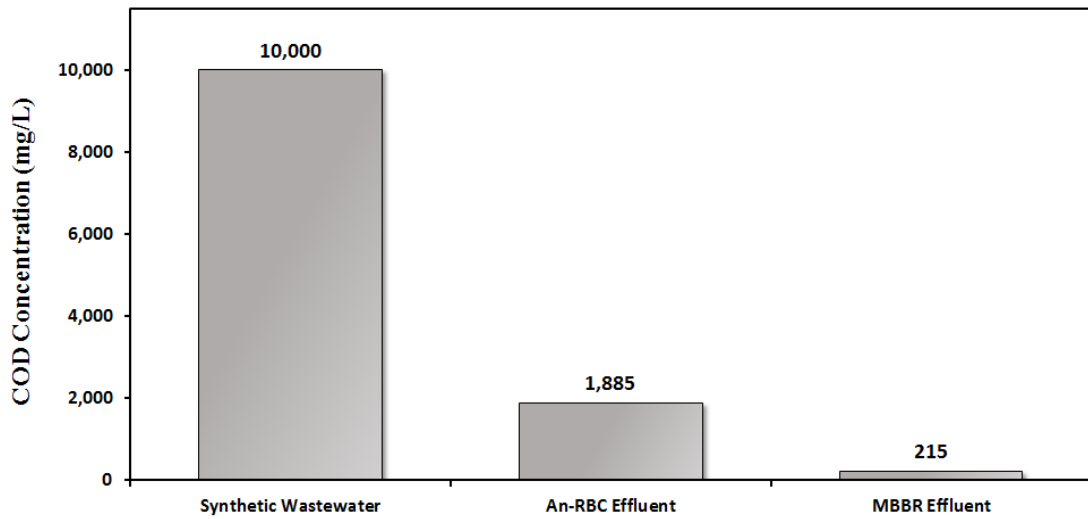


Figure 4-10. COD concentrations under selected optimal operational conditions

4.4. Conclusion

This chapter examined the novel application of a combined system for treatment of high strength industrial wastewater. By conducting individual experiments and through a stepwise analysis, the preferred operational conditions were identified, which led to overall COD removal efficiency of 97.85% and methane gas production of 116.60 L/day. Additionally, analysis of anaerobic biokinetic coefficients showed that using the Stover-Kincannon model had higher prediction accuracy over Grau second-order model. Therefore, the Stover-Kincannon model is suggested for designing and estimating the performance of full size AnRBC reactors.

Finally, it was concluded that using the proposed combined system is highly preferable compared to individual AnRBC. The resultant novel integrated system can provide both maximum removal efficiency and methane production potential. Thus, this system is recommended for treatment of high strength industrial wastewater.

CHAPTER FIVE. AN OPTIMIZED BIOLOGICAL APPROACH FOR TREATMENT OF PETROLEUM REFINERY WASTEWATER

5.1. Introduction

Petrochemical industries and petroleum refineries generate significant amounts of wastewater as crude oil is refined. This wastewater contains a complex set of oxygen-demanding materials and priority pollutants which, if untreated, would be released into the natural environment (Tyagi et al. 1993). Common wastewater pre-treatment methods employed by the industry include coagulation flocculation, adsorption, membrane, and chemical oxidation (Diya'uddeen et al. 2011). Generally, it is challenging to remove small suspended oil particles and dissolved elements by sole use of physical or chemical technologies. In this case, the processes that rely on the ability of microorganisms to use wastewater components for their metabolisms are found to be more cost-effective and sustainable compared to physical and chemical oxidation processes (Vendramel et al. 2015).

The activated sludge biological processes are often employed to remove pollutants from the waste stream as a secondary treatment stage. (Shokrollahzadeh et al. 2008). Biological treatment of oily wastewater can be cost-effective, environmental friendly, and more compatible with existing plant facilities compared to other techniques (Fakhru'l-Razi et al. 2009). However, these systems are typically associated with numerous

operational challenges, including poor sludge settling properties, extra-cellular polymers generation, biological inhibition, prolonged sludge retention time, and extensive period of acclimation or start-up (Singh and Desai 1987; Tyagi et al. 1993).

Excess sludge production, which is a byproduct of biological processes, raises a serious issue during the wastewater treatment. Treatment and disposal of considerably high produced sludge from the biological processes may even account for almost 60% of total associated costs and energy demand of the treatment plants (Wei et al. 2003). Thus, the optimal design of biological treatment systems is essential to reduce the treatment costs of refinery wastewater. A significant number of previous researchers have worked to assess the improvements in pollutant removal efficiency for treatment of petrochemical as well as other industrial wastewater (El-Naas et al. 2014; Gasim et al. 2014; Lu et al. 2013; Mardani et al. 2011; Mirbagheri et al. 2014; Saranya et al. 2014; Vasquez Sarria et al. 2011; Vendramel et al. 2015). However, very few have sought an optimal condition for both maximizing the process removal efficiency and minimizing the amount of produced sludge and with considering a limited range of operational conditions (Mirbagheri et al. 2014; Vasquez Sarria et al. 2011).

To overcome the aforementioned shortcoming of previous research projects, this study identifies the conditions that lead to optimal performance of contact stabilization systems treating petroleum refinery wastewater. Specifically, the study focuses on conditions that maximize the removal performance and minimize sludge production of the system. To achieve this objective, a series of experiments were conducted on a pilot plant. The system was tested under a wide range of operational conditions and the results were

studied through a systematic analysis. The findings from this work serve as a guide for secondary treatment of wastewater from petroleum refineries.

5.2. Material and methods

5.2.1. Contact-Stabilization Process

The development of contact-stabilization process was based on the idea of increasing the capacity and improving the performance of activated sludge biological wastewater treatment systems (Al-Mutairi et al. 2003). In this method the raw wastewater is aerated and mixed with the bacteria, which is in contact with dissolved and insoluble organic matters, in the contact basin. During this bio-oxidation process, the dissolved organic matters are used by bacterial cells and the insoluble organic matters are adsorbed to external skin cells (Metcalf et al. 1979). Some of the biological solid matters is settled in the secondary settling basin and subsequently wasted, while the remaining is returned to the stabilization basin for further bio-regeneration and stabilizing the organic matters received from the contact basin. It has been ascertained that competition between flocc-forming and filamentous microorganism is strongly affected by the organic concentration during mixing of influent and return activated sludge (Hao et al. 1996). Thus, through the optimization of return sludge to the contact tank, the high adsorption capacity of activated sludge is fully utilized and the volume of daily excess production from the system is decreased.

5.2.2. Pilot Plant Description

A pilot-scale biological treatment plant was constructed and examined at the laboratory department of the Tehran petroleum refinery, Tehran, Iran. The treatment process involved three distinct zones: contact, stabilization, and settling tanks, see Figure 5-1. Detailed dimensions and volumes describing the pilot plant are presented in Table 5-1.

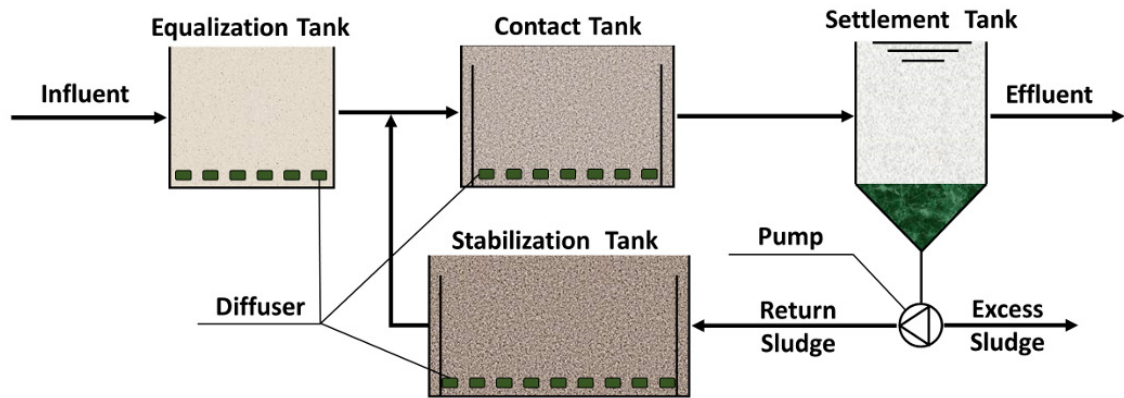


Figure 5-1. The Process of the Contact Stabilization Pilot Plant

Table 5-1. Description of Pilot Plant

Unit	Length × Width × Height (cm)	Total Volume (L)	Effective Volume (L)
Contact tank	40 × 60 × 200	480	456
Stabilization tank	100 × 60 × 200	1200	1140
Settling tank	150 × 100 × 130	1950	1755

To prevent short-circuiting and turbulent flow in the basins, 50 cm × 60 cm partition sheets were installed at the inlet and outlet of the contact and stabilization tanks. An equalization basin, equipped with a diffuser and an air flotation unit, was installed up gradient of the pilot plant. Stone air diffusers were fixed at 10 cm above the bottom of the reactors. The air flow in the reactor ensured a mixing intensity, which simulated the mixing characteristic in an activated sludge process. The sludge was recycled from the settler and then returned into the stabilization tank by using a 3500 L/hr pump. The pilot plant's operation (start and termination) was controlled by programming a logic control. A steady-state condition was assumed, when fairly constant biomass growth and permeate chemical oxygen demand (COD) were attained.

5.2.3. Wastewater

The feed wastewater for the pilot plant was obtained from the biological stage influent of Tehran's petroleum refinery treatment plant. The general characteristics of the influent wastewater are presented in Table 5-2.

Table 5-2. Influent Chemical Characteristics

Parameter	Value
Biological Oxygen Demand (BOD)	229 (mg/L) – 261 (mg/L)
Chemical Oxygen Demand (COD)	377 (mg/L) – 422 (mg/L)
Mixed Liquor Suspended Solids (MLSS)	1865 (mg/L) – 2389 (mg/L)
Mixed Liquor Volatile Suspended Solids (MLVSS)	1462 (mg/L) – 1986 (mg/L)
pH	7.1 – 7.9

5.2.4. Operational Conditions

To achieve optimum treatment performance, a variety of operational parameters need to be adjusted. In this study, the mixed liquor dissolved oxygen (DO) and the percentage of return sludge (RS) from the settling tank to the stabilization tank, were selected as key operational parameters affecting the total sludge production and overall removal efficiency of the system. The dissolved oxygen in the contact tank affects the physical, chemical and biological potential synergic functions of microorganisms in the mixed liquor to adsorb pollutants (Liu et al. 2009). The return sludge parameter impacts the growth rate of organisms from the stabilization tank to maintain a specific level of food to microorganism ratio in the contact tank (Greene and DeLorenzo 2005). Thus, it was hypothesized that minimum sludge production and maximum performance efficiency of the system would be achieved by changing the return sludge rate and oxygen supply of the aeration basin.

The pilot plant was operated for a period of six months. The operation was conducted at fixed inflow rate of 700 L/hr and under different DO concentrations and RS percentage values. In start-up, the system was maintained at a constant hydraulic retention time (HRT) of 0.65 hr and 5.43 hr for contact and stabilization tanks, respectively. Each individual experiment was conducted for four days and a minimum time of one week was selected for the mean cell residence time (MCRT) between subsequent test series, to ensure steady state conditions. The experiments were conducted under four different aeration phases and eight different RS percentages (n=32), see Table 5-3.

Table 5-3. Characterization of Applied Operational Condition for 32 Defined Experiments

Phase	Dissolved Oxygen (mg O ₂ /L)	Return Sludge (%)	Hydraulic Retention Time (hour)
1	0.52		
2	1.94	30, 50, 70, 100, 120,	5.43, 3.26, 2.33, 1.63, 1.36,
3	3.70	140, 160, and 180%	1.16, 1.02, and 0.90
4	5.20		

5.2.5. Sampling and Laboratory Testing

Samples were collected two times per day from the influent wastewater, reactor, and effluent flow. The collected samples were analyzed for various physical and chemical parameters in accordance with the Standard Methods for the Examination of Water and Wastewater (Way 2012). The temperature was kept between 18°C and 24°C during the operation and sampling periods.

5.3. Results and discussion

The data collected during operation of the pilot plant were assessed in a variety of capacities to identify optimal performance operations with respect to maximizing the removal efficiency and minimizing sludge production of the system. First, the biokinetic coefficients for the four experimental phases were examined and compared to established acceptable ranges. Second, the aeration phase associated with optimal removal efficiencies was identified. And third, suitable RS percentages were determined by

examining both the removal efficiencies and the amount of produced sludge in the selected aeration phase.

Concentrations of selected parameters were measured for each individual experiment in all phases of the study. The results of these measurements for the pilot plant's effluent and the mixed liquor are presented in Tables 5-4 and 5-5, respectively.

Table 5-4. Effluent Parameters from the Contact Stabilization Pilot Plant

Phase	BOD ₅ (mg/l)	COD (mg/l)	pH
1	117 - 138	180 - 201	7.1 – 7.8
2	65 - 100	102 – 145	
3	62 - 95	82 - 112	
4	56 - 75	78 - 89	

Table 5-5. Mixed Liquor Characteristics in the Contact and the Stabilization Tanks

Phase	SRT (days)	Contact Tank		Stabilization Tank	
		MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)
1	3.29 – 6.25	5187 - 10221	4335 - 9097	8344 - 14901	7214 - 13045
2	4.1 – 8.75	5262 - 11816	4341 - 9080	9142 - 15515	8024 - 13050
3	6.46 – 9.18	4229 - 11844	3167 - 10365	7249 - 17369	5872 - 15011
4	8.2 – 15.13	5001 - 14385	3813 - 12597	8777 - 19895	7018 - 18711

5.3.1. Biokinetic Coefficients

The Monod model is commonly used to quantify utilization of the growth limiting substrate against microorganisms' growth in activated sludge processes (Equations 1 and 2). The biokinetic coefficients within this model explore the specific relationships between biomass yield and biomass lost. The common ranges of these coefficients in an activated sludge system are presented in Table 5-6 (Al-Malack 2006).

$$1/\text{SRT} = YU - K_d = Y(S_0 - S)/(\theta X) - K_d \quad (1)$$

$$(\theta X)/(S_0 - S) = K_s/(K_s) + 1/k = 1/U \quad (2)$$

where:

SRT = Solid Retention Time, [Day]

Y = Maximum cell yield, [mg VSS/mg COD]

U = Substrate utilization rate, [mg COD/mg VSS.day]

K_d = Endogenous decay coefficient, [day⁻¹]

S = Effluent substrate concentration, [mg COD/L]

S₀ = Influent substrate concentration, [mg COD/L]

θ = Hydraulic retention time, [day]

X = Biomass concentration, [mg VSS/L]

k = Maximum rate of substrate utilization per unit mass of microorganisms [day⁻¹]

K_s = Half velocity constant [mg COD/L]

Table 5-6. Typical Values of Biokinetic Coefficients for Activated Sludge Systems

Biokinetic Coefficient	Typical Range
Y (mg VSS/mg COD)	0.2 - 0.5
Kd (1/day)	0.03 - 0.07
k (1/day)	2 - 8
Ks (mg COD/L)	40 - 120

The biokinetic coefficients for each experimental phase are shown in figures 5-2 and 5-3, and summarized in Table 5-7. The Y parameter represents the biomass yield, which indicates how biomass is produced against the utilized substrate. This parameter, which plays a major role during the design of a treatment facility, provides an estimate of the sludge produced through the treatment process (Metcalf et al. 1979). The higher values of Y indicate higher sludge productions and therefore, require an increase in size of the sludge handling facility. It was observed that after increasing aeration, the parameter Y decreased. The estimated values of Y coefficient were out of the typical range for phases one and two (DO concentrations of 0.52 mg/L and 1.94 mg/L). Inspection of Figure 4-2 also shows that parameter Y for phases three and four (DO concentrations of 3.7 mg/L and 5.2 mg/L) was within the acceptable range. This indicates that by applying more aeration, less sludge is produced.

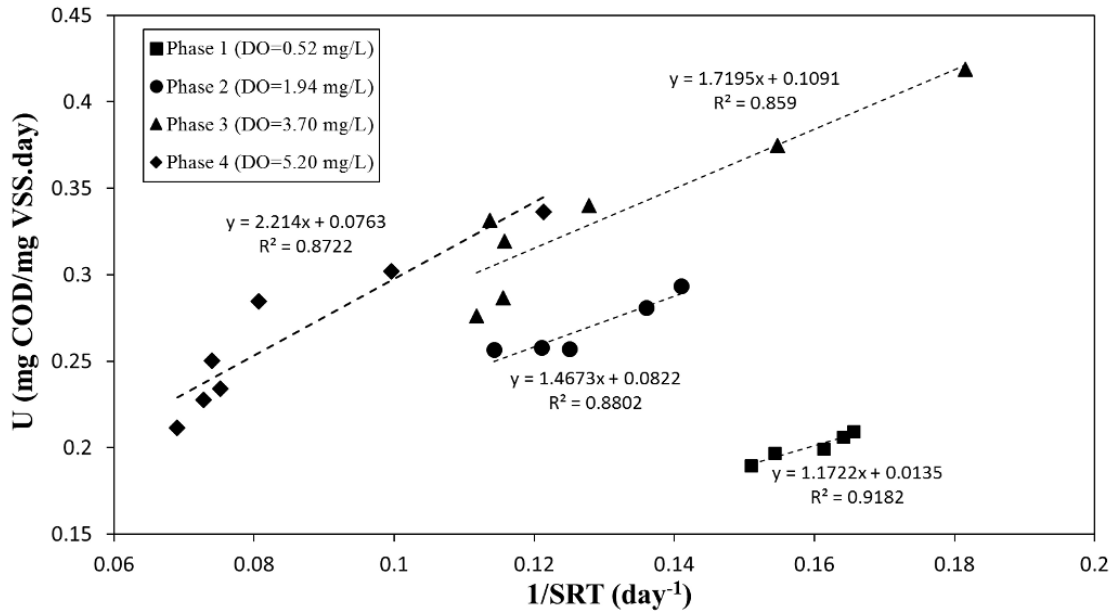


Figure 5-2. Determination of Parameters Y and K_d

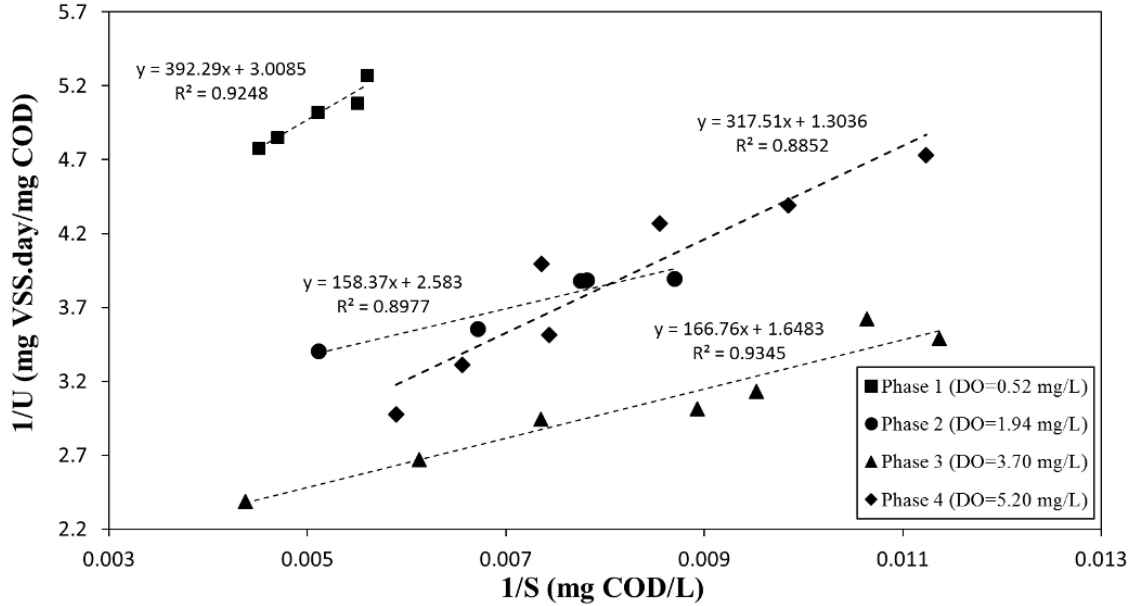


Figure 5-3. Determination of Parameters K_s and k

Table 5-7. Derived Biokinetic Coefficients for Each Phase

Biokinetic Coefficient	Phase 1	Phase 2	Phase 3	Phase 4
Y (mg VSS/mg COD)	0.853	0.682	0.582	0.452
Kd (1/day)	0.012	0.056	0.063	0.034
k (1/day)	0.332	0.387	0.607	0.767
Ks (mg COD/L)	130.394	61.312	101.171	243.564

The parameter Kd indicates the biomass lost to endogenous respiration per unit of biomass per unit time. Kd is used for evaluation of net sludge production and thus, is another key factor for effective design of a treatment facility. Higher values of Kd reduce the net sludge production during the microbiological treatment process. Although the effect of this parameter on sludge production is smaller compared to parameter Y, it can be used to fine tune the size of the sludge handling facility, resulting in economic benefits. The estimated value of Kd at phase four was out of the typical range. The highest value of this coefficient was recorded at phase three, indicating less net sludge production under this aeration condition.

Parameter k affects the total volume of the reactor: the greater the value of k, the smaller the size of the reactor. None of the estimated k values were in the typical range, however it was observed that by increasing the aeration the values of this parameter increased.

Ks, also referred to as half velocity constant, is the maximum growth limiting substrate concentration measured at saturated condition. Higher values of Ks indicate that the maximum specific yield of bacteria occurs at higher substrate concentrations. Unlike parameters Y and K, Ks has no direct application in the design process of a treatment

facility. It has a theoretical application to estimate the changes in specific growth rate of bacteria due to changes of growth limiting concentration substrate. Values of K_s for phases one and four (DO concentrations of 0.52 and 5.2 mg/L) were out of the typical range defined in Table 6. Although the values from the other two phases were well within the typical range, higher specific yield of bacteria were observed in phase three compared to that from phase two.

The discussed results for all four aeration phases indicated that biokinetic coefficients from phase three better fell within the established typical ranges compared to those from other phases. Thus, it can be inferred that application of 3.7 mg/L dissolved oxygen can result in admissible biokinetic coefficients and low sludge production during the treatment process.

5.3.2. Optimum Aeration Phase

Different applied aeration phases resulted in different COD removal efficiencies of the system, see figure 5-4. The least removal efficiencies were achieved under phase one, which is attributed to a lack of oxygen that reduces the microorganisms' activities and subsequently the removal of organic matters. By increasing the amount of dissolved oxygen in higher phases, the overall efficiency of the system increased. Increasing the oxygen concentration in the liquid mixture leads to a deep diffusion of oxygen, which subsequently causes an enlargement of the aerobic volume inside the floc. As a result, the hydrolyzed microorganisms in the floc degraded and efficiency improved (Abbassi et al. 2000).

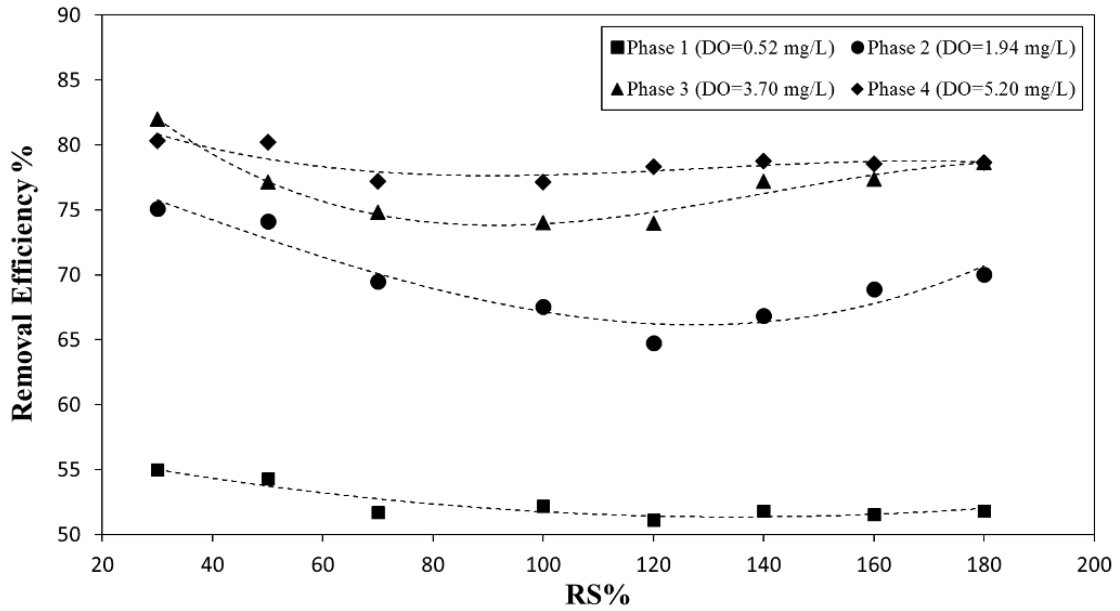


Figure 5-4. COD Removal Efficiency of Pilot Plant at Different Operational Phases

As Figure 5-4 indicates, the system efficiency improved by increasing the DO concentrations. Unlike phases one and two, which resulted in low system's efficiencies, phases three and four led to high (>75%) removal efficiencies. The average observed efficiencies were 77% and 79% for phases three and four, respectively. Figure 5-5 compares the boxplots of achieved removal efficiencies for each aeration phase and confirms the negligible difference between phases three and four.

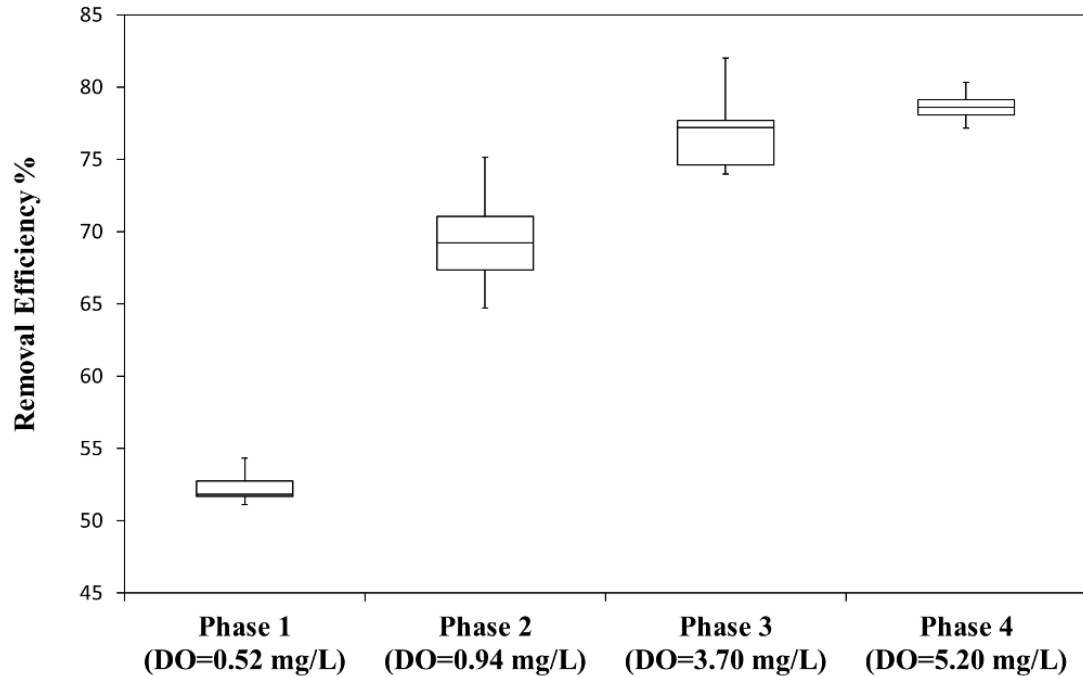


Figure 5-5. The COD Removal Efficiency for All Phases. The box illustrates the 25th percentile, median, and 75th percentile. The top and bottom whiskers represent the highest and lowest values

To make a final selection between phases three and four, a statistical “one-way analysis of variance” (ANOVA) test was used. The ANOVA test determined whether the observed differences in the mean removal of organic matter was statistically significant ($p\text{-value} < 0.005$) or not. Prior to using the ANOVA, all data groups were tested and confirmed for normality distribution assumption. The results from the ANOVA tests for each two consecutive aeration phases are presented in Table 5-8. Significant ($p\text{-value} < 0.005$) differences of COD removals were observed between phases one and two, and phases two and three. However, the ANOVA did not show any significant improvement in COD removal efficiency between phases three and four. Considering

these results, phase three (DO = 3.7 mg/L) is recommended as optimum aeration condition, which confirms the previous findings from biokinetic analysis.

Table 5-8. Statistical Analysis of Observed COD Removal Efficiencies for All Aeration Phases

Aeration Phase	COD Removal %			ANOVA Results	
	Mean \pm St.dv.	Median	Median Difference	Mean Difference	Adjusted R ² % <i>p</i> -value
Phase 1 (n=8)	52.44 \pm 1.41	51.82			
Phase 2 (n=8)	69.60 \pm 3.53	69.21			
Phase 3 (n=8)	76.90 \pm 2.69	77.18			
Phase 4 (n=8)	78.65 \pm 1.18	78.60			
Between Phases 1 & 2			17.39	17.16	92.10 0.000
Between Phases 2 & 3			7.97	7.3	60.70 0.000
Between Phases 3 & 4			1.42	1.75	16.93 0.113

5.3.3. Return Activated Sludge

Once the optimum biological treatment aeration condition was identified (phase three), the process was further refined to determine suitable ranges of RS percentages. To achieve this objective, the effects of this operational parameter on COD removal efficiency, as well as daily biomass (sludge) production (Px), were assessed and analyzed.

Inspection of Figure 5-4 indicates that for all aeration phases, maximum removal efficiency is achieved at the lowest RS percentage. This might be due to the high aeration period to the recycled solids and a high MLVSS concentration in the stabilization basin, which led to endogenous metabolism of microorganisms (Metcalf et al. 1979). Once the

external substrate is completely depleted and the bacteria, which are a food source for higher organisms, are consumed the total amount of biomass decreases. This results in a transfer of food to a higher trophic level and increases the system's removal efficiency. By increasing the RS percentage (30% - 100%), the removal efficiency decreased due to the reduction of aeration time for recycled sludge and depletion in the concentration of active organisms. Further increasing of RS percentage (100% to 180%) led to the rise of active organisms' population in the contact tank, and subsequently a slight improvement of system's removal efficiency.

At an optimal return sludge rate, most of the MLVSS concentration in the contact tank is utilized and as a result, the amount of produced sludge reaches its minimum value. In other words, considerable reductions of sludge production can be achieved by maximizing the energy used for maintenance requirements of microorganisms, rather than for their cellular synthesis (Low and Chase 1999).

The amount of produced biomass for all return sludge percentages in phase three were investigated, see Figure 5-6. The Px values in this phase decreased by increase of the RS and ranged between 1.32 and 1.48 kg/day. Also, it was observed that the amount of produced sludge was minimized at RS value of 100%. Further increase of this ratio, which leads to subsequent growth of system's energy demand, showed insignificant decrease of biomass. It can thus be inferred that using a RS% in the range of 100% to 180% is not suitable since the decrease in the produced sludge and the increase of system's performance are negligible and has no economic justification.

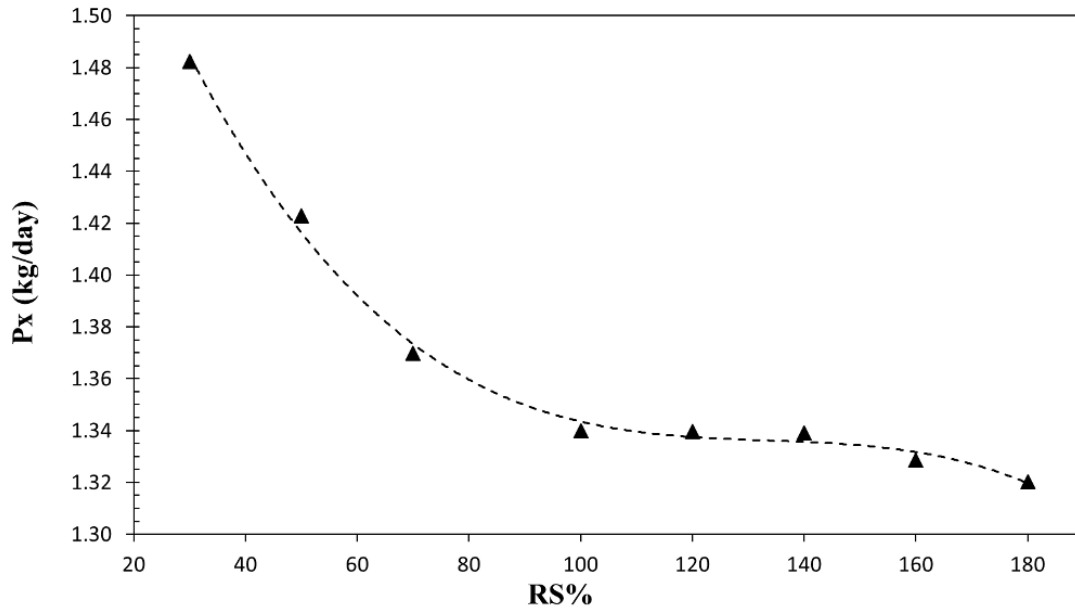


Figure 5-6. Variation of Daily Sludge Production at Phase Three

Within RS percentages ranging from 30% to 100%, the removal performance and the amount of produced sludge show a direct relationship with each other, see Figure 4-7. By increasing the RS% in phase three, lower removal efficiencies (unfavorable) and lower sludge production (favorable) were achieved. Depending on the desired treatment objectives, all RS percentages in this range (30% - 100%) can be acceptable. If the intent is to achieve the highest removal efficiency, then 30% return sludge is the optimal operational condition. Similarly, if the goal is to minimize sludge production, an RS% of 100% is the optimal operational condition.

Using a RS percentage that ensured both the high removal performance and low sludge production was an alternative scenario. It is suggested to use the RS% that corresponded to the approximate averages of removal efficiencies and produced sludge values in Figure 5-7, which were 78% and 1.42 kg/day, respectively. The equations of the observed

trendlines between removal efficiency and RS% for phase three (Figure 4-4), and between Px and RS% (Figure 4-6), were solved to obtain the associated RS%. The results indicated that a RS% approximately equal to 46% would satisfy both equations, see Table 5-9.

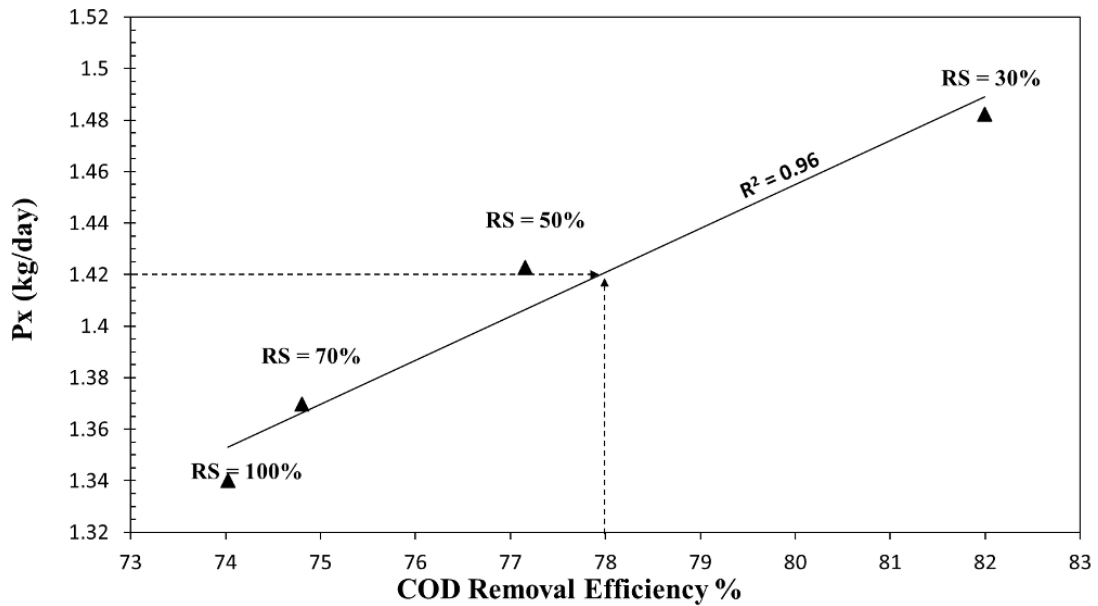


Figure 5-7. The Relationship between Removal Efficiency and Sludge Production for $30\% \leq RS \leq 100\%$, in Phase Three

Table 5-9. Determining Optimum RS Value

Derived Trendline Equation	Y	X (Solved)
$Y = -1E-05X^3 + 0.0044X^2 - 0.5436X + 94.647$	COD Removal % = 78	RS% \simeq 46
$Y = -1E-07X^3 + 5E-05X^2 - 0.0071X + 1.6536$	Px = 1.42 kg/day	

Considering common treatment process objectives, three suitable operational conditions are summarized in Table 5-10. The first two solutions optimize the removal efficiency and sludge production, respectively. The third solution, however, works to satisfy both the high removal efficiency and low produced sludge of the system. This solution uses aeration phase three (DO = 3.7 mg/L) with RS of 46%. Under these operational conditions, the COD removal efficiency and the amount of daily produced sludge will be equal to 78% and 1.42 kg/day, respectively.

Table 5-10. Selected Operational Conditions for System's Optimum Performance

Parameter	Solution One	Solution Two	Solution Three (<i>recommended</i>)
DO (mg/L)	3.70	3.70	3.70
RS (%)	30	100	46
HRT _{Contact} (hr)	0.65	0.65	0.65
HRT _{Stabilization} (hr)	5.43	1.63	3.54
COD Removal Efficiency (%)	82	74	78
Px (kg/day)	1.48	1.34	1.42

5.4. Conclusion

A step by step analysis was performed to optimize the performance of a contact stabilization process for secondary treatment of petroleum refinery wastewater. The results of the biokinetic coefficients analysis indicated that aeration phase three (DO concentration of 3.7 mg/L) was more suitable compared to other three phases, since it resulted in coefficients that better fit the normal range compared to those from other phases. The ANOVA tests showed that removal efficiencies significantly (p -value < 0.05) improved with the increase of DO concentration in the contact tank from phase one to phase three. However, the ANOVA indicated that the improvement in system's efficiency in phase four compared to phase three was not statistically significant (p -value > 0.05). Due to the results from biokinetic analysis and ANOVA tests, phase three was selected as the recommended aeration phase.

The RS values equal to 30% and 100% led to maximum removal efficiency and minimum sludge production, respectively. However, optimizing both removal efficiency and sludge production led to a recommended solution of a 46% RS. This operational condition (RS = 46% and DO = 3.7 mg/L) resulted in both high COD removal (78%) and low produced sludge (1.42 kg/day) in the system. While these selected conditions do not ensure maximum removal performance or the minimum sludge production, they achieved concurrent occurrences of these two criteria and thus, an optimum performance of the system. Considering the results from this study, the contact stabilization activated sludge process is suggested as an effective alternative for secondary treatment of wastewater from petroleum refineries.

CHAPTER SIX. QUALITY APPRAISAL OF GROUNDWATER IN ARID REGIONS BY USING DETERMINISTIC AND PROBABILISTIC APPROACHES

6.1. Introduction

As populations expand and urbanization increases, the associated water demands put significant pressures on natural water resources. Groundwater, as a common source for residential, agricultural, and industrial demands, has been subjected to tremendous deterioration, especially in arid regions. To provide a sustainable source, understanding the temporal and spatial fluctuation of water quality is essential considering climate changes and local environmental pressures. Thus, for arid regions with low rainfall rates and limited groundwater resources, a robust groundwater quality investigation is crucial to promulgate regulations for better environmental management and human health protection.

For arid regions, many studies have worked to understand the groundwater chemistry processes and establish procedures necessary for water quality assessments (Iranmanesh et al. 2014; Kim et al. 2005; Meng and Maynard 2001; Moya et al. 2015; Niu et al. 2017; Vasanthavigar et al. 2010). In general, these studies are either deterministic or probabilistic in their origin. For the deterministic approach, a geochemical analysis of groundwater samples within the aquifer is conducted by using traditional graphical methods and diagrams such as Piper, Wilcox, or US Salinity Laboratory Staff plot

(Ebrahimi et al. 2016; Herczeg et al. 2001; Jamshidzadeh and Mirbagheri 2011; Yidana and Yidana 2010; Zaidi et al. 2016). These studies evaluated the suitability of samples for drinking and irrigation purposes by comparing groundwater physicochemical parameters with pre-established quality standards and indicators. For the probabilistic approach, statistical algorithms such as correlation, clustering, factor analysis, and measurement uncertainty, are used to provide a classification scheme for categorizing the physiochemical properties of aquifer and to identify the anthropogenic sources of contamination governing the groundwater quality deteriorations (Belkhiri et al. 2011; Güler et al. 2002; Machiwal and Jha 2015; Rastogi and Sinha 2011; Waqar et al. 2016).

Both types of studies have presented significant information regarding the aquifer's quality condition. The deterministic approach delivers results pertaining to individual sampling wells. However, it is challenging to compare the overall groundwater quality conditions across several basins or for temporal analyses, by using this approach alone. The probabilistic approach, while strong for comparison purposes, does not provide meticulous results based on individual quality indicators, especially for waters under severe adverse environmental impacts. The combination of statistical methods in conjunction with the traditional water quality assessment techniques, can provide a rigorous procedure to draw meaningful results of the overall groundwater quality for the investigated basins.

The objective of this study is to utilize a methodology that combines the probabilistic and deterministic approaches for assessing aquifer's quality condition. For this purpose, a 300 km² basin under arid weather conditions, was selected as the case study. The intent of this work was to identify: 1) groundwater classification scheme, 2) processes governing

the groundwater chemistry, 3) hydrochemical characteristics of groundwater, and 4) suitability of the groundwater for drinking and agricultural purposes.

6.2. Material and Methods

6.2.1. Methodology

The proposed methodology first uses the probabilistic approach to classify wells based on physicochemical properties of groundwater. Then based upon the obtained results, the deterministic approach is applied for comprehensive assessment of groundwater quality for different applications.

For the probabilistic approach, the multivariate statistical techniques were applied. To determine if the specific parameters were statistically correlated, the Pearson product moment correlation analysis was performed (Cohen et al. 2013). To classify sampling wells into finite statistically distinct hydrochemical groups based on their similarities, the cluster analysis (CA) was used (Kaufman and Rousseeuw 2009). To simultaneously evaluate the correlations among several variables and to reduce the total data set dimension, the principal component analysis (PCA) was conducted (Mackiewicz and Ratajczak 1993).

By concurrent use of probabilistic and deterministic approaches, the processes responsible for groundwater quality deterioration were evaluated. The deterministic approach included traditional groundwater classification techniques. To investigate the suitability of groundwater for drinking, the standards by the World Health Organization

(WHO) were exercised. Additionally, the water quality index (WQI) was developed to score the combined influences of individual quality variables on the overall groundwater quality for human consumption. Finally, to assess the suitability of groundwater for agricultural activities, a hazard-based study of groundwater mineral compounds was conducted.

6.2.2. The Study Area

The 300 km² Shiraz basin lies in south-west Iran and is surrounded on the north and north-west by mountains. On the south, the basin is located at the vicinity of the 250-km² Maharloo Salt Lake, which has dominant water salinity compositions of sodium-chloride-magnesium and sodium-sulfate, see Fig. 6-1. The superficial plain of the study area ranges from 1400 m to 3100 m above mean sea level. The geological formation of the plain is characterized by shales and gypsiferous marls near the ground surface and with sandstone and conglomerate at depth. Based on 50-year recorded data, the average annual temperature for this plain is 18.2°C and the mean annual precipitation is 338 mm. The 106-mm minimum and 578-mm maximum annual recorded precipitations occurred in 1983 and 1995, respectively.

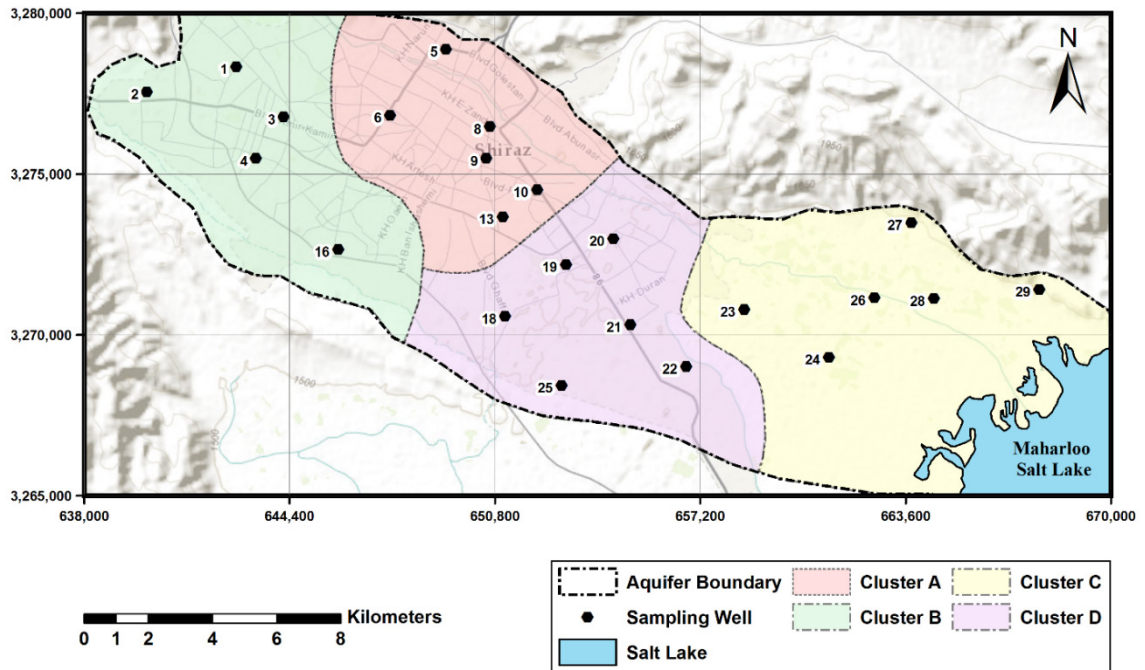


Figure 6-1. Study area

6.2.3. Groundwater Sampling Results

The conducted groundwater quality monitoring program in the Shiraz basin included a total of 310 samples collected from 23 wells during 2014. To determine the physicochemical parameters, all collected samples were tested per the standard methods (Apha 2012). The statistical summary of different quality parameters and major ions is presented in Table 6-1. All parameters were found to be non-normally distributed based on the calculated significance level less than 0.05.

Table 6-1. Descriptive statistics of the groundwater physicochemical parameters

Parameter	Unit	Mean	Median	Min	Max	St. Dev.
pH	-	7.6	7.4	6.9	9.8	0.7
TDS	mg/L	2324.1	1395.0	412.0	11800.0	2525.6
EC	μS/cm	3125.6	2064.0	596.0	10107	2660.7
TH	mg CaCO ₃ /L	1302.2	962.5	182.5	4950.0	1197.7
Ca	mg/L	228.3	183.6	40.8	688.5	172.2
Na	mg/L	304.5	132.9	21.8	3408.5	694
K	mg/L	7.0	3.9	1.0	41.6	9.4
Mg	mg/L	180.5	112.4	20.0	808.0	211.5
CO ₃	mg/L	2.9	0.0 ^a	0.0 ^a	28.5	6.9
HCO ₃	mg/L	424.4	396.6	131.2	732.2	185.4
SO ₄	mg/L	648.9	366.0	18.3	2945.7	747.7
Cl	mg/L	657.0	257.0	61.2	6859.6	1410.9

^a below detection limit

6.3. Analysis and Discussion

6.3.1. Multivariate Statistical Analysis

For probabilistic assessment of the groundwater, a multivariate statistical procedure was employed. The proposed approach, which includes correlation, cluster, and principal component analyses, is a controlling mathematical method for categorizing and interpreting large datasets in environmental monitoring programs (Liu et al. 2003). The numerical analyses performed in this section were conducted by using the statistical software SPSS (Statistical Package for Social Science, version 13.0). Within all analyses, variables were normalized to mean zero and unit variance to prevent misclassifications arising from different parameter scales.

6.3.1.1. Correlation Analysis

Correlation analysis is a technique to measure the relationship between chosen variables. The established coefficient, ranging from negative one to positive one, is the degree of the dependency in the same direction (positive values) or in the opposite direction (negative values) (Cohen et al. 2013). The Pearson product-moment correlation analysis, was applied to each pair of Shiraz groundwater quality parameters, see Table 6-2. As expected, a significant positive correlation was observed between total dissolved solids (TDS) and electrical conductivity (EC), which indicates that same underlying process has influenced both parameters. Also, TDS content exhibited high correlations with total hardness (TH), Ca, K, Mg, SO₄, and Cl, which identify as the main elements contributing to groundwater salinity. The TH value exhibited considerable positive correlations with Ca, Na, K, Mg, Cl and SO₄. It can be interpreted that the groundwater hardness is mainly due to saline compounds resulted from those elements (Udayalaxmi et al. 2010). Na and Cl possessed a considerable high positive correlation which suggests the dissolution of chloride salts within the study area (Belkhiri et al. 2011). High correlations between Cl and Ca, Na, K, and Mg refer to the dissolution of evaporites. Also, the observed high correlation between Cl and SO₄ indicates the impact of agricultural activities on the groundwater vulnerability (Dhanasekarapandian et al. 2016).

Table 6-2. Correlation matrix between the groundwater physicochemical parameters. Numbers in bold indicate significant statistical correlation at 0.05 level

	pH	TDS	EC	TH	Ca	Na	K	Mg	CO ₃	HCO ₃	SO ₄	Cl
pH	1.00											
TDS	-0.07	1.00										
EC	-0.06	0.99	1.00									
TH	-0.21	0.97	0.96	1.00								
Ca	-0.30	0.90	0.90	0.95	1.00							
Na	0.41	0.67	0.68	0.46	0.36	1.00						
K	-0.15	0.96	0.95	0.98	0.89	0.50	1.00					
Mg	-0.15	0.96	0.95	0.98	0.86	0.50	0.99	1.00				
CO ₃	0.92	-0.10	-0.09	-0.23	-0.29	0.35	-0.15	-0.18	1.00			
HCO ₃	-0.63	0.21	0.20	0.34	0.42	-0.31	0.26	0.27	-0.57	1.00		
SO ₄	-0.15	0.94	0.93	0.96	0.94	0.47	0.94	0.92	-0.17	0.16	1.00	
Cl	0.20	0.87	0.87	0.74	0.59	0.89	0.78	0.80	0.15	-0.02	0.67	1.00

6.3.1.2. Cluster Analysis

CA is a technique for classifying samples into a set of finite groups based on their specific similarities. The derived groups represent the overall correspondence of variables in the dataset, (Massart et al. 1983). There are two types of clustering: R-mode and Q-mode methods (Caliński and Harabasz 1974). The Q-mode method works to group similar samples, each containing the same number of variables. Whereas the R-mode method works to reduce the total number of variables by categorizing them into a smaller number. For the purpose of this study, the Q-mode hierarchical cluster analysis was performed to identify statistically distinct hydrochemical groups of sampling wells. To formulate the clustering approach, the Ward's algorithmic method was carried out (Ward Jr 1963). This method is based on the analysis of variance to split different clusters. To

measure the distance between clusters, the Euclidean distance method was employed (Davis and Sampson 1986). This approach organizes the dataset and represents the results with a dendrogram. As a result, four clusters (A, B, C, and D) were distinguished for the Shiraz aquifer, see Fig. 6-2. Cluster A, comprising 27% of sampling wells, mostly covered the center parts of the basin, adjacent to the urban areas. Cluster B included 23% of the wells and encompassed the northwest regions of the basin. Cluster C contained 23% of the sampling wells and expanded on the southeast areas of the basin, nearby the Salt Lake. Cluster D consisted of 27% of the samples and mostly covered the mid-south of the study area.

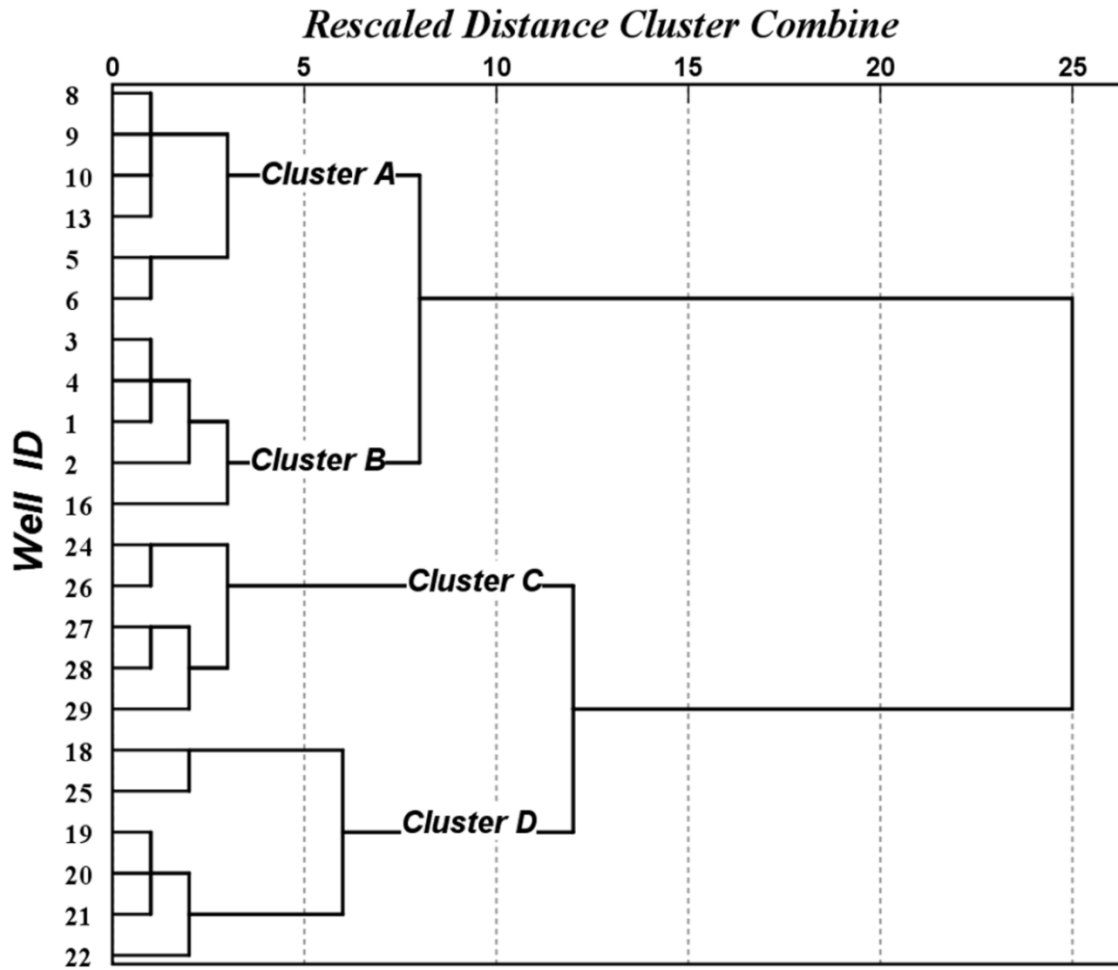


Figure 6-2. Hierarchical dendrogram cluster map for the sampling wells

6.3.1.3. Principal Component Analysis

To investigate the interrelationships among large groups of variables, the PCA can be applied (Jolliffe 2002). This technique identifies variables that are correlated with each other, and converts them into a limited number of uncorrelated components. The resultant components present a specific variance percentage of all studied variables with minimal information loss (Alberto et al. 2001). The overall characteristic of the dataset can be sufficiently described by considering the components with high variance percentages (loadings) (Bayo and López-Castellanos 2016). This approach can be formulated in five separate steps, as comprehensively described in literature (Ebrahimi et al. 2017).

For the Shiraz aquifer, the PCA was applied on the 12 physicochemical parameters to extract the principal components corresponding to different sources of variation. The Kaiser's rule of eigenvalues-greater-than-one and Varimax normalization method for orthogonal factor rotation, were used for this procedure (Kaiser 1974). As a result, two components were generated, which cumulatively accounted for 88.8% of initial dataset variance. Thus, with a minimal information loss of 11.2%, the 12 groundwater physicochemical parameters were reduced into two components, see Table 6-3.

The first component, accounting for 64.4% of the variance, contained absolute loading for TDS, EC, TH, cationic ions, SO₄, and Cl. This component can be considered as an indicator for natural weathering of the minerals (Belkhiri et al. 2011). The second component, which accounted for 24.4% of the total variance, comprised significant loadings for pH, CO₃, and HCO₃. This component can be labeled as an indicator for natural processes and water-rock interactions (Belkhiri et al. 2011). The orthogonal

rotation plots of the samples on the two principal factors, represented reasonable separations along the axes; see Fig. 6-3. High separation of data points from cluster C, indicates that hydrochemical variations of the samples within this cluster were greater than those from the other clusters. This can be attributed to the effect of the Salt Lake, located at the vicinity of cluster C. Also, the highest positive loadings of PC1, which contains high positive scores on the salinity related constituents, were observed for cluster C.

In conclusion, by considering the results from correlation and principal component analyses, along with hierarchical Q-mode cluster analysis, chloride salts dissolution was identified within the aquifer. More specifically, the areas adjacent to the Salt Lake were found to be potentially susceptible to groundwater salinization.

Table 6-3. Rotated component matrix with factor loadings (>0.4) ^a

Attribute	Principal Component	
	PC1	PC2
pH		0.93
EC	1.00	
TDS	1.00	
Ca	0.89	
Na	0.67	0.58
K	0.97	
Mg	0.96	
CO ₃		0.90
HCO ₃		-0.78
SO ₄	0.94	
Cl	0.87	
TH	0.97	
Eigenvalue	7.77	2.88
Initial Variance percentage (Loading)	64.37	24.39
Cumulative Variance percentage	64.37	88.76

^a. Rotation converged in 8 iterations

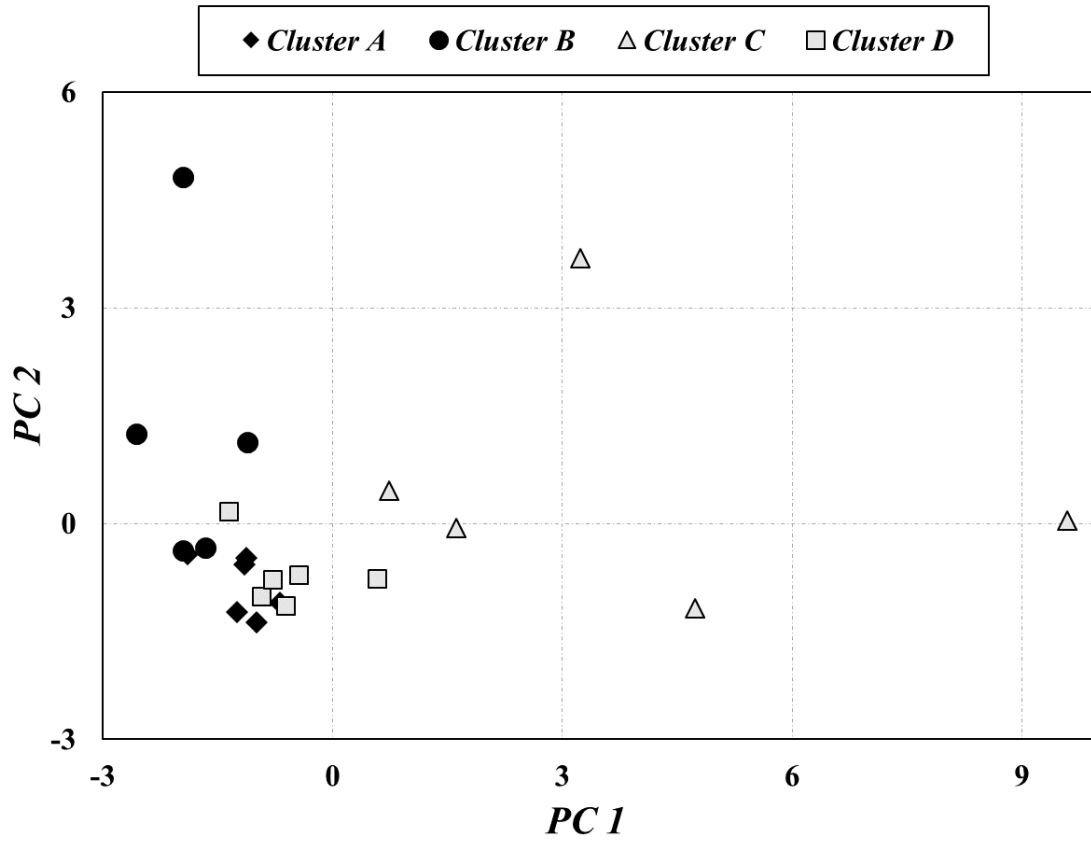


Figure 6-3. PCA scores from samples from different clusters

6.3.2. Groundwater Quality Assessment

The obtained results from the probabilistic approach in previous section were used as the basis for the deterministic assessment of the groundwater. This combined approach evaluates the groundwater's hydrochemical characteristics throughout the study area. Additionally, groundwater suitability potential for drinking and irrigation purposes was comprehensively weighed by developing a water quality index and a multi-hazard risk assessment.

6.3.2.1. Chemical Composition Assessment

Hydrogeochemical studies evaluate the processes responsible for groundwater quality vulnerability. Four different classification methods were selected to recognize hydrochemical types of groundwater. Each method was applied separately on the previously identified clusters within the Shiraz basin. To determine the groundwater ionic order, the average abundances of anion and cation concentrations were compared. To categorize the hydrochemical facies of water samples, the Domenico classification was considered (Domenico 1972). To graphically present the composition of major ions and relationships between the dissolved constituents, the Piper trilinear diagram was used (Piper 1944). Finally, to assess the chemical categories of groundwater samples, the Chadha diagram was analysed (Chadha 1999). Each of the aforementioned methods has been previously reviewed in detail by Ebrahimi et al. (2016).

The average ionic abundance of each individual well was calculated and then averaged for each cluster. For cluster A, the cationic and anionic compositions were found to be dominated by Ca and HCO₃, respectively, see Fig. 6-4. The dominant ionic variation within cluster B was determined as Na-Cl. Thus, the overall groundwater composition at west and center regions of the basin was characterized as Na-Ca-Cl-HCO₃. The samples from cluster C which depicted the Mg-SO₄ type water, showed the highest ion concentration abundances. Cluster D presented lower concentration fluctuations compared to cluster C, however it was also found to have the same dominant water type. Almost all magnesium related saline compounds may exist within the samples from cluster D.

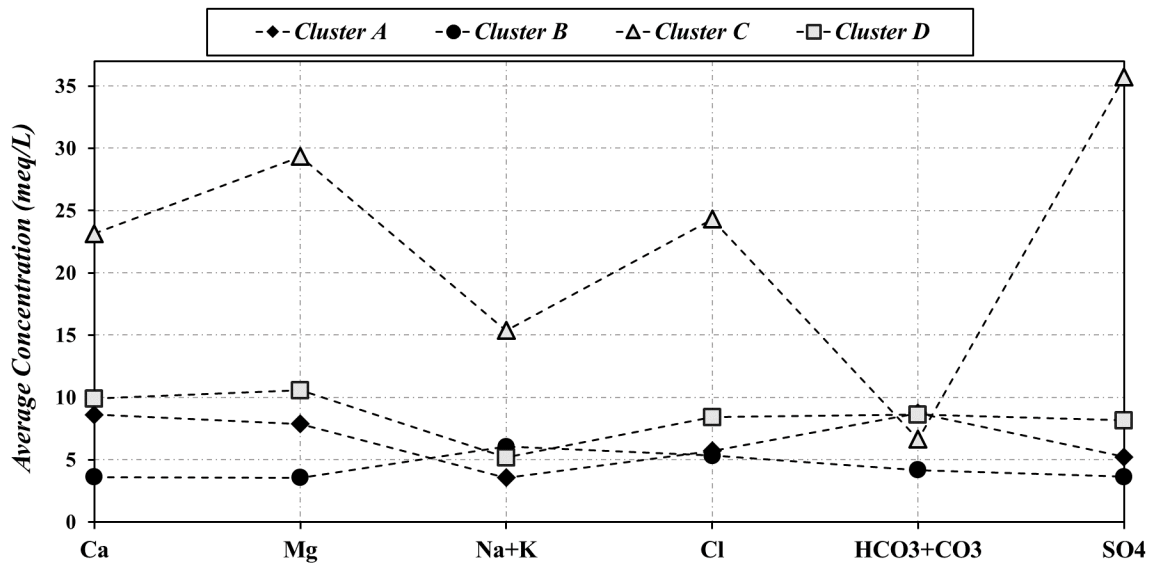


Figure 6-4. Average abundances of ions

Using the Domenico classification, the groundwater cationic facies in most parts of the study area were determined as Ca-Na, see Table 6-4. The Chloride-Sulfate-Bicarbonate was found as the major anionic facies of the groundwater throughout the basin. However, some wells within clusters A and C contained HCO₃-Cl-SO₄ and Cl-SO₄ type anionic hydrochemicals, respectively.

Table 6-4. Domenico Classification of groundwater hydrochemical facies

	Percentage of Constituents				Cluster			
	Ca+Mg	Na+K	HCO ₃ +CO ₃	Cl+SO ₄	A	B	C	D
Cation Facies								
Calcium-Magnesium (Ca-Mg)	90-100	0-10			17%	Nil	Nil	Nil
Calcium-Sodium (Ca-Na)	50-90	10-50			83%	60%	80%	100%
Sodium-Calcium (Na-Ca)	10-50	50-90			Nil	40%	20%	Nil
Sodium-Potassium (Na-K)	0-10	90-100			Nil	Nil	Nil	Nil
Anion Facies								
Bicarbonate (HCO ₃)			90-100	0-10	Nil	Nil	Nil	Nil
Bicarbonate-Chloride-Sulfate (HCO ₃ -Cl-SO ₄)			50-90	10-50	50%	20%	Nil	Nil
Chloride-Sulfate-Bicarbonate (Cl-SO ₄ -HCO ₃)			10-50	50-90	50%	80%	40%	100%
Chloride-Sulfate (Cl-SO ₄)			0-10	90-100	Nil	Nil	60%	Nil

Considering the Piper diagram, most of the sampling wells were characterized as Ca-Cl type water, see Fig. 6-5 and Table 6-5. However, Ca-Mg-Cl type water were found for 33% and 60% of the samples from clusters A and B, respectively.

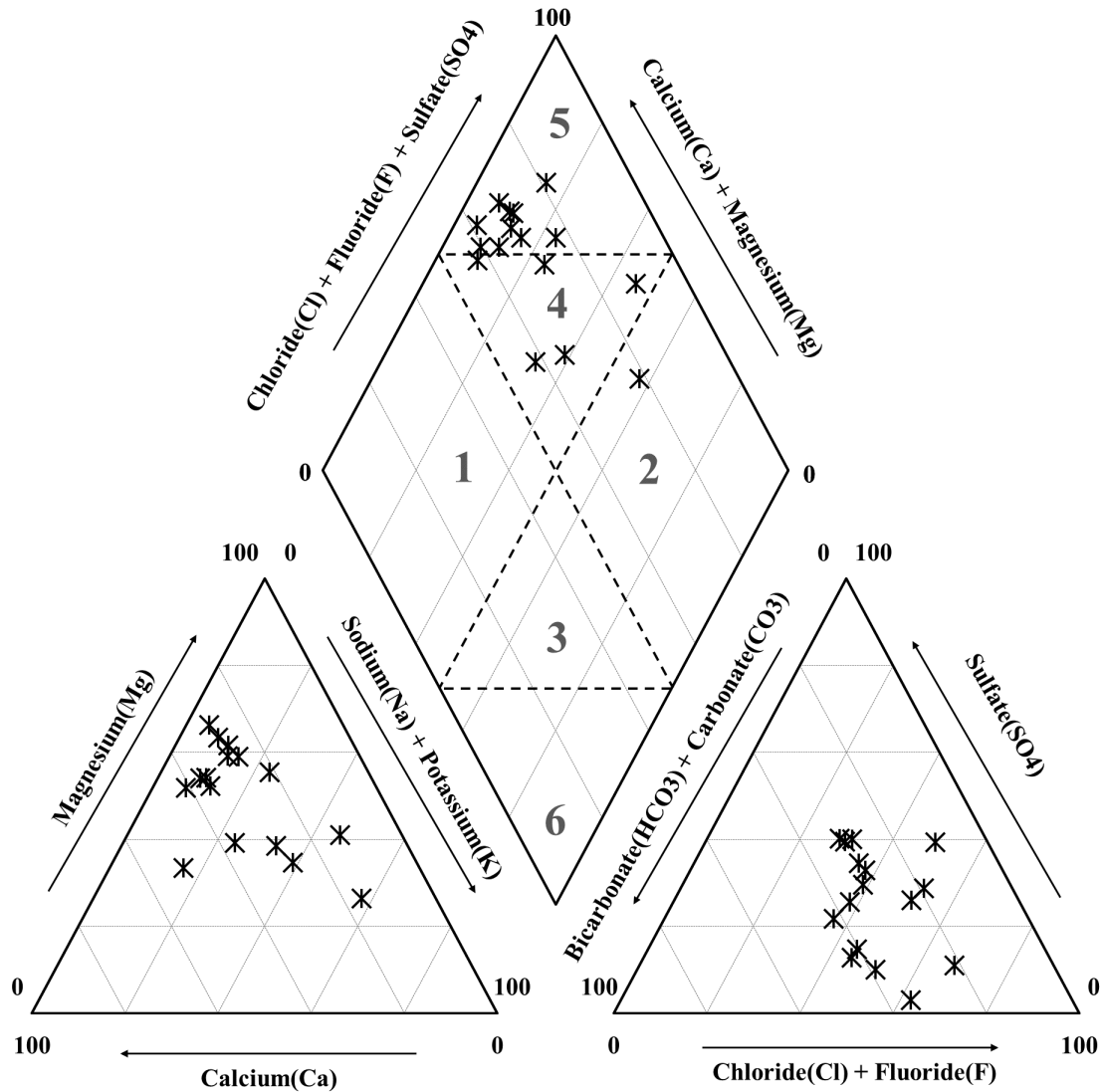


Figure 6-5. The Piper diagram of the samples

Table 6-5. Hydrochemical classification of groundwater based on the Piper diagram

Subdivision	Facies	Cluster			
		A	B	C	D
(1)	CaHCO ₃	Nil	Nil	Nil	Nil
(2)	Na-Cl	Nil	20%	Nil	Nil
(3)	Mixed Ca-Na-HCO ₃	Nil	Nil	Nil	Nil
(4)	Mixed Ca-Mg-Cl	33%	60%	Nil	Nil
(5)	Ca-Cl	67%	20%	100%	100%
(6)	NaHCO ₃	Nil	Nil	Nil	Nil

Considering the Chadha diagram, the Ca-Mg-Cl type water was observed for all the clusters, see Fig. 6-6 and Table 6-6. 50% of the samples for cluster A and 20% from cluster B fell under Ca-Mg-HCO₃ subdivision. Also, Na-Cl type water was confirmed for 40% and 20% of the samples within clusters B and C, respectively. In addition, it was concluded that for the groundwater constitutes in the Shiraz basin, alkaline earths exceeded alkali metals and strong acidic anions exceeded weak acidic anions.

In conclusion, from the aforementioned classification techniques, the overall groundwater chemical composition was found to mainly comprise chloride-based saline compounds.

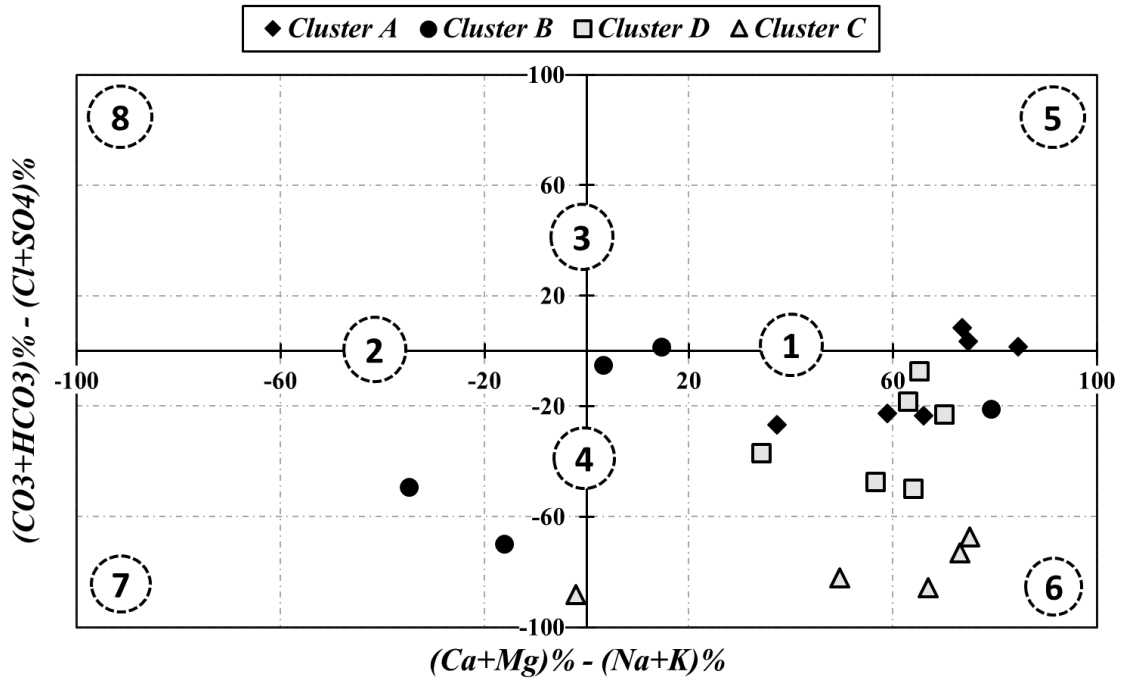


Figure 6-6. Chadha's hydrochemical classification diagram

Table 6-6. Hydrochemical classification of groundwater based on Chadha diagram

Subdivision	Classification	Cluster			
		A	B	C	D
(1)	Alkaline earths exceed alkali metals	Nil	Nil	Nil	Nil
(2)	Alkali metals exceed alkaline earths	Nil	Nil	Nil	Nil
(3)	Weak acidic anions exceed strong acidic anions	Nil	Nil	Nil	Nil
(4)	Strong acidic anions exceed weak acidic anions	Nil	Nil	Nil	Nil
(5)	Ca-Mg-HCO ₃	50%	20%	Nil	Nil
(6)	Ca-Mg-Cl	50%	40%	80%	100%
(7)	Na-Cl	Nil	40%	20%	Nil
(8)	Na-HCO ₃	Nil	Nil	Nil	Nil

6.3.2.2. Drinking Water Quality Assessment

To investigate the suitability of groundwater for human consumption, major water quality constituents should be inspected for their compliance with pre-established standards. For the Shiraz basin the standards defined by the World Health Organization (WHO 2011) was used, see Table 6-7. Also, to identify the sources of contamination, as well as the contaminant transport pattern across the study area, the spatial distributions of water quality parameters were studied using GIS-based variograms, see Fig. 6-7.

Table 6-7. Assessment of groundwater drinking suitability based on the WHO standard

Parameter	WHO Standard	Samples Range	% samples exceeded the limit			
			Cluster			
			A	B	C	D
pH	6.5 - 8.5	6.9 - 9.8	Nil	20%	20%	Nil
EC ($\mu\text{S}/\text{cm}$)	1500	596 - 10107	83%	20%	100%	100%
TDS (mg/L)	1000	412 - 6885	83%	20%	100%	100%
TH (mg/L)	500	182.5 - 4950	100%	20%	100%	100%
Cl (mg/L)	250	61.1 – 1648.4	17%	20%	80%	67%
Na (mg/L)	200	21.8 – 740.2	Nil	Nil	40%	50%
SO ₄ (mg/L)	250	18.2 – 2945.7	50%	80%	40%	83%

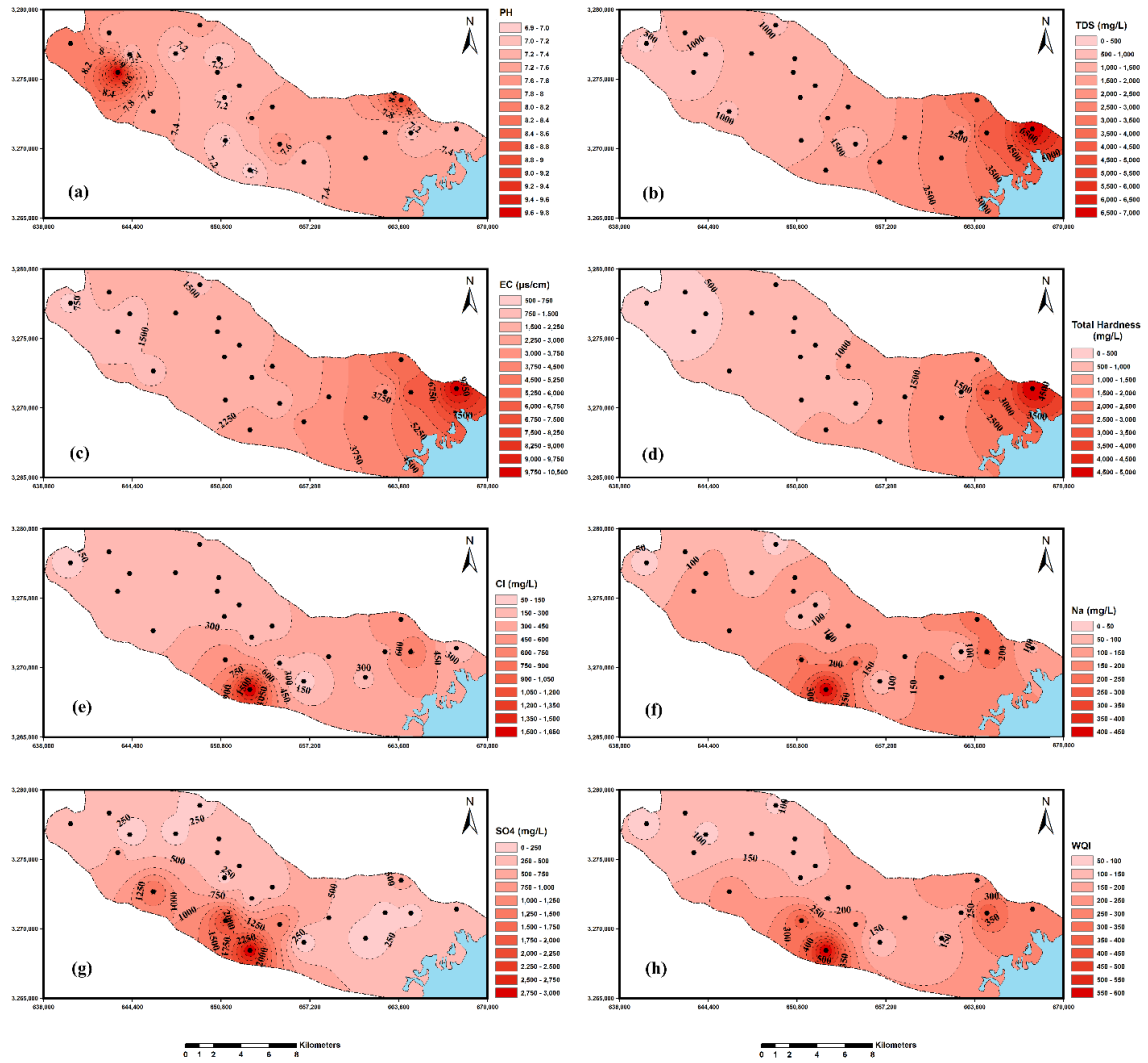


Figure 6-7. Spatial distribution of quality parameters within the study area. (a) pH, (b) TDS, (c) EC, (d) TH, (e) Cl, (f) Na, (g) SO₄, and (h) WQI

Analysis of the results from Table 6-7 revealed high non-compliance with the standard limits within clusters C and D. Most of the observed pH values fell within the recommended range. From the taste aspect, the WHO restricts the consumption of water with a TDS content higher than 1000 mg/L. Also, high TDS concentrations may result in scale formations in household appliances and water pipes. The majority of the studied samples exhibited TDS values greater than the recommended limit. Same results were observed for EC content. EC values greater than 3000 $\mu\text{S}/\text{cm}$ indicate enrichment of salts in the groundwater, which were observed for clusters C and D, see Fig. 6-7(c).

The WHO has specified a maximum allowable limit of 500 mg/L for TH in drinking water. Almost all samples showed TH values higher than 300 mg/L. Thus, they can be classified as hard water type, which has corrosion potential for distribution systems. The WHO has proposed 250 mg Cl/L, as the taste threshold. The groundwater of mid-south and southeast regions, contained Cl values higher than the recommended limit. High observed Cl concentrations within those areas confirm the previous assumption of groundwater salinization. As for the sodium value, same results were interpreted. High SO_4 concentrations, mainly observed in center and southeast parts of the basin, see Fig. 6-7(g), can cause a laxative effect in water consumers.

6.3.2.3. Groundwater Quality Index

The WQI is a dimensionless number that cumulatively expresses the quality of an aggregated set of measured physiochemical parameters from different samples in a given area (Hallock 2002). The lesser values indicate that the quality of water is more adapted with the pre-established standards proposed by the WHO. The established WQI, as a variable indicator, enables decision makers to distinguish different groundwater sources based on their suitability for drinking purposes (Bordalo et al. 2006).

For all sampling wells within the Shiraz basin, the WQI was calculated based on the method proposed by Yidana et al. (2010). All parameters (n) were assigned a weight (wi) on a scale of 1 to 5, based on their influence on drinking water quality and human health, see Table 6-8. The relative weight value (Wi) and the quality rating scale (qi) for each parameter were calculated using equations 1 and 2, in which Ci and Si are the measured concentration and the WHO standard for each parameter, respectively. Finally, the WQI for an individual well was then expressed as the sum of the sub-index (SIi) of all parameters by using equations 3 and 4.

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (1)$$

$$q_i = \frac{C_i}{S_i} \times 100 \quad (2)$$

$$SI_i = W_i \times q_i \quad (3)$$

$$WQI = \sum_{i=1}^n SI_i \quad (4)$$

Table 6-8. Relative weight of groundwater quality parameters

Parameter	Assigned weight (wi)	Relative weight (Wi)
pH	2	0.08
TDS (mg/L)	5	0.2
TH (mg/L)	5	0.2
Ca (mg/L)	2	0.08
Na (mg/L)	3	0.12
SO ₄ (mg/L)	4	0.16
Cl (mg/L)	4	0.16
	$\sum w_i = 25$	$\sum W_i = 1$

The groundwater can be categorized into five classes based on the calculated WQI, see Table 6-9 (Sahu and Sikdar 2008). For the Shiraz basin, the computed indexes ranged from 80 to 661, with an average value of 251, see Fig 6-7(h). It can be interpreted that for the clusters A and B, located further from the Salt Lake, none of the samples exhibited unfit quality for drinking. While all samples from the cluster C, and 83% of the sampling wells from the cluster D, were determined to have water with very poor to unpotable quality. For the wells located at the vicinity of the Salt Lake, the water quality was significantly degraded. However, for those located at the north or west parts of the basin, the suitability of groundwater remained in acceptable conditions.

Table 6-9. Classification of groundwater drinking suitability based on the WQI

WQI	Description	Cluster			
		A	B	C	D
<50	Excellent	Nil	Nil	Nil	Nil
50-100	Good	Nil	40%	Nil	Nil
100-200	Poor	83%	40%	Nil	17%
200-300	Very Poor	17%	20%	40%	50%
>300	Unfit for Drinking	Nil	Nil	60%	33%

6.3.2.4. Agricultural Water Quality Assessment

The most important factor affecting the suitability of groundwater for agricultural applications is the salinity level (Todd and Larry 2005). The presence of saline compounds in irrigation water can highly corrode the soil structure and its vegetation capability. To have an overall assessment regarding the suitability of the groundwater for agricultural activities in the Shiraz aquifer, the Wilcox diagram (Wilcox 1948) was used, which considers the combined effect of sodium percentage and electrical conductivity values, see Fig. 6-8. Most of the sampling wells from clusters A and B were categorized as good to permissible water types. All samples from cluster C were found to be unsuitable for irrigational activities. While, most of the samples from the cluster D were classified as doubtful water. Thus, it can be concluded that the irrigation quality of groundwater within the Shiraz basin was partially degraded.

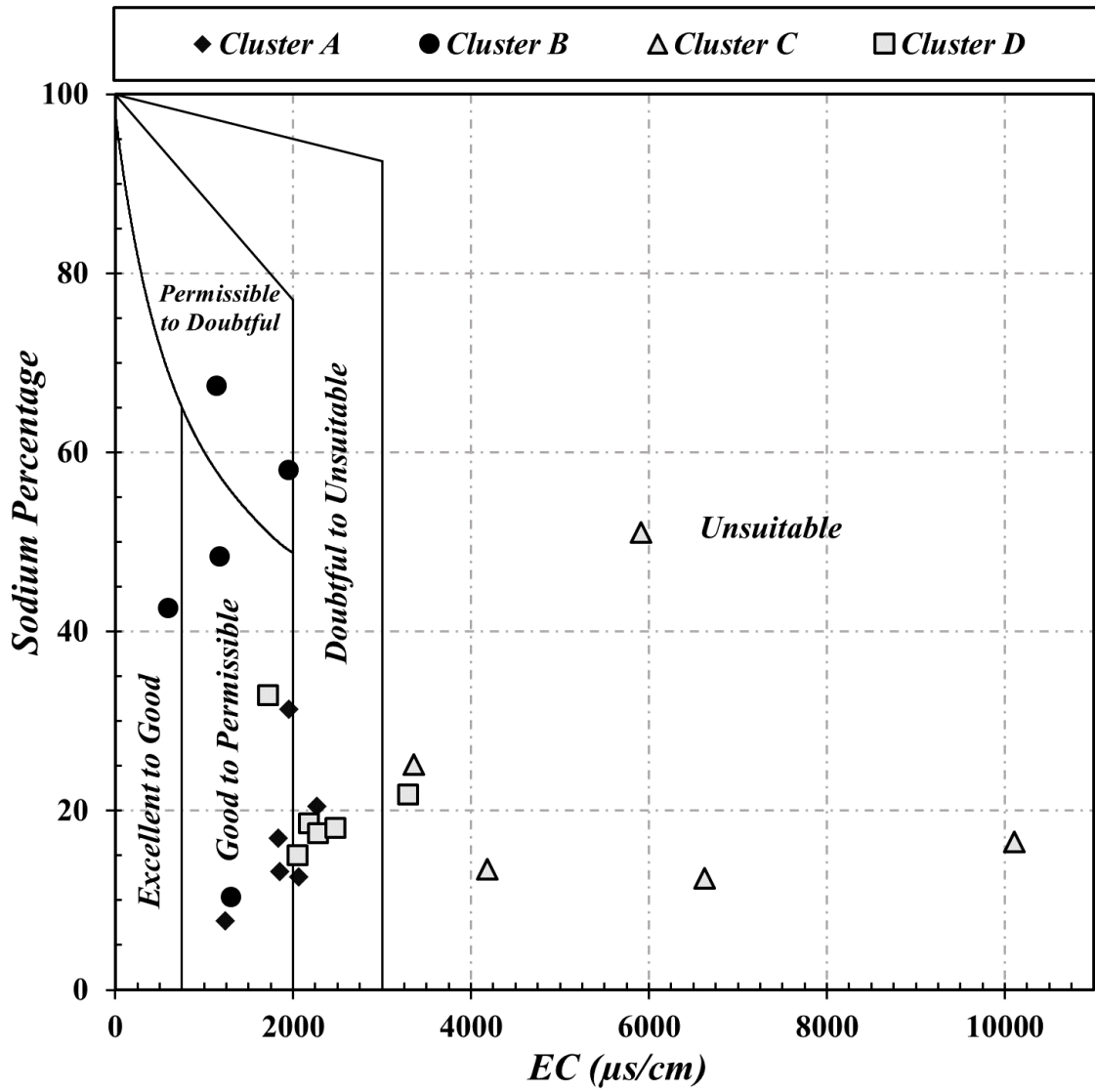


Figure 6-8. Chadha's hydrochemical classification diagram

6.3.2.5. Multi-Hazard Risk Assessment

The mineral compounds have an essential role on the groundwater's agricultural applicability potential. Hazardous levels of different quality indicators, including salinity, sodium, alkalinity, lime deposition, bicarbonate, and chloride, can prohibit cultivation of crops sensitive to saline water. Also, it may even lead to further adverse impacts, such as lower rates of soil permeability, plugging of irrigation systems, and foliar burns (Ebrahimi et al. 2016). Thus, it is necessary to further investigate the effects of mentioned indicators. As a result, a methodical approach was developed to evaluate the hazard potentials associated with high levels of various quality indicators. For the Shiraz basin, the proposed multi-hazard risk assessment was applied, see Table 6-10.

Table 6-10. Irrigation based multi-hazard risk assessment

Parameter	Range	Hazard Potential	Cluster A	Cluster B	Cluster C	Cluster D	
Salt	EC < 0.25	TDS < 160	Very Low	Nil	Nil	Nil	Nil
	0.25 - 0.75	160 - 480	Low	Nil	20%	Nil	Nil
	0.75 - 2.0	480 - 1280	Medium	50%	60%	Nil	17%
	2.0 - 3.0	1280 - 1920	Mid-High	50%	20%	Nil	67%
	> 3.0	> 1920	High	Nil	Nil	100%	16%
Sodium (based on sodium percentage)	Na% < 20		Very Low	67%	20%	60%	67%
	20 – 40		Low	33%	Nil	20%	33%
	40 – 60		Medium	Nil	60%	20%	Nil
	60 – 80		Mid-High	Nil	20%	Nil	Nil
	> 80		High	Nil	Nil	Nil	Nil
Sodium bicarbonate	RSC < 0		Low	100%	100%	100%	100%
	0 - 1.0		Medium	Nil	Nil	Nil	Nil
	1.0 - 2.5		High	Nil	Nil	Nil	Nil
	> 2.5		Very High	Nil	Nil	Nil	Nil
	Alkalinity	SAR < 10		Low	100%	100%	100%
10 – 18			Medium	Nil	Nil	Nil	Nil
18 – 26			Mid-High	Nil	Nil	Nil	Nil
> 26			High	Nil	Nil	Nil	Nil
Chloride		Cl < 70		Low	Nil	Nil	Nil
	70 - 140		Medium	Nil	20%	Nil	Nil
	140 - 350		Mid-High	100%	80%	40%	50%
	> 350		High	Nil	Nil	60%	34%
	Bicarbonate	HCO ₃ < 1.5		Low	Nil	Nil	Nil
1.5 - 7.5			Medium	33%	100%	60%	33%
> 7.5			High	67%	Nil	40%	67%
Lime Deposition		mg Lime/L < 2		Low	Nil	Nil	Nil
	2.0 - 3.0		Medium	Nil	Nil	Nil	Nil
	3.0 - 4.0		Mid-High	Nil	60%	40%	Nil
	> 4		High	100%	40%	60%	100%

All samples from cluster C, located at the vicinity of the Salt Lake, were classified as high saline water and not suitable for irrigation. This confirmed the obtained results from analyzing the Wilcox diagram. Also, medium to medium-high salinity was observed in other parts of the basin. These water types are not suitable for sensitive plants to saline compounds. Considering the sodium percentage (Na%), most of the samples were identified to have very low to low sodium hazards. While, samples from cluster B fell under the range of medium to medium-high hazard classes. High levels of sodium in irrigation water can limit soil's permeability (Raju 2007).

Using the residual sodium carbonate (RSC) content, identified low sodium hazard for all sampling wells. Thus, monitoring the infiltration rates and soil's pH level would not be necessary (Hopkins et al. 2007). Analyzing the sodium absorption ratio (SAR), all samples were categorized as low alkalinity hazard classes. Considering the Cl content, majority of the sampling wells were classified as medium-high chloride hazard. Irrigation with these water types can result in foliar burns on crops. Also, high chloride hazard classes were determined for 60% and 34% of the samples from clusters C and D, respectively. Thus, the assumption of groundwater salinization within those regions of the study area can be confirmed. Irrigation with high-chloride water, can lead to significant negative impacts on agricultural products.

Finally, potential of plugging in irrigation systems was evaluated by using the lime deposition index. Almost all samples showed medium-high to high lime deposition hazard risks. The irrigation limit of 0.5 cm/hr is suggested for these water sources, provided that low evaporation rates exist (Hopkins et al. 2007).

6.3.3. Comparison with Previous Studies

To further present the practicality of the proposed methodology, the overall dynamic of the groundwater quality in the Shiraz basin was compared with two previously studied basins with similar aquifers and lithology of rocks, and under similar climate conditions. The groundwater quality conditions of the Kashan basin located at central Iran (Baghvand et al. 2010; Jamshidzadeh and Mirbagheri 2011), and the Damghan basin located at north-east of Iran (Ebrahimi et al. 2016), were re-analyzed based on the performed methodology in this study, see Table 6-11. First, the chemical composition of each basin was investigated by using the Piper diagram. Then, the suitability of groundwater for drinking purposes was determined based on the developed WQI. Finally, the suitability of groundwater for agricultural applications was assessed by considering the Wilcox classification.

According to the Piper cataloging, most of the groundwater samples within the Shiraz and Damghan basins exhibited the Ca-Cl and Mixed Ca-Mg-Cl type hydrochemical facies. While, for the Kashan aquifer, the Na-Cl type water was found to be dominant. It can be inferred that chloride type saline compounds largely contributed to the groundwater chemical composition in all studied cases.

By developing the WQI, similar drinking water quality was observed for the Shiraz and Damghan basins. Within both aquifers, approximately 25% of the samples were found to be unfit for drinking. However, the groundwater quality within the Kashan basin were determined to be significantly degraded compared to those from the other two basins. More than half of the groundwater resources from the Kashan basin did not meet the

quality limitations and were categorized as unpotable water. One of the benefits of using WQI method is the ease of comparing the overall drinking quality of groundwater across several basins, which was presented here. Based on the Wilcox classification, the groundwater within the Shiraz basin was determined to be more suitable for irrigation compared to those of the other two basins. Similar to the WQI results, the Kashan basin was found to be the most degraded basin and approximately 70% of its samples were determined as unsuitable for agricultural applications.

The overall obtained groundwater quality results agree with the identified hydrochemical facies. Although groundwater types from all the basins were affected by the Cl compounds, the one with dominant Na-Cl type (Kashan basin) were found to be the most degraded, possibly due to extreme saltwater intrusion into this aquifer as reported by Jamshidzadeh et al. (2011).

Table 6-11. Overall groundwater quality assessment for three different basins

Evaluation step	Classification	Shiraz basin	Damghan basin	Kashan basin
Hydrochemical Facies: Piper	CaHCO ₃	Nil	Nil	Nil
	Na-Cl	Nil	33%	71%
	Mixed Ca-Na-HCO ₃	Nil	Nil	29%
	Mixed Ca-Mg-Cl	27%	40%	Nil
	Ca-Cl	73%	27%	Nil
	NaHCO ₃	Nil	Nil	Nil
Drinking based assessment: WQI	Excellent	Nil	Nil	Nil
	Good	9%	Nil	Nil
	Poor	36%	46%	10%
	Very Poor	32%	27%	33%
	Unsuitable	23%	27%	57%
Agriculture based assessment: Wilcox	Excellent	4%	Nil	Nil
	Good	33%	Nil	9%
	Permissible	9%	33%	5%
	Doubtful	27%	27%	19%
	Unsuitable	27%	40%	67%

6.4. Summary and Conclusions

This study demonstrated the effectiveness of combined consideration of deterministic and probabilistic approaches for a robust groundwater quality evaluation. Application of the probabilistic approach, which included multivariate statistical analysis, provided a classification scheme for categorizing the physiochemical properties of aquifer. Further application of the deterministic approach, which was built upon the obtained results from the conducted probabilistic analysis, led to comprehensive evaluation of the groundwater quality. The developed multi-hazard-based procedure was found to be an inclusive tool for irrigation groundwater risk assessment. Additionally, the water quality index proved to be an effective method for assessing the overall drinking quality of groundwater. By using a consistent criterion, this methodology was found to be specifically suitable for

comparing the overall groundwater quality conditions across different aquifers or for a temporal assessment within one.

Application of the proposed methodology on a basin with arid climate, identified chloride based saline compounds throughout the aquifer. The results indicated that less than a third of sampling wells contained potable water and only half of the study area comprised suitable groundwater for irrigation. Finally, the overall groundwater quality condition of this case study was compared with those from two other basins located in similar arid regions. It was concluded that the studied groundwater resources were prone to quality degradations, possibly due to salinization. The presented methodology in this study provides the environmental analysts and governmental decision makers with a comprehensive tool for evaluation of current and future quality conditions within any given aquifer.

CHAPTER SEVEN. SUMMARY AND RECOMMENDATION

The main focus of this research study was to develop an analysis methodology for water related infrastructure systems that would balance the long-term needs of society while protecting environmental resources. For this line of research, many studies and analyses were conducted on wastewater treatment plants and aquifer systems.

In the field of wastewater systems, this study demonstrated procedures and methods to incorporate the temporal variability of data in the effluent evaluation and optimization assessments. Primarily, the research focused on evaluating the wastewater's make-up, transforming the laboratory results into practical information for decision makers, and temporal performance assessment of the systems. By using multivariate data analyses and statistical techniques, a robust overarching methodology was developed for monitoring the performance of full-scale wastewater treatment plants, assessing the temporal and spatial changes of water quality by introducing wastewater quality index, discovering the important relationships among the monitored parameters through descriptive data analysis, and establishing the numerical expressions for predicting the significant properties of the influent and effluent of the treatment plants. The proposed methodology was successfully applied on the "Floyds Fork Water Quality Center" in Louisville, KY. The proposed procedure can be summarized in the following seven steps:

1. Developing the wastewater quality index (WWQI) for influent and effluent streams considering the regional discharge standards and the results of the wastewater monitoring programs.
2. Categorizing the overall flow conditions over the time and, evaluating the treatment process effectiveness by comparing the calculated influent and effluent indexes.
3. Conducting the principal component analysis for all measured quality and quantity variables.
4. Evaluating the overall variation of influent and effluent organic loadings, ion activities, oxygen demanding, and nutrient loading characteristics considering the fluctuation of calculated components' scores.
5. Determining the interrelationship level between the measured data by conducting Pearson product correlation analysis. Consequently, identifying the most highly correlated variables with initial indices like BOD, COD, phosphorus, nitrogen, WWQI, etc.
6. Developing predictive models, using a multivariate regression technique, for initial parameters considering the highly-correlated variables as the predictors.
7. Verifying the accuracy of produced models in terms of fitting with the training and testing data.

The information learned from the temporal performance assessment of treatment plants was extended to other industrial wastewater treatment systems. The main objective of conducting such studies was to optimize the wastewater treatment processes to obtain higher efficiency, lower operational costs, and less negative environmental impacts.

Thus, to identify the most appropriate operating configurations resulting in a sustainable setup for the full-scale plants, the studies were continued for conducting a systematic big-data analysis on the obtained results from full-scale or laboratory-scale plants. Achieving higher removal efficiency, lower sludge production, and increased bio-gas generation was the main objective for all cases.

Specifically, the study first examined the novel application of a combined system for treatment of high strength industrial wastewater. By conducting individual experiments and through a stepwise data analysis, the optimal operational conditions were identified, which led to maximum overall COD concentration reduction as well as high methane gas production rates. As a result, the examined hybrid system was recommended for the treatment of high strength industrial wastewater.

In another case study, a step by step analysis was performed to optimize the performance of a contact stabilization process for secondary treatment of petroleum refinery wastewater. The focus of this study was to identify the optimal operational conditions, in terms of applied aeration rates and recycling sludge flows, which can ensure the concurrent occurrences of maximum pollutant removal performance and minimum sludge production. Considering the results from this study, the contact stabilization activated sludge process was suggested as an effective alternative for secondary treatment of wastewater generated from petroleum refineries.

In the field of aquifer systems, the study demonstrated a procedure for evaluating groundwater quality deterioration due to excessive withdrawal rates and saltwater intrusion. The main objective was to present a baseline for temporal control on the recharge and discharge cycles for basins located in arid areas. To provide true temporal

groundwater quality assessment, a comprehensive study was performed by considering a wide range of quality indicators for both drinking and irrigation uses and by investigating the long-term quantity depletion. The proposed methodology combined the probabilistic and deterministic approaches. Application of the probabilistic approach, which included multivariate statistical analysis, provided a classification scheme for categorizing the physiochemical properties of aquifer. Further application of the deterministic approach, which was built upon the obtained results from the conducted probabilistic analysis, led to comprehensive evaluation of the groundwater quality. The developed multi-hazard based procedure was found to be an inclusive tool for irrigation groundwater risk assessment. Additionally, the water quality index proved to be an effective method for assessing the overall drinking quality of groundwater. By using a consistent criterion, this methodology was found to be specifically suitable for comparing the overall groundwater quality conditions across different aquifers or for a temporal assessment within one.

Overall, the research study used multivariate data analysis algorithms to identify the inherent structure of the wastewater and groundwater physicochemical characteristics from various treatment plants and aquifer systems. The methodologies described herein can provide a scientific basis for a robust control system on the performance of any treatment plant and/or aquifer systems. Also, the presented methods can be used to effectively manage water quality monitoring programs, in both wastewater and groundwater fields, while reducing the number of quality parameters which must be routinely measured and also controlling the quality of sampling efforts and measurements. The presented methodologies in this research study provide the environmental analysts and governmental decision makers with a comprehensive tool for

evaluation of current and future quality conditions within any given environmental system.

Recommendations for future work

The developed methodologies in this study for assessing the temporal performance of wastewater and groundwater systems can be upgraded and transferred to the broader arena of civil infrastructure systems. It would be beneficial to continue the primary research agenda described in this research study for optimization and performance assessment of other environmental infrastructures by using multivariate data analysis and simulation.

Also, to perform the aforementioned studies with the objective of optimization of systems, the main focus could be on the simulation and scenarios analyses by using different simulator software packages. To accomplish this, a step-by-step approach can be summarized as:

- 1- Setting up the physical, biological, and chemical layouts of the system
- 2- Defining the dimension of different physical units
- 3- Inserting the input quantitative and qualitative data like flow rate, COD, TP, NH, and TSS,
- 4- Assigning the control data measurements like DO concentration of aeration tanks, nutrient concentration of chemical dosing stages, and recycled activated sludge rates
- 5- Evaluating the constructed model for hydraulic mass balance

- 6- Calibration phase: developing a robust methodology is required for calibrating the physical, chemical, and biological models by considering both steady and dynamic simulation states
- 7- Scenario Analysis: to obtain the desired management strategies, there is a need to introduce a model-based optimization and scenario analysis platforms
- 8- Cost Analysis phase: evaluating the associated costs from different performed scenarios

The results from conducting those researches can also be used as a framework or guideline to assist decision-makers in considering economic and environmental aspects for designing civil and environmental infrastructures.

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