

جامعة ميدأوشن

كلية الإدارة

قسم / ماجستير إدارة . . المخاطر



تأثير زيادة تركيز الكبريتات عن الحد المسموح على أداء عمليات معالجة مياه الصرف الصحي: بالتطبيق على
شركة مرافق في مدينة ينبع الصناعية

إعداد الطالب/

هتان أبو بكر قطب

242000312

إشراف/

د. الفصيل عبد الحميد

د. فايز جراد

العام الدراسي:

٢٠٢٥



MIDOCEAN UNIVERSITY

College of Management

Department/ Master of Risk Management

**The Effect of Increasing Sulfate Concentration Above the Permissible Limit on the Performance
of Wastewater Treatment Process: Applied to Marafiq Company in Yanbu Industrial City**

Prepared by/

Hattan Abubaker Qutob

242000312

Supervised by/

D. AL Faisal Abdulhameed

D. Faiz Jarad

Year:

2025

Table of Contents

List of Tables:	- 5 -
Table of Figures:	- 6 -
Abstract.....	- 7 -
CHAPTER ONE: Introduction	- 10 -
Introduction:.....	- 11 -
Research Problem:	- 12 -
Importance of the Research:	- 13 -
The Goal of Research:.....	- 14 -
Research Question:	- 15 -
Research Hypotheses:	- 16 -
Study Model:	- 17 -
CHAPTER TWO: Literature Review	- 18 -
Introduction:.....	- 19 -
Previous Studies:	- 20 -
Process inhibition by sulfate salinity:	- 20 -
Favorable conditions for Sulfate-Reducing Bacteria (SRB) growth:	- 20 -
Theoretical Framework:	- 22 -
Consequences of SRB presence in biological nutrient removal plants:	- 22 -
CHAPTER THREE: Research Methodology	- 24 -
Introduction:.....	- 25 -
Research Methodology:	- 26 -
Ways of Research:	- 27 -
Research Tools:.....	- 28 -
Research Limitation:.....	- 29 -
CHAPTER FOUR: Practical Study	- 30 -
Introduction:.....	- 31 -
Data Gathering:	- 32 -
Data provided by Marafiq:	- 32 -
Data Provided by Royal Commission:.....	- 33 -
Data provided by Concern Site:.....	- 34 -
Comparison of data:	- 36 -
Sulfate Load Calculation from Concern Site:.....	- 36 -
Effects of higher Sulfate content in Concern site effluent to Marafiq:	- 37 -

Scenario analysis	- 39 -
Definition of the scenarios	- 39 -
Method of interpretation	- 40 -
Simulation Results:	- 43 -
Verification of material of construction	- 47 -
Plastic materials.....	- 47 -
Equipment in stainless steel	- 47 -
Equipment in carbon steel	- 48 -
Conclusion and Recommendations	- 50 -
REFERENCES	- 53 -
List of References:	- 54 -

List of Tables:

Table #	Description
4.1	Sulfate at Marafiq Inlet
4.2	Sulfate Analysis by RC
4.3	Sulfate at Concern Site Outlet
4.4	Effect on Marafiq of higher Sulfate Content in Concern site Effluents
4.5	Current and Hypothetical Sulfate Conditions (mg SO ₄ -2 /l)
4.6	Wastewater characterizations and operational parameters for IWTP-II modelling

Table of Figures:

Figure #	Description
4.1	Marafiq Sulfates Results
4.2	RC Sulfates Results
4.3	Concern site Sulfate Results
4.4	Simulation 1 (SO ₄₂₋ spike: A → A ₁ → A)
4.5	Simulation 2 (Occurrence of medium SO ₄₂₋ levels both in stable and spike conditions: A → B → B ₁ → B)
4.6	Simulation 3 (Occurrence of high SO ₄₂₋ levels both in stable and spike conditions: A → C → C ₁ → C)
4.7	Simulation 4 (Occurrence of high Cl ⁻ concentration, 1200 mg/L from day 5, and spike SO ₄₂₋ condition: A → A* → A ₁ * → A*):

Abstract

The study has addressed two scenarios additional to that of the present situation, namely:

1. increase to 800 mg/l sulfate from Concern site, keeping unvaried the sulfate load from other industries
2. 800 mg/l sulfate for all industries discharging to Marafiq.

The review of available data provided by Royal commission, Marafiq, Concern site was carried out to assess the present situation; the study was actually performed based on data from Marafiq because of their greater frequency and because are providing a slightly higher concentration of sulphates than data from other entities.

The analysis of data pertaining the present situation highlight that:

- The streams from Concern site is, on average, exceeding the figure of 150 mg/l for sulfate:
- The blended contribution from all other industries within the Yanbu Industrial city area is also exceeding the allowed figure for sulfate:
- Peak of sulfate concentration in Concern site effluent didn't occur, and vice-versa. When peak from single industries is detected, no peak is observed the stream incoming and out-coming the Marafiq:
- When peak of sulfate in the blended stream entering Marafiq happened, concentration in streams from Concern city were below the peak value. Therefore, peak in the blended stream entering Marafiq were determined by other industries. Moreover, in such events, the final effluents from Marafiq didn't show any peak. It means that the well operated Marafiq demonstrate the capability to handle short duration spikes:
- Increase in the sulfate concentration (on average about 100 mg/l) is observed between the inlet and the outlet of Marafiq. This is explained by the injection of chemicals inside Marafiq process scheme. Higher increase in sulfate concentration (> 400 mg/l) are observed. This is explained by the injection of Sulphuric acid for the operation of the Fenton Oxidation Process inside Marafiq, which take place unfrequently (2-3 times per month).

The alternative scenario, when Concernsite is discharging at 800 mg/l sulfate, is expected to determine, at the inlet of Marafiq, a concentration in the blended stream of about 400 mg/l, assuming unvaried flow rate and concentration of sulfate in the streams from other industries. Considering the current average injection of sulfate inside Marafiq, in this scenario, the concentration of sulfate in the effluent

from Marafiq is not expected to exceed the figure of 600 mg/l. In case of the Fenton Oxidation Process is operated, exceeding of the allowed figures may be expected.

The alternative scenario, when all industries are discharging at 800 mg/l sulfate, will determine an exceed of the allowed figure of 600 mg/l in the final effluent from Marafiq.

As to the effect of the increasing concentration of sulfate fed to the process performances of the biological section of Marafiq, the above two alternative scenarios were studied and a mathematical model was utilized to verify the potential interference between the NRB (Nitrate Reducing Bacteria) and the SRB (Sulphate Reducing Bacteria); to make sure that in the existing plant configuration where a nitrification and de-nitrification process is established, the potential increase of the incoming sulfate would not provide the environment for the proliferation of the SRB bacteria at the expenses of the NRB bacteria, with that reducing if not deactivating the nitrification and de-nitrification process.

The first case study, where only Concern site were disposing waste water at 800 mg/l sulfate, while the other industries were maintaining their present quality and quantity of disposals, can be handled by the biological section of Marafiq. SRB bacteria can be present in the biological environment but their effect is considered of low impact.

The second case study, where the average concentration of sulfate entering Marafiq was set at 800 mg/l is providing a certain concern: SRB bacteria can be present in higher quantity and serious impact on the biological section of Marafiq is expected, unless dedicated pilot study is demonstrating the opposite. In this case, the effluent will never be in compliance with law requirements, unless major modifications to the plant configuration are put in place.

The above two scenarios were studied in presence of chlorides as well, where the presence of chlorides at low concentration or high concentration were not modifying the final outcomes of the study.

As to the effect of sulfate on the material of construction of Marafiq, the study came to the conclusion that no risk is expected for localized pitting corrosion and general oxygen corrosion due to high sulfate content, considered in the two scenarios.

It is important to notice that, despite sulfate concentration are a parameter to be respected by all industries contributing to Marafiq, the configuration of the plant is such that sulfate cannot be removed by the plant, and the basis of design for Marafiq.

As to the possibility to replace of use of chemicals containing sulfate, used inside Marafiq, the use of different acids (hydrochloric, phosphoric, nitric or acetic), alternative to Sulphuric acid, currently used,

has been investigate. All the above acids, even providing the benefit of reducing sulfate, shows various adverse effects, which don't recommend their use.

Similarly, the replacement of Aluminum sulfate, currently used as coagulant in Marafiq, with other chemicals is not recommended.

In case any reduction of sulfate concentration in the streams out-coming Marafiq would be required, the introduction of a dedicated unit (RO or IE) is recommended for treatment of a portion of the stream. This has to be considered as a major modification of Marafiq and it will be beneficial also in view of the reduction of chlorides and other compounds in the effluent stream.

Reduction of sulfate, applying the above technologies directly at the point of discharge of each single industry, is not recommended, due to the requirement of pre-treatment steps, which are already foreseen in Marafiq, for the overall combined stream.

CHAPTER ONE: Introduction

Introduction:

One of the most important environmental problems faced by industries is the management of waste. The chemical industry is a major source of wastes that can be harmful, dangerous, poisonous and life-threatening. Proper management of waste helps in recycling and reuse of the available resources, which helps in saving money and energy. The industrial wastewaters are difficult to treat because of the significant variation in characteristics of different industries. Specific treatment methods may be required for particular industrial effluents. Sulfate concentration in one of industrial wastewater that regulatory limited 150 mg/l as acceptable to be received at Marafiq Company.

Subsequently, Marafiq received Sulfate concentration above 150 mg/l in daily basis one petrochemical site. So, in this research will assess the Sulfate concentration levels from that concern site and in blended Wastewater entering Marafiq and evaluate how much effect of high Sulfate to Biological Treatment Unit and the outcomes results from Marafiq.

Research Problem:

One of Petrochemical site located in Yanbu Industrial City loaded Marafiq process with Sulfate concentration from 350 mg/l to 650 mg/l which above acceptable and regulatory limit

Importance of the Research:

The importance of this research is the assessment of the effects of an increasing influent sulfate concentration on the Marafiq treating principally petroleum refining wastewaters, with particular attention to the biological processes for removal of organic compounds (Chemical Oxygen Demand/Total Organic Carbon) and Ammonia compounds: nitrification, denitrification and aerobic Chemical Oxygen Demand (COD) removal.

The Goal of Research:

To identify the possibility to increase the concentration of Sulfate from Western Region companies from 150 mg/l to 800 mg/l without impacting Marafiq process efficiency, piping construction and irrigation system regulation

Research Question:

Q: What is the consequences of high Sulfate concentration to Marafiq?

- i. Is it effect the biological treatment?
- ii. Is it impacting the construction of piping?
- iii. Is it effect irrigation water quality system?

Research Hypotheses:

The increasing of Sulfate concentration up to 800 mg/l for all Western Region companies having a relationship to violate the Irrigation System regulation (outlet results) for Marafiq and affect condition of constructed piping and kills the bacteria in biological treatment system.

Study Model:

- a) Independent Variable: Biological Treatment Unit at Marafiq Company
- b) Dependent Variable: Sulfate Concentration, Quantity and Quality

CHAPTER TWO: Literature Review

Introduction:

In this chapter will discuss the previous studies in the same topic and what the benefits and special for this research. Furthermore, will overview about the Theoretical Framework that goes in this study.

Previous Studies:

Process inhibition by sulfate salinity:

High salt concentrations are detrimental to bacteria. Salinity causes osmotic stress, ionic toxicity (improved membrane permeability and ruined cellular structure due to cations replacing Ca^{2+} in the cell membrane), oxidative stress (increase in intracellular reactive oxygen species), cell dehydration, plasmolysis (shrinking of the cytoplasm due to the diffusion of water out of the cell when salt concentration is above 10 g/l) and direct inhibition of many enzymes resulting in the loss of cell activity and death of micro-organisms (Lefebvre and Moletta, 2006; Zhao et al., 2013).

Most of the studies found in literature about salinity inhibition are related to NaCl that is considered the standard salt for this topic. Hoverer, Campos et al. (2002) tested three salts with different anions and the same cations (Na_2SO_4 , NaNO_3 and NaCl) and found similar inhibitory effects on nitrification autotrophic biomass. Differently, for heterotrophs bacteria, which are also in the biological section, chloride ion appears to have a higher inhibiting effect than sulphate ion (Pernetti and Palma, 2005). That being said and taking into account outcomes of the previous study about effects of chlorides, which indicated that no major evidence of nitrification inhibition was found in literature when considering chloride concentration up to 1,500 mg Cl/l, it can be deducted that, no significant inhibitory effects are expected for nitrification and denitrification, at SO_4^{2-} concentration up to 800 mg/L.

Favorable conditions for Sulfate-Reducing Bacteria (SRB) growth:

Sulfate-Reducing Bacteria (SRB) are bacteria capable of sulfate reduction using CO_2 and H_2 as carbon source and electron donor, respectively (autotrophic SRB) or using organic matter as unique substrate with regards to heterotrophic SRB (Cassidy et al., 2015). Typical substrates are amino acids, sugars (e.g. fructose, glucose, etc.), long-chain fatty acids, aromatic compounds (phenol, etc.), volatile fatty acids (e.g. acetate, formate, propionate, butyrate, lactate), alcohols (e.g. methanol, ethanol, etc.) and hydrocarbons (Ollivier et al., 2007, Hao et al., 2014), whereas the major end-product of SRB is hydrogen sulfide (H_2S), a toxic compound for bacteria, aquatic life and humans (Hao et al., 2014) :

In some wastewater treatment facilities SRB are present in complex treatment scheme for Chemical Oxygen Demand (COD) and/or SO_4^{2-} removal with optimal COD/ SO_4^{2-} ratio for COD removal of 0.6/1.2 and with ratio of 2.4/4.8 for sulfate removal (Hao et al., 2014). In other biological processes SRB can be a danger, instead. In fact, information from the technical and

scientific literature suggests that an increase in sulfate levels in the influent of a Biological Nutrient Removal (BNR) plant can create favourable conditions for the growth of Sulfate-Reducing Bacteria (SRB) in basins where oxygen is not present, such as pre-denitrification and post-denitrification units. Moreover, SRB are able to tolerate molecular oxygen (Manz et al., 1998) and therefore aerobic basins (nitrification and flotation units) do not pose a concern for the survival of these bacteria in the biological process.

The possible presence of SRB in wastewater treatment facilities has been shown by Manz et al. (1998), who found a SRB from 0.5 to 8% of the total cell counts within all stages of an activated sludge process in Germany. Since these bacteria tolerate temperatures between 5 and 75 °C (optimum temperature values of 28 - 32°C), salinity up to 12% and a wide pH range (5.5/10) (Hao et al., 2014) SRBs represent a possible threat for any Biological Nutrient Removal (BNR) plant because, if present, they produce H₂S, that is toxic to nitrifying bacteria and possibly to nitrate-reducing bacteria

However, even though it is clear from the literature that anoxic conditions are favourable for SRB because these bacteria grow on the same substrate (soluble biodegradable COD) of Nitrate-Reducing Bacteria (NRB) and the coexistence of the two bacteria need to be demonstrated at the operational conditions of Marafiq. In general, competition on the same substrate can result in coexistence or exclusion of the slow-growing microorganisms (SRB in this case). In order to investigate the possible presence of SRB a modelling approach is required in this research to simulate possible scenarios of increased sulfates in the influent.

Theoretical Framework:

Sulfate ions are present in natural waters and industrial effluents of the chemical and metallurgical industries. Sulfate anion (SO_4^{2-}) is not considered to be toxic; however, high sulfate content in discharge water can result in an increase in the salinity of receiving water (Nariyan et al., 2018). The high concentration of sulfate in discharge water can also influence the permanent stratification of the receiving water, hence disturbing nutrient and oxygen cycles (Boehrer and Schultze, 2008). Therefore, the industrial wastewater with high sulfate content are required to be treated prior to being discharged into the environment.

Treatment of wastewater is a major step in preventing the pollution of water resources. The process uses to remove pollutants such as metals, debris, microorganisms, and biowaste from the wastewater. After treatment, the treated industrial wastewater (or effluent) may be reused or released to a sanitary sewer or to a surface water or to irrigation system in the environment (wikipedia,2024).

Marafiq with its upstream situated collecting network from western region industries. The design capacity of Marafiq is equal to 48000 m³/d. Marafiq consist THREE treatment stages which is Primary stage to remove settleable solids, Secondary Stage (biological treatment) to removing soluble organic matter solids that escaped primary treatment and finally Tertiary treatment to specification and to treat wastewater for public water systems.

Consequences of SRB presence in biological nutrient removal plants:

The major effect of the SRB presence in a biological nutrient removal plant is the production of H₂S and its inhibiting effects to bacteria other than SRB.

Differently to anaerobic digestion, aerobic and BNR treatments would not normally be considered conducive to the presence of reduced sulphur constituents and the activated sludge process has not been fully investigated with regards to this topic. However, some important studies have been conducted particularly regarding the nitrification process that is generally considered a very sensitive reaction to inhibiting substances.

Sears et al. (2004) investigated the impact of soluble sulphide under aerated and unaerated conditions, focusing in particular on ammonia-oxidizing (AO) bacteria due to their critical first-step role with nitrification. The authors showed that even at low total soluble sulphide concentrations, active ammonia oxidation was inhibited in the aerobic basin. AO promptly recovered, in tests after the depletion of H₂S was achieved, indicating that a degree of recovery

was possible. However, since the depletion rate immediately following sulphide exposure ranged over only 51–74% of the maximum control rate, some measure of a lingering effect was still evident. Ammonia depletion rates measured 24 h after sulphide exposure indicated that additional recovery was possible, but a full recovery to the “pre-sulphide-exposure” AO rates was not achieved within this time interval.

Other tests conducted with inactive ammonia oxidizers exposed at higher dosage levels (0.5 and 5 mgS/L) during anoxic conditions revealed that their subsequent aerobic activity was correspondingly decreased to 72% and 64%, respectively even if H₂S was not present during aerobic conditions. The full recovery of nitrification activity was obtained after 24h (Sears et al., 2004).

The results of these experiments clearly indicate that sulphides contact in anoxic condition and residual sulphide concentration in aerobic condition (after H₂S stripping due to aeration) can reduce nitrification rates.

With regards to denitrification there are very limited studies investigating the effect of sulphide on NRB during wastewater treatment. Some authors tested the depletion of different intermediate compounds of heterotrophic denitrification that overall consists of sequential reductive reactions from nitrate (NO₃⁻) to nitrite (NO₂⁻), nitric oxide (NO), nitrous oxide (N₂O), and finally to nitrogen gas (N₂) (Pan et al., 2013).

They found that also low concentrations of hydrogen sulphide is inhibitory to N₂O reduction.

By comparison, SRB activity decrease when H₂S is higher than 60 - 70 mgS/l (Hao et al., 2014).

CHAPTER THREE: Research Methodology

Introduction:

In this chapter, the methodology and ways followed in the research will be explained. Which include determining the methodology and data collection tools of verifying validity and reliability. Additionally, the limitation of the research will be listed in this chapter as well.

Research Methodology:

Gathering data of Sulfate concentration is essential to start the research, the data will be gathered from Industrial Marafiq, Regulatory body and concern site that have major contributor in order to assess of peak of Sulfate routed to Marafiq. In addition to first step, it's important to assess the Sulfate load within internal Marafiq. After that, the method of interpretation will be used for and it's constituted of three steps:

- Dynamic simulation of Sulfate-Reducing Bacteria (SRB) growth.
- Minimum population sizes for species conservation.
- Magnitude of the possible impacts.

Lastly, Identification of expected degradation mechanisms is important to ensure proper material used in case of Sulfate concentration increased up to 800 mg/l.

Ways of Research:

Study the impact of Sulfate concentration with current situation which is range of 350 mg/l to 650 mg/l and slightly increase the concentration with close monitoring with any deviations observed to treatment system, piping, bacteria and outcomes Sulfate results. In addition, the history data of all stages are very crucial for the study in order to set proper and logic recommendations.

Research Tools:

Mathematical model is a system of differential equations that simulates biochemical phenomena in a real system, in this case the activate sludge system. Once the mathematical model is defined it must implement by a calculation software capable of solving differential equations. For that purpose, AQUASIM software, which is characterized by a strong technical and scientific validity will be used. It is like the use of spreadsheet applications to calculate/solve design formula of activated sludge system.

Research Limitation:

- Lack of previous research in terms of impacting of high Sulfate concentration to Marafiq process, piping and results as well.
- Poor cooperation with Marafiq and Regulatory body to provide the historical data of Sulfate Analysis Results.
- Enforce local regulatory body to follow the new study recommendations.

CHAPTER FOUR: Practical Study

Introduction:

In this chapter, gathering Sulfate data and make comparison between each other. Here, will go an overview of Sulfate-Reducing Bacteria (SRB) condition in case of increasing of Sulfate concentration. In addition, study the effect of Sulfate concentration to Marafiq material of construction. Concluded with research recommendations.

Data Gathering:

Data provided by Marafiq:

Quality of the water incoming Marafiq is monitored by Marafiq for the daily operation of plant itself, as well as by Royal Commission (hereinafter RC), for monitoring of compliance with regulations.

Marafiq analyses the influent water once per day. Following Table 4.1 summarizes the outcomes of statistical analysis made on data provided by Marafiq.

Description	Unit	results
N° of Samples	---	365
Average	[mg/l]	237
Number of samples exceeding 150 mg/l	---	332
Percentage of samples exceeding 150 mg/l	%	91
Number of samples exceeding 300 mg/l	---	43
Percentage of samples exceeding 300 mg/l	%	11.8
Number of samples exceeding 800 mg/l	---	0
Percentage of samples exceeding 800 mg/l	%	0

Table 4.1 Sulfate at Marafiq Inlet

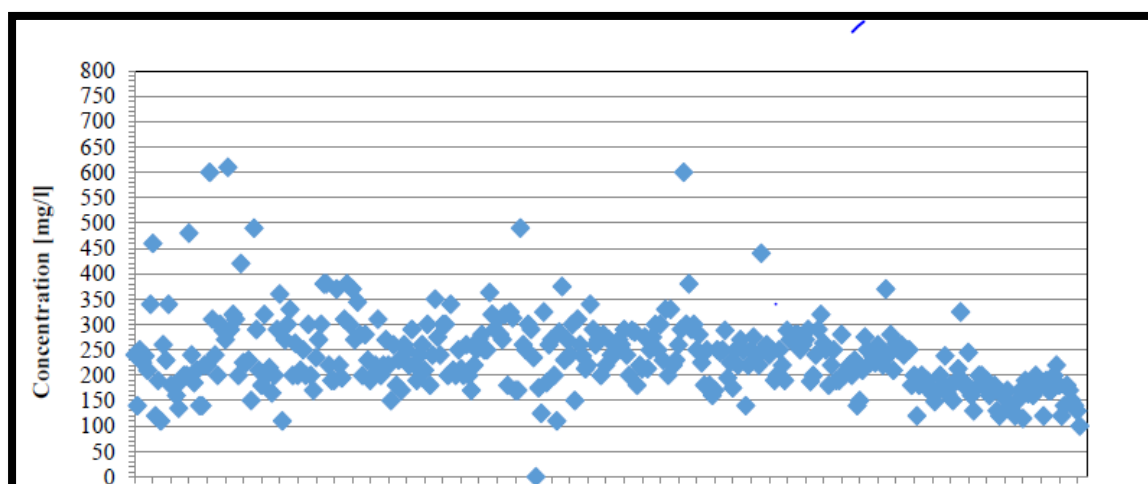


Figure 4.1: Marafiq Sulfates Results

Data Provided by Royal Commission:

Following Table 4.2 summarizes the outcomes of sulfate analysis made by RC.

Description	Unit	results
N° of Samples	---	167
Average	[mg/l]	183
Number of samples exceeding 150 mg/l	---	129
Percentage of samples exceeding 150 mg/l	%	73.3
Number of samples exceeding 300 mg/l	---	8

Percentage of samples exceeding 300 mg/l	%	4.5
Number of samples exceeding 800 mg/l	---	0
Percentage of samples exceeding 800 mg/l	%	0

Table 4.2: Sulfate analysis by RC

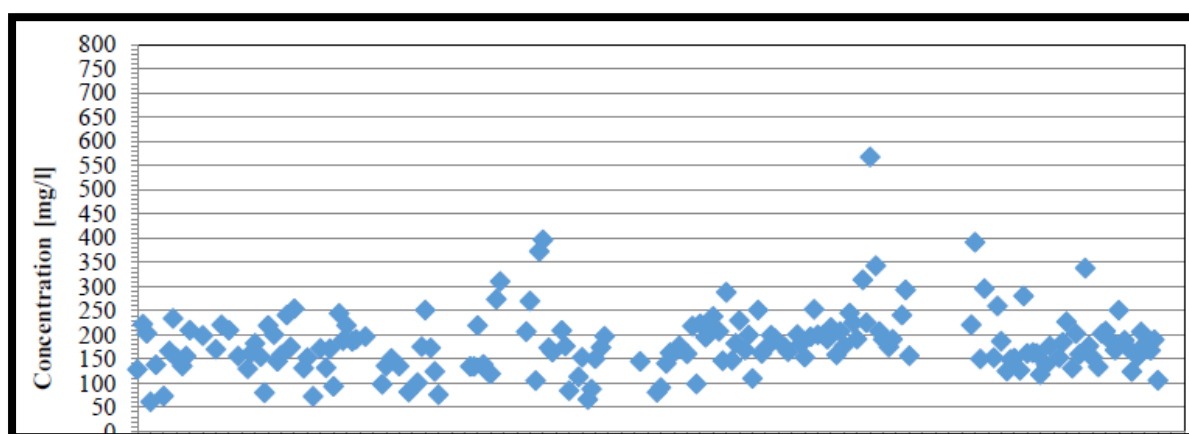


Figure 4.2: RC Sulfates Results

Data provided by Concern Site:

Following Figure 4.3 and Table 4.3 summarize the outcomes of sulfate analysis made by Concern site (based on grab samples).

Description	Unit	results
N° of Samples	---	53
Average	[mg/l]	224.1
Number of samples exceeding 150 mg/l	---	21
Percentage of samples exceeding 150 mg/l	%	39.6
Number of samples exceeding 300 mg/l	---	13
Percentage of samples exceeding 300 mg/l	%	24.5
Number of samples exceeding 800 mg/l	---	0
Percentage of samples exceeding 800 mg/l	%	0

Table 4.3: Sulfate at Concern site outlet

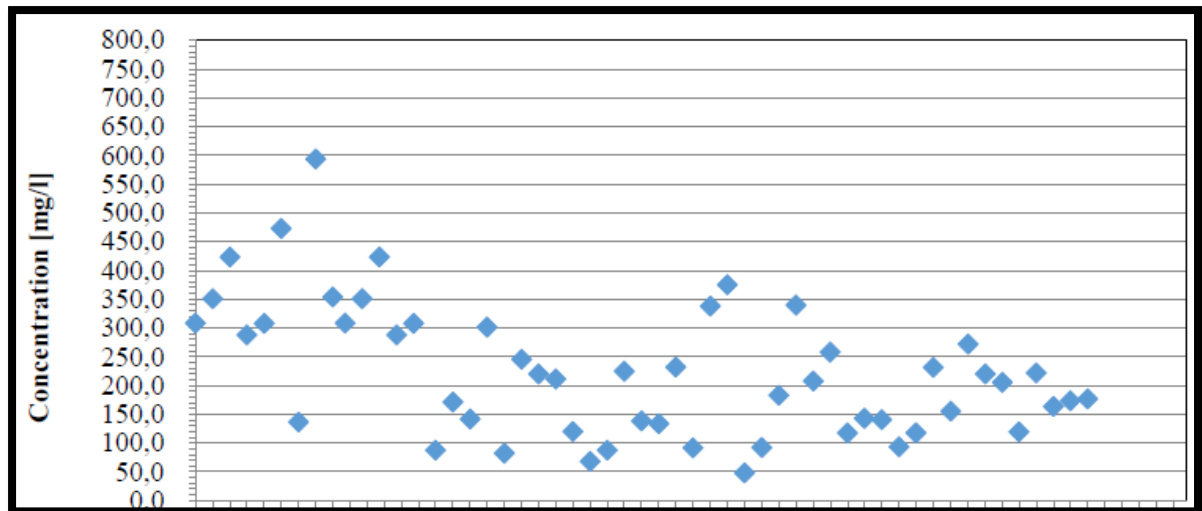


Figure 4.3: Concern site Sulfate Results

Comparison of data:

Values reported in Table 4.2 (RC source) appears a bit different than those reported in the Table 4.3 (Concern site source) and Table 4.1 (Marafiq source).

As the period and the frequency of the analysis are different, both series of data have been subjected to a selection aimed at picking up and compare only figures pertaining to the same day of sampling.

Considering that both Concern site and RC are not monitoring daily the sulfate content in the effluent, in the set of data provided by all parties, only four (4) are pertaining the same day of sampling. Therefore, any comparison of statistical analysis made on such limited sample, is statistically not significant.

Sulfate Load Calculation from Concern Site:

The overall contribution, in terms of Sulfate load of Concern site effluent to Marafiq influent can be estimated as follows:

- Concern site flow rate contribution to Marafiq: 12.9%
- Sulfate at Concern site Effluent: 257 mg/l
- Sulfate Load to Marafiq from Concern site Effluent: $257 \text{ mg/l} \times 5551 \text{ m}^3/\text{day} : 1000$
= 1426.6 kg/day
- Sulfate to Marafiq: 237 mg/l
- Sulfate Total Load to Marafiq: $237 \text{ mg/l} \times 43177 \text{ m}^3/\text{day} : 1000 = 10233.0 \text{ kg/day}$

- Sulfate Load to Marafiq from Concern site Effluent 1426.6 kg/day : **10233.0 kg/day = 13.9 % of total Sulfate load to Marafiq.**

Effects of higher Sulfate content in Concern site effluent to Marafiq:

In case the concentration of Sulfate in Concern site effluent would increase to 800 mg/l, the expected load of Sulfate to Marafiq will be as follows, assuming that the flow rate from each single industry would not be modified:

- Hypothetical sulfate at Concern site Effluent: 800 mg/l
- Hypothetical sulfate Load to Marafiq from Concern site Effluent: $800 \text{ mg/l} \times 5551 \text{ m}^3/\text{day} : 1000 = 4440.9 \text{ kg/day}$

Assuming that load of sulfate and flow rate from other Industries would not be modified, the expected future load will be:

- Expected Sulfate Load to Marafiq: $4440.9 \text{ kg/day} + 5973.2 \text{ kg/day} + 7148.8 \text{ kg/day} = \mathbf{17562.9 \text{ kg/day}}$

Considering the existing average flow rate, the above load corresponds to the following theoretical concentration at Marafiq inlet:

- Sulfate Total Load to Marafiq (future): **17562.9 kg/day**
- Flow rate to IWTP-II: 43177 m³/day
- Sulfate concentration at Marafiq Inlet: $17562.9 \text{ kg/day} : 43177 \text{ m}^3/\text{day} \times 1000 = \mathbf{407 \text{ mg/l}}$

The below Table 4.4 summarizes the expected figures of sulfate at Marafiq inlet in the above case. Additionally, it is reported, in the last column, the worst case of all industries discharging their effluents at 800 mg/l.

	Current Value ⁽⁴⁾ [mg/l]	Future Value Case 1 [mg/l]	Future Value Case 2 [mg/l]
Sulphates at YANPET effluent	257	800	800
Sulphates at YANSAB effluent	222	800	800
Sulphates at Other Industries effluent	-	As existing	800
Sulphates at IWTP-II inlet	237	407	800
Variation at IWTP-II Inlet [mg/l]	-	+ 170	+ 563
Variation at IWTP-II Inlet [%]	-	+ 72%	+ 237 %

Table 4.4: Effect on Marafiq of higher Sulfate Content in Concern site Effluents

Considering that no specific section is currently foreseen within the Marafiq to remove sulfate, the above additional sulfate would be almost transferred to the final Marafiq effluent.

The expected concentration of sulfate at the Marafiq effluent would therefore be, as a minimum, the above table, increased of the amount of sulfate added within the Marafiq existing process scheme, due to various chemical injections.

Moreover, in case the increase of sulfate at Marafiq inlet would determine a reduction of performance in Marafiq, possible increase of chemicals injection may occur to compensate performance reduction, with consequently possible additional injection of Sulfate.

For the sake of transparency data from RC are quickly reviewed, and in case RC data were used instead of those from Marafiq, the situation would change as follows:

- Present total Sulfate Load to Marafiq: $183 \text{ mg/l} \times 43177 \text{ m}^3/\text{day} : 1000 = \mathbf{7901.4 \text{ kg/day}}$
- Sulfate Load to Marafiq from Concern site Effluent: $250 \text{ mg/l} \times 5551 \text{ m}^3/\text{day} : 1000 = \mathbf{1387.5 \text{ kg/day; or 17.6\% of the total}}$
- Sulfate Load to Marafiq from other Industries: $(7901.4 - 1387.5 - 1869.5) \text{ kg/day} = \mathbf{4644.4 \text{ kg/day; or 58.7\% of the total}}$

With similar calculation as reported above, in case Concern site would run at 800 mg/l sulfate, and other industries will maintain their present load, the average concentration at Marafiq would be of:

- $(4440.9 + 5973.2 + 4644.4) \text{ kg/day} : 43177 \text{ m}^3/\text{day} \times 1000 = 349 \text{ mg/l}$

The above would make the sulfate concentration increase of about 91%.

Scenario analysis

Definition of the scenarios

The scenario analysis was performed taking into account all the possible conditions listed in **Error!**

Reference source not found. (A, B, C, A1, B1, C1, A*, B*, C*, A1*, B1*, C1*) and simulating the following 6 scenarios:

1. SO_4^{-2} spike:
 $A \rightarrow A1 \rightarrow A$
2. Occurrence of medium SO_4^{-2} levels both in stable and spike conditions:
 $A \rightarrow B \rightarrow B1 \rightarrow B$
3. Occurrence of high SO_4^{-2} levels both in stable and spike conditions:
 $A \rightarrow C \rightarrow C1 \rightarrow C$
4. Occurrence of high Cl-concentration and spike SO_4^{-2} condition:
 $A \rightarrow A^* \rightarrow A1^* \rightarrow A^*$
5. Occurrence of high Cl-concentration and medium SO_4^{-2} levels both in stable and spike conditions:
 $A \rightarrow A^* \rightarrow B^* \rightarrow B1^* \rightarrow B^*$
6. Occurrence of high Cl-concentration and high SO_4^{-2} levels both in stable and spike conditions:
 $A \rightarrow A^* \rightarrow C^* \rightarrow C1^* \rightarrow C^*$

	Biological process influent (stable concentration)	Biological process influent (spike condition, duration of 3 days)
<u>Current chloride concentration</u>		
Current condition (<u>low</u> SO ₄ ²⁻ levels)	300 (A)	600 (A ₁)
Hypothetical future @ <u>medium</u> SO ₄ ²⁻ levels	500 (B)	800 (B ₁)
Hypothetical future @ <u>high</u> SO ₄ ²⁻ levels	900 (C)	1200 (C ₁)
<u>High chloride concentration</u>		
Current condition (<u>low</u> SO ₄ ²⁻ levels)	300 (A*)	600 (A ₁ *)
Hypothetical future @ <u>medium</u> SO ₄ ²⁻ levels	500 (B*)	800 (B ₁ *)
Hypothetical future @ <u>high</u> SO ₄ ²⁻ levels	900 (C*)	1200 (C ₁ *)

Table 4.5: Current and Hypothetical Sulfate Conditions (mg SO₄⁻² /l)

Method of interpretation

1. Dynamic simulation:

A dynamic simulation is needed even though it is clear from the literature that anoxic conditions are favorable for SRB, because they grow on the same substrate (soluble biodegradable COD) of NRB (denitrification biomass) and the coexistence of the two bacteria need to be demonstrated at the operational conditions of Marafiq.

In general, competition on the same substrate can result in coexistence or exclusion of slow-growing microorganisms (SRB in this case). Moreover, the dynamic simulation allows to quantify the amount of sulfate reduced to H₂S in order to estimate the potential side effects of SRB coexistence.

2. Minimum population size for SRB conservation

Biologists have long known that the smaller the population, the more susceptible it is to extinction from various causes, such as stochastic perturbations (e.g., temporal variation of environmental and process parameters, occurrence of new competitors and predators such as protozoa in activated sludge processes, etc.) that may extinguish populations of a

species even in an environment that, on average, is favourable for their growth and persistence (Shaffer, 1981).

As a rule of thumb, we consider two levels as minimum population sizes for species conservation expressed in relative terms ($\%SRB = \frac{SRB}{SRB+NRB+nitrifiers}$) and three possibilities:

- $\%SRB < 1\%$ no presence of SRB
- $1\% < \%SRB < \%nitrifiers$ possible presence of SRB
- $\%SRB > \%nitrifiers$ presence of SRB

3. Magnitude of the possible impacts

All the possible impacts and side effects on the overall biological process are related to the production of H_2S because of direct inhibition of AO bacteria.

Therefore, the maximum potential concentration of H_2S (as the sum of dissociated and un-dissociated forms) may be estimated conservatively assuming a 100% conversion of the removed SO_4^{2-}

The calculated value of H_2S cannot be taken as a direct index of the magnitude of the possible impacts due to the very conservative assumption made and because of the stripping effect taking place in the oxidation section. The degree of stripping depends on several factors, such as type of aeration system, mixed liquor characteristics and composition, pH, etc. (Sears et al., 2004).

As a consequence the presence of SRB is considered as the more realistic index for the definition of the magnitude of the possible impact as follows:

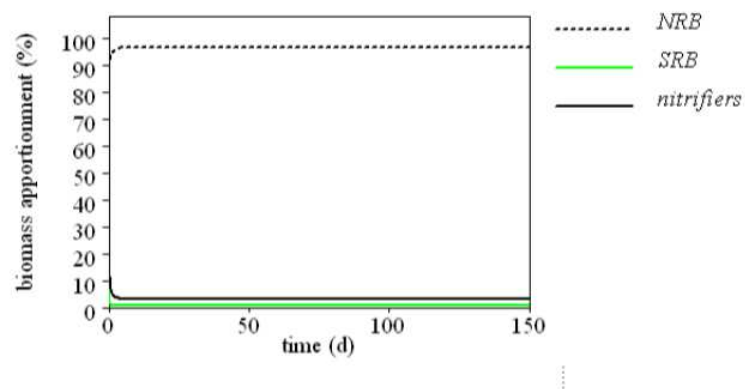
- $\%SRB < 1\%$ no impact
- $1\% < \%SRB < \%nitrifiers$ nitrifiers low/moderate impact
- $\%SRB > \%nitrifiers$ nitrifiers potential high impact

Wastewater characterizations		
parameter	value	unit
COD	1500	mg COD/L
ammonia	80	mg N/L
nitrites	10	mg N/L
pH	7-8	-
temperature	30-35	°C
Operational condition		
parameter	value	unit
influent	18,400	m ³ /d
recycle from nitrification	89,600	m ³ /d
recycle from flottation	8,368	m ³ /d
waste activated sludge (WAS)	426	m ³ /d
Volume denitrification	4,484	m ³
Volume nitrification	10,400	m ³
Volume post-denitrification	780	m ³
flotation concentration ratio of biomass	2.870	-
dissolved oxygen	3.2	mg/L

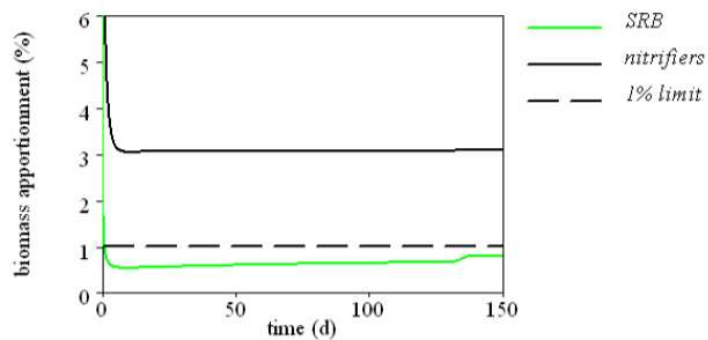
Table 4.6: Wastewater characterizations and operational parameters for IWTP-II modelling

simulation Results:

a) biomass apportionment between SRB NRB and nitrifiers;



b) evaluation of the SRB population size for conservation;



c) concentration of sulfate.

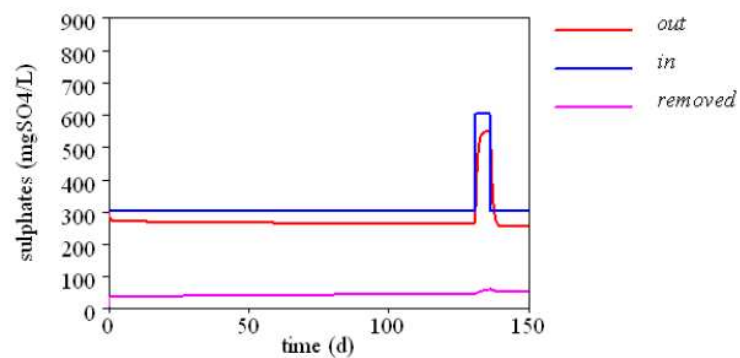
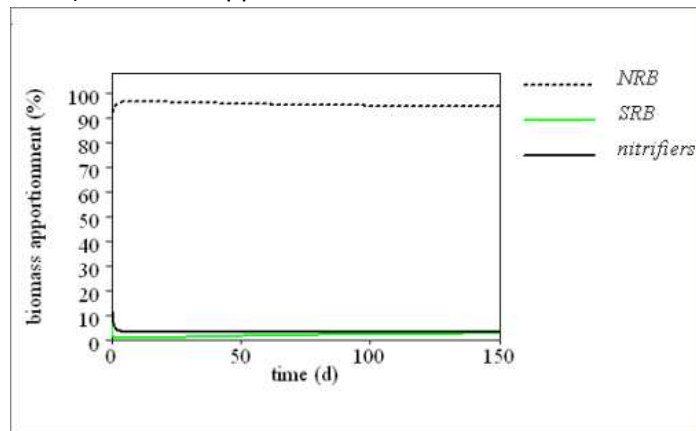
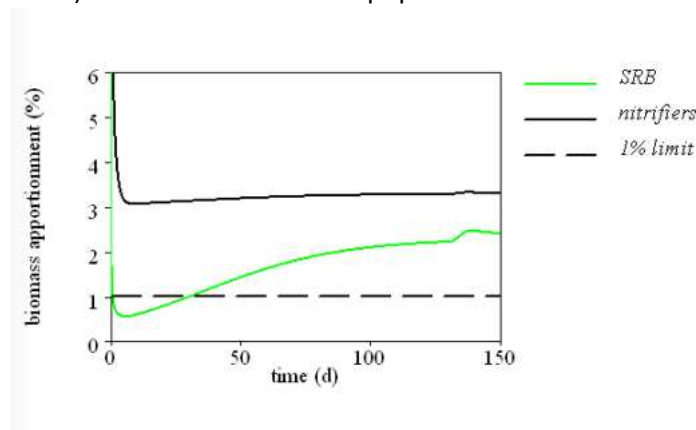


Figure 4.4: Simulation 1 (SO₄₂-spike: A → A₁ → A)

a) biomass apportionment between SRB NRB and nitrifiers;



b) evaluation of the SRB population size for conservation;



c) concentration of sulfate.

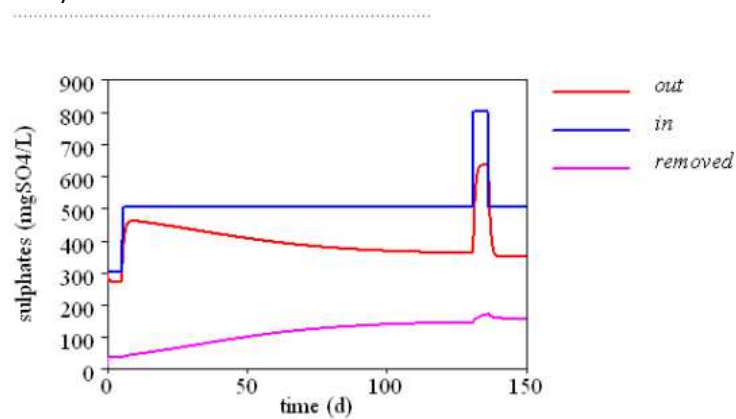
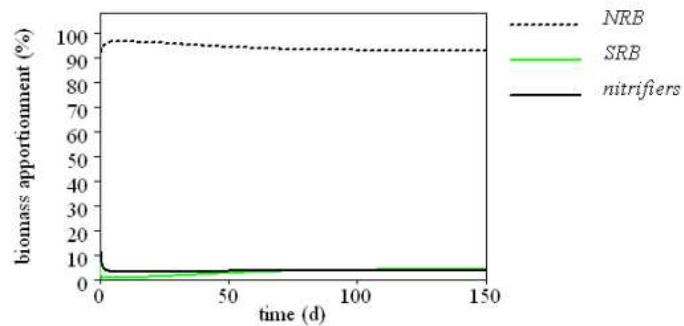
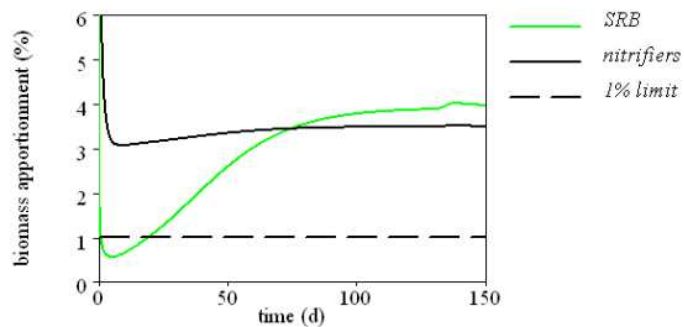


Figure 4.5: Simulation 2 (Occurrence of medium SO₄₂-levels both in stable and spike conditions: A
→ B → B₁ → B)

a) biomass apportionment between SRB NRB and nitrifiers;



b) evaluation of the SRB population size for conservation;



c) concentration of sulfate.

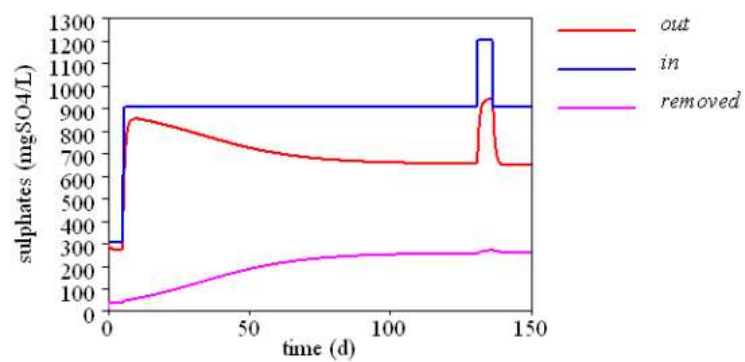
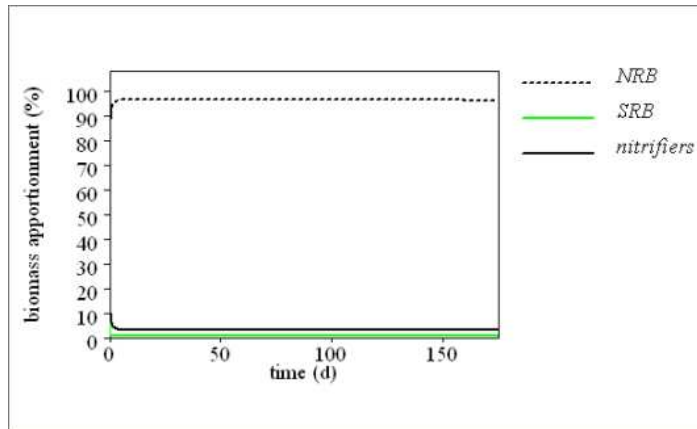
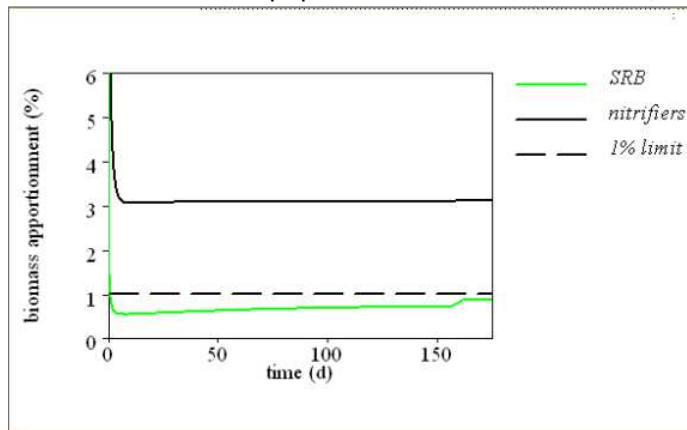


Figure 4.6: Simulation 3 (Occurrence of high SO₄²⁻ levels both in stable and spike conditions: A
→ C → C1 → C)

a) biomass apportionment between SRB NRB and nitrifiers;



b) evaluation of the SRB population size for conservation;



c) concentration of sulfate.

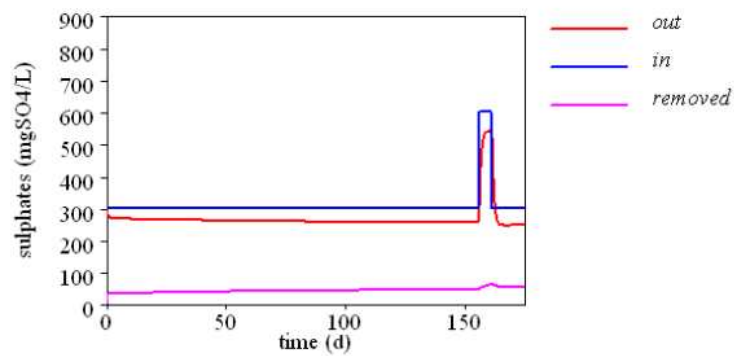


Figure 4.7: Simulation 4 (Occurrence of high Cl⁻ concentration, 1200 mg/L from day 5, and spike SO₄²⁻ condition: $A \rightarrow A^* \rightarrow A_1^* \rightarrow A^*$):

With regards to SRB presence the results of the scenario analysis showed:

- no presence of SRB at current conditions (300 mg $\text{SO}_4^{-2}/\text{L}$) even after the spike sulfate of 600 mg $\text{SO}_4^{-2}/\text{L}$;
- the possible presence of SRB in the hypothetical future condition @ medium sulfate (500 mg $\text{SO}_4^{-2}/\text{L}$);
- the presence of SRB in the hypothetical future condition @ high sulfate (900 mg $\text{SO}_4^{-2}/\text{L}$);
- no significant effects of spikes.
- no significant effects of chloride.

With regards to the magnitude of the possible impacts the results of the scenario analysis showed:

- a moderate impact of SRB presence in the hypothetical future condition @ sulfate concentration of 500 mg $\text{SO}_4^{-2}/\text{L}$, at biological section inlet;
- a possible high impact of SRB presence in the hypothetical future condition @ sulfate concentration of 900 mg $\text{SO}_4^{-2}/\text{L}$, at biological section inlet.

Verification of material of construction

Plastic materials

The main material for the collecting network upstream the plant is in GRP. Only two lines are in PVC. Further plastic materials has been used for some parts of the Marafiq plant.

No corrosion threats are envisaged for piping and equipment built in plastic materials, also considering the higher expected sulfate and chlorides contents in the process fluids at the expected operating temperatures.

Equipment in stainless steel

The materials of construction for some equipment of Marafiq are austenitic and ferritic-austenitic stainless steel. The following stainless steels can be found in the plant:

Austenitic stainless steels

- 304 stainless steel.
- 316 and 316L stainless steel,

Ferritic-austenitic duplex stainless steels:

- SS duplex stainless steel.
- 25 Cr super-duplex stainless steel.

These materials are in contact with waste waters characterized by sulfate contents between 240 mg/l and 1900 mg/l and chloride contents up to about 1200 ppm. At plant inlet the sulfate content is between 240 mg/l and 800 mg/l. Maximum sulfate content within the whole plant is 1900 mg/l, maximum chloride content within the whole plant is about 1200 ppm. For the maximum values the ratio between chloride (Cl-) and sulfate (SO₄) is equal to 1.3:1.

The operating temperatures are between 21 °C and 50 °C.

Main expected corrosion threat for stainless steels is pitting, as shown in paragraph 8.5.1, and risk for pitting has been assessed considering:

- operating temperature.
- pH of process liquids.
- sulfate content.
- chloride content.
- eventual presence of chlorine.
- eventual favourable galvanic coupling.
- stagnant or turbulent conditions.

The verification of the above stainless steels has been carried out based on:

The influence of the high content of sulfate, considering the presence of chloride.

Equipment in carbon steel

Piping of the lift stations I in Marafiq is in carbon steel. Body and impeller of the pumps are in cast iron. Further some casings of pumps to Marafiq plant is in cast iron.

1. O₂ Corrosion Rate:

For the operating life equal to 20 years, corrosion rates have been calculated based on the estimated oxygen concentration, which depends on temperature and water salinity.

For stagnant conditions the estimated oxygen corrosion rates, depending on temperature, are expected to be:

- for an operating temperature of 21 °C equal to 0.18 mm/year (estimated oxygen content of 9 ppm):
- for an operating temperature of 50 °C equal to 0.11 mm/year (estimated oxygen content of 5.5 ppm).

For a 20 years design life, this would result into a cumulative corrosion between 2.2 mm and 3.6 mm. This figure is very conservative as O₂ content in the treated water is for sure much lower than that used for the above calculations due to the presence of organic matter which reduces the actual oxygen content in the water (close to anoxic conditions). The actual expected cumulative metal loss due to oxygen corrosion over the design life is expected to be much less than that calculated above.

2. Predicted MIC corrosion rates

As the environment here under present study is aerated, the formation of anaerobic active colonies is not expected and thus predicted corrosion rates for MIC are zero.

However, in case conditions for the formation of anaerobic conditions are met (e.g. under deposit), the corrosion rate would be very high. The carbon steel piping of the lift stations, is contact with oily water which is characterized by a sulfate content up to about 1000 ppm and an operating temperature equal to 50 °C, the calculated average uniform corrosion rate ($C_{rate,SRB}$) is about 2.9 mm / year. However, at high sulfate contents, as it is for the case here under study, corrosion rates ($C_{rate,SRB}$) due to the mitigating effect of iron sulfide do not exceed 1 mm/y.

Conclusion and Recommendations

Information from the technical and scientific literature suggests that an increase in sulfate levels in the influent of a Biological Nutrient Removal (BNR) plant can create favourable conditions for the growth of Sulfate-Reducing Bacteria (SRB) in basins where oxygen is not present, such as pre-denitrification and post-denitrification unit.

SRB can be a potential threat for BNR plant in general and even more in petroleum industry because of the widespread presence within the oil reservoirs and oil gathering and transferring processes.

Dynamic simulations and the scenario analysis shows in some cases the possible coexistence of SRB and NRB, both the two species competing on soluble biodegradable COD, but using SO_4^{2-} or NO_3^- as electron acceptors.

- no expected presence of SRB at current conditions (300 mg SO_4^{2-} /L) even after the spikes;
- the possible presence of SRB in the hypothetical future condition @ medium sulfate concentration of 500 mg SO_4^{2-} /L at the inlet of the biological section, which is estimated in case of only Concern site would discharge at 800 mg/l sulfate;
- the presence of SRB in the hypothetical future condition @ high sulfate concentration of 900 mg SO_4^{2-} /L at the inlet of the biological section, which is estimated in case of all industries would discharge at 800 mg/l sulfate.
- no significant effects of spikes, due to use of chemicals (Sulphuric acid) for oxidation purposes.
- no significant effects of chlorides on SRB growth.

Information from literature showed:

- a residual presence of H_2S due to the SRB activity may inhibit ammonium oxidation. This process promptly recovers, if depletion of H_2S is achieved, but not at levels as prior the sulfide exposure;
- inactive ammonia oxidizers exposed at higher dosage levels (0.5 and 5 mgS/L) during anoxic conditions suppressed the subsequent aerobic activity.

For most materials here under Study, no risk for localized pitting corrosion and general oxygen corrosion due to higher expected sulfate and chloride contents is likely.

However for some equipment (De-oiling DAF Pressurized Vessels and Secondary DAF Pressurized Vessels), based on a conservative approach, the implementation of a cathodic protection system with galvanic anodes has been recommended in order to protect surfaces in stainless steel, due to the presence of chlorides, and therefore not included in present recommendations pertaining the effects of sulfate.

The effects of sulfate on corrosion is, in general, very small. They have a minor effect on pitting corrosion of stainless steels while, although indirectly, they represent the main driver of microbial induced corrosion (MIC) of carbon steel components.

The effect on pitting corrosion of stainless steels is beneficial: non halide anions such as sulfate can reduce the risk to pitting in chloride containing solutions. However, their inhibiting effect depends on their concentration and chloride content of the solution.

Based on the above facts, and considering the outcomes of the study, we can summarize and concluded that:

- Presence of sulfate, at the current levels considered for the study, are not expected to have significant effects on the performance of the biological section. Possible growth of SRB may occur in case of increase of sulfate in the effluents, which may have effects in terms of reduction of denitrification rate, with possible increase of nitrates content in the effluent
- If Concern site discharged at 800 mg/l each and all other industries discharged at their current conditions of sulfate (average 237 mg/l), the biological section of Marafiq would handle the case and the final effluent would not exceed the value of 600 mg/l (average). The above level of sulfate would have no effects both on performance and on material of construction of Marafiq.
- If Fenton oxidation process is used (2-3 days per month) in combination with the above conditions, the effluent may exceed 600 mg/l.
- An increase of sulfate concentration up to 800 mg/l in the overall stream entering Marafiq will lead to an increase of Sulfate in the final effluent from Marafiq above the Regulatory limits and to an expected reduction of performance of the biological denitrification section, which cannot be accommodate within current facilities inside Marafiq.

- Material of construction are generally adequate to the conditions considered in the study , and limited requirements for improvement are associated only to the presence of chlorides, as investigated in a dedicated study for the same plant.
- Since Marafiq is not designed to remove sulfate and other salts like chlorides; a major modification to Marafiq is required in this case.

Based on the above conclusions, the following is recommended:

- Considering that the current stream incoming and out-coming Marafiq is in compliance with Regulatory requirements for sulfate, no modification of Marafiq is strictly necessary to this purpose only.
- Upgrade the material of construction of the equipment is not required, other than the normal replacement after the design life of the unit has been reached, as it is the case of the network, upstream of Marafiq.
- Replacement of chemicals used in the existing Marafiq with other inorganic acids, to reduce sulfate load, is not viable, as all identified alternatives are providing negative effects in addition to the benefit of reducing sulfate.
- In case of increase of sulfate concentration in the streams from industries, the introduction of a dedicated unit (RO or IE) is recommended for treatment of a portion of the stream. This has to be considered as a major modification of Marafiq and it will be beneficial also in view of the reduction of chlorides and other compounds in the effluent stream.

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