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ENHANCING DRINKING WATER TREATMENT PLANT PERFORMANCES BY THE APPLICATION OF ROBUSTNESS INDICES AND CHEMICAL – PHYSICAL PROCESSES

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Abstract

Surface water quality is declining due to climate change, leading to increased concentrations of soluble metals, natural organic matter (NOM), turbidity, and algal blooms. These changes pose challenges to traditional water treatment plants, needing innovative approaches. In addition, the new regulatory framework (EU 2184/2020) sets stricter limits for turbidity and percentile statistics for continuous compliance, demanding greater robustness of the treatment processes.

In this regard, the initial focus of the study lies on the development and application of a new turbidity robustness index ($\text{TRI}_{95\text{B}}$) to be used as a warning tool for detecting deviations from water quality standards. The proposed $\text{TRI}_{95\text{B}}$ index has two key novelties compared to the existing indices required for adapting to the new drinking water regulation: (i) introduces the 95th percentile as a statistical indicator; (ii) considers an additional term that sets an alert when a threshold value is exceeded. $\text{TRI}_{95\text{B}}$ has been compared with the TRIs existing in the literature. Furthermore, the $\text{TRI}_{95\text{B}}$ validation has been performed by a three-year monitoring dataset of a full-scale DWTP. In addition, the index has been correlated to the characteristics of the raw water at the inlet of plant, in order to identify for which particular load conditions and events, in terms of magnitude and duration, the plant loses robustness. The same approach has been applied for the development and validation of a manganese robustness index ($\text{MRI}_{95\text{B}}$).

The second part of the research explored the use of potassium ferrate(VI) as a potential solution to address the increasing concentration of pollutants in raw water and climate change-related water emergencies and to meet the more stringent regulations of drinking water and, in particular, to cope with losses of robustness of drinking water treatment plants. Conventional chemicals might not be able to ensure compliance with drinking water quality standards; in this light Fe(VI) has been investigated to be used either alone or in combination with conventional reagents to producing potable water.

Results showed that the proposed RIs can identify short-duration and low magnitude failures, thus coping with the purpose of the new regulation for drinking water. Overall, $\text{TRI}_{95\text{B}}$ and $\text{MRI}_{95\text{B}}$ showed a great capability of synthetically and effectively describing the variability of plant performance, allowing highlighting process failures. Additionally, by linking $\text{TRI}_{95\text{B}}$ to the occurrence of turbidity peak events it was observed that there is a threshold value of such events that leads to a serious compromission of the plant's robustness.

Moreover, results showed that Fe(VI) was more effective to remove soluble manganese compared to a conventional oxidant (permanganate), while requiring a lower stoichiometric dosage (<2 mol of Fe(VI) per 3 mol of Mn(II)) as the reaction byproducts of Fe(VI) reduction (eg., Fe³⁺) contributed to manganese removal. A slightly alkaline environment (pH >8.5) was crucial to maximize manganese oxidation since pH closer to neutral caused the reduction of Fe(VI) to Fe(III), thus decreasing its reduction potential. Fe(VI) was also effective toward NOM although its activation was necessary to provide noticeable effects. In combination to conventional coagulant/flocculant agents, Fe(VI) was able to provide noticeable increases in removal of turbidity (<0.30 NTU) while involving a simultaneous decrease in other chemicals requirement (>50%). Besides, Fe(VI) was also capable of providing algae removal of approximately 80% higher than conventional oxidizing agent, through simultaneous oxidation and flocculation.

In conclusion, this study demonstrated that, in a context of climate change, which leads to the occurrence of extreme and short-duration events, the indices can assess the potential vulnerability of the plant and can be used to identify for which magnitude of an event the plant loses robustness, requiring emerging treatment to comply with regulations. In this regard employing Fe(VI) as a treatment method for drinking water is very promising as it can serve as an alternative or complement conventional approaches in tackling the challenges presented by climate change and sustaining high-quality standard potable water.

Keywords: Algal bloom, Climate changes, Drinking water treatment plants, Ferrate, Manganese, NOM, Robustness index

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List of Contents

List of Figures	VII
List of Tables.....	XI
List of Acronyms.....	XIII
Scientific contributions and publications	XV
Introduction	1
Chapter I	5
Effect of climate change on water quality	5
1.1 Climate Change and the Water Cycle	6
1.1.1 Changes in precipitation pattern.....	6
1.1.2 Changes in stream flow	8
1.1.3 Changes in droughts and floods	9
1.2 The impact of climate change on water quality	10
1.2.1 Qualitative characteristics modifications of the water cycle.....	11
1.2.2 Changes in the characteristics of groundwater bodies	13
1.2.3 Changes in the characteristics of surface water bodies	14
1.3 Effects on water service infrastructure.....	15
1.3.1 Effects on drinking water treatment plants.....	15
1.3.1.1 Natural organic matter.....	15
1.3.1.2 Harmful algal blooms.....	17
1.3.1.3 Turbidity.....	17
1.3.1.4 Heavy metals and Manganese	18
1.3.2 Effects on water distribution networks.....	19
1.4 Drinking water safety	20
Bibliography.....	23
Chapter II.....	35
Regulatory framework on water intended for human consumption	35

2.1 Historical Context and Evolution of the Drinking Water Directive	35
2.1.1 The EU Directive 2020/2184.....	36
2.2 The WHO Guidelines for drinking water quality and the origin of Water Safety Plans	39
2.2.1 The Water Safety Plan approach	39
2.3 The Italian regulatory framework.....	43
Bibliography	49
Chapter III.....	51
Process indicators in drinking water treatment plants	51
3.1 Assessment of drinking water treatment performances by means of indicators	52
3.1.1 Reliability	52
3.1.2 Resiliency	52
3.1.3 Robustness.....	53
3.1.4 Risk.....	54
3.1.5 Interrelationship between indicators.....	55
3.2 Detecting the robustness of a drinking water treatment	56
3.2.1 Turbidity Robustness Index.....	57
Bibliography	62
Chapter IV	67
Innovative treatment technologies for waters intended for human consumption.....	67
4.1 Advanced drinking water treatment process.....	68
4.1.1 Membrane processes.....	70
4.1.2 Adsorption on activated carbon and other materials	72
4.1.3 Advanced oxidation processes (AOP)	73
4.1.3.4 Oxidation with potassium ferrate.....	76
4.2 Ferrate(VI).....	76
4.2.1 Ferrate properties	77

4.2.2 Ferrate production	79
4.2.2.1 Dry oxidation method.....	80
4.2.2.2 Wet oxidation method	81
4.2.2.3 Electrochemical method.....	82
4.2.3 Ferrate measurement	84
4.2.4 Ferrate(VI) as a multifunctional chemical reagent.....	87
4.2.4.1 Oxidation.....	87
4.2.4.2 Coagulation	88
4.2.4.3 Disinfection	88
4.2.5 Ferrate(VI) application in drinking water treatment	89
4.2.5.1 Algal removal.....	89
4.2.5.2 NOM removal	91
4.2.5.3 Turbidity removal.....	92
4.2.5.4 Manganese removal.....	92
4.2.5.5 Emerging pollutants removal	95
Bibliography.....	97
Chapter V¹.....	109
Experimental activity: materials and methods	109
5.1 Full-scale plant description	110
5.2 Development of the Robustness Indices	113
5.2.2 Data collection and analysis	114
5.2.3 Development of the modified TRI	114
5.2.3.1 TRIs validation: sensitivity and specificity	117
5.2.3.2 Application of TRI at single-process scale.....	118
5.2.3.3 Definition of a Turbidity Load Index	118
5.2.3.4 Events identification and correlation with TRI _{95B}	120
5.2.4 Development of the MRI.....	121
4.2.4.1 MRIs validation: sensitivity and specificity	121

5.3 Ferrate experimentation.....	122
5.3.1 Jar test experiments	122
5.3.2 Manganese removal procedures	123
5.3.3 Ferrate stability experiment.....	124
5.3.4 NOM and turbidity removal assays	124
5.3.5 Algae removal.....	125
5.3.6 Chemicals	125
5.3.7 Analytical methods.....	125
5.4 Ferrate(VI) electrochemical production	126
Bibliography	129
Chapter VI².....	131
Experimental activity: results and discussion	131
6.1 Results on Turbidity Robustness Indices.....	131
6.1.1 Characteristics of raw water and compliance of treated water with regulations	131
6.1.2 Comparative assessment of TRIs in the framework of the old regulation.....	136
6.1.3 Comparative assessment of TRIs in the framework of the EU 2020/2184	138
6.1.4 Reliability of TRIs	141
6.1.5 Evaluation of TRIs at single-process scale: clariflocculation (CH) and filtration (FS)	146
Clariflocculation (CH).....	146
Filtration (FS)	150
6.1.6 Correlation between TRI _{95B} and TLI at global and single scale process	154
6.1.7 Assessing plant robustness in presence of turbidity peak events....	160
6.2 Results on Manganese Robustness Index	164

6.2.1 Characteristics of raw water and compliance of treated water with regulations	164
6.2.2 Comparative assessment of MRIs in the framework of the EU 2020/2184.....	166
6.2.3 Reliability of MRIs.....	168
Conclusions	170
6.3 Addressing emerging challenges by using Potassium Ferrate. Experimentation Results	171
6.3.1 Manganese removal.....	171
6.3.1.1 Stoichiometry of Mn(II) oxidation by Fe(VI) and Mn(VII).....	171
6.3.1.2 Effect of Fe(III) on Mn(II) removal	175
6.3.1.3 Kinetics of Mn(II) oxidation by Fe(VI) and Fe(III)	176
6.3.1.4 Overall reaction of Mn(II) removal by Fe(VI)	178
6.3.2 Removal of NOM and turbidity	181
6.3.2.1 Removal of NOM with ferrate and permanganate	181
6.3.2.2 Removal of turbidity: using ferrate as enhancer coagulant/flocculant	183
6.3.3 Algae removal	184
6.3.3.1 Performance and mechanisms of algae removal	184
6.3.3.2 Integration of ferrate with conventional flocculating agent for algal removal.....	187
Conclusions	189
6.4 Evaluation of Fe(VI) electrochemical production and stability	190
Bibliography.....	195
Overall Conclusions.....	199

List of Figures

Figure 1.1. Trend of temperature and CO ₂ emissions since Industrial Revolution (https://www.climatecentral.org/climate-matters/peak-co2-heat-trapping-emissions)	5
Figure 1.2. Effect of climate change on the quality of surface water and groundwater resources as well as the effect on human health (Akhtar et al., 2021)	13
Figure 1.3. Seasonal dynamics of Mn content in water (Matveeva et al., 2022)	19
Figure 1.4. Impact of climate change on drinking water safety (Ma et al., 2022)	21
Figure 2.1. Key Components of Water Safety Plans	42
Figure 2.2. Synopsis of risk assessment and management according to D.Lgs 18/2023	48
Figure 3.1. Robustness of a water treatment system	54
Figure 3.2. Interrelationship between reliability, resiliency, robustness and risk	55
Figure 4.1. Scheme treatment for surface water intended for human consumption falling within class A1 (a), A2 (b) and A3 (c)	68
Figure 4.2. Classification of AOPs	74
Figure 4.3. Pourbaix diagram of iron	77
Figure 4.4. Stability of ferrate in the aqueous phase at different pH	78
Figure 4.5. Influence of pH on the speciation of Fe(VI) (Wang et al., 2021) ...	79
Figure 4.6. Methods used to synthesize ferrate(VI) (Sharma et al., 2016)	80
Figure 4.7. Scheme of an electrochemical cell for ferrate production (Alsheyab et al., 2009)	82
Figure 4.8. UV-vis (a), FTIR (b), XRD (c) and Mössbauer (d) absorption spectra of Ferrate(VI)	86

Figure 4.9. Schematic diagram of ferrate(VI) disinfection (Yu et al., 2023) ...	89
Figure 5.1. Panoramic view of the Sambuca drinking water treatment plant and of the Garcia artificial reservoir	111
Figure 5.2. Treatment scheme of water mainstream	113
Figure 5.3. Jar test experimental procedure: rapid mixing (a), slow mixing (b) and settled period (c)	122
Figure 5.4. Electrolytic cell: anode (a), cathode (b) and electrolytic solution (c)	127
Figure 5.5. Ferrate solution (a) and ferrate salt (b)	128
Figure 6.1. Trends of the main statistics (minimum, median, maximum) of flow data in influent water (data between weeks 116-120 are missing)	131
Figure 6.2. Trends of the main statistics (mean, median, maximum) of turbidity data in influent water (a): seasonal variation of turbidity data (b); maximum, 90 th , 95 th percentiles and median of turbidity data measured at the outlet of the DWTP (data between weeks 116-120 and week 125 are missing)	133
Figure 6.3. Trends of the main statistics (mean, median, maximum) of turbidity data in X1 unit	135
Figure 6.4. Comparison of the average turbidity values at the inlet of the plant and in X1 unit	136
Figure 6.5. Trends of TRIs scores during the 2021-2023 period, assuming a T_{goal} of 1 NTU	137
Figure 6.6. Trends of TRIs scores during the 2021-2023 period, assuming a T_{goal} of 0.3 NTU	139
Figure 6.7. Cumulative distribution of T_{50} , T_{90} , T_{95} and T_{100} (a) and TRIs with T_{goal} of 1 NTU (b) and 0.30 NTU (c)	142
Figure 6.8. Boxplot of TRIs within different ranges of turbidity discrepancy .	145
Figure 6.9. Trends of the main statistics (95 th percentile, median, maximum) of turbidity data as average of the clariflocculation process (a) and at the outlet of CH ₁ (b), CH ₂ (c) and CH ₃ (d) units	147

Figure 6.10. Trends of TRIs scores during the 2021-2023 period for the evaluation of clariflocculation process robustness, assuming a T_{goal} of 5 NTU	148
Figure 6.11. Trends of the main statistics (95 th percentile, median, maximum) of turbidity data as average of the filtration process (a) and at the outlet of FS ₁ (b), FS ₂ (c) and FS ₃ (d) units	151
Figure 6.12. Trends of TRIs scores during the 2021-2023 period for the evaluation of filtration process robustness, assuming a $T_{\text{goal}} < 1$ NTU and a T_{goal} of 0.3 NTU in 95% of samples	153
Figure 6.13. Trend of TLI scores during the 2021-2023 period	155
Figure 6.14. Boxplot of TRI within different ranges of TLI	155
Figure 6.15. Boxplot of TRI _{95B} calculated for CH ₁ (a), CH ₂ (b), CH ₃ (c) and as average of the CH process (d) within different ranges of TLI	157
Figure 6.16. Boxplot of TRI _{95B} calculated for FS ₁ (a), FS ₂ (b), FS ₃ (c) and as average of the FS process (d) within different ranges of TLI	159
Figure 6.17. Event identification with threshold value (a) and focus on events duration and score (b)	161
Figure 6.18. Correlation between TRI _{95B} and event score	162
Figure 6.19. Visual representation of a threshold score beyond which the TRI starts to increase and the plant loses robustness	163
Figure 6.20. Trends of the main statistics (mean, median, maximum) of manganese data in influent water (a), and in X1 tank (b) (data in weeks 32 and 33 are missing); maximum, 95 th percentile, median and average of manganese data measured at the outlet of the DWTP (c)	165
Figure 6.21. Trends of MRIs scores during the year 2023, assuming a T_{goal} of 50 $\mu\text{g/L}$	166
Figure 6.22. Cumulative distribution of M ₅₀ , M ₉₀ , and M ₉₅ (a) and MRIs with $T_{\text{goal}} = 0.50$ $\mu\text{g/L}$ (b)	168
Figure 6.23. Relationship between the Fe(VI) (a) and Mn(VII) (b) depleted and the Mn(II) oxidized	171

- Figure 6.24.** Relationship between the Fe(VI) and Mn(II) oxidized at pH 7 and 9 (a); Fe(VI) concentration in a Fe(VI) solution (10 mg/L in deionized water) under different pH (b); UV-vis absorption spectrum of the Fe(VI) solution at different pH (c) 174
- Figure 6.25.** Linear regression between Fe(III) dose and Mn(II) removed (a); relationship between Fe(II) produced during Fe(III)-Mn(II) reaction and Mn(II) depleted (b) 175
- Figure 6.26.** Kinetic of Mn(II) oxidation with Fe(VI) (a); relationship between Fe(VI) depleted and Mn(II) oxidized during the kinetic assay with Fe(VI) (b); Kinetic of Mn(II) oxidation with Fe(III) (c); relationship between Fe(II) produced and Mn(II) oxidized during the kinetic assay with ferric chloride (d) 177
- Figure 6.27.** Relationship between the Fe(VI) dose and the Mn(II) removed . 179
- Figure 6.28.** Trend of residual TOC at increasing dose of permanganate and ferrate with or without Mn(II) in the solution (pH = 8) 181
- Figure 6.29.** Residual turbidity of real surface water samples at different dose of PACl without (■) or with Fe(VI) at 2.5 mg/L (●) and 4 mg/L (●). The red dotted line indicates the limit imposed by Directive EU 2020/2184 183
- Figure 6.30.** Removal of Chl-a with Fe(VI) and Mn(VII) at different dose (a); removal efficiency of Chl-a with increasing dosage of Fe(VI) and Mn(VII) (b); possible mechanisms of algal removal by ferrate and permanganate (c) 185
- Figure 6.31.** Chl-a removal using PACl at different dosage with the addition of 9 mg/L of Mn(VII) and Fe(VI) (a) and 15 mg/L of Mn(VII) and Fe(VI) 188
- Figure 6.32.** Fe(VI) concentration over time during electrochemical production tests 190
- Figure 6.33.** Reduction of ferrate(VI) concentration over time at different boundary conditions (a); ferrate decay and reduction rate after 1 hour (b). Boundary conditions: A. sample exposed to light and kept at room temperature; B. sample kept in the dark and at room temperature; C. sample exposed to light and kept at 4°C; D. sample kept in the dark and at 4°C; E. oxygen saturated sample; F. deoxygenated sample 193

List of Tables

Table 1.1. Meaningful changes observed in the climate system over the past and current centuries (Sohoulande Djebou and Singh, 2016)	7
Table 2.1. Microbiological parameters (Annex I, part A, D.Lgs 31/2001)	43
Table 2.2. Chemical parameters (Annex I, part B, D.Lgs 31/2001)	44
Table 2.3. Indicator parameters (Annex I, part C, D.Lgs 31/2001)	45
Table 2.4. Chemical parameters updated by D.Lgs 18/2023 and comparison with D.Lgs 31/2001	47
Table 2.5. Turbidity reference values and frequency of sampling and analysis	47
Table 3.1. Decision process for selecting different weighting factors (Li and Huck, 2008)	59
Table 3.2. Classification of system operation with robustness index value and mathematical significance (Li and Huck, 2008)	60
Table 4.1 Overview of EPs' removal by AOWT	75
Table 4.2. Redox potential of commonly used oxidants/disinfectants	88
Table 4.3. Summary of studies on the removal of heavy metals by ferrate(VI) (S. Dong et al., 2019)	94
Table 5.1. Existing TRIs in the literature	115
Table 5.2. Classification of system operation with robustness index value and mathematical significance	115
Table 5.3. Decision process for selecting different weighting factors	119
Table 6.1. Occurrence of TRIs within a class of system operation quality ($T_{\text{goal}} = 1 \text{ NTU}$)	138
Table 6.2. Occurrence of TRIs within a class of system operation quality ($T_{\text{goal}} = 0.3 \text{ NTU}$)	140
Table 6.3. Results of sensitivity and specificity of TRIs referred to the old and new regulations	144

Table 6.4. Occurrence of TRIs within a class of system operation quality ($T_{\text{goal}} = 5$ NTU)	149
Table 6.5. Occurrence of TRIs within a class of system operation quality ($T_{\text{goal}} < 1$ NTU and $T_{\text{goal}} = 0.3$ NTU in 95% of samples)	154
Table 6.6. Occurrence of MRIs within a class of system operation quality	167
Table 6.7. Results of sensitivity and specificity of MRIs referred to the new regulations	169
Table 6.8. Results on ferrate(VI) electrochemical production	191

List of Acronyms

Acronym	Description
AOWT	Advanced Oxidation Water Treatment
AOM	Algal Organic Matter
AOPs	Advanced Oxidation Processes
CH	Clariflocculation
DBPs	Disinfection Byproducts
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DSA	Dimensionally Stable Anode
DWD	Drinking Water Directive
DWTPs	Drinking Water Treatment Plants
ED	Electrodialysis
EPs	Emerging Pollutants
EU	European Union
FA	Fulvic Acid
Fe(VI)	Ferrate
FO	Forward Osmosis
FS	Filtration
TR-IR	Fourier Transform-Infrared
FTU	Formazin Turbidity Unit
GHGs	Greenhouse Gases
HA	Humic Acid
HAAs	Halo Acetic Acids
HABs	Harmful Algal Blooms
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IPPC	Intergovernmental Panel on Climate Change
IQR	Inter Quartile Range
ISS	Istituto Superiore di Sanità
M _x	x-percentile of Manganese
MF	Microfiltration
MPs	Microplastics
MRIs	Manganese Robustness Indices
MTBF	Mean Time Between Failures
MTTR	Mean Time To Recovery

MX	3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone
NF	Nanofiltration
NOM	Natural Organic Matter
NTU	Nephelometric Turbidity Units
PACl	Aluminium Sulphate Polychloride
PFAS	Per- and polyfluoroalkyl Substances
PPCPs	Pharmaceuticals and Personal Care Products
RI	Robustness Indices
RO	Reverse Osmosis
SCADA	Supervisory Control And Data Acquisition
SUVA	Specific UV Absorbance
T _x	x-percentile of Turbidity
THMs	Trihalomethanes
TLI	Turbidity Load Index
TOC	Total Organic Carbon
TRIs	Turbidity Robustness Indices
UF	Ultrafiltration
UVA	Ultraviolet Absorption
UV-Vis	Ultraviolet–Visible Spectrophotometry
WFD	Water Framework Directive
WHO	World Health Organization
WPS	Water Safety Plan
WTP	Water Treatment Plant
X1	Pre-oxidation
XRD	X-Ray powder Diffraction
ZLD	Zero Liquid Discharge

Scientific contributions and publications

The research described in this doctoral dissertation has been shared with the scientific community through the following scientific publications:

➤ **Research topic 1**

A modified robustness index for assessing operational performance of drinking water treatment plants: a comparative study within a new regulatory framework

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➤ **Research topic 2**

Ferrate as a sustainable and effective solution to cope with drinking water treatment plants challenges.

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Introduction

The latest Intergovernmental Panel on Climate Change (IPCC) report highlights that climate change is rapid, widespread, and intensifying, with significant impacts on both water quantity and quality. One of the most significant factors affecting surface water quality is temperature, which influences chemical, physical, and biological processes as well as lake stratification and mixing. Research highlights three major concerns related to water quality under climate change: (i) increased levels of soluble metals, such as iron (Fe), manganese (Mn), and aluminium (Al), released from lake sediments under anoxic conditions, (ii) the proliferation of algal blooms caused by rising water temperatures in nutrient-rich lakes, and (iii) increased concentrations of natural organic matter (NOM) and higher turbidity due to extreme precipitation events.

Manganese, in particular, is of concern due to its impact on the raw water used for drinking water treatment. Recent studies have observed abnormal increases in soluble manganese concentrations, especially during autumn and winter, which may be linked to climate change. Changes in temperature, dissolved oxygen, and redox potential in water can alter manganese diffusion, and under anaerobic conditions, microbial processes can reduce metals like manganese, making it harder to remove during treatment. Additionally, many large lakes have seen increases in algal blooms, which complicates water treatment, causing issues such as bad taste and odours, while also making algae removal a significant challenge.

Furthermore, extreme weather events linked to climate change can cause surges in NOM and turbidity, both of which complicate drinking water treatment. NOM, while not toxic, serves as a precursor for disinfection byproducts (DBPs) when chlorinated. It is essential to remove NOM before disinfection to limit DBP formation. Pre-oxidation is a key process in treating water with high NOM concentrations, although it can also alter NOM's characteristics, making it more hydrophilic and harder to remove through coagulation and flocculation.

Therefore, drinking water treatment plants (DWTPs) provide an essential service to communities in developed countries and ensuring a continuous supply of safe drinking water is crucial for safeguarding public health and sanitation. Nevertheless, the impacts of climate change and the increasing concentration of pollutants in water, pose significant challenge to such infrastructure.

In response to these challenges, the European Union's Directive 2020/2184 introduced more stringent regulations to ensure drinking water safety. One of its

key provisions is the stricter control of turbidity levels, an important indicator of water quality. Turbidity is a critical measurement because it can signal the presence of microorganisms like *Cryptosporidium* oocysts and provide insights into NOM concentrations, which contribute to DBP formation during water treatment. The Directive mandates that turbidity must be below 0.30 nephelometric turbidity units (NTU) in 95% of samples and must never exceed 1 NTU. This represents a stricter standard compared to previous regulations (Directive 98/83/CE), where the indicative limit for turbidity was 1 NTU.

This new regulation introduces the concept of robustness in DWTPs, which refers to the system's ability to maintain high water quality despite variations in raw water quality and other operational challenges. Therefore, robustness is a measure of how the system copes with changes. In past studies, Turbidity Robustness Indices (TRIs) were developed to help assess a plant's ability to meet performance goals. However, earlier versions of TRIs had limitations, including arbitrary weighting scores and failure to address performance variability effectively. As a result, the existing TRIs were not fully adequate for measuring the robustness of DWTPs under the stricter requirements of Directive 2020/2184.

Therefore, climate change poses ongoing risks to drinking water quality, necessitating enhanced robustness of DWTPs and innovative approaches to water treatment.

This has led researchers to explore the use of ferrate (Fe(VI)), an emerging oxidant which offers promising broad-spectrum efficacy. Ferrate is advantageous because it produces non-toxic byproducts, has a high oxidation potential, and can be generated electrochemically, making it a cost-effective and environmentally friendly alternative to conventional oxidants.

Studies showed that ferrate effectively removes manganese, NOM, and turbidity, but further research is needed to fully understand its reaction mechanisms, stoichiometry, and interactions with other pollutants and environmental factors such as pH. Ferrate, with its broad-spectrum effectiveness and potential synergy with conventional treatments, offers a promising solution for addressing water quality challenges under climate-driven emergency conditions. However, more research is needed to optimize its use and to understand its full potential in combination with traditional treatment methods.

In this regard, the thesis proposes an initial examination of the regulatory framework, the main impacts of climate change on surface water quality, the

robustness indices in literature and innovative techniques for treating water intended for human consumption

It then follows the experimental section, in which two main objectives are pursued.

In more detail, the first aim of the present thesis was to propose a new manganese robustness index (MRI_{95B}) and a modified turbidity robustness index (TRI_{95B}) for the operational analysis of a drinking water treatment plant and able to overcome the highlighted issues of the existing ones. These indices were applied to the Sambuca di Sicilia plant, which treats surface water drawn from the Garcia reservoir, subjected to clariflocculation, filtration, and subsequent disinfection treatments. Such indices were used as a quantitative measure to assess how well the plant was performing in maintaining water quality standards while providing an early warning system by detecting deviations from desired water quality standards. In this way, it was possible to identify potential issues to specific process units and address emergency situations through the application of alternative treatments.

In this light, the second part of the research project was focused on the evaluation of ferrate(VI) treatment to be used either as an alternative or in combination with conventional reagents. Specific investigations on the mechanisms for removing the main pollutants, the stoichiometry of reactions, as well as potential advantages and disadvantages, have been conducted.

Overall, climate change may not be preventable, it is essential to implement necessary measures to ensure the consistent quality of treated drinking water during both normal conditions and extreme events.

Chapter I

Effect of climate change on water quality

Climate change refers to the long-term alteration of global or regional climate patterns, primarily due to the increased accumulation of greenhouse gases (GHGs), especially carbon dioxide (CO₂), in the atmosphere. Since the Industrial Revolution, the concentration of CO₂ in the troposphere has risen from 290.7 ppm to 407.58 ppm in 2018 (EEA, 2019), alongside a global average temperature increase of 0.08°C (0.14°F) per decade (US Global Change Program, 2018). This warming effect has intensified since 2010, with the 10 warmest years on record occurring within the last 12 years. According to the Intergovernmental Panel on Climate Change (Intergovernmental Panel on Climate Change, 2021), global temperatures have risen by approximately 1.2°C since pre-industrial times, with significant implications for the hydrological cycle (Ma et al., 2022). Figure 1.1 shows the evolution of the increase of temperature and CO₂ emissions since the Industrial Revolution.

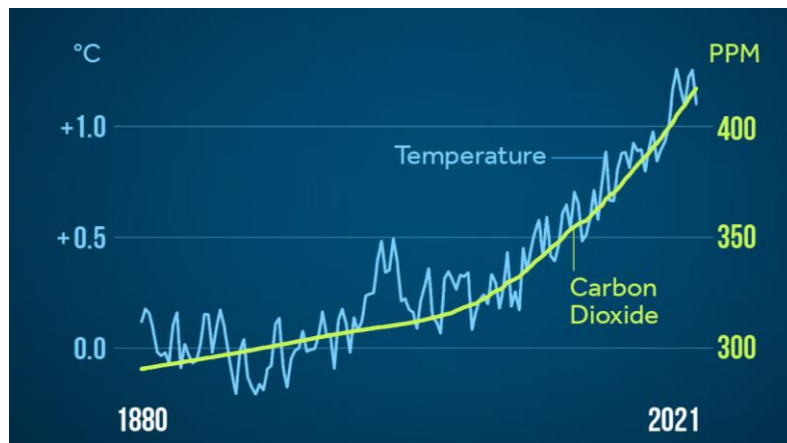


Figure 1.1. Trend of temperature and CO₂ emissions since Industrial Revolution (<https://www.climatecentral.org/climate-matters/peak-co2-heat-trapping-emissions>)

Generally, ambient temperatures are expected to rise in both summer and winter, with higher latitudes experiencing greater warming rates than equatorial regions (Earman and Dettinger, 2011). This accelerated warming in high latitude areas is likely to significantly increase ice melting, with snowfall gradually being replaced by rainfall in polar regions. The rise in temperature also leads to increased atmospheric moisture content, which boosts precipitation in wet

regions with abundant surface water. Concurrently, the rate of evapotranspiration increases, exacerbating drying in arid areas. Consequently, climate change is expected to intensify the differences in precipitation patterns between wet and dry regions. Specifically, high-latitude, equatorial Pacific, and mid-latitude wet regions are experiencing increased precipitation, while mid-latitude and subtropical dry zones are seeing a decrease (Earman and Dettinger, 2011). This means that extreme weather events like droughts will become more frequent in dry regions, while floods will become more common in wet regions. Overall, the impacts of climate change, such as changes in temperature and precipitation patterns, directly affect the water cycle, thereby influencing the quantity and quality of groundwater and surface water in various regions in complex ways (Dao et al., 2024). Surface water and groundwater are interconnected components of the hydrological cycle. Surface water bodies can recharge groundwater aquifers through infiltration, while groundwater can discharge into rivers and lakes, maintaining their flow during dry periods. Climate change-induced alterations in precipitation and temperature patterns disrupt this balance, affecting both surface water and groundwater resources. Understanding this interaction is crucial for comprehensive water resource management in a changing climate.

1.1 Climate Change and the Water Cycle

The hydrological cycle is the continuous movement of water on, above, and below the surface of the Earth. It involves processes such as evaporation, condensation, precipitation, infiltration, and runoff. Solar energy drives the cycle, causing water to evaporate from surfaces like oceans, lakes, and rivers, as well as from soils and vegetation. This water vapor condenses to form clouds, which eventually release precipitation back to the surface, replenishing water bodies and infiltrating the ground to recharge aquifers (Kundzewicz, 2008).

Climate change affects the hydrological cycle by altering the rates and distribution of these processes (Delpla et al., 2009; Mujere and Moyce, 2016). Higher temperatures increase the rate of evaporation and the atmosphere's capacity to hold moisture, leading to more intense and frequent precipitation events in some areas and prolonged droughts in others. These changes have profound implications for surface water quantity and quality.

1.1.1 Changes in precipitation pattern

Climate change is altering precipitation patterns globally, leading to increased variability and more extreme weather events. As reported in Table 1.1, the annual

precipitation scenarios present heterogeneous trends, depending on the latitude band. Some regions experience more intense and frequent storms, while others face prolonged periods of drought. These changes are driven by the increased capacity of a warmer atmosphere to hold moisture, leading to heavier precipitation events.

Table 1.1. Meaningful changes observed in the climate system over the past and current centuries (Sohoulande Djebou and Singh, 2016)

Climate factor	Feature	Changes		Additional fact	Sources
		Period 1	Period 2		
Temperature	Trend of global earth temperature	1906–2005: warming trend is 0.06°C/decade	1956–2005 : warming trend is 0.13°C/decade	–	IPCC 2007
	Average earth temperature	1880–1974: average earth global temperature climbed by 0.3°C.	1975–2010: average earth global temperature increased by 0.5°C	–	IPCC 2007
	Land Surface Air Temperature	1901–1950 : increased by 0.097°C per decade	1951–2012 : increased by 0.175°C per decade	1979–2012 : increased by 0.254°C per decade	Rohde <i>et al.</i> , 2013 ; IPCC 2013
Cryosphere	Glaciers (outside Greenland and Antarctica)	1993–2009: Ice mass loss was 0.76 mm/year	2005–2009: Ice mass loss was 0.83 mm/year	–	IPCC 2013
	Perennial ice covers	1980: the extent was 7.9 × 10 ⁶ km ²	2012: the extent was 3.5 × 10 ⁶ km ²	–	IPCC 2013
	Arctic ice packs	1980: annual mean thickness was 3.6 m	2000: annual mean thickness declined to 2.4 m	since 1978, Arctic sea ice extent decreased by 2.7% per decade	IPCC 2013; Rothrock <i>et al.</i> , 2008
Oceans	Global sea level	1961–2003: global sea level raised by 1.8 mm/year	1993–2003: global sea level raised by 3.1 mm/year	Correlation between sea level rise and the global temperature	IPCC 2013
	Sea Surface Temperature	1901–1950 :increased by 0.066°C per decade	1951–2012 : increased by 0.071°C per decade	1979–2012 : increased by 0.073°C per decade	IPCC 2013; Ishii <i>et al.</i> , 2005
Precipitation	Latitude box : 30°N–60°N	1901–2008: the trend was 3.14 mm/year per decade	1951–2008: the trend was 1.50 mm/year per decade	Estimates using Global Precipitation Climatology Centre GPCP data	IPCC 2013; Becker <i>et al.</i> , 2013
	Latitude box : 30°S–30°N	1901–2008: the trend was –0.48 mm/year per decade	1951–2008: the trend was –4.16 mm/year per decade		
	Latitude box : 60°S–30°S	1901–2008: the trend was 2.40 mm/year per decade	1951–2008: the trend was –0.51 mm/year per decade		

According to Douville et al. (2021) GHG forcing has driven increased contrasts in precipitation amounts between wet and dry seasons and weather regimes over tropical land areas, with a detectable precipitation increase in the northern high latitudes. GHG forcing has also contributed to drying in dry summer climates, including the Mediterranean, southwestern Australia, southwestern South America, South Africa and western North America. Seneviratne et al. (2021) also concluded that the frequency and intensity of heavy precipitation events have likely increased at the global scale over most land regions with good observational coverage. Heavy precipitation has likely increased on the continental scale over North America, Europe and Asia. Regional increases in heavy precipitation frequency and/or intensity have been observed.

As of 2020, approximately 498 million people lived in areas with unfamiliarly wet conditions, defined as long-term changes greater than one standard deviation from the 1891-2016 mean. These areas are primarily in mid and high latitudes. Conversely, around 163 million people lived in unfamiliarly dry areas, mostly in low latitudes (Hawkins et al., 2020). Due to high variability, long-term changes in annual mean precipitation are not distinguishable from variability in many areas. Notably, many regions have seen increased precipitation in part of the year and decreased precipitation at other times, leading to minimal changes in annual mean precipitation but likely more people experiencing unfamiliar seasonal precipitation.

The intensity of heavy precipitation has increased in many regions, including much of North America, most of Europe, most of the Indian sub-continent, parts of northern and southeastern Asia, much of southern South America, parts of southern Africa, and parts of central, northern, and western Australia (Dunn et al., 2020; Qiaohong et al., 2020). Conversely, heavy precipitation has decreased in regions like eastern Australia, northeastern South America, and western Africa. The length of dry spells has changed, with increases in annual mean consecutive dry days in large areas of western, eastern, and southern Africa, eastern and southwestern South America, and Southeast Asia, and decreases across much of North America. Precipitation extremes have changed in some places without trends in annual precipitation. Regions such as southern Africa and parts of southern South America are seeing increased heavy precipitation and longer dry spells. More people (~709 million) live in regions with increased annual maximum one-day precipitation than those with decreased precipitation (~86 million). However, more people are experiencing longer dry spells (~711 million) than shorter dry spells (~404 million) compared to the 1950s.

1.1.2 Changes in stream flow

The trend in annual streamflow generally follows observed changes in regional precipitation and temperature since the 1950s (Jiménez Cisneros et al., 2014). Between the 1950s and 2010s, stream flows showed decreasing trends in parts of western and central Africa, eastern Asia, southern Europe, western North America and eastern Australia, and increasing trends in northern Asia, northern Europe, and northern and eastern North America (Dai, 2016; Gudmundsson et al., 2019, 2017; Li et al., 2020; Masseroni et al., 2021). Significant spatial heterogeneity is also found in streamflow changes at the regional scale. Significant declines occurred at 11% of stations and significant increases at 4% of stations, with most decreases occurring in southern Canada (Bonsal et al.,

2019). An increasing trend (1950–2010) is found in the northern region, mainly due to climate warming.

The spatial differences in annual mean streamflow trends around the world are influenced by climatic factors, particularly changes in precipitation and evaporation (Ficklin et al., 2018; Greve et al., 2014; Hannaford, 2015), as well as by anthropogenic forcing (Gudmundsson et al., 2021).

Precipitation explains over 80% of the changes in discharge of large rivers from 1950 to 2010 in northern Asia and northern Europe, where the impact of human activities is relatively limited (Li et al., 2020). In northwest Europe, precipitation and evaporation changes explain many observed trends in streamflow (Vicente-Serrano et al., 2019). In several polar areas in northern Europe (e.g., Finland), North America (e.g., British Columbia in Canada) and Siberia, many studies reported increased winter streamflow primarily due to climate warming, for instance, more rainfall instead of snowfall and more glacier runoff in the winter period (Bonsal et al., 2020). In contrast, in southwestern Europe, land cover changes and increased water demands by irrigation are the main drivers of streamflow reduction (Vicente-Serrano et al., 2019).

Shi et al. (2019) found that in 40 major basins worldwide, both climatic and direct human impact contribute to observed flow changes to varying degrees. Climate change or variability is the main contributor to changes in basin-scale trends for 75% of rivers, while direct human effects on streamflow dominate for 25%.

1.1.3 Changes in droughts and floods

Droughts are prolonged periods of abnormally low rainfall that led to water shortages. Climate change is expected to increase the frequency, severity, and duration of droughts in many regions. This has significant implications for surface water quantity, as reduced rainfall leads to lower water levels in rivers, lakes, and reservoirs.

While some regions face droughts, others are experiencing increased flooding due to more intense and frequent rainfall events (Seneviratne et al., 2021). Flooding can have immediate and severe impacts on surface water quantity by overwhelming water bodies, leading to temporary surges in water availability.

The frequency and magnitude of river floods have changed in the past several decades in some regions with impacts across human and natural systems. A global flood database based on in situ measurement and satellite remote-sensing

during 1985–2015 show that floods have increased 4-fold and 2.5-fold in the tropics and northern mid-latitudes, respectively (Najibi and Devineni, 2018). Estimates of flood exposure using satellite-derived inundation area and high-resolution population data showed a 20–24% increase during 2000–2018 (Tellman et al., 2021). Analyses of in situ streamflow measurement showed both increases and decreases in the frequency of river floods for 1960–2010 in Europe and the USA (Berghuijs et al., 2017; Blöschl et al., 2019), an overall increase in China, Brazil and Australia but decrease in some areas in the Mediterranean (Tramblay et al., 2019) and southern Australia. Warming in the last 40–60 years has led to a 1–10 days earlier per decade spring flood occurrence depending on the location (the most frequent being 2–4 days per decade) (Blöschl et al., 2017; Dudley et al., 2017; Solander et al., 2017).

1.2 The impact of climate change on water quality

It has long been recognized that climate change leads to significant alterations in both the physical and chemical characteristics of water, including oxygen content, turbidity, and nutrient load, as well as the biological ones that manifest as changes in the structure and functioning of aquatic ecosystems. More recently, it has been observed that other physicochemical parameters that define water quality, such as acidification, salinization, thermal stratification of lakes, and light penetration in the water column, are also changing (Delpla et al., 2009; EEA, 2008).

However, the challenge of distinguishing between temporal modifications in water quality characteristics caused by climate change and those resulting from land use changes (urbanization, desertification, water resource utilization, etc.) has made it difficult to establish clear analytical models and correlations that can be used to evaluate future scenarios for planning strategies.

Nevertheless, the significance of this issue, which directly impacts the usability of water resources for human purposes and the preservation of ecosystems, needs further research based on extensive spatial-temporal data. Equally essential is the implementation of preventive approaches to monitor and manage water quality. The European governance has shown clear interest in this direction by introducing risk assessment procedures for human health in the water cycle, albeit with differentiation between drinking water supply chains and wastewater management. The former is addressed through Water Safety Plans (WSP), which were implemented for all drinking water systems by the EU Directive 2015/1787 and 2020/2084 (DIRECTIVE 2015/1787/EU; 2020/2184/EU).

1.2.1 Qualitative characteristics modifications of the water cycle

Different climatic factors can have consequences on water quality. Among them, the increase in air temperature, the frequency of extreme events, the extreme alternation of wet and dry periods, and the increase in solar radiation appear to be of greater importance (Delpla et al., 2009).

There can be numerous effects of these factors. The main ones include the alteration of chemical and biological balances in ecosystems, which are known to be sensitive to even slight temperature increases. Others include the reduction of dilution effects of anthropogenic compounds during long drought periods, the increased leaching of pollutants into water bodies during flooding events, the increased frequency and duration of eutrophication in poorly circulated basins (such as lakes, reservoirs, and coastal zones) due to longer and deeper thermal stratifications, and the rise in average sea levels, leading to the risk of saline intrusion and salinization of coastal aquifers. It should be noted that these phenomena can also be attributed to causes unrelated to climate change but rather to changes in anthropogenic land use, such as land use evolution, deforestation, urbanization leading to increased surface runoff and reduced flow times, concentrated pollution from urban and industrial activities, and diffuse pollution from agricultural sources (Salerno et al., 2018). The consequences of these phenomena on water quality overlap with those of climatic origin, making them difficult to distinguish. Therefore, it is now common to speak of "global" changes resulting from all the mentioned phenomena, regardless of their origin.

Among the main effects of climate change, the increase in temperature is recognized as having the greatest impact on both the entire hydrological cycle and water quality. The temperature increase influences the kinetics of biogeochemical processes that regulate aquatic ecosystems, thereby modifying their quality (Verweij et al., 2010). This can result in:

- reduction of oxygen content due to increased rates of biological reactions, especially during summer and low flow periods or in the hypolimnetic layers of lakes and artificial reservoirs, causing significant stress to aquatic ecosystems;
- more stable thermal stratification, leading to reduced water mixing in lakes and artificial reservoirs, deoxygenation of deep waters, modification of nutrient cycling, and changes in planktonic communities;

- less ice formation on river or lake surfaces or early breakup or absence of ice in water bodies with cold climates, with consequent impact on planktonic communities;
- increased eutrophication due to higher nutrient loads in warmer climates, resulting from increased mineralization and release of nitrogen, phosphorus, and carbon from soils. Additionally, phosphorus release from lake sediments can occur under hypolimnetic anoxic conditions;
- intensification of harmful algal blooms, often dominated by toxic cyanobacteria, posing threats to lake ecosystems and human health.

The increased biodegradation of organic matter in soils resulting from temperature increase leads to higher concentrations of dissolved humic substances in surface waters due to soil leaching, especially during flooding events. While this increase may stimulate microbial growth and improve the biodegradation of certain pollutants, it can also have negative effects, including reduced effectiveness of solar radiation in natural disinfection of surface waters and significant challenges for water treatment plants (Lipczynska-Kochany, 2018).

The higher intensity and frequency of extreme events and resulting floods increase the load of pollutants washed off from soils (organic substances, nutrients, hazardous substances). They also increase the frequency of wastewater discharge into water bodies through combined sewer overflow outlets.

In regions experiencing significant reductions in precipitation, the decrease in river flows and groundwater recharge can worsen water quality due to reduced dilution of pollutants finding their way into water bodies (Mujere and Moyce, 2016).

Figure 1.2 depicts the decline in the quality of surface water and groundwater resources due to both anthropogenic and natural processes stemming from diverse sources. Additionally, it illustrates the consequential impact on human health resulting from these activities.

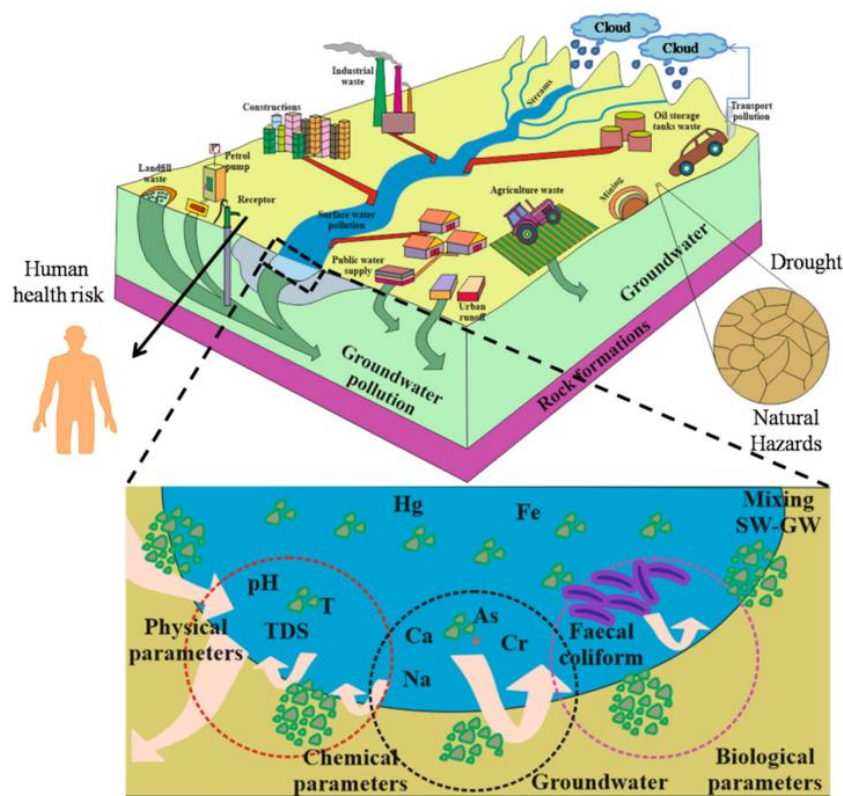


Figure 1.2. Effect of climate change on the quality of surface water and groundwater resources as well as the effect on human health (Akhtar et al., 2021)

1.2.2 Changes in the characteristics of groundwater bodies

Climate change has also been observed to have effects on the quality of aquifers. The main effects are as follows (Şen, 2021):

- increased surface runoff due to more intense precipitation, resulting in reduced aquifer recharge and lower resilience to pollutant inputs;
- greater intrusion of saltwater into coastal aquifers due to rising sea levels, leading to potential salinization of the aquifers;
- variation in CO₂ concentration in the water due to the dissolution of carbonate rocks resulting from changes in the hydrological regime;
- potential slowing of aquifer recharge due to increased organic carbon content in the soil.

1.2.3 Changes in the characteristics of surface water bodies

Significant effects have been observed on the quality of surface waters, particularly within lakes and artificial reservoirs. One of the most reported effects in the literature is the increased frequency of eutrophication processes due to the higher nutrient inputs. Shallow lakes are the most affected by elevated nitrogen and phosphorus concentrations in the water column, resulting from intensive agriculture, urban discharge, and industrial activities within their watersheds. The increased frequency of intense weather events leads to greater water and nutrient runoff into the reservoirs, exacerbating eutrophication phenomena (Rodgers, 2021). As mentioned earlier, higher temperatures can also increase the release of nutrients from lake sediments and soils, promoting faster algal growth.

Another phenomenon associated with climate change is sediment resuspension, which causes a significant increase in turbidity and thus affects water quality. This phenomenon is strongly influenced by sediment characteristics such as size and shape, as well as environmental parameters such as wind, currents, water heating, and organism activity (Choukri et al., 2020).

Due to temperature increases, the ecological balance of lake environments is altered, affecting natural productivity cycles. Specifically, it has been observed that higher temperatures in reservoirs lead to an increase in benthic biomass that surpasses zooplankton and other macroinvertebrates (Kimbrough, 2019). The high activity of these benthic organisms also contributes to the increased frequency of sediment resuspension events (Choukri et al., 2020).

However, it should be noted that artificial reservoirs generally respond differently to climate change compared to natural lakes, due to the different management practices regarding water levels and outflows. Specifically, adjusting the withdrawal depth in artificial reservoirs can be used as a tool to optimize the quality of raw water supplied to water treatment plants.

Another form of pollution in surface waters that has been found to increase with global warming is related to the proliferation of plastic in the environment. The more extreme weather conditions and floods associated with climate change contribute to an increased amount of micro- and nano-plastics reaching lakes and reservoirs through soil runoff. These pollutants can encounter biotic targets once the water is used and intended for human consumption (Ford et al., 2022; Zhang et al., 2020).

1.3 Effects on water service infrastructure

Changes in water quality can also have consequences for water service facilities (water treatment plants, distribution networks). These effects result from both modifications in the characteristics of the water entering the treatment plants and subsequently being distributed through the networks, and from phenomena and processes that occur within the facilities and networks (Proença De Oliveira et al., 2015). Drinking water treatment plants experience a significant reduction in pollutant removal efficiency, while distribution networks are at risk of water quality alteration, particularly due to biological recontamination.

1.3.1 Effects on drinking water treatment plants

Observed effects of climate change on water treatment plants include both quantitative and qualitative aspects. While the impact is initially identified with changes in water quantity, resulting from alternating periods of abundance and extreme drought, the quality of raw water entering the plants can also be significantly affected.

The main climate change effects that potentially impact water treatment involve modifications in the hydrological regime, characterized by less frequent but more intense events, as well as increased water temperature and the frequency of wildfires (Feldbauer et al., 2020).

The combination of these factors leads to a notable deterioration in the quality of raw water entering the treatment plants, including increased turbidity, nutrient levels, dissolved organic matter, algae, heavy metals, and more. Additionally, the variability of water quality characteristics entering the plant, caused by alternating dry and intense events, results in extreme values, particularly for parameters like turbidity, exceeding past averages. Conventional treatment processes used for surface water treatment (such as clarification, filtration, and disinfection), which previously ensured compliance with quality standards required by international and national regulations with minimal intervention, are often challenged and require upgrading due to the increase in extreme events. Moreover, there is no one-size-fits-all solution, as the effects of climate change vary depending on the specific geographic area affected.

1.3.1.1 Natural organic matter

Natural Organic Matter (NOM) is a crucial parameter for the design and operation of water treatment processes. NOM can negatively affect water quality by altering

the colour, causing odour problems, promoting biological growth, and causing corrosion in distribution systems. Additionally, increased levels of NOM can raise the concentration of complexed heavy metals and adsorbed organic micropollutants, posing a health risk (Crittenden et al., 2014). Another concern is the formation of potentially harmful disinfection by-products (DBPs), such as THMs, HAAs, and MX, during water treatment. High levels of NOM require larger amounts of disinfectants and coagulants and complicate the removal of particles and pathogenic microorganisms (Ritson et al., 2014). Changes in raw water quality can affect drinking water supply systems, necessitating more advanced treatment processes and modifications to existing facilities. Since current treatment processes can only remove a fraction of the total NOM, high levels of NOM can also deteriorate tap water quality (Sharma, 2020).

Overall, the deterioration of surface water quality potentially has a negative impact on the ability of treatment plants to meet the limits set by regulations for water intended for human consumption. A study conducted by American researchers simulated the effects of changing surface water quality on the performance of a water treatment plant (Li et al., 2014). The changes in water quality were measured in terms of increased concentrations of DOM, ammonia, and temperature. The simulation results demonstrated that worsening water quality significantly increases the risk of exceeding limits for DOM and trihalomethanes in treated water compared to normal plant operating conditions.

Eikebrokk et al. (2004) quantified the impacts of increasing NOM levels on treatment and found that a long-term increase in source water colour from 20 to 35 mg Pt/L resulted in an increase in coagulant dose by 64% which led to nearly doubling of sludge production and in an increase of 87% in the number of daily backwashes of the filtration system. In addition to the long-term browning, the impacts of acute changes in NOM concentration induced by climate events should also be considered as they can also impact enhanced coagulation on a smaller timescale. Hurst et al. (2004) examined the impact of heavy precipitation events on coagulation and clarifier performance and noted an increase in NOM concentrations (40 %, from 3.9 to 5.5 mg/L to 14.4 mg/L) significantly impaired coagulation resulting in elevated settled water turbidity. Such treatment challenges may occur more frequently given the expected increase in heavy precipitation events because of climate pressures.

1.3.1.2 Harmful algal blooms

Harmful algal blooms (HABs) are formed when toxic or ecosystem disruptive algal species grow to sufficient abundance. In particular, eutrophication caused by excess nutrient supply may trigger HABs, which cause water quality problems such as hypoxia (Diaz and Rosenberg, 2008) and release toxins that affect aquatic organisms (Harrison et al., 2017; Landsberg, 2002) and threaten human public health due to consumption of the contaminated organisms (Sin and Lee, 2020).

Climate change is predicted to increase the severity and prevalence of HABs (Hennon and Dyhrman, 2020). Hallegraeff (2010) reported an increase in the number and shift in the seasonality of HAB events around the world which is thought to be related to climate change. HABs in lakes and drinking water reservoirs such as *Prymnesium parvum* and the cyanobacteria *Microcystis* and *Cylindrospermopsis* are also thought to be exacerbated by climate change and represent a growing concern for public safety (Antunes et al., 2015; Paerl and Paul, 2012; Patiño et al., 2014). Recently, Zhang et al. (2024) reported that, in China, the nationwide occurrence of algal blooms has surged by 113.7% from the 2000s to the 2010s.

HABs in freshwater, particularly nearby the intake of a water treatment plant (WTP), can severely challenge the treatment systems with two negative impacts, including that (Deng et al., 2017):

- algal cells result in a sharp increase in influent turbidity;
- unwanted dissolved organic compounds are produced during cell growth or lysis, such as algal toxins, taste and odor (T&O)-causing compounds, and algal organic matter (AOM) that may serve as disinfection byproduct (DBP) precursors.

1.3.1.3 Turbidity

Increases in precipitation amounts and/or intensities and the corresponding increases in runoff and streamflow can produce problematic turbidity levels (Li et al., 2014), thus overwhelming a water treatment infrastructure and deteriorate treatment performance.

The Bearspaw water treatment plant (WTP) in Calgary, Alberta, experienced 3750 nephelometric turbidity unit (NTU) of turbidity following an extreme rainfall event in 2013, and Red Deer WTP in Alberta faced around 3000 NTU of turbidity spike due to flooding in 2005 (Yarahmadi, 2019). A study reports that,

in 2001, the turbidity in the Tame River in England increased substantially by an order of magnitude to >300-500 formazin turbidity unit (FTU) followed by spring storm events (Lawler et al., 2006). Turbidity peaks ranging from 53-1021 NTU have been observed after rainfall events (>10 mm) in a watershed in Fiji in 2009 and 2010 (Ram and Terry, 2016). The water utility serving New York City (USA) has recognized heavy precipitation events as one of its major climate change related concerns. Intense precipitation events have the ability to elevate turbidity levels in some of the main reservoirs of the city up to 100 times the legal limit for source quality at the intake of the utilities, which can result in additional treatment and monitoring costs (IPCC, 2007). In 2011, a DWTP in Alabama, USA, using the Tennessee River as the raw water source, experienced a surge of finished water turbidity of 15 NTU after a severe winter storm, whereas the standard was 0.3 NTU. As a result, the DWTP was forced to shut down for 3 days, alarming the residents and resulting in huge economic loss. The coagulation-flocculation process was affected by the type and concentration of suspended solids, dissolved organic matter and temperature (Qiu et al., 2019). The treatment process failed to meet the standard due to the storm event, indicating that the system lacked robustness. In 2015, as an aftermath of a hurricane in South Carolina, USA, more than 500 mm of rainfall had taken place in 5 days, which is 5 times more rain than the average precipitation of the entire month, which led to a turbidity spike in water bodies up to 56 NTU during the first few days of flooding, whereas the baseline turbidity was lower than 10 NTU. Moreover, up to 66% of the total annual DOC export occurred during the 5-day long event and the elevated DOC levels in water bodies were observed for 8 weeks (Ruecker et al., 2017).

1.3.1.4 Heavy metals and Manganese

Climate changes also impact water quality in terms of increase of soluble metals (Fe, Mn, Al) which are released from lake sediments under anoxic conditions.

In recent years, repeated cases of high and extremely high pollution levels in water and bottom sediments have been recorded during routine observations of the hydro-chemical network of the Russian Hydrometeorological Service (Ministry of Natural Resources and Ecology of the Russian Federation, 2021).

Among metals, manganese is a contaminant of particular concern for the quality of raw water to be treated in drinking water treatment plant (Krueger et al., 2020; Matveeva et al., 2022). Recently, several studies have observed abnormal increases in soluble manganese concentrations (Mn^{2+}) in raw water (DeSimone and Ransom, 2021; Goodwill et al., 2016), exhibiting strong seasonality with

peaks occurring mainly during autumn and winter (Matveeva et al., 2022) (Figure 1.3). These increases may be closely connected to climate change, as variations in certain environmental parameters (temperature, dissolved oxygen, redox potential) and the presence of certain microorganisms can alter the pathways of manganese diffusion in water. The previously mentioned sediment resuspension phenomenon and alterations in the chemical equilibrium governing manganese oxidation or reduction facilitate its solubilization and transport to water treatment plants, posing significant challenges for its removal (Niemistö and Lund-Hansen, 2019).

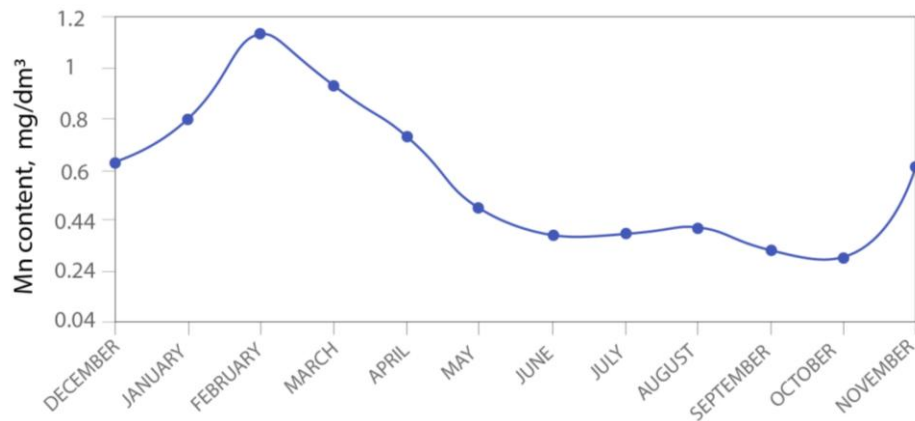


Figure 1.3. Seasonal dynamics of Mn content in water (Matveeva et al., 2022)

The presence of manganese in water is problematic as Mn is easily bioaccumulated; this can lead to unwanted ecotoxicological effects and, in the case of prolonged exposure to high doses of Mn and its compounds, to detrimental human health impacts (Matveeva et al., 2022). For instance, Frisbie et al. (2012) reported that manganese, in high quantities, acts as a neurotoxin, causing learning difficulties and intellectual deficits in children and an increase in the frequency of parkinsonism in adults.

1.3.2 Effects on water distribution networks

Water distribution networks pose a high risk of water recontamination due to the prolonged water residence times resulting from their extensive length. This risk leads to the formation of bacterial biofilms, which act as potential sources of pathogenic contamination (Bloetscher et al., 2014).

A study conducted in Canada highlighted that a modest temperature increase (+1.6°C) resulted in a significant reduction in chloramine concentration and a simultaneous increase in nitrates. This was attributed to the reduced effectiveness of residual disinfectant, which diminished its inhibitory effect on ammonia-oxidizing bacteria (Kimbrough, 2019).

Furthermore, a recent study demonstrated that temperature increases (up to 24°C) associated with climate change can promote physicochemical and microbial alterations in the water transported within distribution networks, influencing the dynamics of biofilm development on pipe surfaces, and contributing to the potential release of pathogens into drinking water (Calero Preciado et al., 2021). The study observed a substantial increase in certain microorganisms, particularly bacteria (*Pseudomonas*) and fungi (*Fusarium genus*). It was also shown that temperature elevation leads to the release of metals and detachment of biofilm from the pipe walls, resulting in increased water turbidity. Other studies highlighted the presence of macroinvertebrates from the *Chironomidae* family (*Paratanytarus grimmii*) and macroinvertebrates (*Asellus aquaticus*) within distribution networks due to temperature increases (Cavicchioli et al., 2019; Christensen et al., 2011).

An identified risk factor in several studies is related to pH alterations within the networks. As water bodies absorb a significant amount of human-produced CO₂, instances of water acidification can occur. It has been demonstrated that such conditions can further contribute to the increased abundance of pathogens within potable water distribution networks (Chadwick et al., 2021).

1.4 Drinking water safety

Given the unpredictable nature of climate change and its effects, ensuring drinking water safety in the face of climate-driven risks will remain an ongoing and persistent challenge. Presently, the risks to drinking water quality are evident during extreme events like intense rainfall, floods, and harmful algal blooms. In response, governments may need to temporarily suspend waterworks operations to address these emergencies. To safeguard drinking water safety in the long term, it is crucial for governments, research institutions, and waterworks to engage in continued discussions and place increased emphasis on monitoring and addressing water quality issues resulting from the impacts of climate change (Figure 1.4).

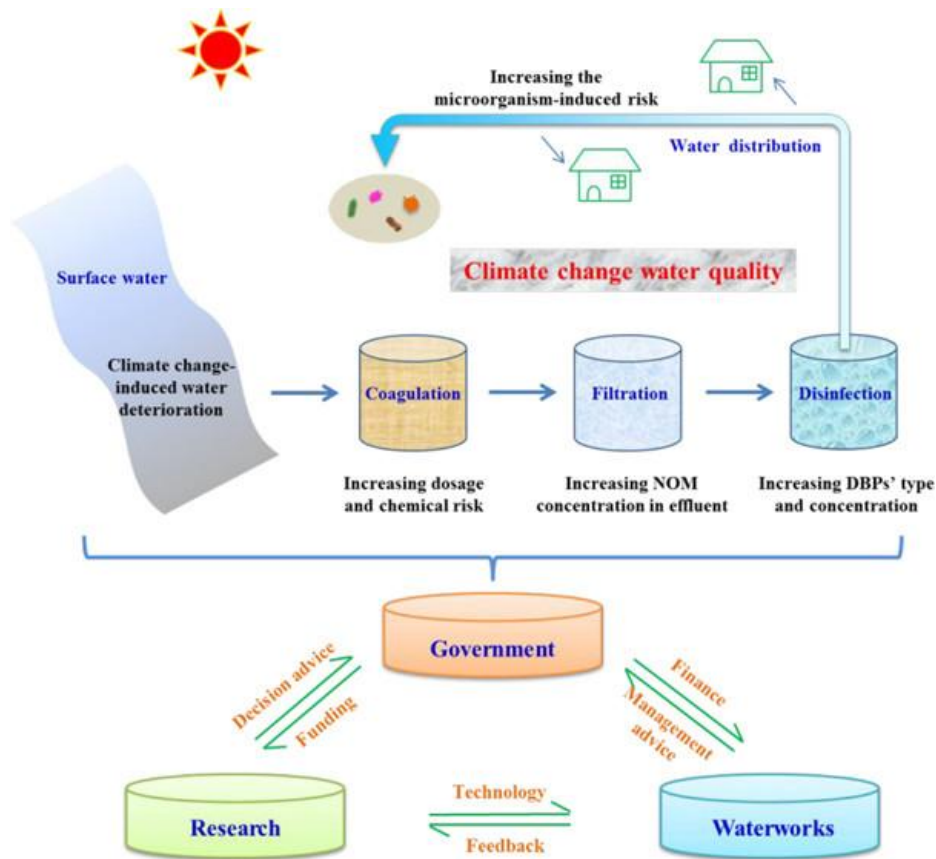


Figure 1.4. Impact of climate change on drinking water safety (Ma et al., 2022)

The issues discussed so far highlight the need to develop resilient water supply systems capable of adapting to the qualitative and quantitative variations of raw water. This is achieved using advanced and more efficient treatment plants that can effectively remove non-conventional contaminants present in raw water at higher concentrations. Reliable management and control methodologies, such as Water Safety Plans (WSPs), are also employed. WSPs are prevention and control tools based on site-specific risk analysis extended to the entire drinking water supply chain. In Italy WSPs were implemented with Decree of the Health Ministry (Ministero della Salute, 2017), in compliance with Directive 2015/1787/EU, adopting the methodology developed by the World Health Organization. This methodology was recently adopted with Directive 2020/2184/EU, concerning the quality of water intended for human consumption,

and has recently been incorporated into Italian law with Legislative Decree nr. 18 of 23/02/2023, imposing the adoption of WSP.

Alongside the development of WSPs, it is good practice for operators of water treatment plants to perform specific functional checks on existing facilities to identify their weaknesses and operational limits. Equally important is the study of technological and management solutions aimed at minimizing the risk of water contamination throughout the entire process, from the point of abstraction to the point of delivery to end users. Among advanced treatments, the use of chemicals with broad-spectrum effects deserves mention, as they ensure the removal of different contaminants in a single solution.

Furthermore, it should be noted that climate change can also indirectly influence water distribution systems for human consumption, primarily through changes in demand by users who adapt their needs based on new conditions (e.g., frequent drought events, rising temperatures, etc.) (Roshani et al., 2022). Demographic shifts and adjustments in industrial activities resulting from new climatic conditions can significantly alter the territorial distribution of water needs and create imbalances between demand and supply capacity for certain supply systems (Proença De Oliveira et al., 2015). Alongside the potential increase in water demand for other uses, such as agriculture and energy production, these changes in water needs could strain the ability to meet water demand in urban areas, especially during milder and summer seasons (Roshani et al., 2022).

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Chapter II

Regulatory framework on water intended for human consumption

Water is a fundamental human right and essential for life, health, and well-being. Ensuring the safety and quality of drinking water is a critical public health priority. In the European Union (EU), the Drinking Water Directive (DWD) provides the regulatory framework to guarantee that water intended for human consumption is safe, clean, and available to all citizens. The directive establishes stringent quality standards, monitoring and reporting obligations, and risk management strategies to protect public health and promote sustainable water management.

Specifically, DWD applies to:

- all water supply systems serving a population of more than 50 inhabitants or supplying more than 10 m³ of water per day;
- systems providing drinking water in tanks, bottles, or other containers;
- food industries that use water, unless the competent national authorities can guarantee that the use of such water does not have consequences for consumers' health.

2.1 Historical Context and Evolution of the Drinking Water Directive

The EU's commitment to ensuring safe drinking water dates back to the 1980s with the adoption of the first Drinking Water Directive in 1980 (DIRECTIVE 80/778/EEC, 1980). This directive marked a significant milestone as it introduced the first set of comprehensive water quality standards for member states. It established maximum allowable concentrations for various contaminants, including microbiological and chemical parameters. It set strict limits on bacteria such as *Escherichia coli* (*E. coli*) and *Enterococci*, as well as chemical pollutants like lead, nitrates, and pesticides. The primary goal was to protect public health by ensuring that drinking water was free from harmful contaminants.

Over the years, scientific advancements and emerging challenges necessitated revisions to the original directive. In 1998, the directive was updated and replaced by Council Directive 98/83/EC (1998). This revision introduced several

significant changes aimed at enhancing water quality management. This revised directive expanded the list of contaminants to include more microbiological, chemical, and indicator parameters; this reflected growing awareness of new contaminants and their potential health impacts.

Directive 98/83/EC was amended with the entry into force of Directive 2015/1787/EU (2015). This directive introduced significant changes to the monitoring and control of drinking water quality. In detail, this DWD required the obligation of accreditation based on the ISO/IEC 17025 (2005) standard for both the analytical methods and the laboratories designated by the competent authorities of the countries for drinking water controls. Additionally, the directive began to incorporate elements of a risk-based approach, requiring Member States to conduct regular monitoring and assessments of water quality at various points in the supply system; Water Safety Plans (WSPs) were introduced in Europe, and the Member States had to implement the legislative and regulatory provisions to comply with this directive by October 27, 2017. Therefore, it represented a significant step forward in ensuring safe drinking water; however, it still faced challenges in addressing emerging contaminants.

The most recent and significant update to the Drinking Water Directive came in December 2020 with the adoption of Directive (EU) 2020/2184 (2020). This update reflects the EU's commitment to addressing contemporary challenges such as emerging pollutants, climate change, and ensuring equitable access to safe drinking water for all citizens. The revised directive aligns with international guidelines, including those from the World Health Organization (WHO, 2017).

2.1.1 The EU Directive 2020/2184

Directive (EU) 2020/2184, adopted by the European Parliament and the Council on December 16, 2020, focuses on the quality of water intended for human consumption. This DWD aims to ensure that water intended for human consumption is safe, clean, and healthy across all member states of the European Union. This theme is articulated through various key objectives and provisions aimed at creating a robust system for water quality management.

One of the foundations of the DWD is the establishment of strict quality standards for drinking water. These standards are designed to protect public health by limiting the concentrations of harmful contaminants. The directive categorizes contaminants into three main groups of parameters:

- microbiological: these parameters include bacteria, viruses, and protozoa that can cause waterborne diseases. Key parameters include *Escherichia coli* (*E. coli*) and *Enterococci*, which are indicators of fecal contamination. The DWD sets zero tolerance for these pathogens in drinking water, ensuring that water is free from harmful microorganisms;
- chemical: this category includes a wide range of chemicals that can pose health risks, both naturally occurring and anthropogenic, such as heavy metals (e.g., lead, arsenic, and mercury), pesticides, nitrates, and disinfection by-products. The directive specifies maximum allowable concentrations for each chemical parameter to protect consumers from acute and chronic health effects;
- indicators: these parameters are used to assess the general quality and treatment efficacy of drinking water; they include pH, colour, turbidity, and conductivity. While not directly harmful at the levels specified, these indicators provide valuable information about the overall condition of the water supply system.

A significant thematic element of DWD is the promotion of a continuous monitoring process; the directive outlines specific monitoring frequencies and methodologies for each parameter, ensuring consistent and reliable data collection. Monitoring programs are designed to cover the entire water supply chain, from the source to the tap, in order to identify potential contamination sources and ensures that corrective actions can be taken promptly. This includes sampling and analysis of water at various points in the distribution system, such as treatment plants, reservoirs, and consumer taps. In this light, Member States are required to implement comprehensive monitoring programs and reporting their results to the European Commission to ensure that drinking water meets the established quality standards.

In addition to continuous monitoring, another key-point emphasized by the DWD is the adoption of a risk-based approach to managing water safety, particularly considering climate change and other emerging threats. This approach involves a thorough assessment and management of risks from the water source to the tap. Water suppliers are required to identify potential hazards and implement measures to mitigate them, ensuring the continuous safety and quality of drinking water. In this regard, the DWD requires Member States to develop and implement Water Safety Plans (WSPs) based on the WHO's Guidelines (WHO, 2017).

Among updates and innovations, the revised DWD significantly focused on:

- emerging contaminants: the DWD recognizes the growing concern over emerging pollutants, including pharmaceuticals, endocrine disruptors, and microplastics. These contaminants can be difficult to detect and remove with conventional treatment methods. Member States are required to conduct risk assessments for emerging pollutants and develop and implement advanced treatment technologies and monitoring systems to reduce their presence in drinking water;
- reducing plastic wastes: in line with the EU's commitment to reducing plastic waste and promoting sustainability, the revised directive encourages the use of tap water over bottled water. Member States are urged to take measures to promote tap water consumption, such as installing water fountains in public spaces and raising awareness about the environmental impact of plastic bottles;
- climate change and climate resilience: climate change poses significant challenges to water quality and availability. Increased frequency and intensity of extreme weather events, such as droughts and floods, can impact water sources and infrastructure. For example, prolonged droughts can lead to reduced water availability and increased concentrations of contaminants in water sources. Conversely, heavy rainfall and flooding can overwhelm water treatment systems, leading to contamination from runoff and sewage overflows. Climate change also influences the distribution and behaviour of contaminants, requiring adaptive risk management strategies. Adapting to these changing conditions requires flexible and robust water management strategies that can respond to a wide range of scenarios and Member States must consider climate resilience in their water management plans to ensure long-term water security.

As DWD has had a deep impact on improving drinking water quality and safety, it is essential ensuring compliance with it to achieving its objectives. For this reason, Member States are responsible for implementing the directive's provisions and ensuring that water suppliers meet the established quality standards. In detail Member States had to transpose the Directive into national legislation and comply with its provisions by 12 January 2023. In cases of non-compliance, Member States can impose penalties and sanctions on water suppliers; in addition, the European Commission can also initiate infringement proceedings against Member States that fail to meet their obligations under the directive.

2.2 The WHO Guidelines for drinking water quality and the origin of Water Safety Plans

The World Health Organization (WHO) is a specialized agency of the United Nations with primary responsibility for international health matters and public health. WHO promotes the development of comprehensive health services, the prevention and control of diseases, the improvement of environmental conditions, the development of human resources for health, the coordination and development of biomedical and health services research, and the planning and implementation of health programmes. WHO guidelines for drinking water are a key tool for ensuring public health and safety. These guidelines provide scientifically based recommendations to manage and mitigate risks associated with drinking water contaminants. Over the years, WHO published four editions of the Guidelines for drinking-water quality (WHO, 2017, 2008, 1993, 1984), as successors to the previous WHO International standards for drinking water, which were published in 1958, 1963 and 1971 (WHO, 1971, 1963, 1958).

The evolution of these guidelines reflects the dynamic nature of scientific advancements; initially focused on microbiological contaminants to prevent waterborne diseases, the guidelines have expanded to include a wide range of chemical and radiological parameters and introducing a risk-based approach for drinking water assessment and management. In detail, in the third Edition of Guidelines for drinking water quality, published in 2004 (WHO, 2008), WHO recommend the Water Safety Plans (WSPs) approach as the most effective way of ensuring continuous provision of safe drinking water.

2.2.1 The Water Safety Plan approach

Water Safety Plan is a proactive risk assessment and risk management approach that encompasses all stages in a water supply from catchment to consumer. It is recommended by WHO as “*the most effective means of consistently ensuring the safety of drinking-water supply*” (WHO, 2023, 2009).

The first guidelines for the development of a WSP, titled “Water Safety Plans, managing drinking-water quality from catchment to consumer”, were published by WHO in 2005 (Davison et al., 2005). Thereafter, in 2009, the manual “Water Safety Plan Manual, step-by-step risk management for drinking water supplies” were published (WHO, 2009); the most recent edition of the latter was published in 2023 (WHO, 2023).

A WSP has three key components, which are guided by health-based targets and overseen through drinking-water supply surveillance (WHO, 2017):

- 1) a system assessment to determine whether the drinking-water supply chain (up to the point of consumption) as a whole can deliver water of a quality that meets identified targets. This also includes the assessment of design criteria of new systems;
- 2) identifying control measures in a drinking-water system that will collectively control identified risks and ensure that the health-based targets are met. For each control measure identified, an appropriate means of operational monitoring should be defined that will ensure that any deviation from required performance is rapidly detected in a timely manner;
- 3) management and communication plans describing actions to be taken during normal operation or incident conditions and documenting the system assessment, including upgrade and improvement planning, monitoring and communication plans and supporting programmes.

The fundamental principle is to consider the entire water supply chain, from source to consumption, and to adopt a preventive risk management approach through the development of drinking water quality management and control plans. This approach also facilitates the flexibility of hazards management of emerging contaminants which are not systematically monitored, and vulnerabilities of water supply systems to direct and indirect impacts due to climate change (WHO, 2017). The WSP approach, in fact, provides that every possible cause of contamination of water intended for human consumption is identified and prevented through the application of specific control measures. In addition, the identification of operational limits that can promptly report possible anomalies and therefore the application of corrective measures, designed to prevent the distribution of contaminated water, are envisaged. To guarantee all this, therefore, monitoring plans for control measures and verification plans are drawn up to assess the effectiveness of the WSP developed (WHO, 2009).

The primary objectives of a WSP in ensuring good drinking-water supply practice are the prevention or minimization of contamination of source waters, the reduction or removal of contamination through treatment processes and the prevention of contamination during storage, distribution and handling of drinking-water.

These objectives are equally applicable to large piped drinking-water supplies, small community supplies and household systems and are achieved through 7 sequential steps (Figure 2.1):

1. assemble a team: the first step in developing a WSP is to assemble a multidisciplinary team with expertise in water quality, treatment, distribution, and public health. This team is responsible for conducting the system assessment and risk analysis, as well as designing and implementing control measures;
2. describe the water supply system (Site Assessment): This involves a detailed evaluation of the water supply system; this includes mapping the catchment area, identifying water sources, outlining treatment processes and documenting the distribution network and points of consumption. The goal is to identify potential hazards and vulnerabilities at each stage;
3. identify hazards and assess risks (Risk Assessment): potential hazards can include microbial contaminants (e.g., bacteria, viruses), chemical pollutants (e.g., pesticides, heavy metals), and physical hazards (e.g., debris, turbidity). Once hazards are identified, the team assesses the risks associated with them by considering factors such as the source of contamination, the effectiveness of existing control measures, and the vulnerability of the population served. This involves evaluating the probability of occurrence and the severity of consequences;
4. determine control measures: based on the risk assessment, the team identifies and prioritizes control measures to mitigate the identified risks. Control measures can range from source protection and improved treatment processes to enhanced monitoring and maintenance practices. The goal is to implement a multi-barrier approach that addresses risks at every stage of the water supply system;
5. establish monitoring and verification procedures: continuous monitoring and verification procedures are essential to ensure that control measures are effective. This involves setting up routine sampling and testing protocols, establishing performance indicators, and implementing corrective actions when deviations are detected. Continuous monitoring helps maintain water quality and provides early warning of potential issues;
6. develop management procedures: in addition to technical control measures, the WSP includes management procedures to address incidents of water contamination or system failures. This involves

creating emergency response plans, defining roles and responsibilities, and establishing communication channels with stakeholders, including the public;

7. documentation and reporting: Comprehensive documentation of all aspects of the WSP is necessary for transparency, accountability, and continuous improvement. This includes detailed records of the system assessment, risk analysis, control measures, monitoring results, and management procedures. Regular reporting to regulatory authorities and stakeholders ensures continuous improvement and fosters trust in the water supply system.

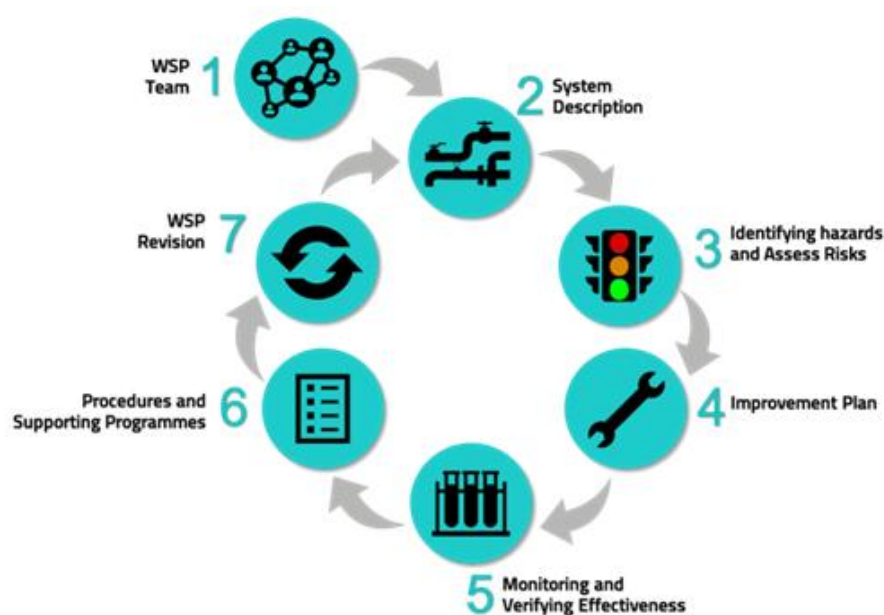


Figure 2.1. Key Components of Water Safety Plans

2.3 The Italian regulatory framework

The regulatory landscape in Italy for drinking water has evolved significantly over the decades; a comprehensive legislative framework has been developed to regulate the quality of drinking water intended for human consumption, aligning with European Union directives and incorporating modern risk management practices. The Decree of the President of the Republic 236/1988 (D.P.R. 236/1988), implemented the EU Directive 80/778/CEE, setting initial standards for drinking water quality in line with European norms. Later, in 2001, Legislative Decree 31/2001 (D.Lgs 31/2001) was enacted to align with the EU Directive 98/83/CE. It marked a significant milestone laying the foundation for the protection and quality assurance of drinking water. It set maximum allowable concentrations for microbiological, chemical and indicator parameters (Table 2.1-2.3), specifying the points of compliance and indicating the methods of sampling and analysis (arts 4-8).

Table 2.1. Microbiological parameters (Annex I, part A, D.Lgs 31/2001)

Parameter	Parametric value [number/100ml]
Escherichia coli (E. coli)	0
Enterococci	0

For water sold in bottles or containers the following values are applied

Parameter	Parametric value
Escherichia coli (E. coli)	0/250ml
Enterococci	0/250ml
Pseudomonas aeruginosa	0/250ml
Colony count at 22°C	100/ml
Colony count at 37°C	20/ml

Table 2.2. Chemical parameters (Annex I, part B, D.Lgs 31/2001)

Parameter	Parametric value	Unit
Acrylamide	0.10	µg/l
Antimony	5	µg/l
Arsenic	10	µg/l
Benzene	1	µg/l
Benzo(a)pyrene	0.01	µg/l
Boron	1	mg/l
Bromate	10	µg/l
Cadmium	5	µg/l
Chromium	50	µg/l
Copper	1	mg/l
Cyanide	50	µg/l
1,2-dichloroethane	3	µg/l
Epichlorohydrin	0.1	µg/l
Fluoride	1.5	mg/l
Lead	10	µg/l
Mercury	1	µg/l
Nickel	20	µg/l
Nitrate	50	mg/l
Nitrite	0.5	mg/l
Pesticides	0.1	µg/l
Pesticides – Total	0.5	µg/l
Polycyclic aromatic hydrocarbons	0.1	µg/l
Selenium	10	µg/l
Tetrachloroethene and Trichloroethene	10	µg/l
Trihalomethanes – Total	30	µg/l
Vinyl chloride	0.5	µg/l
Chlorite	200	µg/l
Vanadium	50	µg/l

Table 2.3. Indicator parameters (Annex I, part C, D.Lgs 31/2001)

Parameter	Parametric value	Unit
Aluminium	200	µg/l
Ammonium	0.5	mg/l
Chloride	250	mg/l
Clostridium perfringens (including spores)	0	number/100ml
Colour	Acceptable to consumers and no abnormal change	
Conductivity	2500	µS/cm at 20°C
Hydrogen ion concentration	6.5 – 9.5	pH units
Iron	200	µg/l
Manganese	50	µg/l
Odour r	Acceptable to consumers and no abnormal change	
Oxidisability	5	mg/lO ₂
Sulphate	250	mg/l
Sodium	200	mg/l
Taste	Acceptable to consumers and no abnormal change	
Colony count 22°C	No abnormal change	
Coliform bacteria	0	number/100ml
Total organic carbon (TOC)	No abnormal change	
Turbidity	1	NTU
Hardness	15 – 50	°F
Dry residual at 180°C	1500	mg/l
Residual disinfectant	0.2	mg/l

Subsequently, the Decree of the Ministry of Health of 14 June 2017 (Ministero della Salute, 2017) entered into force, which constitutes the transposition of EU Directive 2015/1787 and which has made amendments to the legislative decree. Among the novelties introduced by the decree there are:

- the introduction of the concept of risk assessment, which must be conducted on the entire water supply system and must be based on international or national WSP guidelines;

- the modification of the minimum frequency of sampling and analysis for compliance monitoring.

The principles of WSPs have been adopted, in Italy, by the Istituto Superiore di Sanità (ISS) and Ministero della Salute guidelines (Lucentini et al., 2014) and became mandatory in 2017. These guidelines are a technical document designed to assist the competent authorities and water service managers in the preparation and implementation of WSPs. The WSP model consists of the overall risk assessment and risk management from catchment to tap, to protect the water to be destined to human consumption and the system, as well as to control any process potentially affecting water quality, with the aim of assuring on a continuous way the absence of physical, biological and chemical hazards in drinking water. Risk based approach also facilitates the flexibility of hazards management of emerging contaminants which are not systematically monitored, and vulnerabilities of water supply systems to direct and indirect impacts due to climate change. The objective of these guidelines was to provide, in clear and practical terms, methods and procedures necessary to develop and implement WSP in drinking water supplies.

In 2022, in order to reposition the criteria and methods governing the WSPs and the application guidelines of Legislative Decree 18/2023 (D.Lgs 18/2023), implementing Law 127/2022 (Legge 127/2022) and transposing Directive 2020/2184/EU (DIRECTIVE 2020/2184/EU), the guidelines were replaced by a revised volume titled “*Linee guida nazionali per l’implementazione dei Piani di Sicurezza dell’Acqua (PSA)*” (Gruppo Nazionale di lavoro per la redazione delle Linee guida nazionali per l’implementazione dei PSA, 2022).

The primary objective of D.Lgs 18/2023 is to protect human health from the negative effects of contaminated drinking water. This goal is achieved by setting stringent quality standards and ensuring that water intended for human consumption is wholesome and clean. The decree outlines general obligations and minimum requirements for drinking water quality, emphasizing the need for continuous monitoring and risk management to prevent contamination, thus aligning with the DWD 2020/2184.

With the entry into force of the decree, the chemical parameters have undergone a major revision, with the modification of the values for some parameters but especially with the introduction in the list of new substances (Table 2.4), such as

bisphenol-A, lead, PFAS, uranium, for which scientific studies have demonstrated their toxicity for humans and therefore the need to be regulated.

Table 2.4. Chemical parameters updated by D.Lgs 18/2023 and comparison with D.Lgs 31/2001

Parameter	D.Lgs 18/2023	D.Lgs 31/2001	Unit
Antimony	10	5	µg/l
Bisphenol-A	2.5	-	µg/l
Boron	1.5	1	mg/l
Chlorate	250	-	µg/l
Chlorite	250	200	µg/l
Chromium	25	50	µg/l
Copper	2	1	mg/l
Haloacetic acids (HAAs)	60	-	µg/l
Microcystin-LR	1	-	µg/l
Total PFAS	0.5	-	µg/l
Sum of PFAS	0.1	-	µg/l
Selenium	20	10	µg/l
Uranium	30	-	µg/l

The decree also defines and implements an appropriate operational monitoring programme; pursuant to this, the operational monitoring programme shall include the monitoring of the parameter ‘turbidity at the water supply plant’ in order to regularly control the efficacy of physical removal by filtration processes, in accordance with the reference values and frequencies indicated in Table 2.5.

Table 2.5. Turbidity reference values and frequency of sampling and analysis

Operational parameter	Reference value
turbidity at the water supply plant	0.3 NTU in 95% of samples and none to exceed 1 NTU
Volume (m ³) of water distributed or produced each day within a supply zone	Minimum frequency of sampling and analysis
≤ 1000	Weekly
> 1000 to ≤ 10000	Daily
> 10000	Continuous

The decree also stresses the importance of monitoring and preventing microplastics in drinking water, which are not currently regulated. To this end, it is planned to identify by 2024 a methodology for the monitoring of microplastics in water intended for human consumption, which will allow the inclusion of the latter in the “Watch List”, the Control list containing emerging substances which potentially may pose a risk to the consumer if present in water intended for human consumption (AS0017, 2022).

Another key element of D.Lgs 18/2023 is the introduction of a risk assessment and management of the drinking water supply system that includes the collection, treatment, storage and distribution of water intended for human consumption up to the point of delivery. This should be based on the general principles of risk assessment and management established by the WHO (WHO, 2023, 2009), transposed into the National Guidelines for the implementation of the Water Safety Plans by the ISS (Gruppo Nazionale di lavoro per la redazione delle Linee guida nazionali per l’implementazione dei PSA, 2022) (Figure 2.2). Furthermore, according to the decree, climate change-related phenomena must be included in the risk analysis.



Figure 2.2. Synopsis of risk assessment and management according to D.Lgs 18/2023

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Chapter III

Process indicators in drinking water treatment plants

Drinking water treatment plants (DWTPs) are essential facilities that ensure the provision of safe and clean water to the public (Zhang et al., 2012). These plants are designed to remove contaminants and impurities from raw water sources, making it suitable for human consumption. The treatment process typically involves several stages, each employing different technologies and methods to achieve the desired water quality. The raw water that enters a DWTP can come from various sources, including rivers, lakes, reservoirs, and groundwater; surface water from rivers and lakes is generally more susceptible to pollution and requires more extensive treatment compared to groundwater. Anyway, DWTPs face several challenges in ensuring the consistent provision of safe drinking water:

- emerging contaminants, such as micro- and nano-plastics, PFAS, pharmaceuticals and endocrine-disrupting compounds, aren't able to be removed by conventional treatments, requiring advanced processes;
- compliance with regulations and standards to ensure the safety and quality of drinking water necessitates continuous monitoring, reporting, and sometimes, upgrades to treatment processes;
- the aging of treatment plants, distribution systems and infrastructures can lead to a worsening in water quality and thus an increase in risk for human health;
- the quality of raw water can vary significantly due to seasonal changes, weather events, and human activities. In particular, in the last decades, climate changes and extreme weather events led to the worsening of water quality (Delpla et al., 2009; Yadava et al., 2023).

DWTPs must be adaptable and capable of handling these challenges. Quantifying performance is crucial for the effective operation of water treatment plants to maintain high quality control standards (Hartshorn et al., 2015). Therefore, having tools, such as process indicators, to effectively monitor, control, quantify the performance of the treatment processes allows for targeted modifications, replacements, or upgrades. These indicators provide real-time and historical data

on the performance of different processes, ensuring that the water treatment plant operates efficiently and produces safe, high-quality drinking water.

3.1 Assessment of drinking water treatment performances by means of indicators

Scientific literature (Hartshorn et al., 2015; Zhang et al., 2012; Vieira et al., 2008) reports that are four main indices to assess the performances of a DWTP; these are reliability, resiliency, robustness and risk. In the following paragraphs each of them is deepened.

3.1.1 Reliability

The term reliability is defined as “the ability of a water treatment system to consistently perform its required functions under stated conditions for a specified period” (Blanchard, 1992). Thus, it is the probability that failure does not occurs within a fixed period of time (Karamouz et al., 2003). In drinking water treatment, this means the system’s capacity to continuously deliver water that meets quality standards without significant interruptions (Kumar Gupta and Shrivastava, 2006).

Reliability of a DWTP, or the frequency of failure events over a given period, is often characterised using the mean time between failures (MTBF) (Upton et al., 2017). Mathematically, it can be expressed as (Eq. 3.1):

$$MTBF = \frac{\sum_{i=0}^{i=n} (start\ of\ spike_i - end\ of\ spike_{i-1})}{n} \quad [3.1]$$

3.1.2 Resiliency

The term resiliency was initially proposed by Holling (1973) to describe a system’s capacity to persist in a stable state when it is subject to perturbations. Later, Gunderson and Pritchard (2002) and Dalziell and Mcmanus (2004) defined the engineering resilience as “the speed with which a system returns too its former state following a perturbation”.

In the context of DWTP, resilience describes how quickly a system recovers from failure, once failure has occurred. It can also be defined as a measure of the duration of an unsatisfactory condition (Hartshorn et al., 2015; Nazif and Karamouz, 2009). According to Karamouz et al. (2008) system resiliency can be quantified as (Eq. 3.2):

$$Resiliency = \frac{n_{FS}}{n_{F*}} \quad [3.2]$$

where n_{FS} and n_{F*} are the total number of system failures during evaluation period and the number of system failures which are followed by success full operation, respectively in the evaluation period. A failure happens when a WTP cannot supply water with desired quality and quantity.

Resiliency can also be described using the mean time to recovery (MTTR) (Eq. 3.3) (Upton et al., 2017):

$$MTTR = \frac{\sum_{i=0}^{i=n} (end\ of\ spike_i - start\ of\ spike_{i-1})}{n} \quad [3.3]$$

3.1.3 Robustness

Robustness is defined as the competence of a system to perform excellently under normal conditions, deviate minimally during periods of challenges, and continue to provide the desired service (Huck and Coffey, 2004, 2002). When a system is robust, the output of the system does not have a wide variation with changing operating conditions. Referring to DWTPs, it is considered robust if its performance is insensitive to the variation of source water quality and changing operational conditions, thus continuing to achieve the desired drinking water quality (Jung et al., 2019; Zakarian et al., 2007; Zhang et al., 2012). Figure 3.1 illustrates the concept of robustness of a water treatment system.

According to scientific literature (Hartshorn et al., 2015; Huck and Coffey, 2004; Hurst et al., 2004; Li and Huck, 2008; Nemani et al., 2023; Upton et al., 2017; Zhang et al., 2012), turbidity is a universally and routinely monitored parameter with which it is possible to develop robustness indices to evaluate DWTP performances. Robustness indices are discussed in paragraph 3.2.

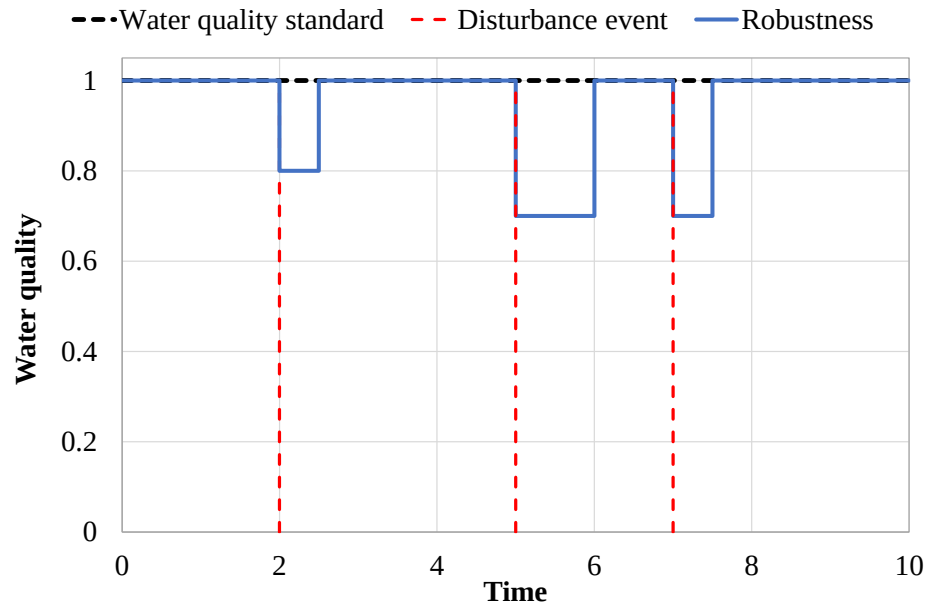


Figure 3.1. Robustness of a water treatment system

3.1.4 Risk

Risk (R) has two dimensions: the likelihood of occurrence of an adverse event (P) and its severity and consequence (D) (Hartshorn et al., 2015; Zhang et al., 2012). Therefore, the mathematical definition of risk is given as (Eq. 3.4):

$$R = P \times D \quad [3.4]$$

Risk in drinking water treatment encompasses the potential for adverse outcomes resulting from system failures, contamination events, or other hazards. Risk assessment involves identifying, analysing, and mitigating these potential adverse outcomes. In this light, WSPs are the main frameworks used for controlling and regulating risk, and their implementation is mandatory (DIRECTIVE 2020/2184/EU; Hartshorn et al., 2015; WHO, 2017).

Reliability and risk describe the failure conditions from a probabilistic perspective. Water planners commonly use reliability to reduce the risk of a system failure. Risk defines the probability of failure and can be understood as 1 minus the reliability (Shuang et al., 2019).

3.1.5 Interrelationship between indicators

The interrelationship between reliability, resiliency, robustness, and risk is central to understanding the overall performance of a system over time, particularly during and after adverse events. The graph shown in Figure 3.2 visually represents these concepts.

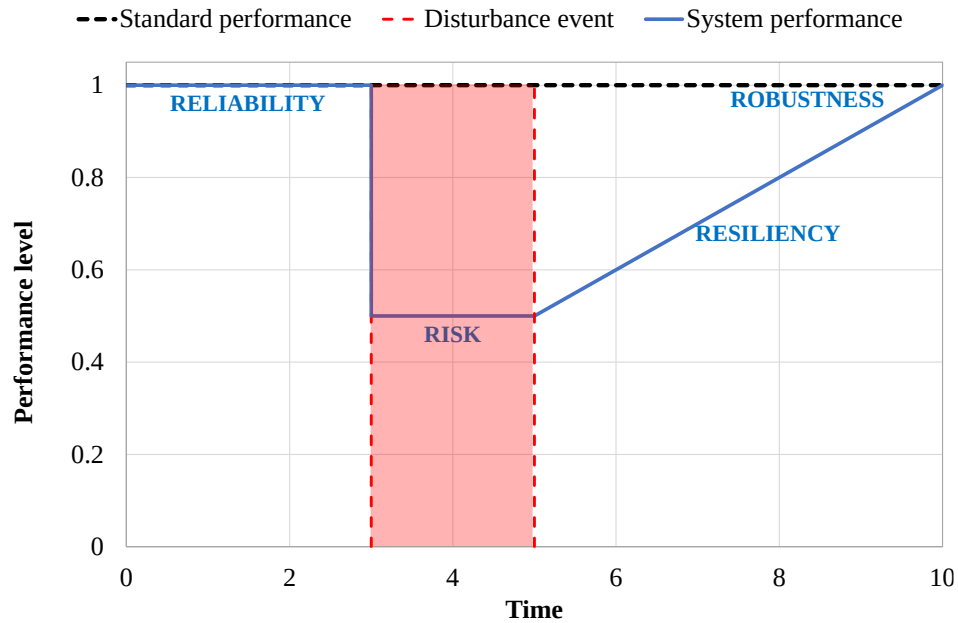


Figure 3.2. Interrelationship between reliability, resiliency, robustness and risk

In the graph reported in Figure 3.2 reliability is indicated by the system's consistent performance level before the disturbance event, resiliency is shown by the recovery of performance after the disturbance event (the period during which the system recovers its performance), robustness shows the system's ability to maintain its performance level across various conditions, even after recovery and risk is represented by the zone where the performance of the system is negatively impacted by the disturbance event.

In a reliable system, the consistent of performances reduces the frequency of disturbances needing recovery, thus enhancing and supporting resiliency. Higher reliability typically means lower risk, as reliable systems are less likely to fail; however, even reliable systems can experience failures, making resiliency crucial for recovery. Therefore, a resilient system manages risk by recovering quickly

from disturbances, minimizing downtime and impact and by ensuring adaptation to adverse events. Usually, a reliable system incorporates robustness to prevent failures from external disturbance events; in fact, robustness ensures consistent performances even under varying and adverse conditions. Consequently, a robust system, being less susceptible to the impact of unpredictable and disturbance events that can compromise performances, lower the risk of failure. However, a system can be robust but not resilient (resisting failure but taking long to recover if it fails), or vice versa (quickly recovering from failures even if frequently disrupted).

In conclusion, these concepts are interdependent; improving one of them often enhances the others, thus creating a more secure and efficient system. Referring to DWTPs, ensuring reliable, resilient, and robust systems while managing risks involves a comprehensive approach that integrates system design, operational practices, and proactive risk management. Balancing all four aspects ensures the continuous provision of safe and clean drinking water under both normal and adverse conditions.

3.2 Detecting the robustness of a drinking water treatment

Safe drinking water is one of the most important factors for protecting public health and sanitation and DWTPs are required to continuously supply it (Hartshorn et al., 2015; Huck and Coffey, 2004; Li and Huck, 2008; Upton et al., 2017; Zhang et al., 2012). In recent years, DWTPs are facing significant challenges with regards to water quality. Most of such infrastructures use surface water (e.g. lakes and rivers) as their raw water sources. Nevertheless, it is known that climate change is impacting the duration, intensity and frequency of extreme hydrological events that contribute to deteriorating the surface water quality (Delpla et al., 2009; Yadava et al., 2023). Moreover, predictions from various climate models suggest that raw water quality might deteriorate further in the future, thereby increasing challenges to DWTP (Quevedo-Castro et al., 2022).

Specifically, changes in precipitation patterns enhance the erosion and transport processes, leading to increased suspended and dissolved particles in surface waters, thus increasing turbidity level (Khan et al., 2015; Skaland et al., 2022). Therefore, the turbidity in the influent raw water to DWTP increases, thus posing a significant operational challenge for maintaining high standards of treated water quality in compliance with regulatory requirements (Mi et al., 2019). Moreover, elevated raw water turbidity caused by extreme rainfall has been associated with several waterborne diseases and gastrointestinal hospitalizations (De Roos et al.,

2017; Delpla et al., 2009); and, in addition, a high level of turbidity is associated with an increased risk of *Cryptosporidium* oocysts and other microorganisms in drinking water (Hartshorn et al., 2015). Moreover, turbidity also serves as an indicator of organic matter, making it useful for evaluating the formation of disinfection by-products (Doménech et al., 2022; Pešić et al., 2020).

As mentioned before, turbidity is the most widely used parameter for monitoring plant performances since its measurement is simple, rapid and economical and it can be monitored continuously (Hartshorn et al., 2015; Huck and Coffey, 2004; Hurst et al., 2004; Li and Huck, 2008; Nemani et al., 2023; Upton et al., 2017; Zhang et al., 2012). Therefore, turbidity is a regulated parameter and water utilities are expected to keep water turbidity levels in compliance with regulatory requirements to mitigate the risk of bacteriological failure and the formation of disinfection byproducts. Considering all these facts, turbidity is the selected parameter to develop robustness index.

Nevertheless, one of the primary challenges in calculating TRI is dealing with non-normal data distributions. In fact, turbidity data often exhibit skewed distributions due to events like heavy rainfall, filter backwashing, operational anomalies, etc. These events can introduce outliers, making it difficult to accurately assess the system's performance.

3.2.1 Turbidity Robustness Index

The presence of robustness in the design and operation of DWTPs can substantially overcome the challenges brought by climate change on water quality. Therefore, quantifying the robustness is important to improve the DWTP performances and aid in continuing provide high-quality drinking water.

Several researchers have evaluated the robustness of filtration units as well as clarification processes based on turbidity (García-Ávila et al., 2021; Hartshorn et al., 2015; Li and Huck, 2008; Zoric et al., 2020). However, there has been limited focus on the robustness of the other treatment units and the overall robustness of full-scale plants (Zhang et al., 2012).

Robustness for water filtration plants was defined by Coffey et al. (1998) as “*the ability of a filtration system to provide excellent particle/pathogen removal under normal operating conditions and to deviate minimally from this performance during moderate to severe process upsets*”. The authors developed the first turbidity robustness index (TRI) considering the index as a function of ripening,

turbidity, water production and breakthrough. Later, the index was improved by Huck et al. (2001) and Huck and Coffey (2002) according as follows (Eq. 3.5, 3.6, 3.7):

$$TRI_{90E} = \frac{1}{2} \left(\frac{T_{90}}{T_{50}} + \frac{T_{50}}{T_{goal}} \right) \quad [3.5]$$

$$TRI_{95E} = \frac{1}{2} \left(\frac{T_{95}}{T_{50}} + \frac{T_{50}}{T_{goal}} \right) \quad [3.6]$$

$$TRI_{99E} = \frac{1}{2} \left(\frac{T_{99}}{T_{50}} + \frac{T_{50}}{T_{goal}} \right) \quad [3.7]$$

where:

- TRI_{90E} , TRI_{95E} and TRI_{99E} are the turbidity indices (dimensionless) using the 90th, 95th and 99th percentile of the turbidity distribution;
- T_{50} , T_{90} , T_{95} and T_{99} , expressed in NTU (nephelometric turbidity units), are the 50th, 90th, 95th and 99th percentile of turbidity;
- T_{goal} is the turbidity goal (expressed in NTU).

In the equations, the first term represents the uniformity/variability of performance over a specific duration; the second term represents how well the filter is performing (the compliance against the goal). A lower value of the robustness index indicates that the filtered water is meeting the goal with relatively low variation for the specific duration. In contrast, a higher TRI indicates that either the treatment has failed to meet the goal value, or the performance variability is high for the specific duration of time.

Huck et al. (2001) reported that the TRI_{90E} and TRI_{95E} were more suitable to compare major differences in filter performance, whereas the TRI_{99E} got heavily influenced by noise in the turbidity data. In any case, the attribution of the same weight (1/2) to both terms was a limitation.

Although the TRI was first developed for filters, in several studies, the TRI method was used to evaluate the robustness of the other treatment steps for a given period. Hurst et al. (2004) used Equation (3.6) to evaluate the robustness of the coagulation and clarification process of a DWTP in England for different raw water conditions during certain rainstorm events and concluded that the TRI was an excellent method for analysing and compacting large volumes of data.

To overcome the limitation of the previous TRIs, Li and Huck (2008) improved the index introducing different weighting factors (A_1 and A_2) as shown in Eq. 3.8:

$$TRI_{90D} = \left(A_1 \frac{T_{90}}{T_{50}} + A_2 \frac{T_{50}}{T_{goal}} \right) \times 100 \quad [3.8]$$

In Eq. 3.8 if the weighting factor A_1 is set at a higher value than A_2 , this means that the index emphasizes the variation in performance, whereas a higher A_2 indicates that the index is focusing on the average performance. The higher value for A_1 or A_2 was chosen to be 0.9 and the lower value was set at 0.1. This was based on an evaluation by Li (2004); in fact, the author found that the use of other weighting factors did not have an impact on the general trends observed.

As a means to establish if A_1 is higher or lower than A_2 , the authors used two new factors:

- N, which is a critical value set to 50 to provide an initial determination of the robustness of a specific filter run;
- W, which gives a preliminary indication of robustness for a given run by considering the upper half of the cumulative turbidity distribution curve and which is compared to N. W is calculated for each cycle as (Eq. 3.9):

$$W = \left(\frac{T_{50}}{T_{goal}} + \frac{T_{60}}{T_{goal}} + \frac{T_{70}}{T_{goal}} + \frac{T_{80}}{T_{goal}} + \frac{T_{90}}{T_{goal}} \right) \times 100 \quad [3.9]$$

The procedure of selecting different weighting factors by comparing W and N is summarized in Table 3.1.

Table 3.1. Decision process for selecting different weighting factors (Li and Huck, 2008)

System designation	Comparison of W and N	If	Then
Robust	$W \leq N$	$\frac{T_{90}}{T_{50}} \leq \frac{T_{50}}{T_{goal}}$	$A_1 > A_2$
		$\frac{T_{90}}{T_{50}} > \frac{T_{50}}{T_{goal}}$	$A_1 < A_2$
Less robust	$W > N$	$\frac{T_{90}}{T_{50}} \leq \frac{T_{50}}{T_{goal}}$	$A_1 < A_2$
		$\frac{T_{90}}{T_{50}} > \frac{T_{50}}{T_{goal}}$	$A_1 > A_2$

On the basis of TRI value, Li and Huck (2008) proposed a classification system in terms of operational quality (Table 3.2). The TRI classes imply how the treatment step was performing during the filter run or selected timeframe based on the variation of T_{50} and T_{90} with respect to T_{goal} .

Table 3.2. Classification of system operation with robustness index value and mathematical significance (Li and Huck, 2008)

Class	TRI value	Implication	Mathematical significance
Very stable	<60	the system produces high quality water for the entire run	(1) $T_{50}, T_{90} \approx 50\%$ of T_{goal} (2) $T_{50} << T_{goal}$ and $T_{90} > 50\%$ of T_{goal}
Stable	60–100	the system produces high quality water for the entire run	(1) $T_{50}, T_{90} = 60\text{--}75\%$ of T_{goal} (2) $T_{50} = 60\text{--}75\%$ of T_{goal} and $T_{90} \approx T_{goal}$
Slightly disturbed	100–130	the system produces high quality water for most of the run	(1) $T_{50}, T_{90} \approx T_{goal}$ (2) $T_{50} < T_{goal}$ and $T_{90} = 30\%$ over T_{goal}
Moderately disturbed	130–160	the system produces water that is not high quality for a short duration during the run	(1) $T_{50}, T_{90} = 30\text{--}50\%$ over T_{goal} (2) $T_{50} = 20\%$ over T_{goal} and $T_{90} = 60\text{--}80\%$ over T_{goal}
Upset	160–200	the system produces water that is not high quality for most of the run	(1) $T_{50}, T_{90} = 60\text{--}80\%$ over T_{goal}
Severely upset	>200	the system produces high quality water at no time during the run	(1) $T_{50}, T_{90} = 100\%$ over T_{goal}

However, this approach showed limitations in terms of the arbitrary assignments of weighting scores and the method complexity.

A further investigation (Hartshorn et al., 2015) allow to update the index with an adapted version (TRI_{90J}). Hartshorn and coauthors replaced the weighting factors A_1 and A_2 with the concept of $G\%$, which is the percentage of time when the turbidity was below T_{goal} (Eq. 3.10).

$$TRI_{90J} = \left[\left(1 - \frac{G\%}{100} \right) \times \frac{T_{90}}{T_{50}} + \frac{T_{50}}{T_{goal}} \times \frac{G\%}{100} \right] \quad [3.10]$$

According to Eq. 3.10, a greater relevance is given to the second term when the turbidity is lower than the goal value most of the time during the run. In more

detail, the higher the value of the G%, the less influence the overall variance of the system is taken into account (first term); thus, variability in performance was not considered when the turbidity was lower than the goal. Nevertheless, this method did not properly address performance variations.

Moreover, Nemani et al. (2023) have recently observed that a low TRI value was obtained when the limit value was continuously exceeded, and the data distribution was quite uniform. Therefore, the existing TRIs fail as a tool indicating the risk.

Despite its limitations, TRI represents a useful evaluation tool for DWTP managers to identify and address potential issues (e.g. units' overload, significant variability of influent turbidity). Such an approach can also be helpful in identifying process units that exhibit criticality and vulnerability to specific load conditions. In this sense, by monitoring TRI during time, operators could proactively manage risks associated with process upset, thus contributing to minimize process vulnerability (Zhang et al., 2012).

In addition, as water quality standards become increasingly stringent (DIRECTIVE 2020/2184/EU), the importance of metrics like TRI in ensuring sustainable water management, safeguarding public health, and addressing both immediate and long-term environmental challenges grow substantially.

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Chapter IV

Innovative treatment technologies for waters intended for human consumption

Surface water intended for human consumption comes from sources such as rivers, lakes, reservoirs, and streams. This type of water often contains a variety of contaminants including microorganisms, organic and inorganic pollutants. Therefore, it requires thorough treatment to make it safe for drinking.

The general criteria for choosing the best applicable treatment solution are based on a series of factors, including, for example, the applicability of the process, the potential of the plant, and the characteristics of the raw water. The latter is what most influences the choice of treatment to be adopted. Indeed, Legislative Decree 152/2006, by transposing Directive 75/440/EEC, laid down quality standards for surface water intended for human consumption. The decree (art. 80) classifies water into three categories (A1, A2, and A3) based on the assumed values of 46 parameters relating to physical, chemical and microbiological characteristics (Tab.1/A, Annex 2, part III). According to the regulation, depending on the category, the waters are subjected to specific treatments (Figure 4.1):

- **A1:** High quality, requiring simple physical treatment and disinfection;
- **A2:** Moderate quality, requiring normal physical and chemical treatment and disinfection;
- **A3:** Lower quality, requiring intensive physical and chemical treatment and disinfection.

Surface waters falling within class A1 generally need a filtration treatment, followed by disinfection. For water of class A2, a pre-oxidation and clarification treatment is provided upstream. For waters falling in class A3 further refinement by means of activated carbon filters upstream of the disinfection is required.

Although in the past, the treatments listed above were sufficient to guarantee the quality standards required by the regulations, to date most of traditional DWTPs aren't able to ensure compliance with it (Leveque et al., 2021).

Indeed, the variation in raw water quality and the increased concentration of contaminants caused by factors such as climate change and input of anthropogenic pollutants (emerging pollutants), accompanied by the recent Directive 2020/2184/EU concerning the quality of water intended for human

consumption and the imposition of much stricter limits, pose challenges for drinking water facilities.

This leads to the need to develop new technologies and/or improve existing technologies utilised in DWTPs (Pivokonsky et al., 2024).

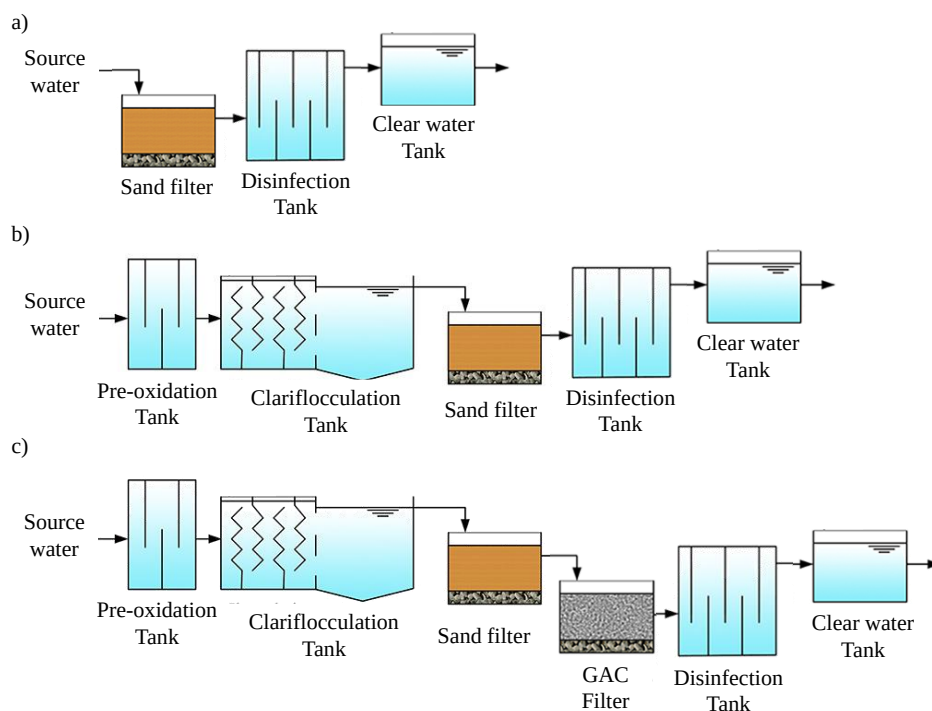


Figure 4.1. Scheme treatment for surface water intended for human consumption falling within class A1 (a), A2 (b) and A3 (c)

4.1 Advanced drinking water treatment process

According to a throughout literature review, it arose that the main contaminants affecting water quality are manganese, NOM, turbidity, algae and emerging pollutants (EPs) such as disinfection by-products and micro- and nano-plastics (Gobler, 2020; Hashempour et al., 2020; Jarsjö et al., 2020; Teodosiu et al., 2018).

Manganese is commonly removed by using strong oxidants that convert soluble manganese (Mn^{2+}) into insoluble (Mn^{4+}) that can be separated through filtration (Tobiason et al., 2016). Removal of NOM in drinking water treatment plant is of particular concern. Although NOM is not toxic, its presence in drinking water

sources is highly detrimental because it is an important source of disinfection byproducts (DBP) precursors. Recent studies demonstrated that a key approach for controlling DBP in drinking water is to maximize NOM removal before chlorination (Jiang et al., 2016). To this aim, pre-oxidation is commonly performed to partially oxidize NOM and DBP before clarification process. As regard this point, previous studies reported that strong oxidants (e.g., ozone) may alter the structure and characteristics of NOM, which become more hydrophilic and fragmented and thus impacting its removal by subsequent coagulation/flocculation process (Graham et al., 2010). Algae removal from water is difficult because of their small size and the low specific gravity. Various treatment processes for removing of algae from water have been tested. Typically, pre-oxidation followed by coagulation/flocculation and filtration is the most applied treatment stages for algae removal from drinking water (Kubiňáková et al., 2017). Even in this case, pre-oxidation is a crucial step for algae removal. Indeed, previous studies observed that a decrease of algal cell activity and chlorophyll concentration enhanced the coagulation process (Ma and Liu, 2002). Nevertheless, DBP production poses a substantial ongoing risk and remains a significant threat that demands attention and mitigation efforts.

Based on what above stated, pre-oxidation is a key process for removal of these pollutant from water both because it is necessary for the removal of the specific pollutant and to prevent the formation of byproducts in subsequent downstream treatments. However, conventional oxidants, like ozone (O_3), chlorine compounds (e.g., ClO_2), permanganate (MnO_4^-) might lead to disadvantages among which high production costs and complex onsite generation facilities (ozone), byproducts generation (chlorine compounds) and overproduction of particulate manganese (permanganate) (Ma et al., 2023). Furthermore, due to the heterogeneity of pollutants and the inability to predict in some cases the sudden increase in their concentrations, it is necessary to rely on oxidizing agents capable of acting on a wide range of compounds and being ready for use in any situation.

In addition to pre-oxidation, coagulation is also a fundamental process in DWTPs (Pivokonsky et al., 2024). Originally, the main purpose of coagulation was to decrease the turbidity of water, caused primarily by inorganic colloidal particles (Gheraout and Gheraout, 2012). However, over time, coagulation was found to be effective for the removal of many other impurities, provided that the coagulation conditions were appropriately adjusted. For instance, substantial attention was given to the optimisation of coagulation to effectively remove

dissolved NOM, which is sometimes denoted in the literature as “enhanced coagulation” (Gheraout and Gheraout, 2012; Jiang, 2015).

On the whole, coagulation is currently expected to remove various impurities, such as inorganic colloids, algal and cyanobacterial cells, NOM, and even some anthropogenic pollutants (Baresova et al., 2017; Gheraout, 2020; Ren et al., 2022). Although modern DWTPs perform several treatment steps, the role of coagulation is irreplaceable, particularly in facilities supplied by surface waters, and coagulation efficiency significantly affects the performance of downstream treatment processes and ultimately the quality of treated drinking water (Jiang, 2015; Pivokonský et al., 2022).

In addition to the applicability of the traditional treatment process for the elimination of incoming undesirable compounds, novel coagulants are being developed and tested (Lee et al., 2012). Conventional and still widely employed coagulants include hydrolysing metal (Al or Fe) salts – typical representatives are aluminium sulphate $\text{Al}_2(\text{SO}_4)_3$ (often designated “alum”), ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$, and ferric chloride FeCl_3 (Gheraout and Gheraout, 2012; Gregory and Duan, 2001; Pivokonský et al., 2022; Ren et al., 2022). However, there are many alternatives, such as prepolymerised Al- or Fe-based coagulants (e.g., polyaluminium chloride, polyaluminium sulphate, polyferric sulphate) (Pernitsky and Edzwald, 2003; Wang et al., 2004); natural (e. g., chitosan) or synthetic (e.g., polyamines, polyacrylamides) organic polymers (Ding et al., 2018; Li et al., 2017); coagulants based on metals other than Al or Fe (e.g., coagulants comprising Ti or Zr) (Thomas et al., 2020); and composite coagulants (Lee et al., 2012). While some of the mentioned compounds are currently being applied instead of or in addition to the Al/Fe salts at DWTPs, some remain a subject of investigation.

The research advancement in the field of innovative and advanced approaches (e.g. membrane, advanced oxidation, adsorption on activated carbon and other materials) for the removal of the above contaminants are presented in the following paragraphs.

4.1.1 Membrane processes

The use of membranes for water treatment has risen significantly in recent decades. Membrane processes effectively remove a wide variety of organic, inorganic and solid particles from surface and seawater, through semipermeable

materials that allow the separation of water (permeate) and of the concentrate (retained at the membrane surface).

Membranes are produced from different materials, which provide specific characteristics (pore size, surface charge and hydrophobicity) that determine what type of contaminants can be retained (Gupta and Ali, 2013a). A wide variety of chemically and thermally stable polymers or polymer blends, but also other materials, such as ceramics, metals, glasses or mixed matrix membranes may be used (Arribas et al., 2015).

For drinking water production, several membrane processes may be used, which can be classified considering the force that drives the separation (Arribas et al., 2015):

- pressure driven processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO);
- electric potential gradient: electrodialysis (ED);
- concentration gradient: forward osmosis (FO).

DWT requirements, the influent quality, the necessity to remove specific target pollutants and their concentrations dictate the process type and membrane material. The major operational parameters refer to: driving force characteristics (pressure, electric potential), mode of operation (cross flow, dead-end), water flow and initial solute concentrations, pH, membrane material, pore size and retention capacity (Qi et al., 2024). The risk of fouling, clogging or concentration-polarisation depends on the water matrix (concentrations and type of contaminants), membrane material and process control, and therefore different cleaning methods (flushing, backward flushing, air flushing or chemical cleaning) have been developed (Teodosiu et al., 2018). A disadvantage of membrane processes when comparing them to advanced oxidation processes is that pollutants are transferred into the concentrate streams and not destroyed, therefore the concentrate requires further treatment and disposal (Rodriguez-Narvaez et al., 2017). This is compensated by advantages as: ease of operation and adaption to existent treatment facilities, modular design, very small chemical requirements, low energy consumption.

The most suitable membrane processes for EPs removal, due to their small pore sizes are UF, NF and RO (Arribas et al., 2015). Among these processes, RO is the most effective in removing pesticides, PPCPs, toxic metals and cyanides (Teodosiu et al., 2018). Over 99% of total organic and inorganic species were

removed from surface waters and groundwater through RO (Gupta and Ali, 2013b; Schoonenberg Kegel et al., 2010). Ion-exchange membranes (cation/anion exchange and bipolar membranes) are used in DWT, especially for sea water desalination by ED or reverse electrodialysis (Alzahrani and Mohammad, 2014; Singh, 2015). The most effective membrane processes that may be used for EPs removal at pilot and full-scale level are presented in Table 4.1, either as stand-alone or combined treatment.

4.1.2 Adsorption on activated carbon and other materials

Adsorption is an important advanced oxidation water treatment (AOWT) process that is efficient and cost-effective if the adsorbent has high porosity and specific surface area, is easy to operate and regenerate (thermally or chemically) and is available in sufficient quantities. The adsorbents' removal capacity depends on densities (material, particle and bulk), porosities (particle and bulk), external surface area, internal surface area, pore-size distribution (among macropores, mesopores and micropores), surface chemistry and operational parameters (temperature, pH, contact time) (Kulabhusan and Campbell, 2024). Various studies demonstrated that granular or powder activated carbon adsorption is one of the best technologies used for EPs' removal from surface water (Rodriguez-Narvaez et al., 2017) along with silica gel (Sharma and Bhattacharya, 2017), activated alumina, zeolites (Teodosiu et al., 2018) and metal oxide adsorbents (Kulabhusan and Campbell, 2024), but the energy used to produce adsorbents is very high. In order to increase EPs' removal efficiencies, organic or inorganic materials were developed to obtain nano-adsorbents or engineered nanomaterials (which possess a minimum of one external dimension ranging from 1 to 100 nm) with improved adsorption properties, being able to remove efficiently EPs with various molecular sizes, hydrophobicity and speciation behaviour (Thines et al., 2017). Engineered nanomaterials are classified as: carbonaceous nanomaterials (C-ENMs, carbon nanotubes, carbon nanofibers, fullerenes, graphenes and carbonaceous composites), metal and metal oxides (nanoscale zero-valent iron, TiO₂, Ag and ZnO) and magnetic-core composite nano/micro particles that have cores made with magnetic elements such as iron, nickel, cobalt or their oxides and alloys with ferromagnetic or superparamagnetic properties, and shells (silica, alumina or polymers or surfactants) (Teodosiu et al., 2018).

4.1.3 Advanced oxidation processes (AOP)

AOPs are based on the production of hydroxyl radicals ($\bullet\text{OH}$), one of the strongest oxidants (oxidation potential 2.8 V) that may be used for the removal/destruction of EPs for several purposes: raw water pre-treatment, DWT, wastewater treatment (Antonopoulou et al., 2014). The production of hydroxyl radical can be achieved by many pathways, which allow to choose the adequate AOP according to the specific characteristics of the raw water and the necessary treatment targets (Dhamorikar et al., 2024).

AOPs may be classified by considering the method to generate hydroxyl radicals into chemical, electro-chemical, sono-chemical and photochemical processes, combinations of AOPs with other processes being also frequently used (Molinari et al., 2017). Depending on how reactants get in contact, AOPs may be homogeneous or heterogeneous processes. In the heterogeneous processes, a catalyst such as metal supported catalysts, clays, carbon materials or semiconductors such as TiO_2 , ZnO , WO_3 , Cu_2O or composite materials are used (Enesca et al., 2016; Orha et al., 2017). EPs' removal efficiencies in homogeneous processes is dependent on the interactions between the chemical reagents and target compounds; while in heterogeneous processes, the adsorption of reactants and desorption of products that occur at the active sites of the catalyst surface are also very important (Dhamorikar et al., 2024; Teodosiu et al., 2018).

The most common radical generators/catalyst systems for AOPs include (Dhamorikar et al., 2024): Fenton's reagent involving iron species (Fe^{2+} or Fe^{3+}) and hydrogen peroxide (H_2O_2), ozone (O_3), UV light, $\text{H}_2\text{O}_2/\text{UV}$, $\text{H}_2\text{O}_2/\text{O}_3$, $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$, photocatalysts/UV or solar radiation, Fenton combined processes (ultrasound/electro/photo Fenton with addition of H_2O_2 and Fe^{2+}). Hybrid processes that combine membrane separation and heterogeneous photocatalysis such as the photocatalytic membrane reactors are also interesting because each process complements the advantages and overcomes the challenges of the other (Molinari et al., 2017). Figure 4.2 shows AOPs classification.

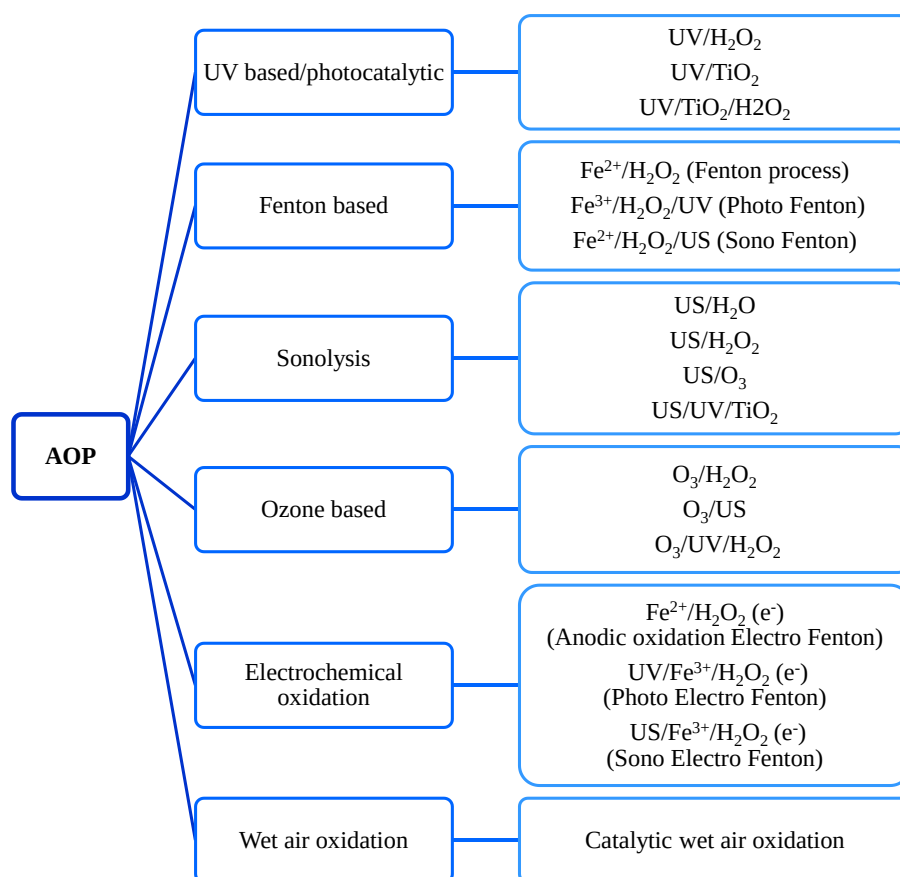


Figure 4.2. Classification of AOPs

Although there are many lab-scale applications of AOPs for EPs removal from water, there are only few studies performed at pilot-scale (Antonopoulou et al., 2014; Bui et al., 2016). It is worth mentioning that the major challenges referring to the use of AOPs for EPs' removal from water are related to:

- the small concentrations of these compounds in water;
- the generation of reaction intermediates (when complete mineralization of target compounds is not achieved);
- relatively high cost of processes when large scale installations are considered.

The most effective AOPs that may be used for EPs' removal at pilot and full-scale level are presented in Table 4.1.

Table 4.1. Overview of EPs' removal by AOWT

Treatment processes	EPs class target	Removal	References
Ozonisation	Pharmaceuticals	>98%	Talib and Randhir, 2016
UV-photolysis	Pharmaceuticals	30-70%	Pal et al., 2010
Nanofiltration	Pharmaceuticals	15-100%	García-Vaquero et al., 2014
GAC adsorption	Pharmaceuticals and pesticides	20-50%	Kennedy et al., 2015
Dioxychlorination, coagulation, sand filtration, ozonation, carbon filtration and chlorine disinfection	Pharmaceuticals and drugs	>98%	Boleda et al., 2011
Coagulation, UF, and GAC filtration	Pharmaceuticals, hormones, antibiotics and flame retardants	99%	Kim et al., 2007
UV pre-disinfection, filtration, NF/RO, remineralization and chlorine disinfection	Pharmaceuticals	>85%	Radjenović et al., 2008
Chlorine, coagulation, sedimentation, filtration, chloramine, ozonation, GAC filtration, chlorine disinfection	Drugs	89-100%	Huerta-Fontela et al., 2008
Chlorine, coagulation, filtration, ozonation, GAC, final chlorination	Drugs	88-100%	Boleda et al., 2011
Advanced oxidation	Pharmaceuticals	>99%	Klavarioti et al., 2009
UF and NF	Estrogens	>90%	Sanches et al., 2012
Photocatalysis and solar photolysis	Pharmaceuticals	66-82%	Kanakaraju et al., 2014
UV/H ₂ O ₂	Pesticides, pharmaceuticals, microorganisms	60-100%	Kruithof et al., 2007)
UV – photolysis	Pharmaceuticals	80%	Lekkerkerker-Teunissen et al., 2013
Dioxychlorination, coagulation, settling, sand filtration, UF, UV disinfection, RO and remineralization	Perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA)	>99%	Flores et al., 2013

4.1.3.4 Oxidation with potassium ferrate

Ferrate(VI) (i.e., FeO_4^{2-}) has been recently proposed as one of the most broad-spectrum chemical toward several contaminants (Li et al., 2021). Fe(VI) contains iron in its +6 oxidation state with a high reduction potential of up to 2.2 V (Luo et al., 2022). The main advantage of Fe(VI) is that nontoxic by-products are formed after the reduction of Fe(VI). Besides, Fe(VI) reduction process provides reaction iron-intermediates which may accelerate oxidation process (Fe^{5+} and Fe^{4+}) or act as useful precipitants (Fe^{3+}), thus reducing the required dose of conventional chemicals (Zhang et al., 2021). Moreover, the possibility of producing Fe(VI) via electrochemical processes using metal scraps makes it to be considered as a green chemical in line with circular economy approaches and potentially cheaper than conventional oxidizing agents (Wang et al., 2020). In the past years, several studies have been carried out using Fe (VI) for drinking water treatments. High removal performances toward manganese (Goodwill et al., 2016), turbidity and NOM (Ma and Liu, 2002; Zhang et al., 2020) have been reported in literature using Fe(VI).

The following paragraph is devoted to a deeper look at ferrate(VI).

4.2 Ferrate(VI)

Typically iron (Fe) exists in two oxidation states either as ferrous (Fe(II)) or ferric (Fe(III)). However, under strong oxidizing conditions, a higher oxidation state (i.e. +IV, +V and +VI) of iron can be achieved, which is referred to as a ferrate (Karim et al., 2020). Based on the ϵ_0 -pH diagram (Figure 4.3), which is also known as Pourbaix diagram of iron, it is possible to visualize the presence of various forms of iron at different pH and under oxidative/reductive environment. A reducing environment is represented by low ϵ_0 values; high ϵ_0 values represent an oxidizing environment. Ferrates are predominating in the top region of the ϵ_0 -pH diagram, whereas iron exists as Fe(0) at the bottom. Among the various higher oxidation state, the +VI state of iron is comparatively stable and easier to produce.

According to literature (Jiang and Lloyd, 2002; Mácová et al., 2009), ferrate(VI) has a tetrahedral structure, in which centrally placed Fe^{+6} is covalently bonded to four equivalent oxygen atoms at the corner of the tetrahedron.

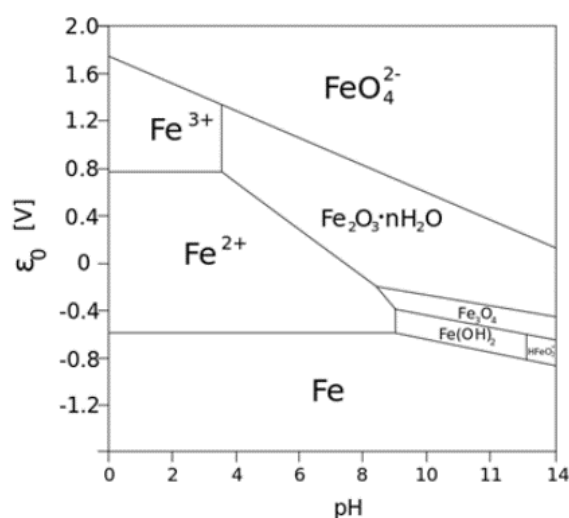
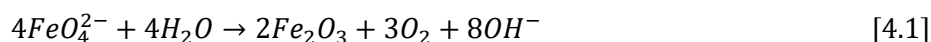


Figure 4.3. Pourbaix diagram of iron

4.2.1 Ferrate properties

The solubility and stability of ferrate(VI) salts are among the most important characteristics when using ferrate(VI) (Máková et al., 2009). The solubility indicates how easily the ferrate(VI) salt can be transferred from solution, where it is mostly produced, to the solid state. The solid state is necessary for long-term storage because the stability of the ferrate(VI) is negatively influenced by moisture (Koltypin et al., 2006). The solubility of K₂FeO₄ was studied by several authors (Jiang and Lloyd, 2002; Sharma, 2004; Wang et al., 2021) in KOH:NaOH solutions of varying relative compositions. In detail, it was found that in a KOH:NaOH mixture of constant OH⁻ concentration, the solubility of ferrate(VI) decreases with increasing potassium ion concentration.

Due to its strong oxidizing properties, ferrate(VI) is relatively unstable in the presence of water (Karim et al., 2020; Wang et al., 2021). Ferrate ions and water molecules react to form ferric oxide (Fe₂O₃), oxygen gas, and hydroxyl ions (Equation 4.1). Due to the release of hydroxyl ions, the resulting pH of the solution is highly alkaline.



Under the acidic environment, ferrate is quite unstable and rapidly undergoes exothermic degradation. In aqueous solution of pH 5, the ferrate (1 mM) was reported to be completely degraded within 7 min (Tiwari et al., 2007). The

stability of ferrate tends to improve with an increase in pH (Figure 4.4). For pH 10, the ferrate concentration remained almost constant. At pH of above 10, the stability of ferrate also tends to deteriorate. For a ferrate concentration of 0.25 mM and a pH of 12, reductions of 60% were reported within 10 min (Graham et al., 2004).

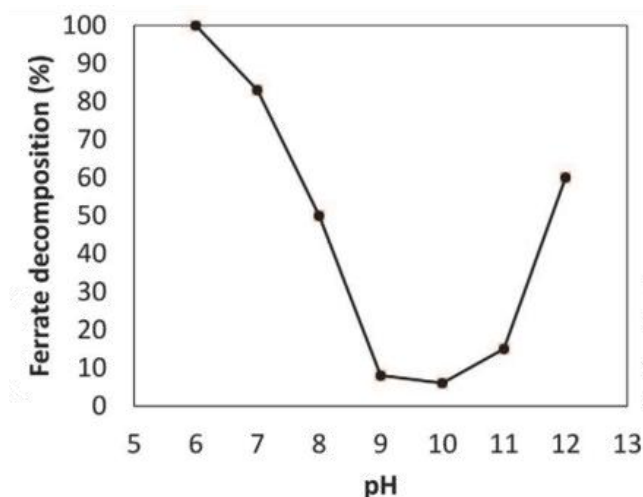


Figure 4.4. Stability of ferrate in the aqueous phase at different pH

A diluted ferrate solution is reported to be more stable than a concentrated solution. The critical ferrate concentration is 0.025 M; a ferrate concentration higher than this (0.025 M) in solution tends to degrade rapidly. When comparing the stability of ferrate at different concentrations, it was reported that 89% of ferrate concentration remained as ferrate for 0.02 and 0.025 M strength for 1 h. However, complete degradation was reported for solution with a 0.03 M concentration in that specific duration (Karim et al., 2020).

The temperature of the aqueous phase can also influence the stability of ferrate. Ferrate solution (0.01 M) kept at 0.5°C was reported to remain stable (2% reduction) even after 2 h. On the other hand, the ferrate concentration was found to be reduced by 10% at a temperature of 25°C. External factors such as light are not known to have any significant influence on the stability of ferrate (0.01 M) (Jiang and Lloyd, 2002).

Depending on the pH of the solution, four different species of ferrate can exist (Figure 4.5). Initially, two unstable species of Fe(VI) (i.e. H_2FeO_4 and HFeO_4^-) were reported in phosphate buffer (0.2 M solution). Three protonated species of

Fe(VI) were reported in phosphate/acetate buffer (0.025). In the alkaline environment, most of the ferrate exist as FeO_4^{2-} . In neutral conditions, HFeO_4^- is the dominating species (Wang et al., 2021).

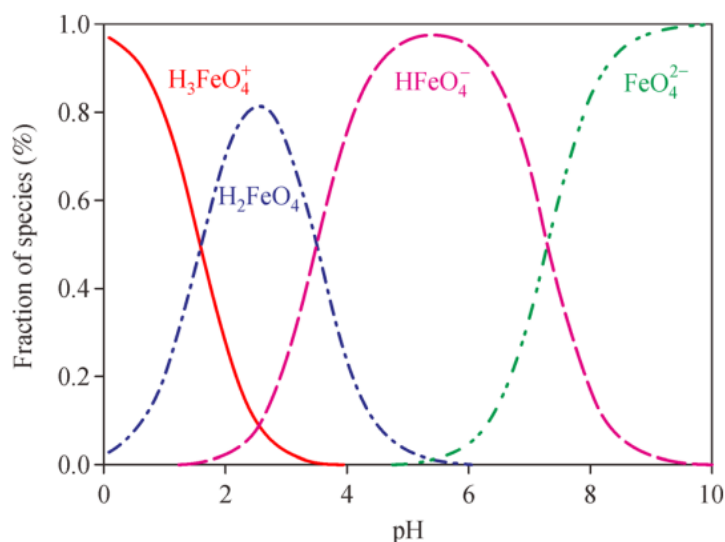


Figure 4.5. Influence of pH on the speciation of Fe(VI) (Wang et al., 2021)

4.2.2 Ferrate production

Georg Ernst Stahl (1702) a chemist and physician, observed a red-purple color during a reaction between potassium nitrate and iron filings (Talaiekhosani et al., 2017b). The red-purple colour was eventually identified as hexavalent potassium ferrate (K_2FeO_4). Eckenberg and Becquerel in 1834 reported that a red-purple colour appeared during heating of a mixture of potassium hydroxide and iron ore. Fremy in 1840 reported that this colour can be ascribed to the production of a type of high-capacity iron having the chemical formula of FeO_3^{2-} . Luo et al. (2011) reviewed all methods for ferrate(VI) measurement. Although FeO_3^{2-} was identified during these studies, its production principles were not discovered until one century ago (Tsapin et al., 2000). Up to now, there are two basic methods for ferrate production (Alsheyab et al., 2009): chemical and electrochemical (Figure 4.6). The chemical methods are based on contacting iron compounds, such as iron(III) nitrate and iron oxide, with an oxidizing material in either an alkaline environment (wet route), or under extreme temperatures in a controlled atmosphere (dry route). The drawback of this method is that it requires additional processes and reagents to obtain high yield and purity which makes it expensive.

On the other hand, the electrochemical method usually consists of a sacrificial iron anode in an electrolysis cell containing a strongly alkaline solution with an electric current serving to oxidize the iron to Fe(VI) (Alsheyab et al., 2009).

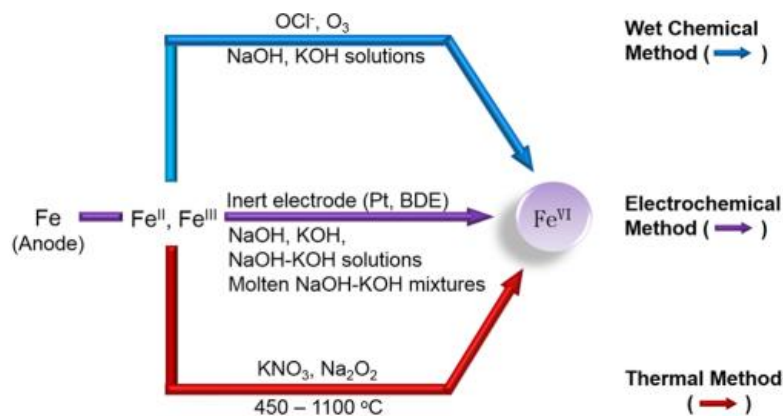


Figure 4.6. Methods used to synthesize ferrate(VI) (Sharma et al., 2016)

4.2.2.1 Dry oxidation method

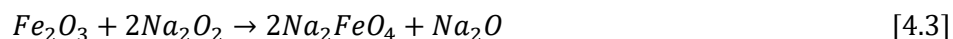
The dry oxidation method, which is also known as the thermal method, is an old method for preparing the ferrate salts and is considered to be quite dangerous and difficult, since the synthesis process could cause detonation at elevated temperatures. Efforts have been made by different investigators (Jiang et al., 2006; Jiang and Lloyd, 2002; Sharma et al., 2005), where the potassium or sodium ferrate(VI) was prepared either by calcination of a mixture of ferric oxide and potassium peroxide at 350–370°C, or by oxidation of iron oxide with sodium peroxide at a temperature of 370°C, under the conditions of continuous flow of dry oxygen (free from carbon dioxide). The resulting product was considered to contain FeO_5^{4-} anions, which were instantaneously hydrolysed to form a tetrahedral ion FeO_4^{2-} when they dissolved in water, resulting in a red-violet solution (Eq. 4.2) (Jiang and Lloyd, 2002).



The percentage of recovery of ferrate was not higher than 55%.

Thompson et al. (1951) introduced a method to produce ferrate(VI) from galvanized waste. In this method, wastes were mixed with ferric oxide in a muffle furnace at 800°C and the sample was cooled and stirred with solid sodium

peroxide and heated gradually for a few minutes. The mixtures were melted and then cooled resulting in the formation of sodium ferrate (Eq. 4.3):



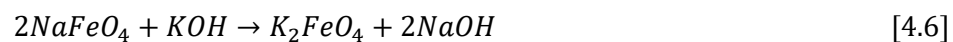
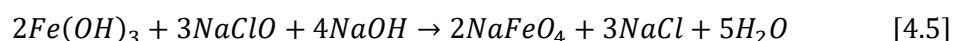
Rush et al. (1996) developed another dry method to produce ferrate(VI). In this method, potassium or cesium super oxides are mixed with iron oxide powder. Then, the mixture heated up to 200°C and is retained at this temperature for 10 more hours. Potassium and cesium ferrates(VI) are the final product of this process (Talaiekhosani et al., 2017b).

4.2.2.2 Wet oxidation method

The wet oxidation method involves the oxidation of a ferric containing solution to form ferrate(VI) solution under high alkaline conditions. As the ferrate solution will be decomposed rapidly, the subsequent procedures of precipitation, washing and dry are required in order to obtain a solid stable product (Jiang and Lloyd, 2002).

Various efforts have been made to prepare solid sodium ferrate; however, there were difficulties in isolating any solid products from the resulting solutions, as Na_2FeO_4 has relatively high solubility in a saturated NaOH solution. By changing the preparation procedures, where the chlorine gas flowed through a ferric salt with a saturated NaOH solution, a solid product was obtained with a weight content of 41.38% as Na_2FeO_4 (Talaiekhosani et al., 2017b).

Preparation of potassium ferrate using wet oxidation method has also been studied since the 1950s (Thompson et al., 1951). The procedure first involves the formation of sodium ferrate by reacting ferric chloride with sodium hypochlorite (NaClO) in the presence of sodium hydroxide, and then by adding potassium hydroxide to precipitate the potassium ferrate from the solution mixtures. Even though a percentage recovery of potassium ferrate as high as 96% could be obtained, the maximum yield percentage obtained by continuous efforts was 75%. The basic chemical reactions are shown in Equations 4.4, 4.5 and 4.6.



4.2.2.3 Electrochemical method

Electrochemical method is considered as a potential in-situ method for production of ferrate(VI) (Talaiekhosani et al., 2017b). Synthesis of ferrate(VI) by using electrochemical methods was first carried out in 1841 (Poggendorf, 1841). According to literature, this method is the simplest way to produce ferrate (VI) solution with high purity [112]. Preparation of ferrate usually consists of a sacrificial anode in an electrolysis cell containing a strongly alkaline solution such as NaOH or KOH with an electric current serving to oxidize the iron to Fe(VI) (Alsheyab et al., 2009) (Figure 4.7). The basic principle of production is shown in Equation 4.7, 4.8, 4.9 and 4.10.

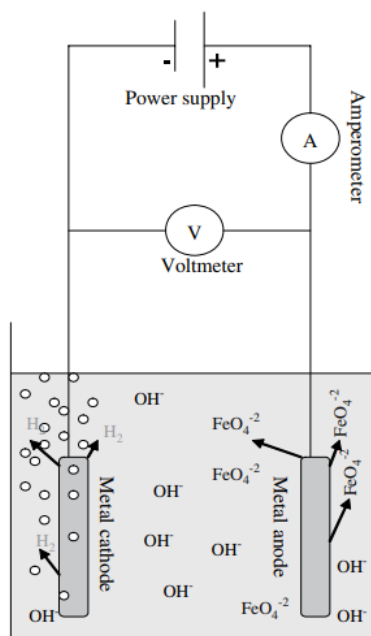
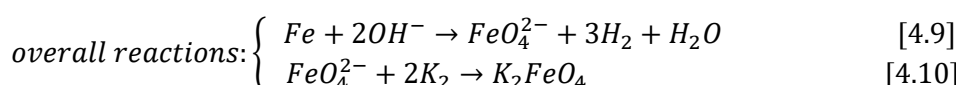
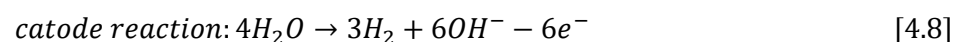
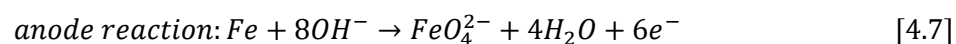


Figure 4.7. Scheme of an electrochemical cell for ferrate production (Alsheyab et al., 2009)

Many studies have been conducted to find the optimum values of electrolytic concentration, current densities, temperature, electrode distance, anode electrode material and hydraulic retention time to achieve the highest production efficiency. It was reported that, among these factors, the composition of the anode, the current density and the type and concentration of electrolytes have significant effects on the ferrate production (Alsheyab et al., 2009; Mácová et al., 2009; Munyengabe and Zvinowanda, 2019; Talaiekhosani et al., 2017b).

Anode composition. Several researchers studied the anode material for ferrate production (Lapicque and Valentin, 2002; Licht et al., 2005). The ideal electrode material should be totally stable in the electrolysis medium permitting the desired reaction with high current efficiency and at low over potential. The anode is sacrificial, usually consisting of tightly wound iron wire (either pure iron or carbon steel). The anode may have iron content between 90% and 100%, preferably above 99%. Both the anode and cathode may be selected from: iron, cast iron, malleable iron, ductile iron, carbon steel, stainless steel and combinations, with different configurations: expanded metal mesh, wire mesh, woven metal cloth, flat plate, rod and combinations. The shape of the electrode is selected to obtain the maximum surface area. It was found that the current yield during electrochemical production increased with the carbon content in the iron anode material used. The current yields were 15% for raw iron, 27% for steel and 50% for cast iron at a current density 10 A/m² and NaOH concentration 16.5 M. The highest current yield was obtained using a cast iron anode containing 3.16% C in the form of iron carbide (Fe₃C), 20°C and 14 M NaOH, where the current yield was 65% in the beginning and 55% after three hours (Bouzek et al., 1996a, 1999a). Other researchers studied the effect of carbon content on the current efficiency, where it was found that the current efficiency was greater than 70% when a silver steel with carbon content of 0.9% was used. Whilst in the same conditions, the current efficiency was reduced to 12% when the carbon content was 0.08% (Alsheyab et al., 2009). The gray iron was described as the ideal anode material for electrochemical synthesis of ferrate where with 14 M NaOH, 20°C and the current density of 4.54 mA/cm², the highest current efficiency 68.5% was achieved and NaOH was reported to be better than KOH as an electrolyte for the ferrate production (Xu et al., 2004).

Electrolyte. The electrolyte solution may include a hydroxide selected from sodium hydroxide, potassium hydroxide, lithium hydroxide, cesium hydroxide, barium hydroxide and combinations between them. It was reported that when comparing LiOH, NaOH and KOH solutions, the NaOH solution provides the

highest ferrate and current yields (Bouzek et al., 1999b). Several studies have demonstrated that increasing NaOH concentration in electrolyte solution has a significant effect on the rate of synthesis of ferrate (VI) (Máková and Bouzek, 2012). Bouzek et al. (1996a; 1996b, 1993) have demonstrated that the best NaOH concentration for electrochemical production of ferrate (VI) is 14 molar. He et al. (2005) reported that KOH is by far the better electrolyte for electro-synthesizing ferrate(VI) than NaOH as a whole. The results showed that under similar conditions, the obtained current efficiency in the concentrated NaOH solution was 55%, while it could reach 73.2% in the solution of KOH, with a purity of 95.3-98.1%. Among different forms of hexavalent irons, sodium ferrate (Na_2FeO_4) and potassium ferrate (K_2FeO_4) are utilized in water and wastewater treatment more than other forms are. Na_2FeO_4 solution in water can remain more stable compared with other forms of ferrate if its environment is saturated with NaOH (Talaiekhosani et al., 2017b). As ferrate(VI) solution is not stable for a long time, it is very important to produce a dry powder. Although production of dry powder of sodium ferrate(VI) is very difficult, production of potassium ferrate(VI) due to being insoluble in NaOH-saturated water is quite convenient. Dry potassium ferrate (VI) is considered as the best dry resource of ferrate (VI), because it is capable of storing for a long period and using in large-scale water and wastewater treatment applications.

Current density. Máková et al. (2009) studied the effect of current density on the ferrate yield with anodes of pure iron and cast iron at various temperatures. For pure iron anode, a current yield of 60% can be achieved at a current density of 20 A/m^2 at 30°C, and 50 A/m^2 at 40°C. For white cast iron anode, the highest current yield of 55% was achieved at 80 A/m^2 and 20°C. It was also found that the current efficiency for ferrate electro-synthesis is related to the electrolyte temperature (Alsheyab et al., 2009).

4.2.3 Ferrate measurement

There are many techniques which are utilized to characterize the produced ferrate(VI) according to its physical and chemical properties (Wei et al., 2015):

- UV-Visible (UV-Vis) spectroscopy. This technique also known as a direct colorimetric method is suitable for quantification of liquid ferrate(VI) solution. It is founded on determining the concentration of a given solution due to the intensity of the color absorbed. In the case of ferrate(VI), the characteristic darkish purple color corresponds to the

visible spectrum between 500 and 800 nm (Rai et al., 2018). Bielski and Thomas (1987) observed a valuable peak at 510 nm at pH 10 with a shoulder of 275 and 320 nm (Figure 4.8a);

- Fourier transform-infrared (FT-IR) spectroscopy. The FT-IR is a method which is frequently used by many researchers to characterize different ferrate salts in a powder form. FT-IR provides a primary peak for ferrate salt around 808 cm⁻¹ and a shoulder peak can also be observed approximately at 780 cm⁻¹ (Barişçi et al., 2016) (Figure 4.8b).
- X-Ray powder Diffraction (XRD) method. The XRD is a method to confirm the crystallinity, structures and magnetic properties of the ferrate(VI) salts. The XRD is one of the analytical facilities used to indicate the presence of ferrate(VI) by demonstrating the isomorphism with other ferrate salts obtained in the literature (Lei et al., 2013). Characteristic peak at 2 Θ values is 30.40°; other secondary peaks are 31.29°, 32.54°, 39.36°, 40.51°, and 57.30 (Munyengabe et al., 2021a) (Figure 4.8c);
- Mössbauer spectroscopy. This method is suitable for determining the oxidation states of iron, ranging from +2 to +6, in a mixture of compounds. The Mossbauer spectrum determines the parameters including isomer shift, which varies with the valence of iron in the sample (Luo et al., 2011). The spectrum is characterized by doublet (-0.5 mm/s and +0.5 mm/s), due to the asymmetrical distribution of electrons around the Fe(VI) center. The absorption peaks are symmetrically positioned around the isomer shift close to 0 mm/s (Figure 4.8d);
- Inductively coupled plasma – mass spectrometry (ICP-MS) method. It can be used for measuring ferrate(VI) indirectly by detecting the iron content in the sample. Since ICP-MS measures elemental concentrations (e.g., Fe), the ferrate(VI) must be converted to a stable iron species, typically Fe(III), through controlled decomposition or reduction. This can be done by acidifying the solution with a strong acid like hydrochloric acid (HCl) or sulfuric acid (H₂SO₄). In this way, by isolating ferrate(VI), the concentration value of total iron can represent the Fe(VI) concentration (Licht et al., 2001);
- Titrimetric (chromite) method. This method is applicable only to the analyses of solutions containing low concentrations of the ferrate(VI) ion

(Jiang and Lloyd, 2002). According to this methodology, the Fe(VI) sample is dissolved into solution as FeO_4^{2-} to oxidise chromite, Cr(III) to chromate, Cr(VI) (Equation 4.11). The generated chromate is then titrated with a standard ferrous ammonium sulphate solution.

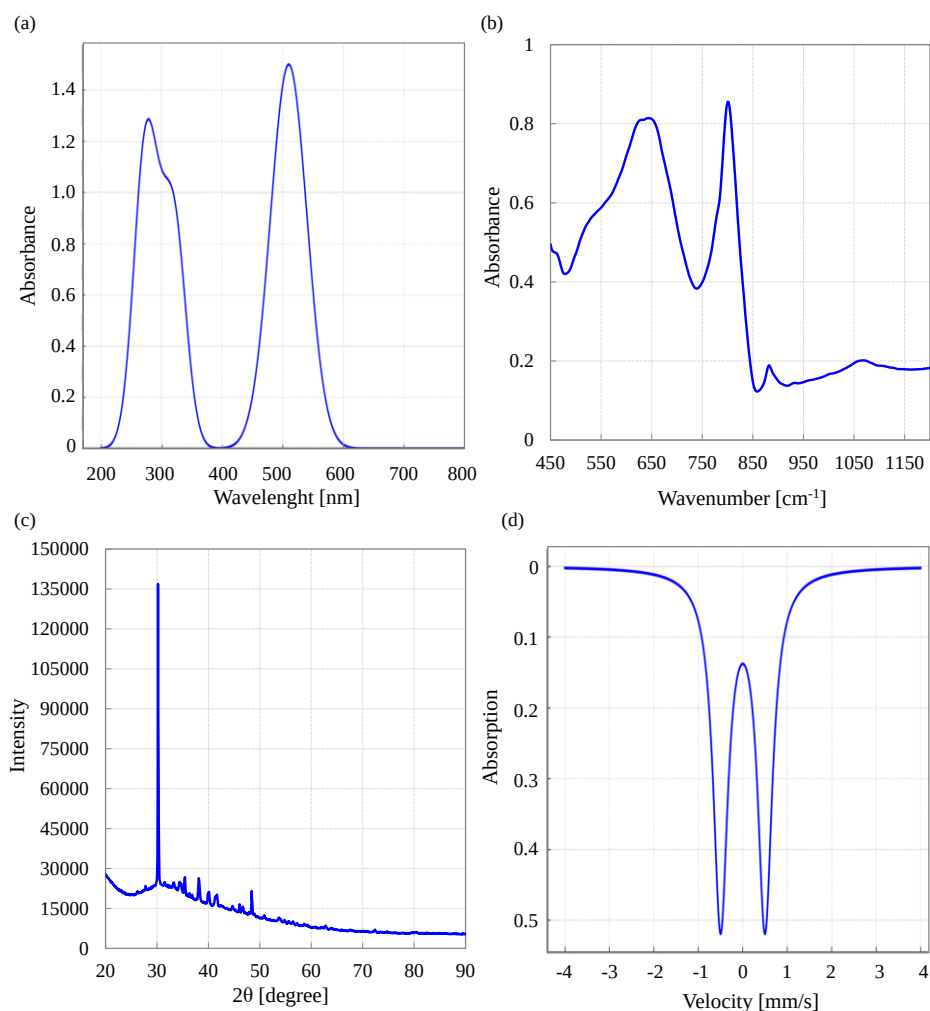
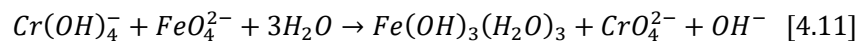


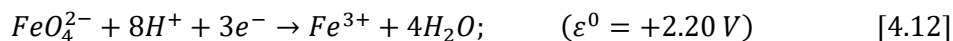
Figure 4.8. UV-vis (a), FTIR (b), XRD (c) and Mössbauer (d) absorption spectra of Ferrate(VI)

4.2.4 Ferrate(VI) as a multifunctional chemical reagent

All water chemical treatment processes can consist of three primary sections, i.e. oxidation, coagulation and disinfection. There is a wide range of chemicals which can be utilized for these purposes. The most common coagulants used include ferric sulphate, aluminium sulphate, and ferric chloride, and the oxidants/disinfectants used are chlorine, sodium hypochlorite, chlorine dioxide, and ozone. However, these common used chemical reagents have limitations, one example of which is the formation of potential harmful disinfectant/disinfection by-products (DBPs) in the chlorination and ozonation process. In order to meet the more stringent regulations/standards of drinking water, an ideal water treatment chemical reagent should not form any harmful by-products in the treatment processes but give more efficient inactivation of microorganisms, partially degrade and oxidise the organic and inorganic impurities, and remove colloidal/suspended particulate materials and heavy metals (Jiang et al., 2006). Potassium ferrate(VI) possesses all above functions and it is the sole potential candidate which can be employed for oxidation, coagulation and disinfection simultaneously (Talaiekhosani et al., 2017b). In the following sections the application of this chemical for these three processes is discussed in terms of influencing parameters such as by products, efficiency and pH.

4.2.4.1 Oxidation

Ferrate(VI) was reported as one of the most powerful oxidants known for water treatment. The reduction potentials of ferrate in acidic and alkaline solutions are reported in Equation 4.12 and 4.13 (Song and Ma, 2013), respectively.



Under acidic conditions, the oxidation – reduction potential of the ferrate(VI) ions (2.2 V) is greater than other common oxidants (Table 4.2), such as ozone (O₃), hydrogen peroxide (H₂O₂), chlorine (Cl₂), chlorine dioxide (ClO₂), and potassium permanganate (KMnO₄).

Table 4.2. Redox potential of commonly used oxidants/disinfectants

Oxidants/Disinfectants	Reaction Type	ϵ^0 [V]
Cl_2	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	1.358
ClO_2	$\text{ClO}_2 + e^- \rightarrow \text{ClO}_2^-$	0.854
O_3	$\text{O}_3 + 2\text{H}^+ + 2e^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	2.076
KMnO_4	$\text{MnO}_4^- + 4\text{H}^+ + 3e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.679
	$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.507
Fe(VI)	$\text{FeO}_4^{2-} + 8\text{H}^+ + 5e^- \rightarrow \text{Fe}^{3+} + 4\text{H}_2\text{O}$	2.20
	$\text{FeO}_4^{2-} + 4\text{H}_2\text{O} + 3e^- \rightarrow \text{Fe(OH)}_3 + 5\text{OH}^-$	0.76

4.2.4.2 Coagulation

As well as the high oxidation capacity, the ferrate(VI) also possesses the coagulation function, since it is reduced to form trivalent iron or ferric hydroxide (Fe(OH)_3) (Talaiekhosani et al., 2017a). Therefore, reaction products of Fe(VI) act as coagulants to capture colloidal particles in water or precipitate undesirable inorganic pollutants (Zhang et al., 2020). An advantage in using ferrate(VI) is that it can destabilize the colloidal particles within 1 min, whilst ferric and ferrous salts can only achieve the destabilization after 30 min mixing (Song and Ma, 2013). This phenomenon points to the possibility of a highly efficient application of ferrate coagulant in direct filtration (Jiang and Lloyd, 2002). In addition, ferrate can achieve the same coagulation performance (e.g., for the removal of turbidity) at a smaller dose and with a lower sludge generation in comparison with ferric chloride and aluminium chloride (Yu et al., 2023).

4.2.4.3 Disinfection

Ferrate(VI) can be used as a strong disinfectant for water sterilization and disinfection. Compared with traditional chlorine disinfection, ferrate(VI) effectively removes microorganisms, and reduces the precursors of disinfection by-products. The schematic diagram in Figure 4.9 illustrates the disinfection of microorganisms such as bacteria by ferrate(VI). Furthermore, ferrate(VI) kills microorganisms by oxidizing their nucleic acids and destroying their protein structures. Moreover, the iron hydroxide colloids obtained by ferrate(VI) reduction can adsorb bacteria and viruses and cause microorganisms to aggregate and precipitate (Yu et al., 2023).

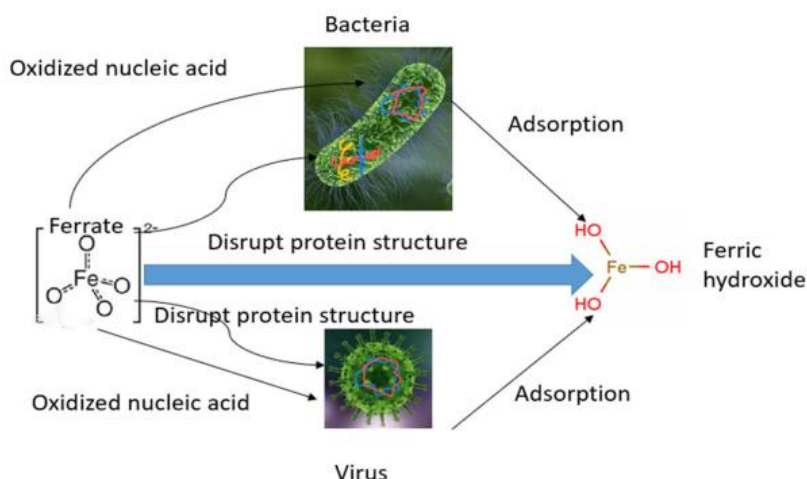


Figure 4.9. Schematic diagram of ferrate(VI) disinfection (Yu et al., 2023)

The disinfecting properties of ferrate(VI) were first observed by Murmann and Robinson (1974) when they investigated the effectiveness of ferrate as a disinfectant to kill two pure laboratory cultures of bacteria (*Non-recombinant Pseudomonas* and *Recombinant Pseudomonas*). The authors found that with a dose range of 0–50 ppm as FeO_4^{2-} , the bacteria could be completely destroyed. Later, the study by Gilbert et al. (1976) showed that ferrate(VI) has sufficient disinfection capability to kill *Escherichia coli* (E. coli).

4.2.5 Ferrate(VI) application in drinking water treatment

In last decades ferrate(VI) has been well investigated (Delaude et al., 1995; S. Dong et al., 2019; Goodwill et al., 2016; Graham et al., 2010; Jiang et al., 2006, 2016; Karim et al., 2020; Khoi et al., 2020; Kubiňáková et al., 2017; Lim and Kim, 2009; Sharma, 2004; Yu et al., 2023) as an alternative water treatment chemical for the removal of a broad spectrum of contaminants. In the following sections the use of iron for the removal of certain contaminants of interest (manganese, algae, natural organic matter, turbidity) is explored.

4.2.5.1 Algal removal

Reservoir eutrophication and algal bloom outbreaks in drinking water sources have become significant threats to the current water ecological environment. The over-growth of algae can easily cause a series of problems such as foul odour and deterioration in water quality. At the same time, algae itself is also a precursor of

DBPs, so removing algae is of great benefit for the control of DBPs (Yu et al., 2023).

Numerous studies have shown that ferrate(VI) is more effective at removing algae than other methods. For example, Ma et al. (2014) compared the effectiveness of potassium ferrate(VI), polyferric chloride (PFC), and potassium permanganate in removing algae in water. The results showed that the removal effect of K_2FeO_4 on algae was better than that of PFC and $KMnO_4$, and the removal rate was as high as 92.4%. Similarly, Kubiňáková et al. (2017) used ferrate(VI) to remove chlorella, and when 8.34 micromole of ferrate(VI) was added, the removal rate of chlorella was 89%. The mechanism by which ferrate(VI) removes algae is mainly through oxidation, which destroys the surface structure of algae cells, this causes the extracellular sheath to crack and the intracellular substances to discharge, which leads to the death of the algae. Additionally, the reduction product $Fe(OH)_3$ of ferrate(VI) has a flocculation effect, which can further adsorb and remove algal cells (Yu et al., 2023).

He et al. (2021) found that after the oxidation treatment with ferrate(VI), not only was the structure of the algae cells destroyed, but the particle size and zeta potential of the algae also increased by 20% and 55%, respectively, which promotes the aggregation of algae and improves algae removal efficiency. Increasing the dosage of ferrate(VI) or the reaction time can also improve the algae removal rate. Dong et al. (2019) used ferrate(VI) to remove cyanobacteria, and the dosage of ferrate(VI) was increased or the oxidation time was prolonged; consequently, the removal of algal cells and algal organic matter (AOM) by ferrate(VI) increased. Ferrate(VI) can effectively inhibit algae growth, enhance the flocculation effect of water bodies, and increase the purification capacity of a water body. Zhou et al. (2019) found that ferrate(VI) pre-oxidation can remove algae cells by destroying the protective organic layer. Therefore, ferrate(VI) is also an effective bactericidal disinfectant and algaecide. At the same time, when used as a disinfectant, ferrate(VI) is not like disinfection by-products (DBPs) that are harmful to the human body and produced during chlorination treatment, such as trihalomethanes (THMs); on the contrary, ferrate(VI) can effectively control the formation of chlorination disinfection by-products (Huang et al., 2016).

Xia et al. (2021) used ferrate(VI)–photocatalysis to remove algal toxins from water. When the dosage of ferrate(VI) was 10 mg/L, the removal rate of algal toxin by the combination of ferrate(VI) and photocatalytic technology increased from 63% to 100%, which could quickly remove the algal toxin.

4.2.5.2 NOM removal

Several studies (Jiang et al., 2006; Jiang and Wang, 2003; Qu et al., 2003) have demonstrated that potassium ferrate can perform better than ferric sulphate (FS) at lower doses for treating humic and fulvic acids (HA and FA) in terms of removing UV₂₅₄ absorbance and dissolved organic carbon (DOC) and lowering the trihalomethane formation potential. Jiang et al. (2006) demonstrated that in drinking water treatment, ferrate(VI) can remove 10–20% more UV₂₅₄-abs and DOC than ferric sulphate for the same dose compared for natural pH range (6 and 8). Qu et al. (2003) reported that the ultraviolet absorption (UVA) of fulvic acids in water can be reduced about 90% when the weight ratio of ferrate to FA was 12:1. Moreover, it emerged that adsorption to and coprecipitation with Fe(OH)₃ precipitate produced by ferrate decomposition can also result in additional FA reduction. In addition, in the presence of turbidity, ferrate can oxidize and adsorb simultaneously and over 95% of UVA was reduced with the same weight ratio of 12:1. Jiang and Wang (2003) demonstrated that potassium ferrate can perform better than ferric sulphate at lower doses for treating waters containing humic and fulvic acids in terms of removing UV₂₅₄ absorbance and dissolved organic carbon (DOC) and lowering the trihalomethane formation.

In the study of Lim and Kim (2009), natural organic matter (NOM) present in river and stream water was removed using potassium ferrate. The authors observed more than 70% removal of humic and fulvic acids by varying the Fe(VI) dosage, pH and temperature of the solution.

According to previous literature, at an alkaline condition the reduction potential of Fe(VI) is lower than at pH lower than 7, thus leading to poor NOM mineralization capacity (Lim and Kim, 2009; Zhang et al., 2020). In this context, Deng et al. (2018) reported that NOM removal by ferrate increased as ferrate decomposition was improved. Therefore, as at high pH Fe(VI) is stable in its form, poor NOM removal was observed. In a recent study (Khoi et al., 2023), it was observed that the single use of ferrate for NOM removal was effective at pH of 5, thus suggesting that the more reactive forms towards NOM removal derived from Fe(VI) decomposition.

In the study of Song et al. (2016), ferrate(VI) decay and reactions with NOMs in a typical surface water matrix was evaluated. Results showed that ferrate(VI) decay exhibited a pseudo 2nd-order reaction pattern, suggesting that self-decomposition is principally responsible for ferrate(VI) consumption. Ferrate(VI) tended to attacked electron-rich moieties in NOM molecules, but had

limited capability to mineralize NOMs. Consequently, ferrate(VI) effectively reduced UV_{254} and specific UV absorbance ($SUVA_{254}$), but poorly removed dissolved organic carbon (DOC).

In other literature studies (Jiang et al., 2016; Liao et al., 2017), it was reported that ferrate pre-oxidation had positive effect on coagulation/flocculation of NOM because of Fe(III) production. Indeed, negatively charged compound of NOM are removed by iron ions by formation of colloidal hydroxides.

4.2.5.3 Turbidity removal

Several studies have been conducted on the use of ferrate(VI) for the removal of turbidity.

Zhang et al. (2020) explored the effects of different doses of Fe(VI) at pH 4 and 8. In particular, at pH 4.0, removal rates of 95% and 98% were achieved with a ferrate dose of 3.0 mg/L and 6.0 mg/L, respectively. Different turbidity removal patterns with ferrate(VI) dose were observed at pH 8. Turbidity removal of 77% was achieved at 1.0 mg/L Fe(VI); however, as ferrate(VI) dose was increased to 6.0 mg/L, the residual turbidity slightly increased to 3.54 NTU, corresponding to a 69% removal of turbidity.

Similarly, Ma and Liu (2002) investigated the effects of pH and ferrate(VI) dosage on turbidity removal. The authors reported that a 89% efficiency was achieved when dosing 4.26 mg/L (as Fe) at pH 3.

Jiang et al. (2015) pointed out that a very low doses of ferrate(VI) (0.2 mg/L as Fe) could perform superiorly to other coagulants. Jiang and coauthors found that for a dose between 0.3 and 1.0 mg Fe/L, ferrate(VI) allowed for achieving 99.9–99.99% reduction while ferric chloride sulphate and polyacrylamide could only reduce 5–30% for the same dose range.

4.2.5.4 Manganese removal

Ferrate(VI) is interested to use in metals removal due to its multifunctional features (S. Dong et al., 2019). Table 4.3 lists studies of metal removal by ferrate(VI).

Many researchers have conducted studies with a particular focus on manganese.

For instance, White and Franklin (1998) obtained a residual manganese concentration close to zero when dosing 3ppm of ferrate(VI); nevertheless, by

increasing ferrate(VI) concentration up to 15 ppm, the residual manganese increased too.

Gui et al. (2009) obtained 72.5% removal with a ferrate dose of 3.0 mg/L at pH 10. Similarly, in the study of Khoi et al. (2020) a removal efficiency of manganese was achieved at around 50% in a wide range of pH and ferrate concentration. Moreover, In the study proposed by Munyengabe et al. (2021b) the removal percentage of manganese ranged between 82.70 and 99.20%.

In the study conducted by Bartzatt (2016), visible spectroscopy showed that potassium ferrate substantially reduced manganese (II) cations after treatment.

Lim and Kim (2010) investigated how to simultaneously remove both manganese and natural organic matters. In water sample including 0.1 mM manganese, removal efficiency ranged 22–73% at the ferrate(VI) doses of 0.03– 0.7 mM (as Fe) and increased with increasing pH. In the mixture of manganese (0.1mM) and NOM (10 mg/L) at the ferrate(VI) doses of 0.03–0.7 mM (as Fe) the removal efficiency was 31–81% for manganese and 33-86% for NOM.

Lastly, Goodwill et al. (2016) investigated the stoichiometry of the oxidation-reduction reaction between Fe(VI) and Mn(II), assessed the impact of pH and initial Mn(II) concentrations across ranges typical to drinking water treatment, evaluated the impact of competition from NOM on the stoichiometry of Fe(VI) and Mn(II), evaluated the kinetics of the reaction and examined the characteristics of resulting Mn and Fe particles with respect to oxidation state and size. The authors found that Fe(VI) oxidizes Mn(II) at a stoichiometric ratio of 2 moles of Fe(VI) to 3 moles of Mn(II). This reaction was consistent across different pH levels (6.2 and 7.5) and in the presence of natural organic matter (NOM), indicating that Fe(VI) selectively oxidizes Mn(II) even in complex water matrices. The presence of NOM slightly affected the oxidation process but did not significantly alter the stoichiometry, thus indicating that Fe(VI) was effective at selectively oxidizing Mn(II) even in the presence of competing substances like NOM. Results from kinetic evaluation highlighted that the rate of the Mn(II) oxidation reaction was fast relative to typical time scales in drinking water treatment, with an estimated second order rate constant of approximately $1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at pH 9.2 and more than $9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at pH 6.2, thus making ferrate a viable option for pre-oxidation in water treatment. Finally, X-ray photoelectron spectroscopy confirmed that the oxidation of Mn(II) by Fe(VI) resulted in the formation of Fe(III) and Mn(IV) particles, including nanoparticles.

Table 4.3. Summary of studies on the removal of heavy metals by ferrate(VI) (S. Dong et al., 2019)

Heavy metal	Condition	Results/findings	Remarks	Reference
As, Pb	As=Pb=2mg/L, pH=6.5, Fe/As=16 ^a , Fe/As=4 ^a	Removal efficiency was greater than 99,5% for all metals.	Removal of metals by ferrate (VI) through oxidation and surface complexation sequentially.	Wang et al., 2015
Cd, Co, Ni, Cu, Al	Initial concentration of metals, 100mg/L; Fe/M=2/1 for Co, Ni, Cu, Al; Fe/Cd=15/1; pH=6.6	Good candidate for the remediation of Co, Ni, Cu, Al. Lower removal rate of the Cd (70%) even at a high Fe/Cd of 15:1	The role of ionic radius and metal valence state cannot be ignored during the removal of metals.	Prucek et al., 2015
As, Sb	As=Pb=2mg/L, pH= 4-7, K ₂ FeO ₄ = 50mg/L	Removal rate: As >98.5%, Sb= 27–96%, The maximum adsorption capacity of As was 162.02 mg (g K ₂ FeO ₄) at pH 6.5 and of Sb was 129.93 mg (g K ₂ FeO ₄) at pH 4.0	The pH dependence of Sb was more pronounced than As. The consideration of synergistic effect on simultaneous removal of As and Sb is required	Lan et al., 2016
Tl	Tl=1µg/L, pH= 7, K ₂ FeO ₄ =0.5–3 mg/L, T= 20 °C	Removal rate: Tl= 40–92%, K ₂ FeO ₄ can removal of trace Tl in actual water but require more K ₂ FeO ₄	The hydrodynamic size of the reduced particle from K ₂ FeO ₄ are in nanoscale and in situ formed ferric nanoparticle plays an important role in Tl removal.	Liu et al., 2017
As	As=501ppm, time=12h, pH=7.3, Fe/As=(2-6)/3	Removal rate: As=45.6–81.8%, the efficiency of As removal increases with an increase of Fe/As	Reaction temperature and reaction time also have an effect on the removal of As.	Fan et al., 2002
As	As = 517 µg/L, pH = 6.3–6.6, K ₂ FeO ₄ =2 mg/L	The As concentration can be lowered to below 50 µg/L. As(III) was oxidized to As(V) by Fe(VI), with a stoichiometry of 3:2 [As(III): Fe(VI)]	The reaction of As(III) with Fe(VI) was first-order with respect to both reactants and its observed second order rate constant decreased nonlinearly with an increase of pH	Lee et al., 2003

4.2.5.5 Emerging pollutants removal

More than 1000 substances, gathered in 16 classes (algal toxins, antifoaming and complexing agents, antioxidants, detergents, disinfection by-products, plasticizers, flame retardants, fragrances, gasoline additives, nanoparticles, perfluoroalkylated substances, personal care products, pharmaceuticals, pesticides, anticorrosives), are classified as Emerging Pollutants (EPs) (Teodosiu et al., 2018). In recent years, many researchers investigated the use of ferrate(VI) for EPs removal.

Lee et al. (2023) examined the flocculation/coagulation for efficiently removing microplastics (MPs), polyethylene (PE) and polyethylene terephthalate (PET)) in water by applying ferrate treatment. Fe(VI) coagulation removed >80 % of PE and PET in a range of ~0.9–3.6 mg/L of coagulant dose. In particular, 99% of PE was removed with 2.7 mg/L coagulants, whereas PET removal efficiency reached 75% at the highest dose (3.6mg/L). However, the presence of organic humic acid (HA) significantly enhanced PET removal efficiency, reaching 99% at the highest dose. Moreover, in the real surface natural water condition, 98% of MPs removal efficiency was achieved by - twofold decreased ferrate dose (1.8 mg/L) without microfiltration membrane process.

Jiang et al. (2023) studied the performances of ferrate(VI) in comparison with that of ferric chloride and ozonation in the treatment of some EPS of interest. The results showed that 10% of metformin, benzotriazole and acesulfam can be removed by ferrate(VI) at a dose of 0.1 mg/L from raw water, but FeCl₃ with or without pre-ozonation cannot achieve the same performance. Moreover, the degradability of three additional micropollutants by ferrate(VI) oxidation followed the sequences of bisphenol-S (BS) > azithromycin (AZM) > imidacloprid (IMP) was evaluated, and 100% concentration reduction of BS was achieved.

In the study of Wu et al. (2018), the degradation efficiencies and mechanisms of atrazine, a recalcitrant herbicide, were investigated using ferrate (Fe(VI)) and peroxymonosulfate (PMS) process. In comparison with Fe(VI) or PMS alone, Fe(VI)/PMS process significantly enhanced the degradation of atrazine, and its degradation efficiency was higher than that of Fe(VI)/persulfate or Fe(VI)/H₂O₂ process at pH 6.0. Complete degradation of atrazine at an initial concentration of 46.5µM could be achieved within 20 min at initial concentrations of 6.0mM Fe(VI), 5.0mM PMS, pH 6.0, and 25°C. Fe(VI)/PMS could efficiently degrade atrazine within a wide range of pH values (5–9). NOM concentration lower than 4.0 mg/L was favourable for atrazine degradation.

Hu et al. (2009) conducted experimental studies to examine the oxidation of carbamazepine, an anticonvulsant drug widely detected in surface waters, by potassium salts of potassium permanganate (KMnO_4) and ferrate. Results showed that both Mn(VII) and Fe(VI) rapidly oxidize carbamazepine; furthermore, Mn(VII) reaction rates exhibited no pH dependence, whereas Fe(VI) reaction rates increased dramatically with decreasing pH, due to changing acid-base speciation of Fe(VI) .

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Chapter V¹

Experimental activity: materials and methods

The primary objective of this research work is to deepen with more details some aspects of the management and treatment of water intended for human consumption. This goal was achieved through two main research topics, each dealing with a different aspect.

The initial focus of the study lies on the development and application of a new turbidity robustness index for the evaluation of the water treatment plant performance of Sambuca di Sicilia. The underlying reason for this is the need to overcome the highlighted issues of the existing TRIs. This is necessary due to the entry into force of the new drinking water regulation (D.Lgs 18/2023, Directive 2020/2184/EU), which introduced the concept of robustness and imposed more restrictive limits. In addition, the proposed index has been correlated to the characteristics of the raw water at the inlet of plant, in order to identify for which particular load conditions and events, in terms of magnitude and duration, the plant losses robustness. The same approach has been applied for the development and validation of a manganese robustness index (MRI).

The second part of the research explored the use of potassium ferrate(VI) as a potential solution to address the increasing concentration of pollutants in raw water and climate change-related water emergencies, to meet the more stringent regulations of drinking water and, in particular, to cope with losses of robustness of drinking water treatment plants. Conventional chemicals might not be able to ensure compliance with drinking water quality standards; in this light Fe(VI) has been investigated to be used either alone or in combination with conventional reagents to producing potable water.

¹ Part of this chapter, under the consent of the publisher, was redrafted after:

1. De Marines, F.*, Corsino, S.F., Castiglione, M., Capodici, M., Torregrossa, M., Viviani, G., 2024. Ferrate as a sustainable and effective solution to cope with drinking water treatment plants challenges. *J. Environ. Chem. Eng.* 12, 112884. <https://doi.org/10.1016/j.jece.2024;>
2. De Marines, F.*, Corsino, S.F., Cosenza, A., Capodici, M., Torregrossa, M., Viviani, G. A modified robustness index for assessing operational performance of drinking water treatment plants: a comparative study within a new regulatory framework. *Water Res.* 268, 122668. <https://doi.org/10.1016/j.watres.2024.122668>.

Moreover, part of the research was focused on ferrate(VI) production. In fact, different solutions, as well as techniques for an effective production process still deserve further investigation and so far there is lack of full-scale application of ferrate (VI) in the water remediation due to difficulties associated with: (i) the instability of ferrate (VI) depending on its production method and (ii) the low yield of ferrate(VI) production.

5.1 Full-scale plant description

The Sambuca DWTP selected for the present study is located in Sicily (Italy) and treats surface water derived from a reservoir, which is classified as A2 according to the Water Framework Directive (WFD) (Directive 2000/60/EC).

Surface waters are taken from the Garcia artificial reservoir, managed by the Reclamation Consortium of Palermo 2, and through a lifting system are delivered to the water treatment plant (Figure 5.1).

The plant is divided into two process lines:

- water treatment mainstream, consisting of all the chemical and/or physical treatment steps, aimed at clarifying the raw water entering the plant;
- sludge stream, that is the set of processes aimed at treating the sludge coming from the water line.

The Sambuca plant is designed for a nominal flow of 900 L/s; but the effective flow rate treated is 640 L/s (520 L/s of raw water and 120 L/s of recirculation).

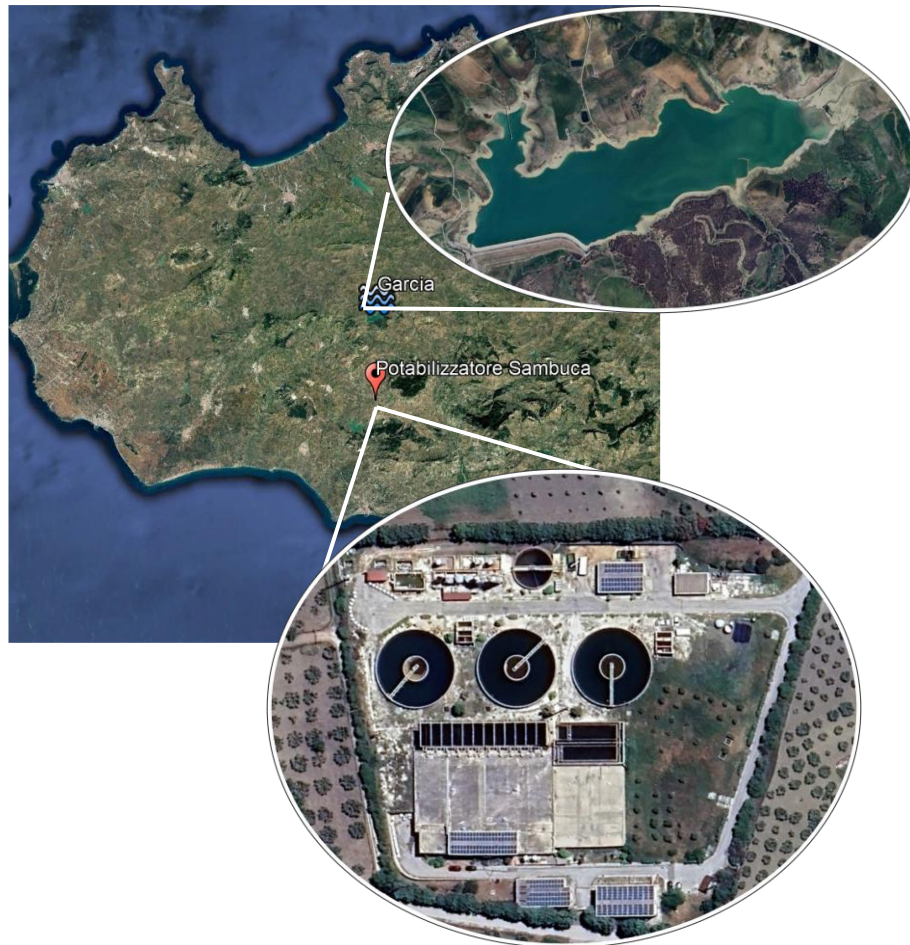


Figure 5.1. Panoramic view of the Sambuca drinking water treatment plant and of the Garcia artificial reservoir

The DWTP operates as a closed-cycle system, technically classified as Zero Liquid Discharge (ZLD), meaning that the complete recovery of the liquid fraction occurs within the process. The only waste product generated is dewatered sludge. This setup ensures that all treatment process residues are recirculated through various sections of the plant. Specifically:

- the filter backwash water, which is temporarily stored in a tank, is pumped back upstream to the load dissipation tank;

- the supernatant from the thickener, collected in a perimeter trough and temporarily stored in an adjacent well, is also pumped back upstream to the load dissipation tank;
- the eluate, which is the liquid fraction separated from the dewatered sludge during the dewatering process in the two belt presses, is recirculated to the thickener.

The water mainstream (Figure 5.2) is divided into three lines operating in parallel, each with equal treatment potential (300 L/s). In detail, each line consists of:

- a load dissipation and pre-oxidation/disinfection unit (X1) in common with the others;
- a clariflocculation unit (CH₁, CH₂ and CH₃) with sludge recirculation;
- a filtration unit (FS₁, FS₂ and FS₃) through quartz sand;
- a final disinfection unit in common with the others.

The pre-oxidation/disinfection phase is carried out by adding chloride dioxide and potassium permanganate. Moreover, disinfection by-products (chlorites) are abated by dosing ferrous chloride. The coagulation-flocculation phase is carried out by adding a coagulant, aluminium sulphate polychloride (PACl), and a cationic polyelectrolyte flocculant. The effluents from the filtration units of the three lines are mixed in a storage tank and subjected to final disinfection with chloride dioxide and sodium hypochlorite.

The dosage of chloride dioxide, potassium permanganate, ferrous chloride and sodium hypochlorite is automatically controlled by a supervisory control and data acquisition (SCADA) system based on the water flow. Similarly, PACl and cationic polyelectrolyte are dosed by the SCADA system based on the raw water turbidity.

Water flow, turbidity and manganese are measured at various points of the plant. In more detail, the turbidity limit to be respected at X1 exit is 500 NTU, above which the plant is bypassed and the supply interrupted; moreover, at the outlet of each clariflocculation unit the objective is to maintain a turbidity level around 5 NTU in operating and design conditions, to ensure water quality that meets drinking standards.

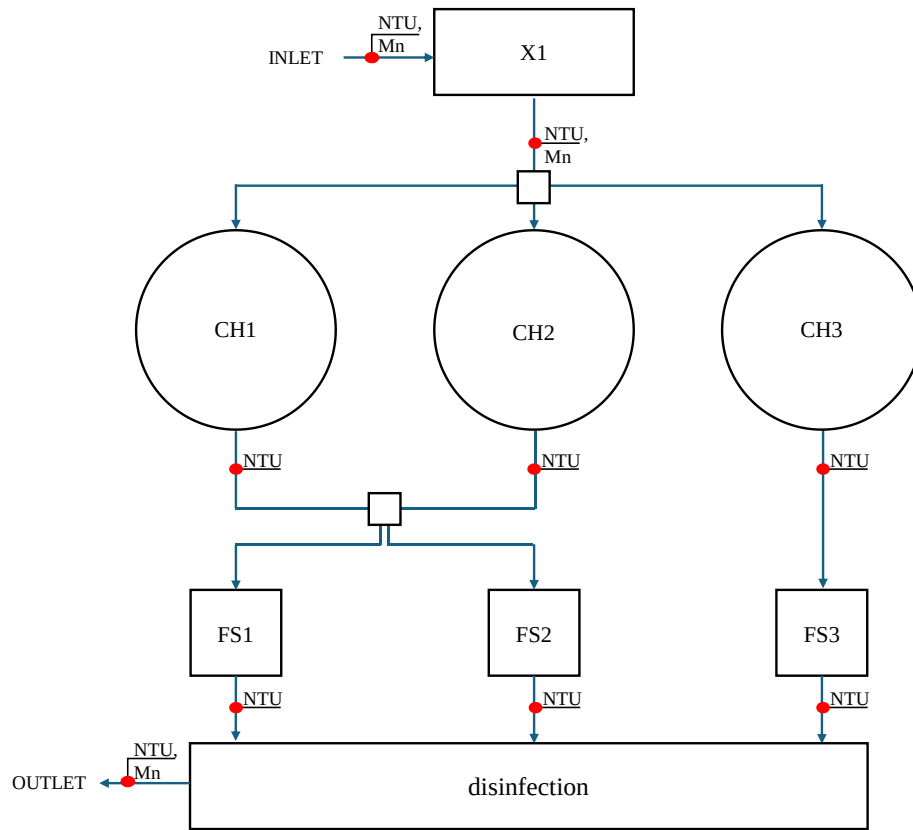


Figure 5.2. Treatment scheme of water mainstream

5.2 Development of the Robustness Indices

The concept of robustness indices was applied to the Sambuca DWTP. To distinguish the robustness index RI (Robustness Index) based on the parameter to which it is applied, the acronym RI is associated with an initial letter corresponding to the specific parameter being measured. Thus, in this study, the Turbidity Robustness Index (TRI) and the Manganese Robustness Index (MRI) were calculated, where “T” refers to turbidity and “M” refers to manganese.

The application of robustness indices does not include hypothetical scenarios but is based on historical data and therefore uses already available information.

5.2.2 Data collection and analysis

Water flow, turbidity and manganese are managed by a SCADA system that acquires the values measured by online sensors. Water flow and turbidity data are recorded by the SCADA within a 4-hour time interval, while manganese within a 5-hour time interval. Consequently, each data point represents the average value measured over the previous hours.

Full-scale plant data were collected for 2 distinct time intervals, depending on their availability:

- 3 years (from 1 January 2021 to 1 January 2024) for water flow and turbidity data;
- 1 year (from 1 January 2023 to 1 January 2024) for manganese data.

RI_s were calculated by using one week of data (42 and 35 average data points for turbidity and manganese, respectively) for each run.

Since the TRI_s were calculated on both at global plant scale and at the level of individual treatment processes, turbidity data recorded at the outlet of X1, the outlet of disinfection tank, and downstream of each treatment unit within the plant were considered. For manganese, however, the MRI_s were calculated on a global scale, using only concentration data from the outlet of X1 and the outlet of the disinfection unit.

5.2.3 Development of the modified TRI

As discussed in Chapter III, three turbidity robustness indices are available in the literature (resumed in Table 5.1) and, according to previous studies, on the basis of the TRI value, six classes of system operation quality can be defined (Li and Huck, 2008) (resumed in Table 5.2).

Table 5.1. Existing TRIs in the literature

Existing TRIs	Reference
$TRI_{90E} = \frac{1}{2} \left(\frac{T_{90}}{T_{50}} + \frac{T_{50}}{T_{goal}} \right)$	(Huck et al., 2001)
$TRI_{90D} = \left(A_1 \frac{T_{90}}{T_{50}} + A_2 \frac{T_{50}}{T_{goal}} \right) \times 100$	(Li and Huck, 2008)
$TRI_{90J} = \left\{ \left[\left(1 - \frac{G\%}{100} \right) \times \frac{T_{90}}{T_{50}} \right] + \left[\frac{T_{50}}{T_{goal}} \times \frac{G\%}{100} \right] \right\} \times 100$	(Hartshorn et al., 2015)

Table 5.2. Classification of system operation with robustness index value and mathematical significance

Class	TRI values	Mathematical significance
Very stable	<60	$T_{50} \ll T_{goal}$ and $T_{90} < 50\%$ of T_{goal}
Stable	60–100	$T_{50} = 60\text{-}75\%$ of T_{goal} and $T_{90} \approx T_{goal}$
Slightly disturbed	100–130	$T_{50} < T_{goal}$ and $T_{90} = 30\%$ over T_{goal}
Moderately disturbed	130–160	$T_{50} = 20\%$ over T_{goal} and $T_{90} = 60\text{-}80\%$ over T_{goal}
Upset	160–200	$T_{50}, T_{90} = 60\text{-}80\%$ over T_{goal}
Severely upset	>200	$T_{50}, T_{90} = 100\%$ over T_{goal}

The proposed TRI, namely TRI_{95B} , is reported in Eq. 5.1.

$$TRI_{95B} = \left\{ \left[B \times \left(1 - \frac{G\%}{100} \right) \times \frac{T_{95}}{T_{goal}} \right] + \left[B \times \frac{T_{50}}{T_{goal}} \times \frac{G\%}{100} \right] + \left[(1 - B) \left(\frac{T_{100}}{T_{max}} + 1 \right) \right] \right\} \times 100 \quad [5.1]$$

in which:

- T_{50} , T_{95} and T_{100} are the 50th, 95th and 100th percentile of turbidity distribution;
- T_{goal} is equal to 0.3 NTU;
- T_{max} is equal to 1 NTU;
- $G\%$ is the percentage time below the turbidity goal within the run;
- B is a switch term.

The main modification is the introduction of the 95th percentile, as imposed by regulations (D.Lgs 18/2023, 2023; Directive 2020/2184/EU, 2020). In fact, the new legislation introduces for the first time a statistical parameter, the 95th percentile, as a reference value for turbidity, therefore representing the minimum target value of the water-purification process. Consequently, the ratio T_{95}/T_{goal} represents the effectiveness of the process according to current regulation ($T_{\text{goal}}=0.3$ NTU and compliance with the turbidity limit in 95% of the samples).

Additionally, the ratio T_{90}/T_{50} (representing the performance uniformity over a specific duration) was replaced by the ratio T_{50}/T_{goal} , thus indicating how the distribution aligns on average with the target value. This substitution was made in order to avoid that, being the time scale relatively short (one week), the extreme values of the distribution had too much influence in the calculation of the index. Nonetheless, the introduction of the 95th percentile allows considering the extreme values in the data distribution. Therefore, including T_{90}/T_{50} in the index as well would give excessive weight to the extreme values in the distribution, resulting in index with absolute values that are too high and not reflective of the plant's actual performance. Therefore, the term T_{50}/T_{goal} represents the new performance uniformity, more precisely indicating how the distribution aligns on average with the target value.

Furthermore, the term T_{100}/T_{max} has been added to $\text{TRI}_{95\text{B}}$. It signifies whether the highest measured turbidity value during a run exceeded the threshold value set by the EU regulation (1 NTU). T_{100} , that is the maximum value of the distribution, excludes outliers. The latter have been removed from the historical data by the Z score method (Eq. 5.2) and having set a threshold score equal to 3.

$$Z = \frac{x - \mu}{\sigma} \quad [5.2]$$

In Equation 5.2, x represents the single value within the data set, μ is the mean of data distribution and σ is the standard deviation of data distribution.

Regardless of the data distribution, if the threshold value is exceeded by even a single data, the index must be able to signal an anomaly. To include this concept into the index, a switch term (B) was introduced.

The factor B is equal to 1 if the threshold value is never exceeded into the run; whereas it is equal to 0 if at least one data point exceeded 1 NTU. Therefore, if no data point exceeds 1 NTU, the B value is equal to 1, and the term T_{100}/T_{max} is null. However, if even one data point exceeds 1 NTU, the B value is 0, and the

TRI value depends only on $T_{100}/T_{\max}$. Consequently, when the $T_{\max}$ is exceeded, since the regulation does not assign any weight to the data distribution during the run, both T_{50} and T_{95} were excluded from the index formulation. In this latter case, in view of ensuring that the value of the TRI is greater than 200 (thereby falling into the “severely upset” class), the term “+1” was added.

All the TRIs were calculated both according to old ($T_{\text{goal}} < 1$ NTU) and new ($T_{\text{goal}} < 0.3$ NTU) regulations.

5.2.3.1 TRIs validation: sensitivity and specificity

To evaluate the performances of TRIs, the sensibility and specificity of each of them were calculated.

Specifically, the sensitivity was aimed at measuring the true positive rate, meaning the ability of TRIs to correctly identify both the run during which the T_{goal} exceedance occurred (true positive – TP) and the belonging to the quality class. Sensitivity was calculated as follows (Eq. 5.3):

$$\text{Sensitivity} = \frac{\text{True positives}}{\text{True Positives} + \text{False Negatives}} \times 100 \quad [5.3]$$

On the other hand, specificity was aimed at measuring the ability of TRIs to correctly identify both the runs during which the exceedance of the T_{goal} does not occur (True negative rate) and the belonging to the quality class. Specificity was calculated as follows (Eq. 5.4):

$$\text{Specificity} = \frac{\text{True negatives}}{\text{True Negatives} + \text{False Positives}} \times 100 \quad [5.4]$$

According to the mathematical significance of TRIs based on the values of T_{goal} and T_{90} (Table 5.2), for each run, the right TRI class was established. Then, true and false positives, as well as true and false negatives, were determined as follows:

- true positive (TP): the number of runs in which TRI fall into the slightly disturbed or superior classes and are correctly identified;
- false negative (FN): the number of runs in which TRI falls into the class stable or very stable but is incorrectly identified;
- true negatives (TN): the number of runs in which TRI falls into the class stable or very stable and is correctly identified;

- false positive (FP): the number of runs in which TRI fall into the slightly disturbed or superior classes but are incorrectly identified.

5.2.3.2 Application of TRI at single-process scale

In order to highlight any critical issues due to malfunctions within the individual treatment units or individual processes, single-process scale TRIs were applied, so as to evaluate their response in terms of robustness.

In more detail, TRIs were first determined on the three clariflocculation (CH₁, CH₂, CH₃) and filtration (FS₁, FS₂, FS₃) units, and then evaluated at single-process scale (CH_{med}, FS_{med}).

In the case of clariflocculation, since there is only one limit to be respected (T_{goal} < 5 NTU), the term B is equal to 1. Instead, for filtration both limits must be respected in line with what is foreseen for the overall process (T_{goal} < 0.3 NTU for 95% of runs and T_{MAX} < 1 NTU).

5.2.3.3 Definition of a Turbidity Load Index

Since in managing the process, in order not to overload the plant, the influent flow to be treated is regulated based on the variation of the incoming turbidity, it is difficult to find a correlation between this latter and the TRIs. In terms of load (flow x concentration), this is kept constant by balancing the increase of the influent concentration with the reduction of the flow. Therefore, the link between the TRIs and the incoming turbidity load was investigated. Nevertheless, since turbidity is measured by an optical size (NTU), it cannot be related to flow (physical size) in dimensional terms. Consequently, the input turbidity load could not be estimated.

To overcome this limitation, a turbidity load index (TLI) has been developed (Eq. 5.5). The index has been elaborated to predict the expected TRI at global and process scales, based on the quality characteristics of raw water entering the plant, and to determine which process (clariflocculation/filtration) is more “sensitive” to input load fluctuations. In this sense, it has been designed as a predictive index of the robustness of the plant and individual processes, and therefore it can act as an alert for DWTPs managers. Even in this case, TLI was calculated by using one week of data for each run.

$$TLI = \left[w_1 \frac{Q_m}{Q_D} + w_2 \frac{T_{50}}{T_D} \right] \times 100 \quad [5.5]$$

In Equation 5.5:

- Q_m is the average value of the instantaneous water flow, measured upstream of the X1 tank and started to treatment, during each run; its maximum value is 520 L/s;
- Q_D is the design flow rate, equal to 640 L/s;
- T_{50} is the 50th percentile of the instantaneous turbidity values, measured in X1 tank, during the run;
- T_D is the design turbidity, which is the maximum turbidity that does not require the implementation of emergency management measures. A value of 100 NTU has been set, which corresponds to the full scale value of the turbidimeter of the tank X1;
- w_1 and w_2 are complementary weighting factor. If the weighting factor w_1 is set at a higher value than w_2 , this means that the index emphasizes the variation in water flow, whereas a higher w_2 indicates that the index is focusing on turbidity variation. The higher value for w_1 or w_2 was chosen to be 0.8 and the lower value was set at 0.2. The procedure for weights assignment is based on the value of $\frac{Q_m/Q_D}{T_{50}/T_D}$ ratio (indicated by n) and is reported in Table 5.3.

Table 5.3. Decision process for selecting different weighting factors

Comparison of $\frac{Q_m}{Q_D}$ and $\frac{T_{50}}{T_D}$	If	Then
$\frac{Q_m}{Q_D} \geq \frac{T_{50}}{T_D}$	$n \leq 1.5$	$w_1 = w_2 = 0.5$
	$1.5 < n \leq 3$	$w_1 = 0.6; w_2 = 0.4$
	$3 < n \leq 4.5$	$w_1 = 0.7; w_2 = 0.3$
	$n > 4$	$w_1 = 0.8; w_2 = 0.2$
$\frac{Q_m}{Q_D} < \frac{T_{50}}{T_D}$	$1.5 < 1/n \leq 3$	$w_1 = 0.4; w_2 = 0.6$
	$3 < 1/n \leq 4.5$	$w_1 = 0.3; w_2 = 0.7$
	$1/n > 4.5$	$w_1 = 0.2; w_2 = 0.8$

5.2.3.4 Events identification and correlation with TRI_{95B}

In order to assess the robustness of the plant, or certain processes, in the context of climate changes, which lead to the occurrence of extreme and short-duration events and therefore which cause turbidity peaks in the influent, an analysis was carried out to relate the TRI_{95B} to such turbidity peaks. Even in this case, the aim was to identify for which magnitude of the event (hereinafter referred as “score”) the robustness index starts to increase or exceeds a certain threshold value.

For the definition of an “event”, a threshold value was set to distinguish between “normal” or “acceptable” turbidity conditions and those with “elevated” turbidity. Specifically, a threshold value equal to 1.5 times the median of the turbidity values entering the plant (19.1 NTU) over the three years considered was used as discriminator. Periods longer than 3 days, during which the threshold value was exceeded, were classified as “events”.

Once the events were identified, each one was assigned a score, weighted according to its duration and the average turbidity and flow values during the event itself (Eq. 5.6).

$$score_i = \frac{\sum_i T_{50,i}}{T_D} \times \frac{Q_{50,i}}{Q_D} \times \frac{d_i}{d_D} \quad [5.6]$$

In Equation 5.6:

- the term $\sum_i T_{50,i}$ is the sum of the medians of turbidity values during the i -th event, normalized with respect to the design turbidity ($T_D = 100$ NTU);
- $Q_{50,i}$ represents the median of the influent flow values during the i -th event, and it is normalized with respect to the design flow rate ($Q_D = 640$ L/s);
- d_i is the duration of the i -th event, normalized with respect to the minimum event duration ($d_D = 3$ days).

The score assigned to each event was subsequently correlated with the robustness indices (both at a global and process scale) calculated at the time the event occurred. In this way it was possible to detect a threshold score beyond which the plant, by losing robustness, is no longer able to meet the quality standards required for the treated water.

5.2.4 Development of the MRI

As with turbidity, the performance and robustness of the plant were evaluated in relation to manganese. In this case, MRIs have been applied only at global plant scale.

The structure of the proposed index, MRI_{95} , is similar to the previous one, with the only difference that, since there is only one limit to be respected (50 µg/L), the switch term B is always equal to 1. For simplicity, the formula of the index in question is shown in Eq. 5.7 without the term B. Symbols have the same meaning as already discussed.

$$MRI_{95} = \left[\left(1 - \frac{G\%}{100} \right) \times \frac{M_{95}}{M_{goal}} \right] + \left[\frac{M_{50}}{M_{goal}} \times \frac{G\%}{100} \right] \times 100 \quad [5.7]$$

Since no MRIs are available in the literature, the proposed index was compared with existing TRIs but calculated for manganese concentrations.

4.2.4.1 MRIs validation: sensitivity and specificity

To evaluate the performances of MRIs, the sensibility and specificity of each of them were calculated. The procedure is the same as for TRIs (Section 5.2.3.1).

5.3 Ferrate experimentation

Specific investigations on the mechanisms of Fe(VI) for removing the main water pollutants, the stoichiometry of reactions, as well as potential advantages and disadvantages, have been conducted.

5.3.1 Jar test experiments

Jar test experimental procedure (Figure 5.3) was used to assess the effect of Fe(VI) for removing manganese, NOM and algae. For all the experiments, jar test procedure involved a rapid mixing at 200 rpm for 1 minute followed by a slow mixing at 30 rpm for 20 minutes and finally a settled period for 60 minutes. In each of the assay, 6 batch reactors at different operating conditions (i.e., chemicals dose, pH, etc.) were studied. At the end of settling phase, a sample from the supernatant of each test was withdrawn and stored for the analyses. Each of the above pollutants was studied individually to eliminate possible interference or synergistic effects.

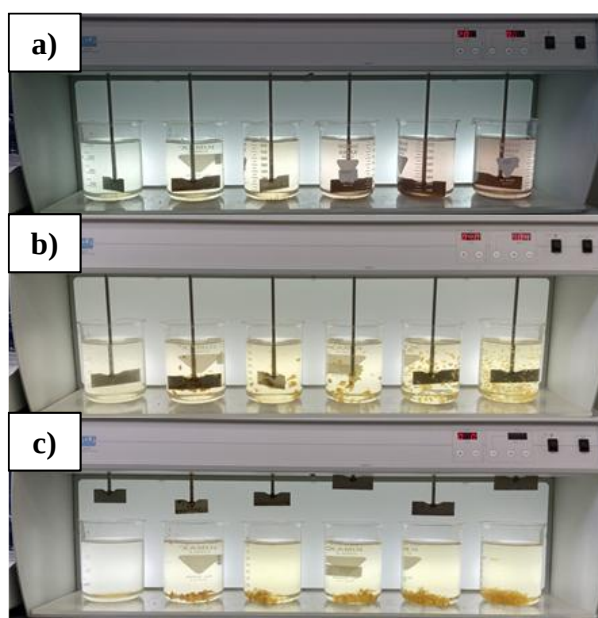


Figure 5.3. Jar test experimental procedure: rapid mixing (a), slow mixing (b) and settled period (c)

5.3.2 Manganese removal procedures

Stoichiometry of soluble manganese (Mn(II)) oxidation by potassium ferrate and permanganate was assessed by carrying out 15 experimental repetitions for each chemical. Initially, these assays were performed with high Fe(VI) dosage to allow for measurable absorbance of residual Fe(VI). Batch reactors were filled with 800 mL of deionized water (pH 7.1 ± 0.1) to avoid having other oxidant demand except to manganese. A concentrated solution of MnCl_2 in deionized water was prepared and a precise volume was dosed in the batch reactors to achieve a target concentration of Mn(II). The initial Mn(II) concentration ranged between 2-14 μM (100-900 mg/L), whereas oxidants (Fe(VI) and Mn(VII)) doses were in the range 2-10 μM . The Mn(II) concentrations were based on the typical value observed in the Garcia reservoir during the late summer/autumn season when influent soluble manganese concentrations usually increased up to 800-1000 $\mu\text{g/L}$. After supplying manganese chloride, Fe(VI) was added under rapid mixing conditions. In these assays, pH was measured by an ion-selective electrode probe (WTW) but not controlled. At the end of the settling phase, the residual concentrations of the Mn(II) and Fe(VI) in the filtrated water were measured to assess the moles of manganese oxidized per mole of Fe(VI) or Mn(VII) reduced.

Two additional assays, including 6 experimental trials each, were executed with Fe(VI) at pH of 9 and 7. pH was adjusted to the target values using drop-wise addition of HCl or H_2SO_4 . Residual Mn(II) and Fe(VI) were measured at the end of the settling phase in the supernatant after samples filtration through 0.45 μm membrane.

The same experimental approach was used to assess the removal of Mn(II) using Fe(III). Ferric chloride (FeCl_3) (purity 99%), was used as source of Fe(III). Fe(II) was measured to prove Mn(II) oxidation by ferric chloride via a colorimetric method.

To focus on Mn(II) oxidation kinetics with Fe(VI) and Fe(III) two assays were carried out. In a 800 mL batch reactor filled with deionized water, Mn(II) was added at the beginning of the experiment at an initial concentration of approximately 4.5 mg/L and 0.35 mg/L in the test performed with Fe(VI) and ferric chloride, respectively. Subsequently, Fe(VI) and Fe(III) were dosed. The reactors were mixed for 30 minutes with a mechanical impeller operating at rapid mixing conditions (100 rpm). Samples for Mn(II) analyses were withdrawn every 20 seconds for Fe(VI) and 4 minutes for Fe(III), then filtered through a 0.45 μm membranes to exclude particulate manganese (Mn(IV)).

5.3.3 Ferrate stability experiment

Stability of Fe(VI) in water solution was determined as a function of pH. The initial concentration of Fe(VI) in the solution was approximately 45 μM and the resulting pH was close to 8.4 without any addition of alkaline agent. Hereafter, the pH was stepwise decreased up to pH of 4 by adding 1 M of HCl solution. The adsorption spectra between 200-600 nm was examined by an UV-VIS spectrophotometer to measure the residual Fe(VI) concentration (510 nm) and the occurrence of Fe(III) (270 nm).

5.3.4 NOM and turbidity removal assays

Deionized water was artificially contaminated with NOM contained in the eluate from a mature compost sample derived from a domestic composting system fed with vegetable and pruning residues. A compost sample (1 kg) was placed in a 5 L laboratory beaker and filled with deionized water, then was mixed for 24 hours. Hereafter, the sample was left to settle for 1 h and 3 L of supernatant were collected and centrifuged at 4000 rpm for 30 minutes to remove residual particles. The supernatant was characterized in terms of total organic carbon (TOC) content and stored at 4°C. To assess NOM removal by Fe(VI), six batch reactors were filled with deionized water and the supernatant derived from compost elution until reaching a target TOC value of approximately 7 mg/L. Then Fe(VI) was supplied at different doses between 0-2 mgFe(VI)/L. This assay was replicated by adding a constant dose of soluble manganese (0.90 mgMn(II)/L) to assess Fe(VI) reactivity in presence of a reducing agent.

Turbidity removal assays were carried out on real water samples collected at the entrance of the Sambuca drinking water treatment plant. Initial turbidity of samples was approximately 6.5 NTU and pH was close to 7.6. Jar test procedure was carried out on 18 samples without any pH adjustment. Specifically, in six batch reactors increasing conventional coagulant/flocculant (polyaluminum chloride - PACl) between 5-25 mg/L and a constant dose of cationic polyelectrolyte (0.10 mg/L) were dosed. The same test was replicated twice while adding a constant dose of potassium ferrate (2.5 and 4 mgFe(VI)/L). In the latter case, the pH slightly increased at about 8.1-8.3.

5.3.5 Algae removal

A mixture of natural algae (mostly *Chlorella* sp.) was used to artificially contaminate deionized water and simulate algal bloom. Two experimental assays were carried out using potassium ferrate and permanganate as oxidating agents. In each of the assays, six batch reactors were filled with deionized water and a mixture of natural algae (initial Chl-a concentration of 0.45 µg/L), then Fe(VI) and Mn(VII) were dosed at different doses (0-15 mg/L). Direct measurement of chlorophyll-a (Chl-a) in the supernatant after the settling phase was assessed to evaluate the effect of Fe(VI) and Mn(VII) on algae removal.

5.3.6 Chemicals

Commercial potassium ferrate (Aaron Chemical, purity 99%) was used in all the assays. Before each test, a concentrated solution of Fe(VI) was prepared by dissolving 1 g of K_2FeO_4 in 1 L of deionized water. Then, the solution was dosed in different volume to achieve the desired Fe(VI) concentration in each reactor. The concentrations of Fe(VI) in the solution and in each reactors were measured to verify the initial value. A concentrated solution of potassium permanganate ($KMnO_4$) (1.4% v/v) was used as comparison with ferrate for manganese and algae removal. Manganese chloride ($MnCl_2$) (Sigma Aldrich, purity 99%) was used as soluble manganese (Mn(II)) source for the relative assays. 1 M HCl or H_2SO_4 solutions were used to adjust pH if required by target operating conditions.

5.3.7 Analytical methods

Fe(VI) determinations were performed using an UV-VIS spectrophotometer by measuring the absorbance at 510 nm. A calibration line (0-10 mgFe(VI)/L) was constructed using commercial potassium ferrate (purity 99%) as a standard to measure the Fe(VI) concentration in the samples. All the samples for Fe(VI) measurement were previously filtered through 0.45 µm cellulose membrane to remove impurities. Samples for Mn(II) measurements, were filtered through 0.45 µm cellulose membrane to remove particulate manganese compounds, then analysed with an inductively coupled plasma optical emission spectrometry (ICP OES). Total organic carbon was measured by a TOC analyser (Shimadzu). Chlorophyll-a was extracted from algae samples and measured according to the literature (Liu et al., 2011). Turbidity was measured using a portable turbidity-meter (Hanna, HI93703).

5.4 Ferrate(VI) electrochemical production

To solve the above-mentioned difficulties about the applicability in the use of ferrate (Chapter IV), a part of the research was focused on the assessment of its electrochemical production, pointing on increasing product stability and production yield. This part of the experimental activity was carried out at the “Applied Electrochemistry Laboratory” in collaboration with chemical engineering colleagues.

To date, ferrate is not available on the market as a reagent that can be used for drinking water treatment processes, except for analytical chemistry products of very high purity, which are therefore unsuitable for large-scale applications due to cost. Therefore, the technically most optimal method for using ferrate in potable water production is its in-situ production through electrochemical methods. However, there are few studies in the literature regarding the production and stability of ferrate produced via electrochemical methods.

To this aim, several tests were carried out with different operating conditions for the electrochemical production of ferrate. Tests were carried out in a 100 mL glass beaker, which represented the electrolytic cell, inside which anode, cathodes and electrolytic solution were inserted (Figure 5.4). In particular, a carbon steel plate was used as anode and two titanium DSAs (dimensionally stable anodes) were used as cathodes; sodium hydroxide and potassium hydroxide were used for the preparation of the electrolytic solutions. Tests were conducted in galvanostatic mode, i.e. applying a constant current intensity between worker (anode) and counter (cathode) and measuring the potential difference between a reference electrode and the worker.

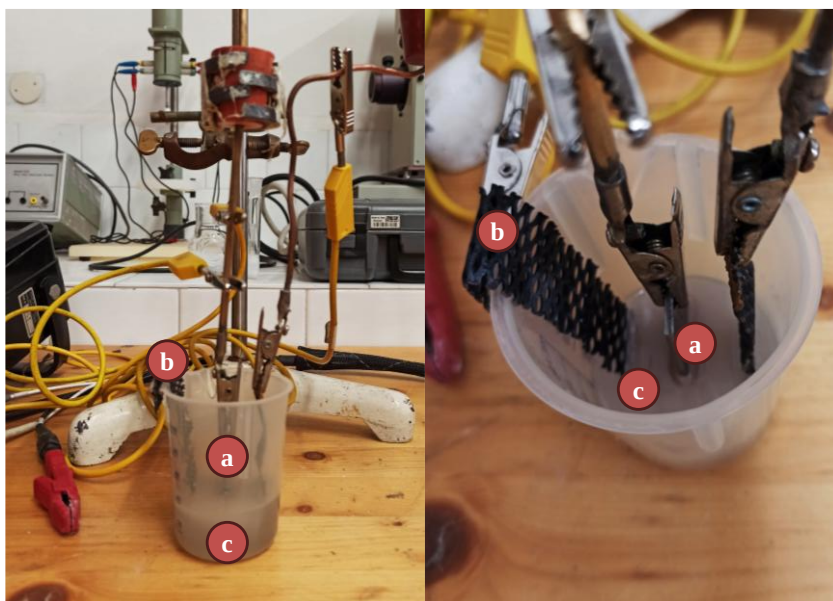


Figure 5.4. Electrolytic cell: anode (a), cathode (b) and electrolytic solution (c)

The operating conditions of the tests carried out are shown below:

- 1st test: anode dimension 2cm x 2cm, 40 mL of electrolytic solution with NaOH 6M, current density of 20 mA/cm² and applied current intensity of 160 mA;
- 2nd test: anode dimension 2cm x 2cm, 40 mL of electrolytic solution with NaOH 10M, current density of 20 mA/cm² and applied current intensity of 160 mA;
- 3rd test: anode dimension 2cm x 2cm, 40 mL of electrolytic solution with NaOH 10M, current density of 125 mA/cm² and applied current intensity of 1000 mA;
- 4th test: anode dimension 2cm x 2cm, 40 mL of electrolytic solution with KOH 6M, current density of 20 mA/cm² and applied current intensity of 160 mA;
- 5th test: anode dimension 2cm x 2cm, 40 mL of electrolytic solution with KOH 10M, current density of 20 mA/cm² and applied current intensity of 160 mA;
- 6th test: anode dimension 2cm x 2cm, 40 mL of electrolytic solution with KOH 10M, current density of 125 mA/cm² and applied current intensity of 1000 mA.

At the end of each test, the electrolytic solution was evaporated in an oven in order to allow the precipitation of the ferrate salt (Na_2FeO_4 or K_2FeO_4). The final product obtained after the electrochemical synthesis and after evaporation is shown in Figure 5.5.

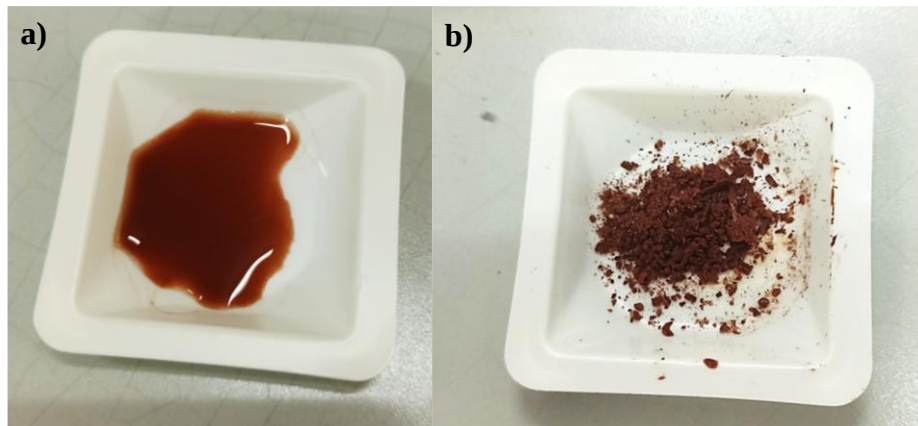


Figure 5.5. Ferrate solution (a) and ferrate salt (b)

Subsequently, characterization analyses were conducted to confirm if the expected product was formed. UV-VIS spectrophotometer technique was used for its determination.

Finally, decay tests were carried out on the sample obtained from the test which had given the higher production yields. In particular, the influence of temperature, light exposure and oxygenation conditions were evaluated on the reduction rate of ferrate. The boundary conditions studied are as follows:

- A. sample exposed to light and kept at room temperature;
- B. sample kept in the dark and at room temperature;
- C. sample exposed to light and kept at 4°C;
- D. sample kept in the dark and at 4°C;
- E. oxygen saturated sample;
- F. deoxygenated sample.

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Chapter VI²

Experimental activity: results and discussion

6.1 Results on Turbidity Robustness Indices

6.1.1 Characteristics of raw water and compliance of treated water with regulations

Flow rate and turbidity data collected from the SCADA system in the raw and the effluent disinfected water are reported in Figure 6.1 and 6.2, respectively.

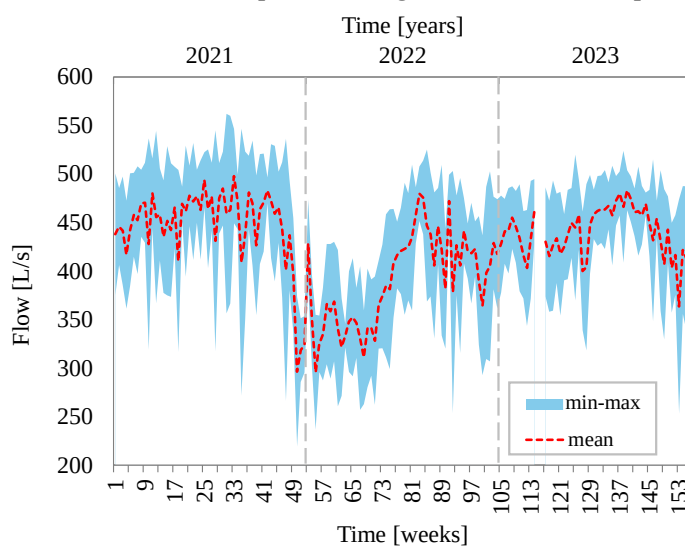


Figure 6.1. Trends of the main statistics (minimum, median, maximum) of flow data in influent water (data between weeks 116-120 are missing)

² Part of this chapter, under the consent of the publisher, was redrafted after:

1. De Marines, F.*, Corsino, S.F., Castiglione, M., Capodici, M., Torregrossa, M., Viviani, G., 2024. Ferrate as a sustainable and effective solution to cope with drinking water treatment plants challenges. *J. Environ. Chem. Eng.* 12, 112884. <https://doi.org/10.1016/j.jece.2024;>
2. De Marines, F.*, Corsino, S.F., Cosenza, A., Capodici, M., Torregrossa, M., Viviani, G. A modified robustness index for assessing operational performance of drinking water treatment plants: a comparative study within a new regulatory framework *Water Res.* 268, 122668. [https://doi.org/10.1016/j.watres.2024.122668.](https://doi.org/10.1016/j.watres.2024.122668)

In Figure 6.1 a high variation in flow rate is observed. Although water treatment plants are supposed to operate at a constant flow rate, this doesn't happen. In fact, the flow rate is adjusted based on critical treatment parameters (e.g., inlet turbidity) to avoid overloading the plant. In detail, flow rates below 300 L/s indicate periods of plant overload caused by high turbidity levels.

The average flow rate remains relatively constant at around 450 L/s, with occasional reductions due to the reasons mentioned earlier. The gap between the 116th and 120th week indicates that the plant was bypassed during that period.

The turbidity (maximum, mean, and median) over the three-year dataset available showed significant fluctuations (Figure 6.2). During 2021 and 2022, the maximum turbidity in raw water exceeded 50 NTU in several runs, while reaching a maximum above 450 NTU in one case. In 2023, the maximum values were below 50 NTU, except for two runs when turbidity was above 200 and 450 NTU. The mean and median of turbidity data were comparable, suggesting an approximately symmetric data distribution around a central value approximately equal to 18 NTU. As depicted in Figure 6.2b, the average turbidity in raw water ranged between 5 and 20 NTU for most of the three years, whereas turbidity values between 40 and 60 NTU were measured in the autumnal period, specifically between November and December. Thus, the DWTP was affected by turbidity fluctuations, especially during the rainy season. These types of fluctuations are likely due to the increase in solid transport due to erosion (Zeng et al., 2022) or sediment resuspension into the reservoir (Mi et al., 2019).

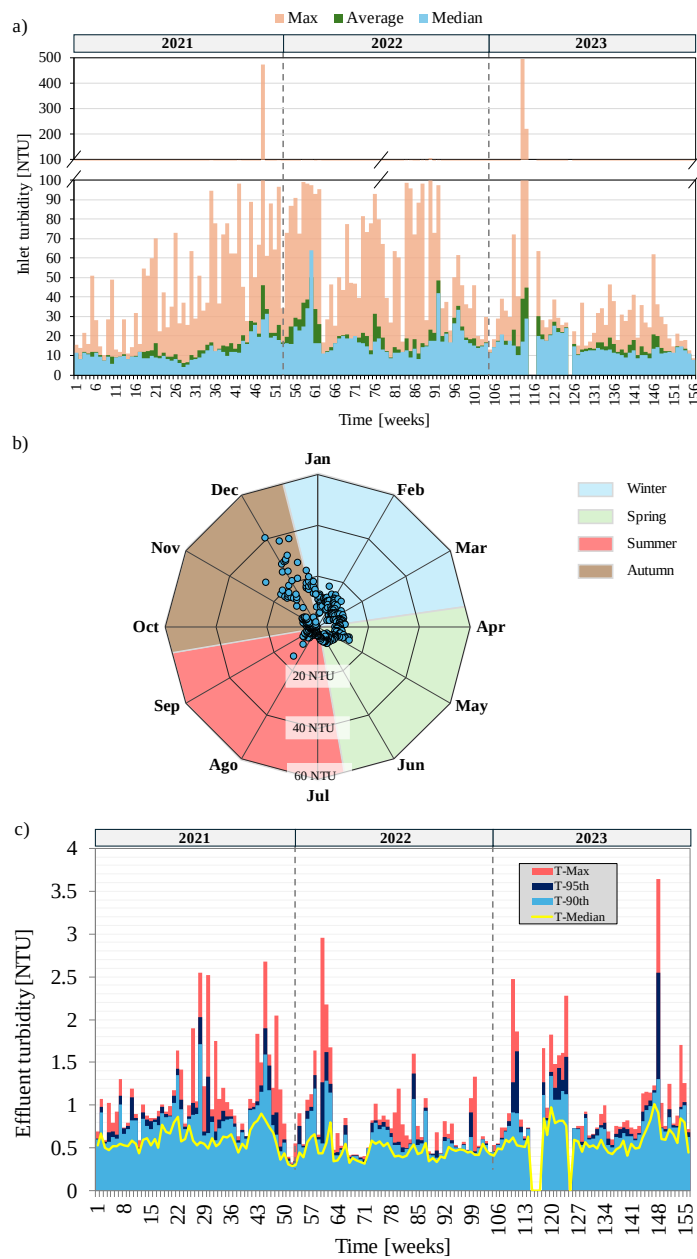


Figure 6.2. Trends of the main statistics (mean, median, maximum) of turbidity data in influent water (a); seasonal variation of turbidity data (b); maximum, 90th, 95th percentiles and median of turbidity data measured at the outlet of the DWTP (data between weeks 116-120 and week 125 are missing)

In Figure 6.2c, the trends of the maximum, 90th, and 95th percentiles, coupled with the median of the effluent turbidity data are depicted. The median turbidity showed a quite regular trend around 0.55 ± 0.15 NTU over the three-year period. On the contrary, 95th percentile and the maximum values showed a less regular trend, characterized by greater fluctuations. In particular, the 95th percentile was on average 0.81 ± 0.34 NTU, while the maximum was 1.01 ± 0.54 NTU. In any case the turbidity limit of 1 NTU (the indicative value of Directive 98/83/EC in force in Italy until March 5, 2023) was not exceeded if one refers to the median of turbidity. Conversely, referring to the 95th and to the lower turbidity goal as required by the new regulation, several exceedances of the turbidity limit were observed. Based on the obtained results, it was clear that the 95th percentile of turbidity was more variable compared to the median. This result is mainly because the 95th percentile was more affected by extreme values and outliers than the median. This result has relevance, especially in cases of extreme turbidity values in the inlet raw water affecting the system's performance. Contrarily, both mean and median, although they are widely used to compare process performances, were characterized by a lower sensibility, thus not allowing us to consider effluent turbidity spiking (Upton et al., 2017). From this perspective, the new regulation introduced a more cautious approach, as it requires the water treatment process to be effective even in the case of turbidity short-term fluctuations. Overall, when considering the 95th percentile of turbidity as a reference parameter, the DWTP demonstrated a lower capacity to maintain a constant value in the effluent. This implies that the novelty introduced by the new regulation requires a thorough and accurate analysis of the plant's robustness.

The trend of the statistical indicators of turbidity was also evaluated at the outlet to the dissipation tank X1 (Figure 6.3).

Even in this case, the turbidity (maximum, mean, and median) values over the three-year dataset showed significant fluctuations, mainly due to the recirculation of the filter backwash water.

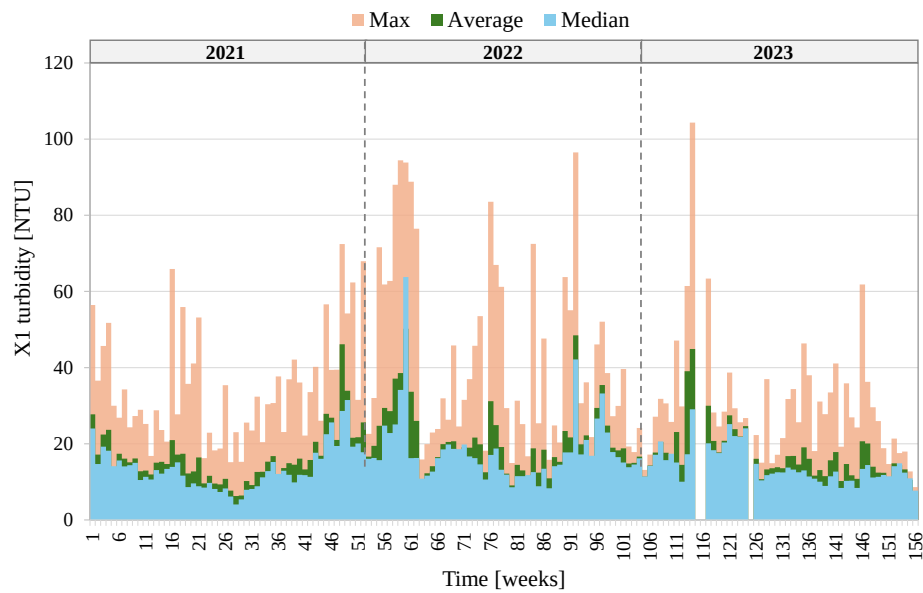


Figure 6.3. Trends of the main statistics (mean, median, maximum) of turbidity data in X1 unit

In order to investigate the existence of a link between turbidity at the inlet of the plant and turbidity in X1 unit, the two-time series were represented in the same graph (Figure 6.4). As it is possible to observe, there is no correlation between the two-time series and there is no correspondence between the turbidity peaks in the influent and in the X1 unit. Moreover, turbidity in the X1 tank is significantly higher than that in the inlet, with recirculating water contributing to almost 40% of the turbidity.

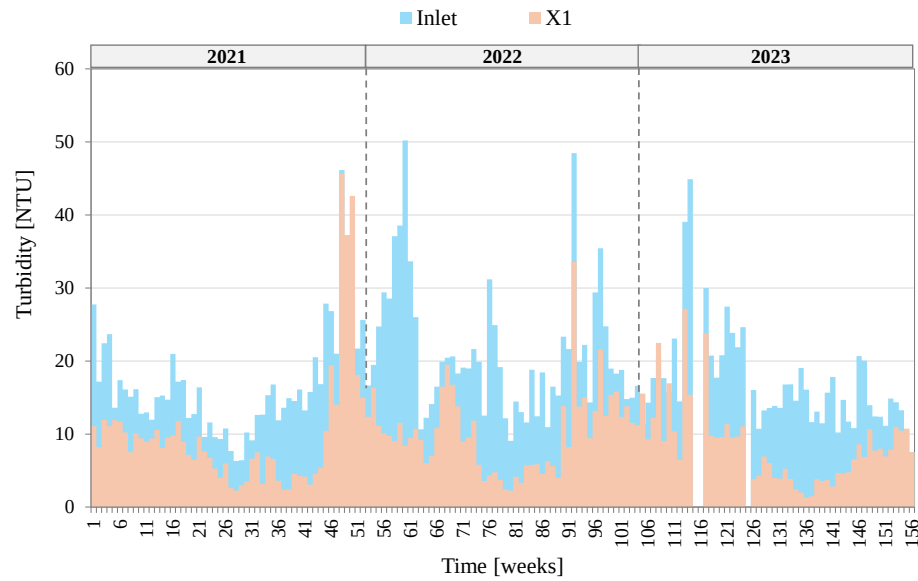


Figure 6.4. Comparison of the average turbidity values at the inlet of the plant and in X1 unit

6.1.2 Comparative assessment of TRIs in the framework of the old regulation

In this section, the results of the comparison between the proposed index and the literature indices are discussed. The turbidity robustness indexes available in the literature and the one proposed in this study were applied to the turbidity values dataset from the DWTP. The turbidity dataset referred to 156 weeks, although data were missing for 4 weeks (116th-120th) because of acquisition failure.

In a first stage of the study, these TRIs were calculated assuming a T_{goal} equal to 1 NTU (according to EU 2020/2184). For the calculation of TRI_{95B} , it was assumed that parameter B was equal to 1, since in old regulation any indication about a limit not to be exceeded was reported. Figure 6.5 shows the trends of the TRIs.

As reported in the previous section, the median of turbidity data in the effluent resulted below 1 NTU during the entire observation period. Therefore, any exceedance of the suggested threshold value for turbidity was observed when referring to T_{50} . In contrast, T_{95} exceeded the target in 20 weeks (< 15%).

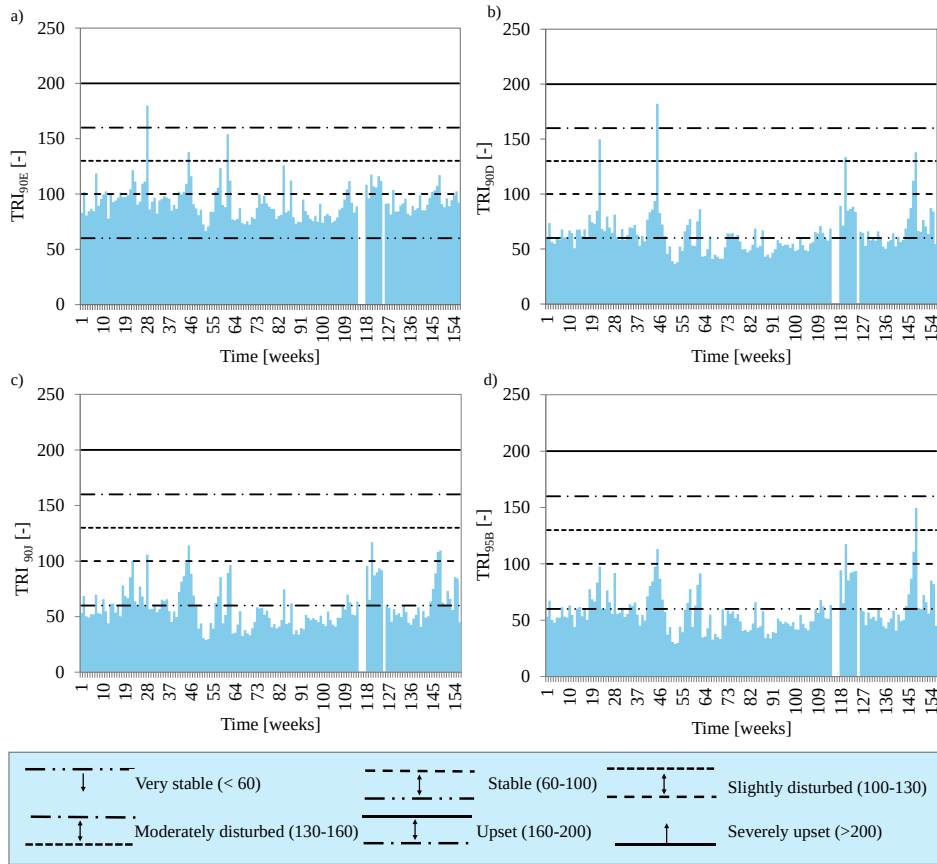


Figure 6.5. Trends of TRIs scores during the 2021-2023 period, assuming a T_{goal} of 1 NTU

The TRIs resulted on average close to 92.5 ± 15 (TRI_{90E}), 64.3 ± 19 (TRI_{90D}), 58.4 ± 18 (TRI_{90J}), 57.8 ± 19 (TRI_{95B}). The TRI_{90E} proposed by Huck and Coffey (2004) showed the highest values, being approximately 25-30% higher than the others. Overall, all TRIs fell within the “very stable” and “stable” classes for over 90% of the runs, except for TRI_{90E}, which fell in the “slightly disturbed” class in 22% of runs (34 out of 156 weeks) (Table 6.1). Moreover, only TRI_{90E} and TRI_{90D} fell into classes higher than “moderately disturbed” for about 3 weeks, while in only one case there was an exceedance of the “upset” limit (TRI > 160). This indicated that both the 50th and 90th percentiles of turbidity were greater than the turbidity limit (1 NTU). Therefore, TRI_{90E} and TRI_{90D} suggested that the DWTP did not generate effluent water of the desired quality for a short duration during those weeks.

Table 6.1. Occurrence of TRIs within a class of system operation quality ($T_{goal} = 1$ NTU)

TRI class	TRI _{90E}	TRI _{90D}	TRI _{90J}	TRI _{95B(*)}
Very stable	0	69	98	100
Stable	115	78	48	48
Slightly disturbed	34	1	6	3
Moderately disturbed	2	3	0	1
Upset	1	1	0	0
Severely upset	0	0	0	0
Not available	4	4	4	4
Total	156	156	156	156

When defining the TRI_{90E}, the authors assumed that the turbidity variability in the effluent (T_{90}/T_{50}) had the same weight as achieving a precise target value (T_{50}/T_{goal}) (Huck and Coffey, 2004). As reported in previous studies, assigning equal weights to these terms made the robustness index less sensitive to the presence of extreme values that deviated significantly from the central value of the distribution (Hartshorn et al., 2015; Li and Huck, 2008). The novel TRI_{95B} was found to be very consistent with TRI_{90J}. The TRI_{90J} was more affected by system performances, while the overall variance was given less consideration, especially in runs where the limit value was exceeded a few times. In fact, in this specific case, the percentage of time for which turbidity was found to be lower than the T_{goal} (G) was very high (>98%). Consequently, the weight of the first term of the TRI_{90J} and TRI_{95B} (i.e., T_{90}/T_{50} and T_{95}/T_{goal}) was very low. Therefore, the second term (T_{50}/T_{goal}) had a greater weight in the final value of these TRIs, which resulted in similar results. Certainly, this result was affected by the value of T_{goal} because a lower value could significantly change the weight attributed to the first term of the TRI.

6.1.3 Comparative assessment of TRIs in the framework of the EU 2020/2184

The TRIs were calculated referring to the EU 2020/2184, specifically reducing the T_{goal} to 0.30 NTU. The trends of the TRIs are shown in Figure 6.6, whereas the frequency of their occurrence within the robustness classes is reported in Table 6.2.

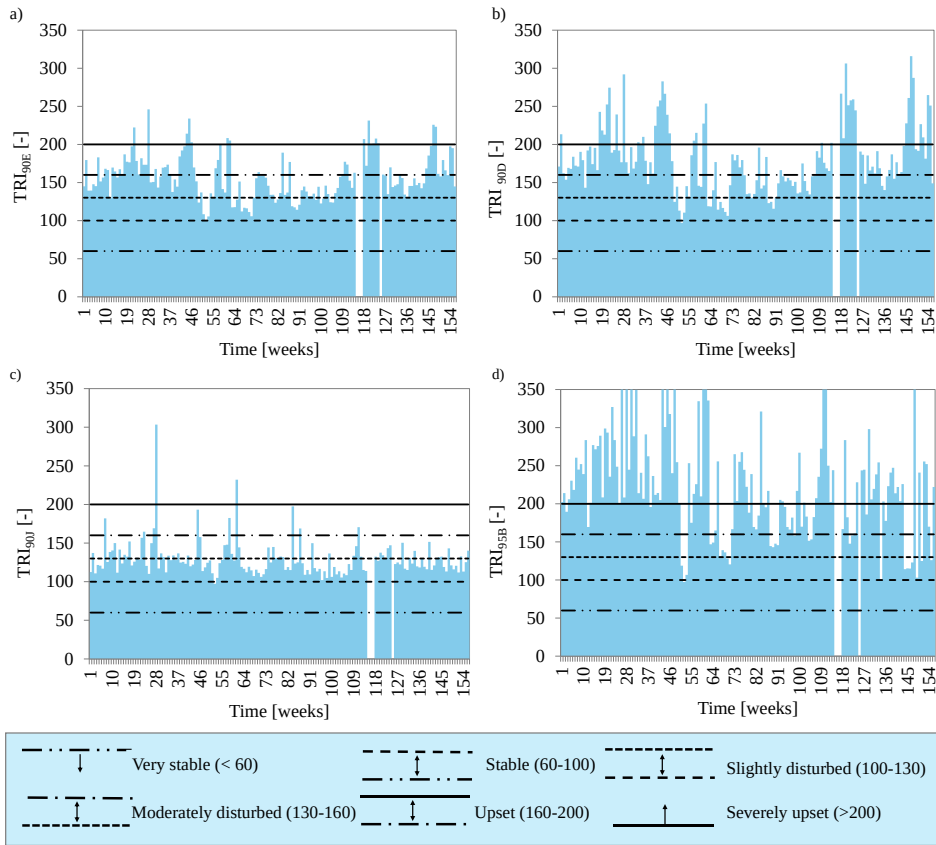


Figure 6.6. Trends of TRIs scores during the 2021-2023 period, assuming a T_{goal} of 0.3 NTU

In this case, the response of the TRIs was different than that obtained considering T_{goal} equal to 1 NTU. Specifically, TRI_{90E} and TRI_{90J} resulted quite low, with average values of 157 ± 29 and 129 ± 23 , respectively. Thus, according to the response provided by those TRIs, the plant fell mainly within the “slightly disturbed” and “moderately disturbed” classes (Table 6.2) despite the main statistical indicators of the effluent turbidity (median and T_{90}) consistently exceeded the 0.30 NTU limit.

Table 6.2. Occurrence of TRIs within a class of system operation quality ($T_{goal} = 0.3$ NTU)

TRI class	TRI _{90E}	TRI _{90D}	TRI _{90J}	TRI _{95B}
Very stable	0	0	0	0
Stable	0	1	1	1
Slightly disturbed	25	15	91	12
Moderately disturbed	66	38	50	14
Upset	46	60	8	24
Severely upset	15	38	2	101
Not available	4	4	4	4
Total	156	156	156	156

The results provided by the TRI_{90E} indicated that the DWTP was affected by severe process instability. However, the absolute values of the index were generally low, and only a few runs indicated an “upset” class or higher. Similarly, regarding the TRI_{90J} this occurrence was even more evident. As reported in previous studies, TRI_{90J} was not a reliable indicator of performance against a target because it favoured variation rather than performance against a goal (Hartshorn et al., 2015; Nemani et al., 2023). Indeed, exceeding the T_{goal} resulted in “G” was zero during most of the runs. Consequently, the term containing T_{goal} was zero, and the robustness index depended only on the ratio T_{90}/T_{50} . Therefore, paradoxically, the value of this ratio was close to one, the corresponding value of TRI was low, despite the T_{goal} could be constantly exceeded in the long run. TRI_{90D} value was higher than that obtained by previous TRIs (180 ± 45). However, it still highlighted the same critical aspects already discussed for the previous indices, mainly linked to the fact that the T_{goal} exceedance was not adequately identified by the TRI value. TRI_{95B} resulted much higher compared to the other TRIs, averaging 228 ± 84 . Overall, TRI_{95B} was the index that fell more frequently (101 out of 156 weeks) into the “severely upset” class (Table 6.2), indicating a significant exceedance of the maximum turbidity value at the DWTP outlet. Unlike the previous TRIs, TRI_{95B} showed a close correspondence to the real trend of the effluent turbidity. Firstly, the use of the 95th percentile instead of the 90th percentile enabled to better consider more extreme values within the turbidity dataset. Consequently, this TRI was more sensitive to point out smaller variations in turbidity within the run. Additionally, by relating T_{95} to T_{goal} , a greater weight to process performance was given. Finally, the introduction of the B parameter clearly enabled to highlight occurrences when the effluent turbidity exceeded the maximum turbidity limit. This is a very important alert that the already existing TRIs did not allow to identify.

6.1.4 Reliability of TRIs

The investigated TRIs showed conflicting results, indicating the occurrence of different robustness classes. As previously demonstrated, the response of TRIs reported in the literature and the one proposed in this study became even more evident when the T_{goal} was decreased to 0.30 NTU. Figure 6.7 illustrates the cumulative distribution of the median, the 90th, the 95th and 100th percentiles of turbidity (Figure 6.7a) and that of TRIs when considering a T_{goal} of 1 NTU (Figure 6.7b) and 0.30 NTU (Figure 6.7c).

As previously stated, the T_{50} was less than 1 NTU for over 99% of runs, whereas the T_{90} was nearly 90% (Figure 6.7a). Consistently, none of the TRIs exceeded the “upset” class (Figure 6.7b). As mentioned earlier, among the TRIs, only $\text{TRI}_{90\text{E}}$ significantly deviated from the other robustness indices. Specifically, $\text{TRI}_{90\text{E}}$ was the only that indicated a significant exceedance (> 30%) of the “slightly disturbed” class. This result suggests that T_{50} was very close to T_{goal} and T_{90} exceeded this value for at least 30% of runs (Huck and Coffey, 2004). However, none of these conditions occurred, indicating that $\text{TRI}_{90\text{E}}$ was not able to accurately describe the real operating performance of the plant. On the other hand, the response of the other TRIs was more precise. Specifically, $\text{TRI}_{90\text{D}}$, $\text{TRI}_{90\text{J}}$, and $\text{TRI}_{95\text{B}}$ fell within the “very stable” and “stable” classes for approximately 45 and 50% of runs, indicating that the system ensured high-quality effluent in compliance with T_{goal} , for most of the observed period (> 96%). In fact, the T_{90} exceeds the T_{goal} only for a few runs. Accordingly, these TRIs indicated an exceedance of the “stable” class falling into the “slightly disturbed” class. These results enabled to observe that when assigning fixed weights to the terms constituting the indices did not enable to consider the high variance of turbidity data, which increases especially if monitoring is continuous and consequently include possible hotspots (Nemani et al., 2023). Furthermore, in this case, the new $\text{TRI}_{95\text{B}}$ did not provide significant new insights compared to those already present in the literature. This was likely due to the low discrepancy in turbidity data compared to the target value.

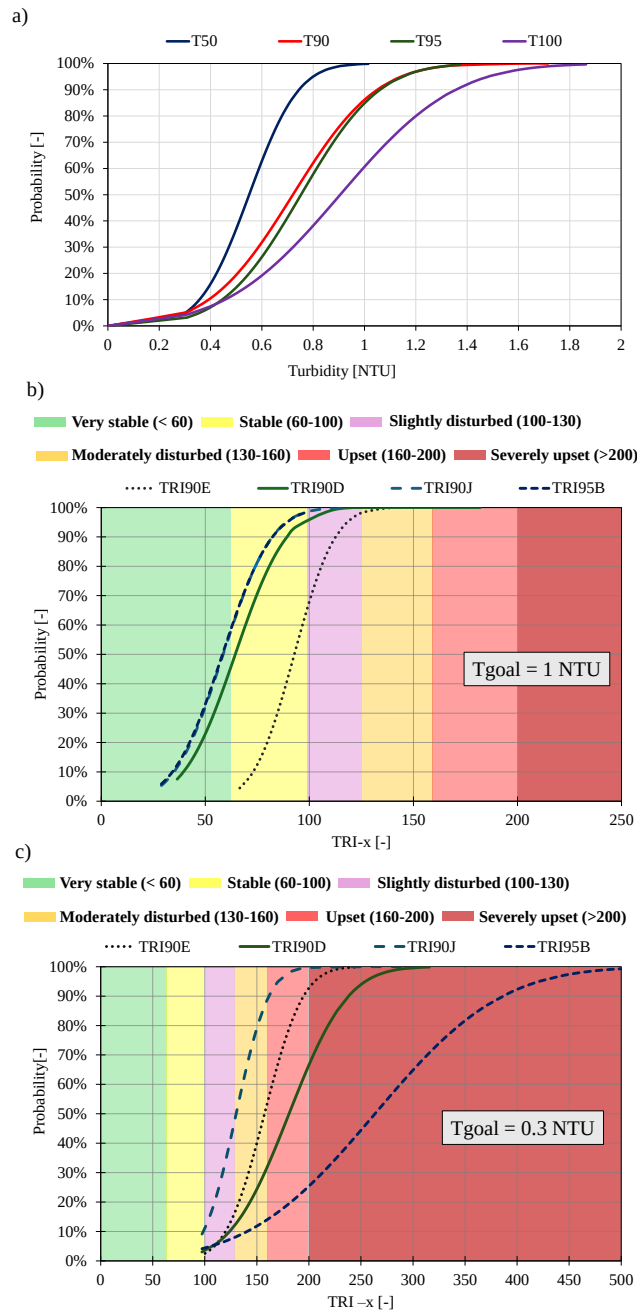


Figure 6.7. Cumulative distribution of T_{50} , T_{90} , T_{95} and T_{100} (a) and TRIs with T_{goal} of 1 NTU (b) and 0.30 NTU (c)

Indeed, the results changed drastically when considering a lower T_{goal} , thereby leading to an increase in the discrepancy between the measured turbidity data and the recommended value (0.30 NTU) (Figure 6.7c). While the previous regulation did not explicitly refer to which statistical turbidity data had to be used for comparison with the recommended value, the new regulations unequivocally identify it as the T_{95} . From Figure 6.7a, it can be observed that T_{95} exceeded 0.30 NTU for over 95% of runs. Furthermore, even the maximum value of 1 NTU was exceeded for approximately 40% of runs. However, not all the TRIs provided results that clearly represented this performance. Indeed, according to Table 5.2 (Chapter V – Classification of system operation with robustness index value and mathematical significance), falling within the “upset” class should indicate that T_{90} was beyond 50% of T_{goal} . In contrast, TRI_{90J} fell into the “upset” or higher class only for 10% of runs, TRI_{90E} for about 45%, TRI_{90D} for about 70%, and TRI_{95B} for over 85%. Therefore, although the T_{goal} was exceeded for over 95% of runs, none of the old TRIs showed a realistic correlation to plant performance. Among all the robustness indices, only TRI_{95B} indicated a significant exceedance of T_{goal} . Furthermore, it fell within the “severely upset” class for over 70% of the runs, indicating a good correlation to the exceedance of the limit value of 1 NTU. Therefore, when considering a lower T_{goal} , the response of TRIs was significantly different, indicating that the oldest showed a lower correspondence with the actual conditions and performance of the plant compared to the new TRI_{95B} .

To better point out this aspect, the sensitivity and specificity of the TRIs were calculated, referring to both the old and the new regulations. It should be highlighted, that because when referring to the new regulation, TRIs never fell within the stable or very stable classes, it was assumed that the true positive values were the number of runs in which TRI fell into the upset or severely upset classes and were correctly identified, whereas the true negatives were assumed to be the number of runs in which TRI fell into a class lower than the upset. The achieved results are reported in Table 6.3.

Table 6.3. Results of sensitivity and specificity of TRIs referred to the old and new regulations

	TRI _{90E}	TRI _{90D}	TRI _{90J}	TRI _{95B}
Directive 98/83/EC – Turbidity 1 NTU				
Sensitivity [%]	29	43	71	86
Specificity [%]	21	87	92	88
Directive EU 2184/2020 – Turbidity 0.30 NTU				
Sensitivity [%]	11	29	1	97
Specificity [%]	35	59	41	91

Referring to the old regulation, TRI_{90J} (71%) and TRI_{95B} (86%) showed a significantly higher sensitivity compared to the other TRIs, indicating a better capacity to detect true positive values. The specificity was comparable among all the TRIs (90%), apart from TRI_{90E}, which showed the lowest capacity to detect true negative values. When considering the Tgoal of 0.30 NTU, the sensitivity of the existing TRIs collapsed. Only the TRI_{95B} showed a very high sensitivity (> 95%), thus confirming that it can accurately identify the run during which the turbidity threshold is significantly exceeded and minimize the chances of missing any actual cases. This is particularly important because it can significantly impact treatment outcomes. Similarly, even the specificity of TRI_{95B} was significantly higher than the other TRIs (88%). Therefore, TRI_{95B} showed the highest capacity to minimize the chances of incorrectly identifying some runs as positive when they are not. It is worth noting that when referring to a lower Tgoal, both the sensitivity and specificity of TRI_{95B} increased. Increasing both sensitivity and specificity indicated that the TRI_{95B} was very accurate if considering a more restrictive limit for turbidity. This improvement is crucial for enhancing the reliability and effectiveness of TRI, as it enables better water quality control.

To provide more insights about the response of the TRIs to the plant operating conditions, all the indices were related to the discrepancy between the T₉₅ in each run and the target turbidity of 0.30 NTU (Figure 6.8).

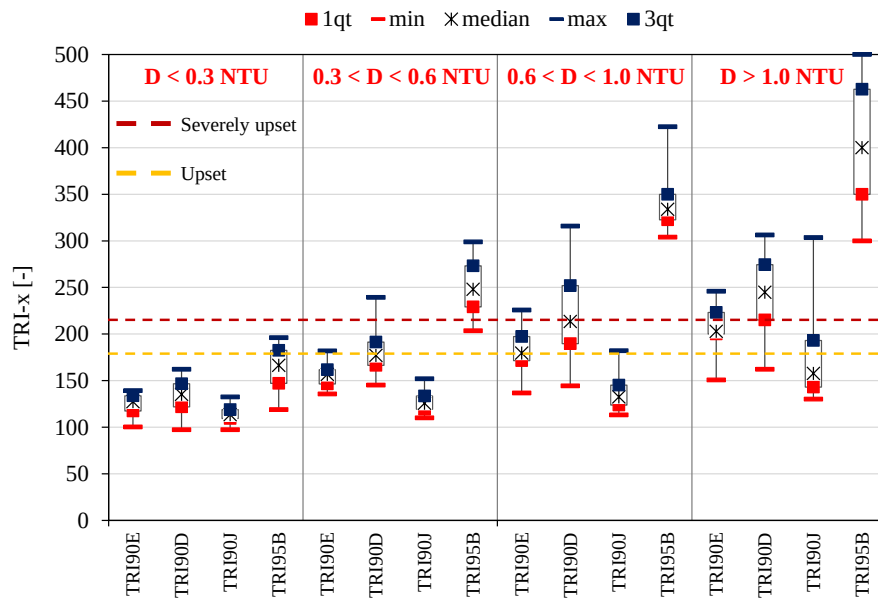


Figure 6.8. Boxplot of TRIs within different ranges of turbidity discrepancy

TRI_{95B} fell within the “upset” class, starting from a discrepancy with T_{goal} lower than 0.30 NTU. On the other hand, the other TRIs indicated a predominantly “moderately disturbed” operating condition. The “upset” condition was reached by TRI_{90E} and TRI_{90D} only for discrepancy values greater than 0.6 NTU. This indicated that only when the effluent turbidity exceeded 0.9 NTU the old TRIs indicate that the system was unable to produce high-quality water for most of the run. Conversely, TRI_{95B} showed a nearly linear relationship with the turbidity goal discrepancy. This was certainly because the T_{95}/T_{goal} ratio increased as the discrepancy rose. Overall, TRI_{95B} was the only index to fall into the “upset” or higher class at lower discrepancy values.

The above results suggested that TRI_{95B} had greater accuracy and reliability toward the DWTP operations than the other indices. Indeed, TRI_{95B} was able to point out failures of plant operation even when the target turbidity was only slightly exceeded. Furthermore, considering the 95th percentile rather than the 90th allowed including extreme turbidity data within the run. Consequently, this was useful for identifying undesired process conditions even if they occur for a brief duration. Moreover, the introduction of the “B” term enabled to better highlight the occurrence of an extremely severe condition that is mandatory for the new regulation, thus providing additional reliability to the robustness index.

6.1.5 Evaluation of TRIs at single-process scale: clariflocculation (CH) and filtration (FS)

In order to highlight any critical system due to malfunctions within the individual treatment units or individual processes, the single-process scale TRI (CH, FS) were applied, in order to evaluate its response in terms of robustness to the variation of the load conditions of the plant.

Clariflocculation (CH)

To evaluate and compare the TRIs related to the clariflocculation process, each TRI was initially applied to the historical set of turbidity data at the outlet of the three CH units. The index values were then calculated as the arithmetic average of the values obtained for each unit.

The performance of TRIs was evaluated qualitatively by comparing the weekly trend of statistical indicators (median, 95th percentile and maximum value) relating to the turbidity data set at the outlet of the clariflocculation process (Figure 6.9) and the weekly trend of TRIs values as a function of quality classes, with reference to the target value $T_{\text{goal}} = 5$ NTU to be respected downstream of the process (Figure 6.10).

In the graph in Figure 6.9a, it is observed that during the three years 2021-2023 there were differences in the fluctuations around the average value.

Specifically, the median turbidity showed a quite regular trend around 4.06 ± 1.15 NTU over the three-year period. On the contrary, 95th percentile and the maximum values showed a less regular trend, characterized by greater fluctuations; in particular, the 95th percentile was on average 5.91 ± 2.30 NTU, while the maximum was 7.14 ± 2.98 NTU. In any case the turbidity limit of 5 NTU was exceeded if one refers both to 95th percentile and to the median of turbidity. In more detail, referring to the median of turbidity, the limit was exceeded for 26 weekly runs, which were concentrated especially in the third year of observation.

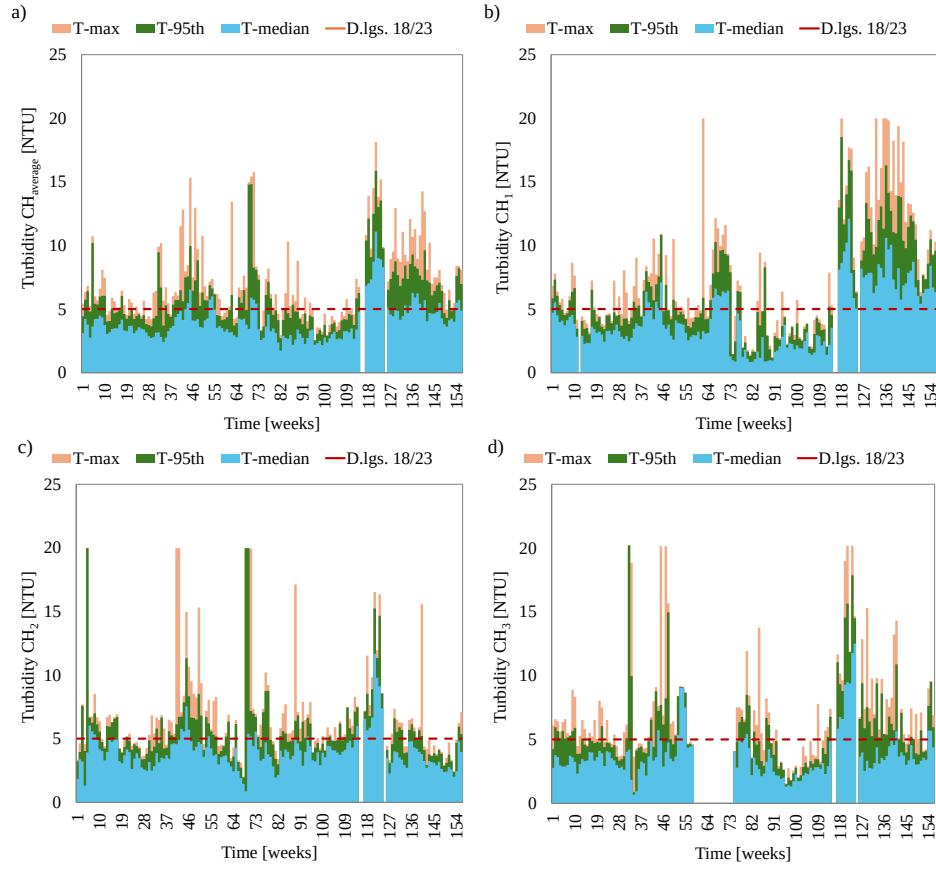


Figure 6.9. Trends of the main statistics (95th percentile, median, maximum) of turbidity data as average of the clariflocculation process (a) and at the outlet of CH₁ (b), CH₂ (c) and CH₃ (d) units

This trend is the result of what happens on average in the single clariflocculation units. Indeed, analysing the same statistical indicators output to individual tanks, it turns out that:

- in CH₁, the median (4.33 ± 2.46 NTU), the 95th percentile (6.36 ± 3.68 NTU) and the maximum value (7.66 ± 4.74) are quite regular, except during the third year of observation;
- in CH₂, statistical indicators remain fairly constant around the average value, except for some occasional peak (median = 3.99 ± 1.43 NTU, 95th percentile = 5.74 ± 2.19 NTU, maximum value = 6.84 ± 3.74 NTU);

- in CH₃, the median (3.79 ± 1.88 NTU) and the 95th percentile (5.78 ± 3.07 NTU) have lower values than other CH units, while the maximum value (7.16 ± 4.02) is greater.

Therefore, CH₁ is the unit which contributes most to the highest turbidity values.

Based on these observations, the graphs in Figure 6.10 have qualitatively demonstrated that TRI_{95G} reported values which more accurately reflect the actual trend of turbidity data downstream of the clariflocculation process.

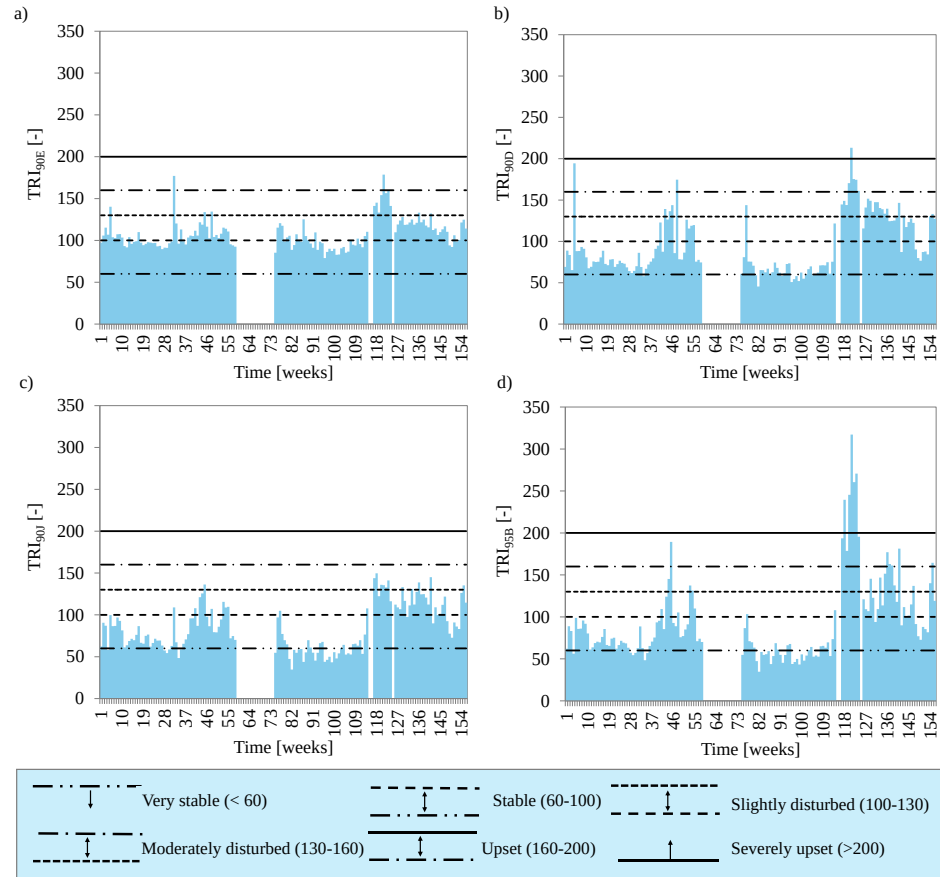


Figure 6.10. Trends of TRI scores during the 2021-2023 period for the evaluation of clariflocculation process robustness, assuming a T_{goal} of 5 NTU

The mean value and standard deviation of the set of TRIs values resulted as follow:

- TRI_{90E} showed the highest values of the average value, equal to 108.15 ± 17.73 , resulting from 12% to 21% higher than the other indices;
- TRI_{90D} had slightly higher fluctuations around a lower average value of 94.95 ± 35.31 ;
- TRI_{90J} had the lowest average value, equal to 85.16 ± 28.07 ;
- TRI_{95B} was slightly lower than the previous ones, but with greater fluctuations, with an average value of 93.61 ± 49.12 .

Table 6.4 shows the number of weeks and their percentage value in which the indices fall into each quality class. All the TRIs are placed in the three classes “very stable”, “stable” and “slightly disturbed” for about 80%-90% of weekly runs. In particular, the “stable” class was the one with the highest overall occurrence frequency. The percentage of runs in which the TRIs were in the “very stable” class was lower: the TRI_{90E} never entered into the class, unlike the TRI_{90J} and TRI_{95G} , which showed the higher frequency among the indices.

The runs in which the TRI were classified as “upset” and “severely upset” were significantly less frequent, ranging from 0% to about 10%.

Based on these results, the TRI_{95G} provided a better and more representative response to the actual operating conditions of the process, as the plant fell into “severely upset” class for five weeks and into “upset” for nine runs, unlike the other TRI who have never been in this category (except the TRI_{90D} , which was only in the “severely upset” class for one week).

Table 6.4. Occurrence of TRIs within a class of system operation quality ($T_{goal} = 5$ NTU)

TRI class	TRI_{90E}	TRI_{90D}	TRI_{90J}	$TRI_{95B(*)}$
Very stable	0	11	29	29
Stable	55	81	67	67
Slightly disturbed	68	17	29	18
Moderately disturbed	12	21	12	9
Upset	2	6	0	9
Severely upset	0	1	0	5
Not available	19	19	19	19
Total	156	156	156	156

Filtration (FS)

The same procedure was used to evaluate and compare the TRI for the filtration process, thus applying the TRI to the historical data set of turbidity output from the three filtration units.

The performance of TRIs was evaluated qualitatively by comparing the weekly trend of statistical indicators (median, 95th percentile and maximum value) relating to the turbidity data set at the outlet of the filtration process (Figure 6.11) and the weekly trend of TRIs values as a function of quality classes, with reference to the target value $T_{MAX} < 1$ NTU and $T_{goal} = 0.3$ NTU in 95% of samples (Figure 6.12).

In the graph in Figure 6.11a, it is observed that during the three years 2021-2023 the fluctuations around the average turbidity value recorded downstream of the filtration process were relevant, with a significant increase in the third year. The trend of the maximum value of the distribution shows more clearly the irregular trend, characterized by extremely high turbidity peaks that exceed by far the permitted limits. Specifically, the median of the turbidity data downstream of the process showed an average value of 0.66 ± 0.34 NTU, the 95th percentile showed average values of 1.00 ± 0.50 NTU and the maximum value was on average 1.72 ± 1.57 NTU. Observing the weekly trend of the 95th percentile of the turbidity data distribution, the limit of 0.30 NTU was exceeded during all weekly runs. In addition, the maximum value of the turbidity data set was kept below the 1 NTU limit for only about 21% of weekly runs. These data show that the filtration process was not able to meet the requirements of the current legislation.

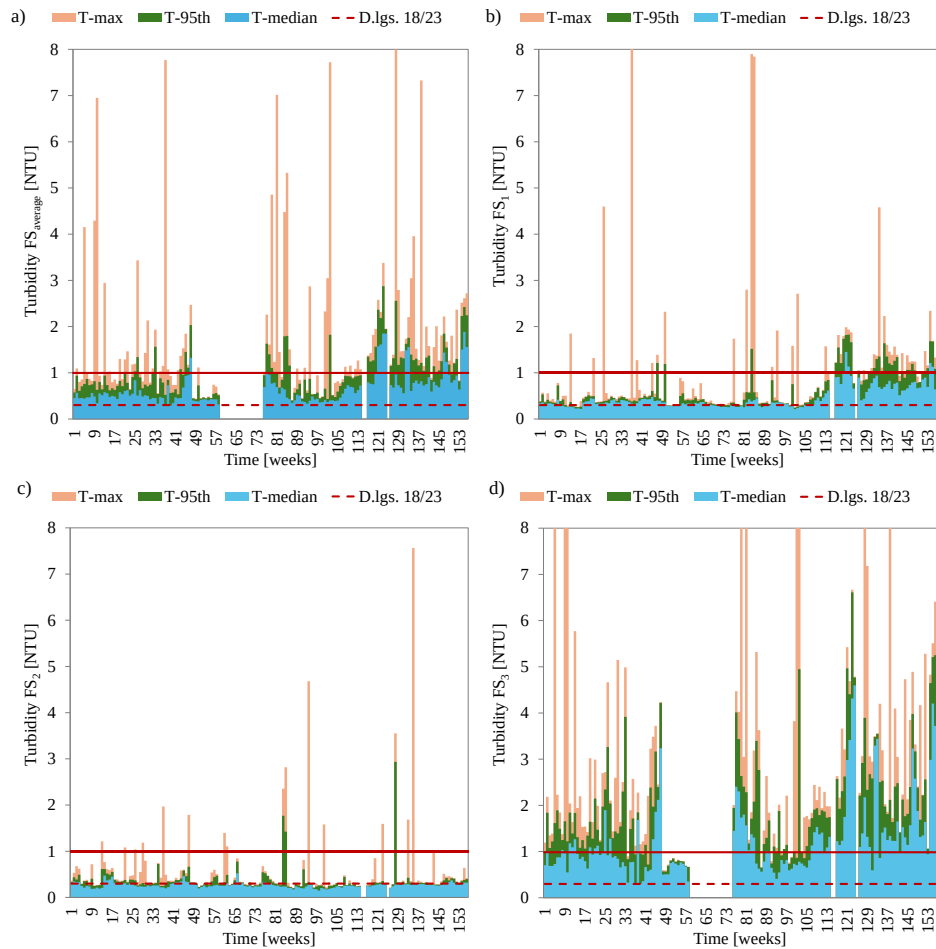


Figure 6.11. Trends of the main statistics (95th percentile, median, maximum) of turbidity data as average of the filtration process (a) and at the outlet of FS₁ (b), FS₂ (c) and FS₃ (d) units

This trend is mainly due to the turbidity values at the outlet of FS₃ units (Figure 6.11d), which are much higher than those at the outlet of FS₁ and FS₂ units (Figure 6.11b and 6.11c), and which, in no case, comply with the limits imposed by the legislation. The FS₁ filter can guarantee, in most cases, that the maximum value of 1 NTU will not be exceeded; however, the 95th percentile was found to be on average twice the value allowed by regulations (0.3 NTU). FS₂ unit, although not in line with the requirements of the regulations, guarantees the best performance,

with a maximum value that is kept below 1 NTU and the 95th percentile slightly above 0.3 NTU.

In particular, the median, the 95th percentile and the maximum value in FS₁, FS₂ and FS₃, respectively, had an average of:

- 0.45 ± 0.23 NTU, 0.63 ± 0.39 NTU and 1.06 ± 1.88 NTU, respectively (Figure 11b);
- 0.27 ± 0.05 NTU, 0.37 ± 0.27 NTU and 0.58 ± 0.81 NTU, respectively (Figure 11c);
- 1.25 ± 0.83 NTU, 1.97 ± 1.14 NTU and 3.42 ± 3.89 NTU, respectively (Figure 11d).

Even in this case, based on these observations, the graphs in Figure 6.12 have qualitatively demonstrated that TRI_{95G} reported values which more accurately reflect the actual trend of turbidity data downstream of the filtration process, thus providing a more accurate and timely response to the exceeding of limits.

The mean value and standard deviation of the set of TRIs values resulted as follow:

- TRI_{90E} had the higher mean value among literature TRIs (102.18 ± 20.98), although it showed the lowest fluctuations;
- TRI_{90D} showed slightly lower average values (77.37 ± 37.51) than the previous one, but with greater fluctuations;
- TRI_{90J} had the lowest average value, equal to 68.85 ± 30.55 ;
- TRI_{95B} showed significantly higher average values, equal to 366.45 ± 303.76 , resulting from 72% to 81% higher than the other indices.

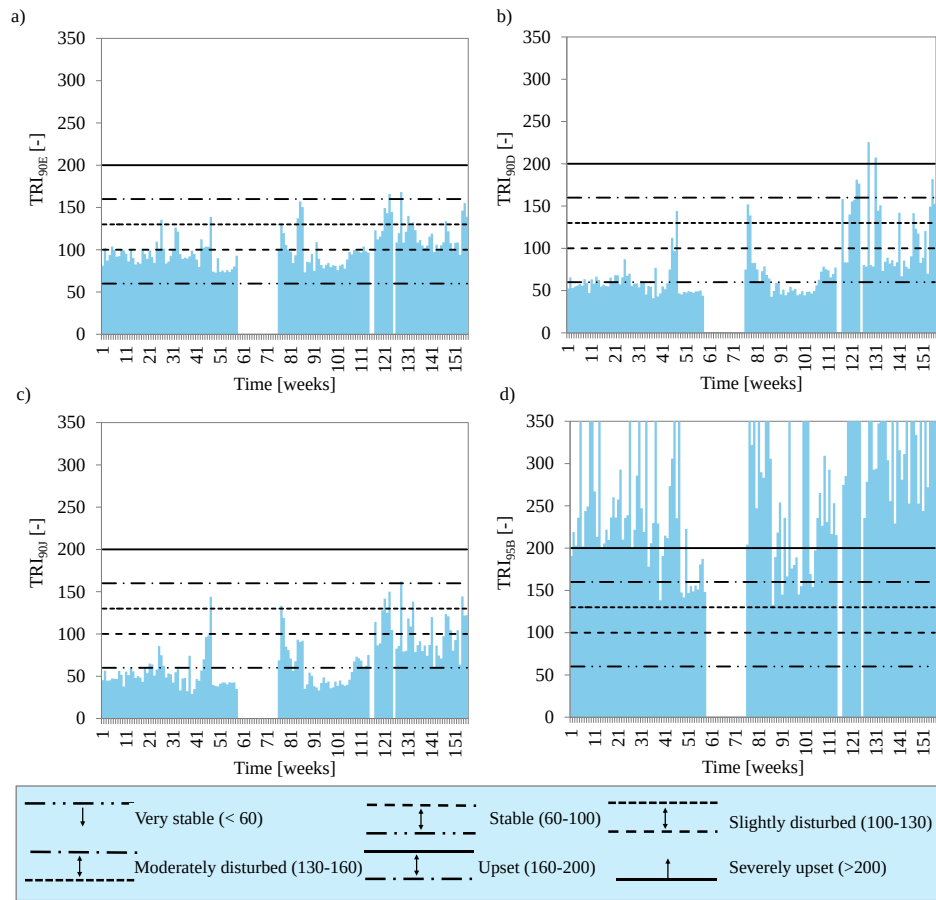


Figure 6.12. Trends of TRIs scores during the 2021-2023 period for the evaluation of filtration process robustness, assuming a $T_{goal} < 1$ NTU and a T_{goal} of 0.3 NTU in 95% of samples

Table 6.5 shows the number of weeks and their percentage value in which the indices fall into each quality class.

The TRIs in the literature are classified into the classes “very stable”, “stable” and “slightly disturbed” for a percentage of approximately 85% to 95% of weekly runs. The TRI_{95B} has never been classified in any of these categories in any run. In fact, it recorded the highest frequency of occurrence (~70%) in the “severely upset” class (110 weekly runs out of 156), clearly highlighting the high instability of the filtration process.

Table 6.5. Occurrence of TRIs within a class of system operation quality ($T_{goal} < 1$ NTU and $T_{goal} = 0.3$ NTU in 95% of samples)

TRI class	TRI _{90E}	TRI _{90D}	TRI _{90J}	TRI _{95B(*)}
Very stable	0	58	70	0
Stable	78	56	45	0
Slightly disturbed	42	4	14	0
Moderately disturbed	14	13	6	14
Upset	2	3	1	12
Severely upset	0	2	0	110
Not available	20	20	20	20
Total	156	156	156	156

Based on these results, unlike the clariflocculation process, there was a clear difference in the response given by the indices. In particular, the TRI_{95B} provided a better and more representative response to the actual operating conditions of the process, making it more difficult for the plant to meet the treatment objective.

6.1.6 Correlation between TRI_{95B} and TLI at global and single scale process

In order to find a link between TRI_{95B}, the variation of the water quality at the inlet of the plant and load conditions, TLI was calculated, and its trend is shown in Figure 6.13.

In general, the graph shows a quite regular trend of the TLI over the observed period, remaining fairly stable between 50 and 60 and with an average value equal to 53.59 ± 6.73 . However, a sensible decrease of the index was detected between weeks 49-58 and 61-74, mainly due to the reduction of the flow at the inlet of the plant (Figure 6.1), caused by an increase of the raw water turbidity (Figure 6.2a).

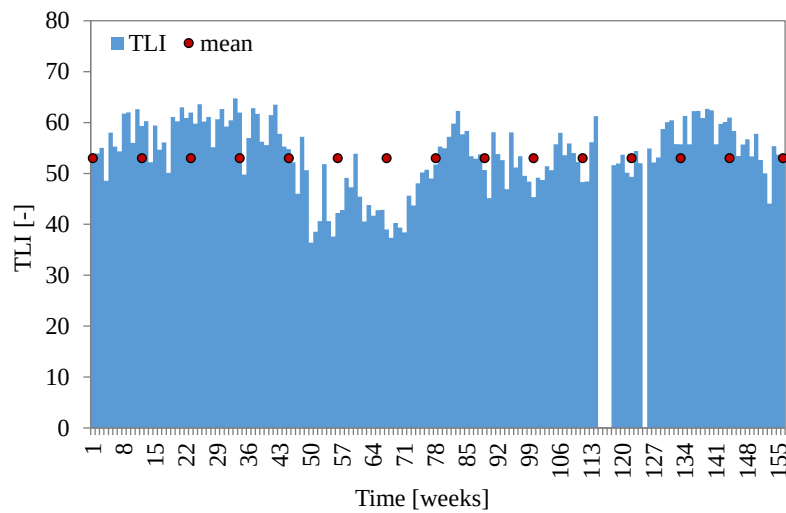


Figure 6.13. Trend of TLI scores during the 2021-2023 period

Figure 6.14 show the overall TRI_{95B} in function of different ranges of TLI.

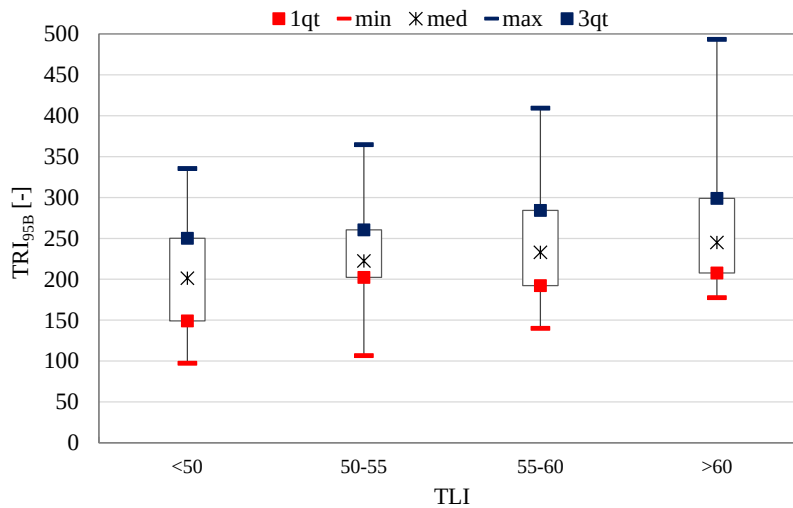


Figure 6.14. Boxplot of TRI within different ranges of TLI

The graph provides a clear representation of how TR_{95B} and then the plant performance changes across different TLI ranges, showing that higher TLI values tend to lead to greater variability in the TR_{95B} .

For all TLI ranges, the median values of TRI_{95B} remains relatively stable around 200-250, with slight variations between the categories. The interquartile range (IQR), the difference between the 1st and 3rd quartile, is fairly consistent across all TLI ranges, suggesting that TR_{95B} values are relatively stable in each TLI range. However, the interquartile range increases slightly in the >60 TLI range, indicating a wider dispersion of TR_{95B} values. Furthermore, the maximum and minimum TR_{95B} values for each TLI category show that there is more variability in the higher TLI ranges (>60).

Therefore, it seems that for <50 TLI range, the smaller dispersion and less variability of the data suggests a more predictable and stable performance; on the contrary, in the higher TLI ranges, the higher maximum value of TRI_{95B} and the larger interquartile range suggest the instability of the performance.

In each case, it must be stressed that, in all TLI ranges, the TRI_{95B} falls into the “upset” or “severely upset” class.

TLI was also correlated with TRI_{95B} of clariflocculation and filtration. This link with the process scale is like a warning signal to the DWTP manager, useful for identifying which process is more sensitive, thus providing information to understand whether the system is going into crisis due to a specific malfunction of a process unit or sub-optimal operating conditions.

Figures 6.15 and 6.16 show the relation between TRI_{95B} and TLI considering clariflocculation and filtration process, respectively.

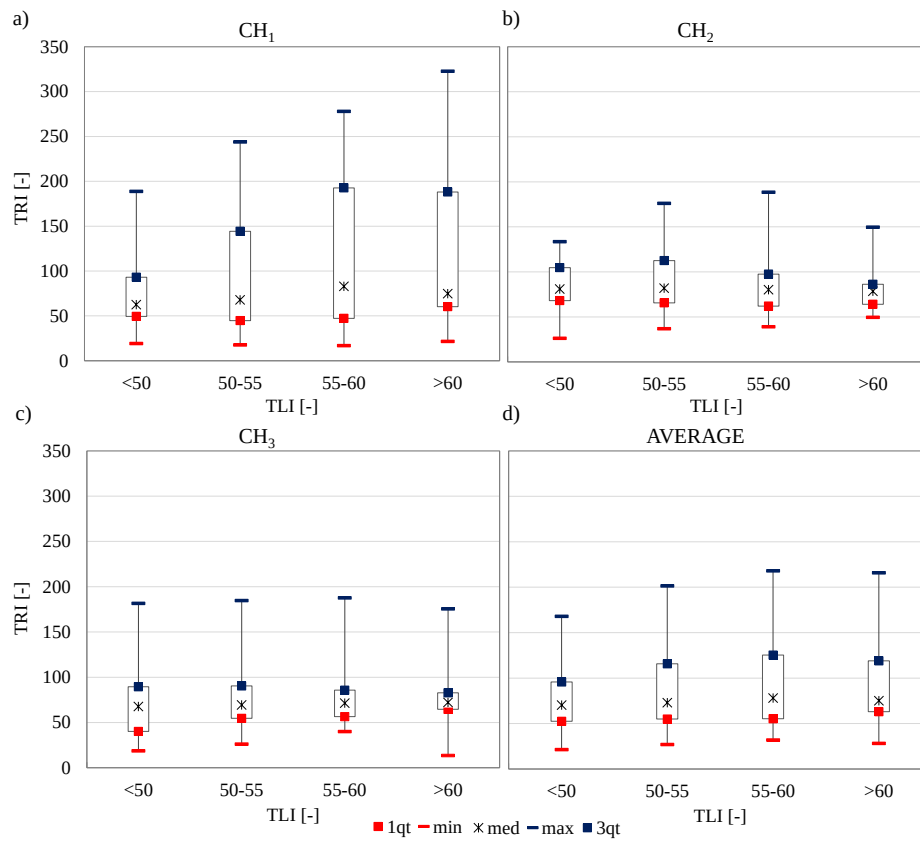


Figure 6.15. Boxplot of TRI_{95B} calculated for CH_1 (a), CH_2 (b), CH_3 (c) and as average of the CH process (d) within different ranges of TLI

In the graph reported in Figure 6.15a it is observed that for all TLI groups, the IQR is quite wide, indicating variability in the TRI values. As the TLI increases, there is an upward trend in the TRI values, with higher values in the 55-60 and >60 categories compared to <50 and 50-55. The range is largest in the 55-60 TLI group, where the maximum reaches nearly 300, and the minimum extends down to around 20. The medians remain almost constant (between 63 and 74) for all TLI ranges, with a slightly increase for the 55-60 category (~85).

Referring to Figure 6.15b, across all TLI categories, the medians show a minimal variability, staying relatively close to 80 for all ranges. Even the IQR is more restricted, suggesting a lower variability of TRI values. Although there are slight

differences in the upper ranges, no clear trend of increasing or decreasing values across TLI groups is observed.

A similar behaviour is observed in the graph reported in Figure 6.15c. There is a quite regular trend across the TLI ranges, with TRI values remaining quite consistent throughout the categories. In fact, even in this case, across all TLI ranges, the median values remain almost constant, hovering around 70. The interquartile range is also relatively narrow for all groups, suggesting less variability in TRI values.

In summary, while TRI values in CH₁ (Figure 6.15a) unit increase with higher TLI ranges, those in CH₂ (Figure 6.15b) and CH₃ (Figure 6.15c) show less variation across these groups, with a narrower spread and more consistent medians. Therefore, it emerged that CH₂ and CH₃ units can guarantee approximately constant performances independently of the load conditions; on the contrary, CH₁ unit resulted more sensitive to such conditions.

Finally, in the graph reported in Figure 6.15d, it is observed a modest increase in the trend of the average TRI across the TLI ranges. This is mainly due to the contribution of TRI in CH₁, which shows a clear upward trend with increasing TLI. However, TRI in CH₂ and CH₃ remain relatively stable and don't follow the same increasing pattern, contributing less to the rising of the average TRI as a whole. Overall, the TRI distribution indicates that the clariflocculation process is somewhat stable but with significant fluctuations. By considering the average TRI for the clariflocculation process, it emerged that it should fall in the "stable" class, as median value, for all the TLI ranges, thus ensuring the robustness and stability of the clariflocculation process.

The filtration process showed a different behaviour in linking TRI_{95B} and TLI (Figure 6.16).

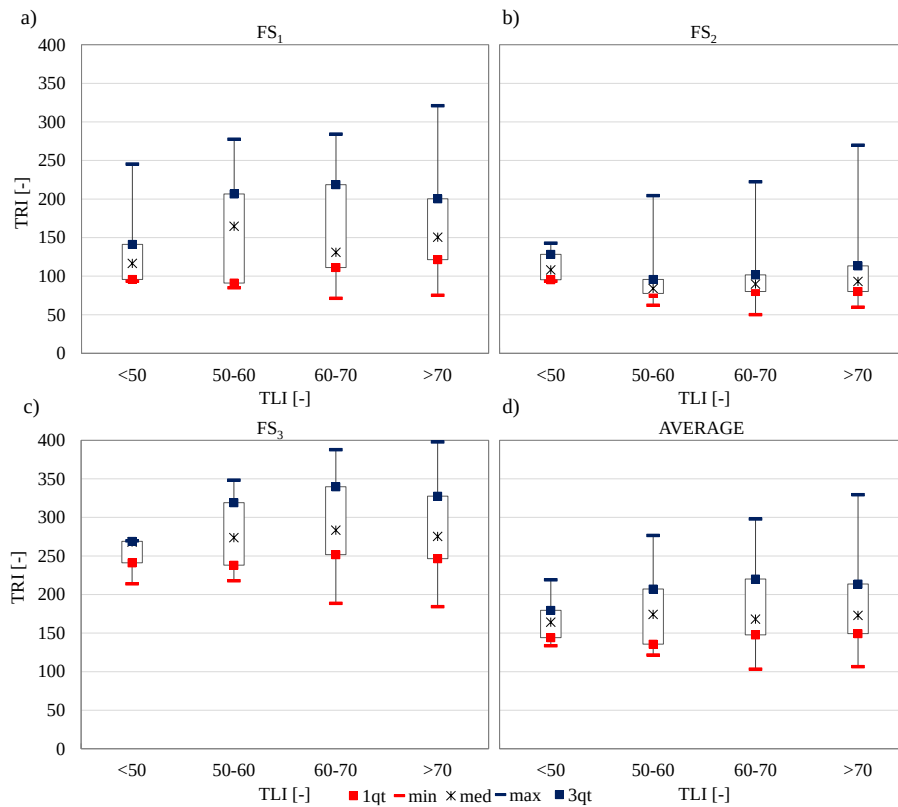


Figure 6.16. Boxplot of TRI_{95B} calculated for FS_1 (a), FS_2 (b), FS_3 (c) and as average of the FS process (d) within different ranges of TL

Figure 6.16a shows a tendency for TRI values to increase in both magnitude and variability as TL rises. In particular, for low TL range (<50), the interquartile range is relatively small, and the minimum value and the 1st quartile are also more compressed; on the contrary, the maximum value shows a greater variability. However, as TL increases to 50-60, 60-70, and >70 ranges, the spread of the data tends to become larger; in fact, the overall range (from min to max) broadens and the IQR also becomes bigger.

In Figure 6.16b it is observed a different variability in TRI values. In fact, for the lower TL class (<50), the overall TRI range is narrow (min~100 and max~150); nevertheless, at higher TL classes, although the median remains relatively stable and the IQR is limited, the spread between the maximum and minimum values increases with larger whiskers, indicating more variability.

In Figure 16.6c, the range and variability of TRI considerably increases as TLI increases, the median values are significantly higher than those in previous graphs (Figure 16.6a and Figure 16.6b) and both IQR and whiskers are wider across all TLI ranges.

Therefore, from the observation of these three graphs and the TRI variability, it resulted that FS₂ unit (Figure 16.6b) is able to ensure higher stability of the filtration process than FS₁ (Figure 16.6a) and FS₃ (Figure 16.6c) units.

Finally, in the graph reported in Figure 6.15d, it is observed a general increase in TRI trend across the TLI ranges. In more details, the median values remain almost constant, while the IQRs and the whiskers extend as TLI ranges increase. Overall, the TRI distribution indicates that the filtration process is highly sensitive to input load variations. By considering the average TRI, it emerged that the filtration process should fall in the “moderately disturbed” class, as median value, for all the TLI ranges, thus suggesting a loss of robustness and stability.

6.1.7 Assessing plant robustness in presence of turbidity peak events

In order to assess the potential vulnerability of the plant, or certain processes, in the case of the occurrence of extreme and short-duration events, such as turbidity peaks, the index has been related to such events.

Figure 16.7a depicts the threshold value of turbidity (19.1 NTU) above which there is the occurrence of the events, and the system may be considered vulnerable or experiencing stress; each identified event is indicated by an arrow. Therefore, the graph highlights how system performance could be periodically challenged, especially in response to certain events that surpass the threshold.

Figure 16.7b focuses on turbidity peaks that correspond to events and for each of them the duration and the score are specified. It is observed that, over the three years considered, 10 events took place; in particular, 3 in 2021, 5 in 2022 and 2 in 2023; moreover, 2022 resulted those with the most extreme and longest-lasting events. Each event had different duration, from 4 days (E6) to 30 days (E5) and their assigned score is proportional to that duration.

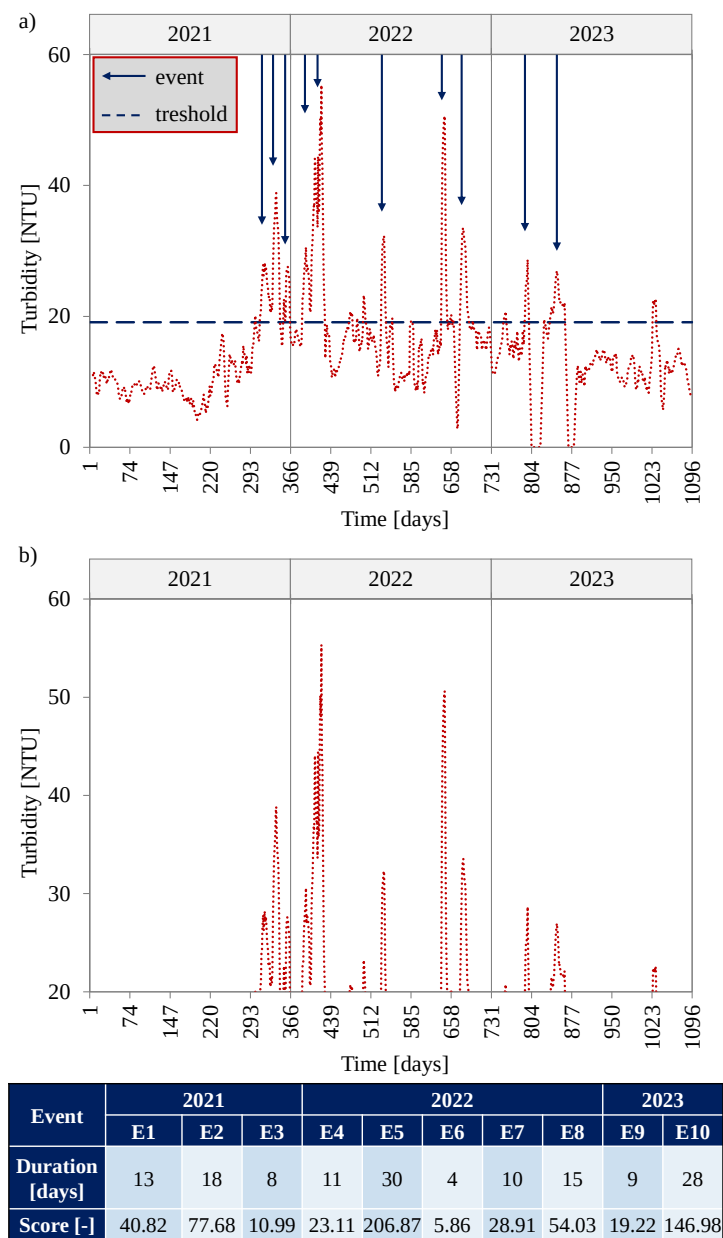


Figure 6.17. Event identification with threshold value (a) and focus on events duration and score (b)

The scores assigned to each event have been subsequently correlated with the TRI_{95B} , both at a global and process scale, calculated at the time the event occurred (Figure 6.18).

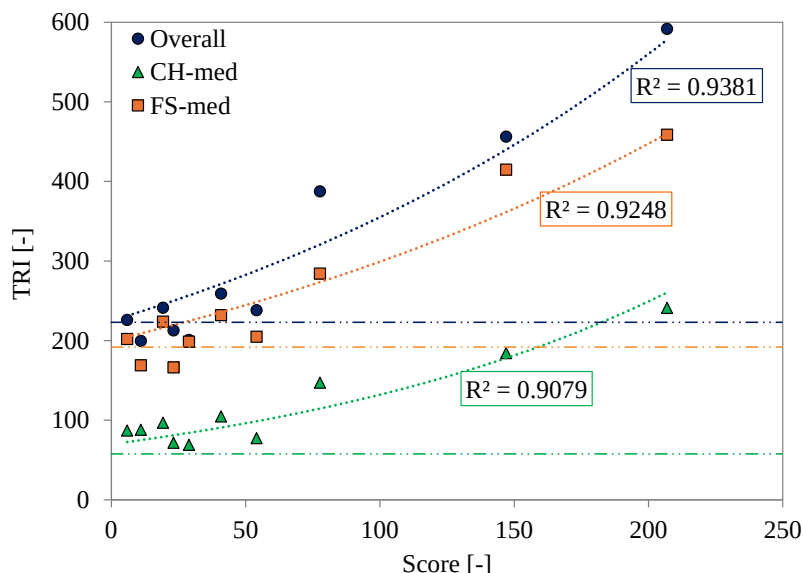


Figure 6.18. Correlation between TRI_{95B} and event score

The graph indicated a strong correlation between the Score and TRI. In fact, all three datasets showed a positive, nonlinear relationship between the two terms, with very high values of R^2 : 0.93 for “overall”, 0.92 for “FS-med” and 0.90 for “CH-med”. This indicated that the Score was a good predictor of TRI_{95B} .

The differences in the slopes of the lines suggested that each category reacts differently to changes in the Score, particularly “CH-med”, which had a more gradual increase, and a lower TRI response compared to “FS-med” and “Overall”. In this sense, the clariflocculation process was found to be more robust and less sensitive to turbidity peaks. On the contrary, the filtration process and the overall performances of the plant exhibited greater vulnerability to such events. In any case, it was observed that in the left side of the graph, and therefore for the lowest values of the Score, there was a trend to align horizontally, thus indicating that for small entity events, both the plant and the single processes guaranteed a certain robustness, without compromising performances. However, by increasing the Score, the trend tended to become exponential, with significant rise in TRI values and thus in the loss of robustness.

In this regard, a useful approach would be to identify a threshold value for a given event that leads to a significant increase of the index and therefore to the robustness loss of the plant. A visual representation of this concept is shown in Figure 6.19.

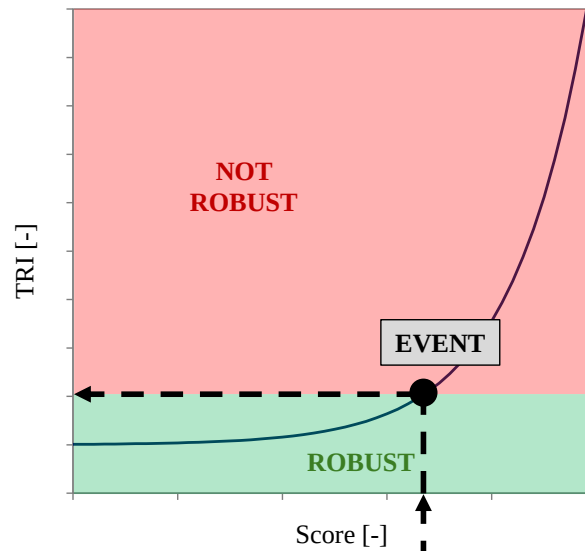


Figure 6.19. Visual representation of a threshold score beyond which the TRI starts to increase and the plant loses robustness

The vertical dashed arrow marks the occurrence of an event, which aligns with a significant increase in the TRI. Therefore, it is considered as the critical point at which the plant's stability rapidly declines, entering a state where it is no longer able to maintain its robustness.

The graph shows that when the magnitude of the event is low (left side of the arrow), the system remains robust (green zone). As the score of the event increases and exceeds the marked threshold, the system reaches a condition where the TRI increases sharply, and the system's robustness is severely compromised (red zone).

6.2 Results on Manganese Robustness Index

6.2.1 Characteristics of raw water and compliance of treated water with regulations

Manganese data collected from the SCADA system in the raw, in X1 tank and in the effluent disinfected water are depicted in Figure 6.20.

The manganese concentration in the raw water at the inlet of the plant (Figure 6.20a) showed periodic fluctuations, with significant peaks (weeks 8, 46 and 47) where the concentration increased sharply reaching values close to 1000 µg/L. On the contrary, the average and median concentrations were mostly aligned and remained comparatively low during most of the weeks, except for week 46 where the median and average values also increased. The overall trend indicates that manganese concentrations generally increase in the latter half of the year thus suggesting possible episodic pollution events (e.g. sediments resuspension).

Figure 6.20b shows that manganese concentration in X1 tank is significantly higher than that at the inlet of the plant, resulting on average doubled. This considerable increase could be due to the fact that the plant operates as a closed-cycle system, thus completely recovering the liquid fraction across all the processes. Such recovery implies that the filter backwash water, that are manganese-laden, are pumped back to the X1 tank. More precisely, the high presence of manganese could be linked to the use of potassium permanganate in pre-oxidation, which leads to the formation of Mn^{4+} (insoluble). In reducing conditions, such as those that develop within storage backwash tanks, this is transformed into Mn^{2+} (soluble), thus contributing to an increase in manganese in the water to be treated.

Figure 6.20c depicts the main statistic of manganese in the effluent water. It is observed that there is a notable increase in manganese levels over time, especially after week 14. The maximum value and the 95th percentile of the distribution showed an irregular trend, characterized by several fluctuations. In particular, the maximum value was on average 49.97 ± 30.67 µg/L, while the mean value of 95th percentile was equal to 43.11 ± 26.14 µg/L. The median and the average values of the manganese distribution showed a similar trend, except during weeks 13-16 in which the average values were characterized by a significant peak. More specifically, the mean values of median and average were equal to 30.72 ± 21.14 µg/L and 32.37 ± 20.60 µg/L, respectively. Referring to average value of manganese concentration, the limit of 50 µg/L was exceeded in 12 weekly runs.

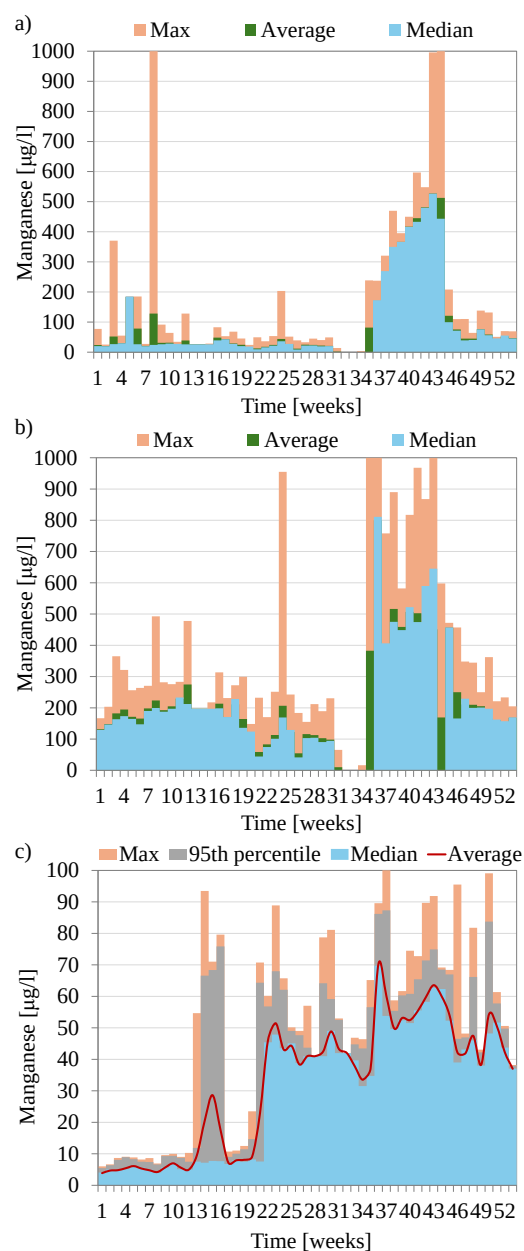


Figure 6.20. Trends of the main statistics (mean, median, maximum) of manganese data in influent water (a), and in X1 tank (b) (data in weeks 32 and 33 are missing); maximum, 95th percentile, median and average of manganese data measured at the outlet of the DWTP (c)

6.2.2 Comparative assessment of MRIs in the framework of the EU 2020/2184

In this section, the results of the comparison between the proposed index and the literature indices are discussed. Since no MRIs are available in the literature, the existing TRIs were applied to the manganese values dataset from the DWTP.

MRIs were calculated assuming a T_{goal} equal to 50 $\mu\text{g/L}$ (according to EU 2020/2184). For the calculation of $\text{MRI}_{95\text{B}}$, it was assumed that parameter B was equal to 1, since there is only one limit for manganese. Figure 6.21 shows the trends of the MRIs.

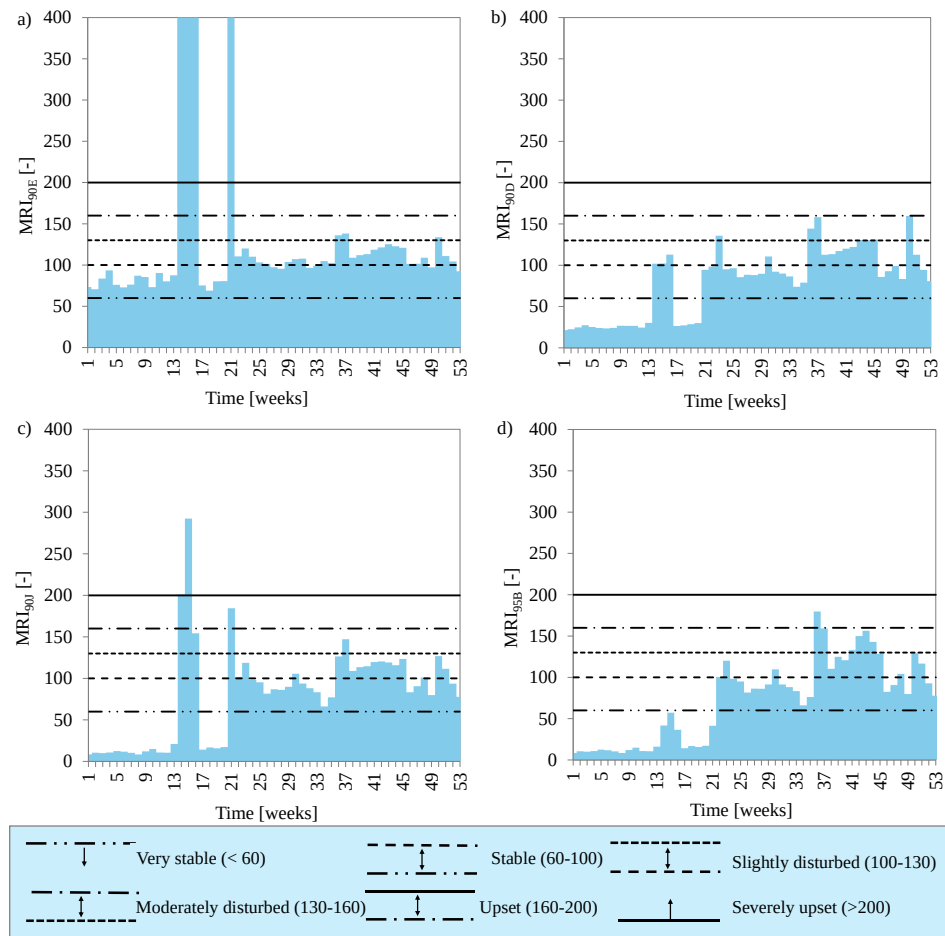


Figure 6.21. Trends of MRIs scores during the year 2023, assuming a T_{goal} of 50 $\mu\text{g/L}$

According to Table 5.2 (Chapter V – Classification of system operation with robustness index value and mathematical significance), if the median value of the data distribution (M_{50}) is lower than the target value ($M_{\text{goal}} = 50 \mu\text{g/L}$) and if the 90th percentile (M_{90}) is greater or equal to 30% of the M_{goal} , then the index falls into the class “slightly disturbed”. The distinction between the quality classes from “slightly disturbed” to “severely upset” depends on the extent and frequency of exceedances occurring in the single weekly run. Consequently, even when the MRI falls in the range “disturbed” (slightly/moderate), it means that exceedances occur in the run, but these can be of small magnitude and short duration.

The MRIs resulted on average close to 126.18 ± 95.69 ($\text{TRI}_{90\text{E}}$), 80.17 ± 41.78 ($\text{TRI}_{90\text{D}}$), 81.03 ± 58.64 ($\text{TRI}_{90\text{J}}$), 72.48 ± 49.91 ($\text{TRI}_{95\text{B}}$). The $\text{TRI}_{90\text{E}}$ showed the highest values, being approximately 35-40% higher than the others. Overall, all MRIs fell within the “very stable” and “stable” classes for ~70% of the runs, and in the “slightly disturbed” or higher classes for ~30%, except for $\text{TRI}_{90\text{E}}$, which never fell in the “very stable” class and mostly fell in the “stable” and “slightly disturbed” class (43% of runs in both classes) (Table 6.6). Therefore, all MRIs indicated that the 90th percentiles were greater than the manganese limit ($50 \mu\text{g/L}$) and consequently that the DWTP did not generate effluent water of the desired quality during those weeks. However, only $\text{TRI}_{90\text{D}}$ and $\text{TRI}_{95\text{B}}$ seem to show a close correspondence with the mean manganese concentration in the effluent.

Table 6.6. Occurrence of MRIs within a class of system operation quality

MRI class	$\text{MRI}_{90\text{E}}$	$\text{MRI}_{90\text{D}}$	$\text{MRI}_{90\text{J}}$	$\text{MRI}_{95\text{B}}(*)$
Very stable	0	17	17	21
Stable	23	19	16	16
Slightly disturbed	23	10	15	10
Moderately disturbed	3	7	2	5
Upset	0	0	1	1
Severely upset	4	0	2	0
Not available	0	0	0	0
Total	53	53	53	53

6.2.3 Reliability of MRIs

The investigated MRIs showed conflicting results, indicating the occurrence of different robustness classes. Figure 6.22 illustrates the cumulative distribution of the median, the 90th and the 95th percentiles of manganese (Figure 6.22a) and that of MRIs (Figure 6.22b).

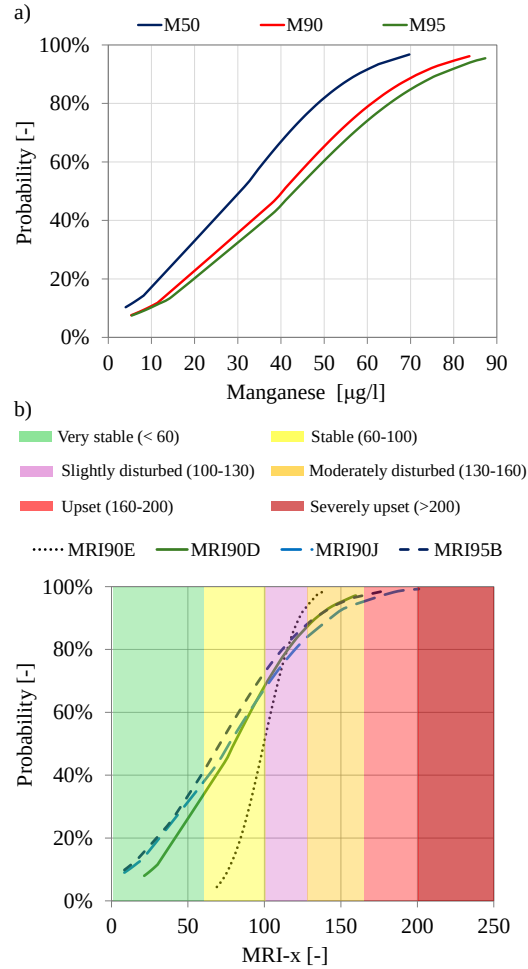


Figure 6.22. Cumulative distribution of M_{50} , M_{90} , and M_{95} (a) and MRIs with $T_{\text{goal}} = 0.50 \mu\text{g/L}$ (b)

The M_{50} was less than 50 $\mu\text{g/L}$ for over 80% of runs, whereas the M_{90} and M_{95} were nearly 63% (Figure 6.22a). As mentioned earlier, among the MRIs, only $\text{MRI}_{90\text{E}}$ significantly deviated from the other robustness indices (Figure 6.22b). Specifically, $\text{MRI}_{90\text{E}}$ was the only that indicated a significant exceedance (> 57%) of the “stable” class. This result suggests that M_{50} was very close to M_{goal} and M_{90} exceeded this value for at least 30% of runs. However, none of these conditions occurred, indicating that $\text{MRI}_{90\text{E}}$ was not able to accurately describe the real operating performance of the plant. On the other hand, the response of the other MRIs was more precise. Specifically, $\text{MRI}_{90\text{D}}$, $\text{MRI}_{90\text{J}}$, and $\text{MRI}_{95\text{B}}$ fell within the “very stable” and “stable” classes for approximately 70% of runs, indicating that the system ensured high-quality effluent in compliance with M_{goal} , for most of the observed period.

To better point out this aspect, the sensitivity and specificity of the MRIs were calculated (Table 6.7). It should be highlighted that, exceeding the limit of 50 $\mu\text{g/L}$ implies the “slightly disturbed” class index ranking. For this reason, it was assumed that the true positive values were the number of runs in which MRI fell into the “slightly disturbed” or higher classes and were correctly identified; whereas the true negatives were assumed to be the number of runs in which MRI fell into the “stable” or “very stable” class.

Table 6.7. Results of sensitivity and specificity of MRIs referred to the new regulations

	$\text{TRI}_{90\text{E}}$	$\text{TRI}_{90\text{D}}$	$\text{TRI}_{90\text{J}}$	$\text{TRI}_{95\text{B}}$
Sensitivity [%]	55	50	50	73
Specificity [%]	19	100	100	100

Results reported in Table 6.7 showed that all MRIs had a very high specificity (100%), indicating that they can accurately identify the run during which the manganese threshold is not exceeded, except for $\text{TRI}_{90\text{E}}$, which showed the lowest capacity to detect true negative values (19%). The sensitivity was comparable among all the MRIs, apart from $\text{MRI}_{95\text{B}}$, which exhibited higher accuracy (73%). However, this value is not very high, and this is due to the limited availability of data (1 year). Despite this, $\text{TRI}_{95\text{B}}$ showed the highest capacity to minimize the chances of incorrectly identifying some runs as positive when they are not.

Conclusions

This study proposed two new robustness indices, named TRI_{95B} and MRI_{95B} . These indices have the ambitious goal of overcoming the limits of the existing indices in the literature. TRI_{95B} has a more stable response when faced with a new regulation on DWTPs effluent quality (EU 2184/2020) that introduces statistical indicators to be compared with more stringent limits. Indeed, results showed that, compared to previous robustness indices, TRI_{95B} has higher accuracy and reliability when considering the requirements of the new regulation (turbidity < 0.30 NTU). TRI_{95B} also demonstrated better alignment with plant performance. When turbidity exceeded the T_{goal} within a run, TRI_{95B} fell within the “upset” class more frequently compared to other indices. Additionally, while other TRIs identified a critical condition (exceeding the threshold of the “upset” class) for high values of the discrepancy between the turbidity measured in the run and the target value, TRI_{95B} highlighted a failure condition for much lower values. Equally, MRI_{95B} was more accurate in the identification of critical conditions and instabilities of the process, showing a close correspondence with plant performance. Nevertheless, the accuracy of the assessments was lower than in TRI_{95B} , due to the limited availability of data and to the limited observation period. Moreover, TRI_{95B} was linked to variation of raw water quality at the inlet of the plant and to the occurrence of extreme and short-duration events. This will help identify the process unit most prone to performance fluctuations and their relationship with key process parameters. Overall, robustness indices can be considered an excellent diagnostic tool to detect deviations from desired water quality standards and reduce DWTP vulnerability.

6.3 Addressing emerging challenges by using Potassium Ferrate. Experimentation Results

6.3.1 Manganese removal

6.3.1.1 Stoichiometry of Mn(II) oxidation by Fe(VI) and Mn(VII)

To simulate the manganese removal by ferrate under ordinary and emergency situation, Mn(II) concentration in the raw water ranged between 0.100 mg/L (ordinary situation) and 0.900 mg/L (emergency). Results for Mn(II) oxidation by potassium ferrate and permanganate are depicted in Figure 6.23. As pH was not controlled in both the tests, it resulted slightly different when potassium ferrate or permanganate were used. Specifically, potassium ferrate involved a slight increase of pH that ranged between 8.2-8.6, showing an increasing trend with the Fe(VI) dose in accordance with previous study (Lim and Kim, 2009). In contrast, pH slightly decreased from 7.6 to 7.2 when the potassium permanganate dose was increased.

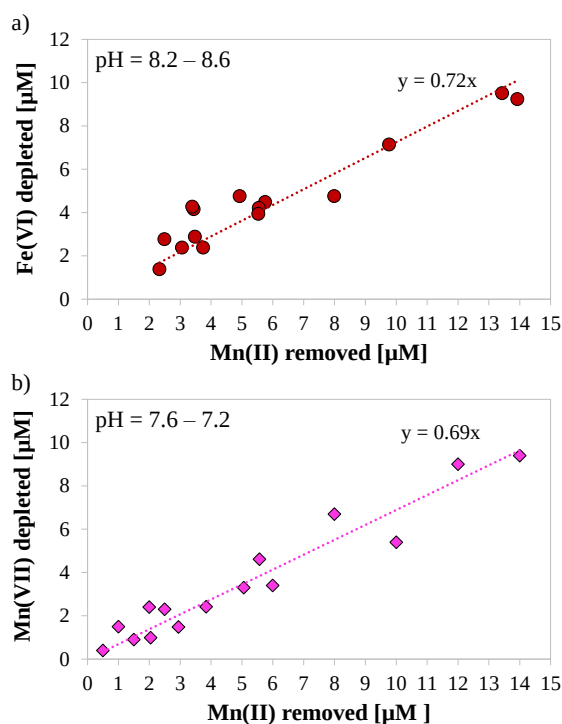
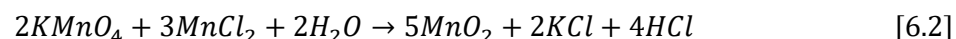
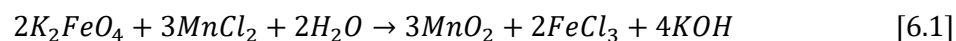


Figure 6.23. Relationship between the Fe(VI) (a) and Mn(VII) (b) depleted and the Mn(II) oxidized.

Linear regression of Fe(VI) and Mn(VII) depleted with Mn(II) removed resulted very similar, showing a slope of 0.72 and 0.69 for Fe(VI) and Mn(VII), respectively. In both the cases, the y-intercept was set to zero in order to consider no Mn(II) oxidation at zero oxidant dose. The above results indicated that the overall molar stoichiometry of the Mn(II) oxidation by Fe(VI) and Mn(VII) without any other oxidant demand was approximately 2:3 according to the following global reactions (Equation 6.1 and 6.2):



The above reactions indicated that the Mn(II) removal mechanisms exerted by Fe(VI) and Mn(VII) involved the transfer of two electrons to Mn(II) that formed manganese dioxide (Mn(IV)-Pyrolusite) in insoluble form precipitated at the end of settling phase.

Considering Equation 6.1, it should be noted that at the end of the reaction, Fe(VI) was reduced to Fe(III), which might react as coagulant-flocculant agent, thus providing additional removal capacity toward other pollutants. Nevertheless, any contribution of Fe(III) to Mn(II) removal was observed in these assays. The production of hydroxyl group (potassium hydroxide) was in line with the pH increase observed during the batch assays. In contrast, Mn(VII) was reduced to Mn(IV) thus contributing to the increase of manganese dioxide in the sludge (+40% than Fe(VI)), as reported in previous literature (Gregory and Carlson, 2003; Tobiasson et al., 2016). From a management point of view, special attention should be paid on this aspect, especially when flocculation and clarification is performed in sludge blanket units (Fouad and Hassan, 2018). Indeed, if sludge blanket is retained for a long period, eventually occurrence of reducing conditions within the sludge bed could lead to transformation of Mn(IV) to Mn(II) and its release in the effluent. Therefore, since the amount of manganese dioxide produced is approximately 40% lower when using potassium ferrate, the latter utilization in place of potassium permanganate could contribute to reduce the risk of Mn(II) release from sludge.

Overall, the stoichiometry of Mn(II) oxidation by Fe(VI) observed in this study was very similar to what reported in previous literature (Goodwill et al., 2016b). Specifically, these authors observed that the overall molar stoichiometry between Fe(VI) and Mn(II) was 0.67 under similar operating conditions of the present

study (absence of other oxidant demand). In contrast with what reported in the above study, in the present work pH was slightly higher (8.2-8.6 vs 6.5-7.5), thus indicating that at higher pH the stoichiometry of the Mn(II) oxidation reaction did not change significantly.

Other studies referred that Fe(VI) reduction resulted to intermediates like Fe(V) and Fe(IV) having higher reactivity than Fe(VI) that could reacted with Mn(II) (Sharma et al., 2022; Zhao et al., 2023). However, the Fe(VI) intermediates were not measured in this study and their presence was only hypothesized. Nevertheless, as reported in previous literature (Goodwill et al., 2016a), if Fe(V) and Fe(IV) were formed as intermediates in the reaction and they did not oxidize Mn(II), the slope of Fe(VI)/Mn(II) would result higher as more Fe(VI) would be necessary for Mn(II) oxidation.

To assess the effect of pH on the stoichiometry of Mn(II) oxidation by Fe(VI), two additional assays were carried out at pH 7 and 9. The results are reported in Figure 6.24.

In contrast to what reported in previous studies, ferrate was not observed at pH lower than 6 (Zhang et al., 2020). In a recent study, it was demonstrated that Fe(VI) decay was faster at pH lower than 9 and its complete disappearance occurred at $\text{pH} < 6.0$ (Wang et al., 2022). The same authors observed that Fe(V) and Fe(IV) started to generated from Fe(VI) decay at pH lower than 8. The above results indicated that when Mn(II) oxidation by Fe(VI) was carried out at pH lower than 9, the oxidative effect of Fe(VI) noticeably decreased, whereas in contrast the contribution of other intermediated likely increased. In this sense, other studies focusing on the role of Fe(V) and Fe(IV) on Mn(II) oxidation mechanisms should be necessary.

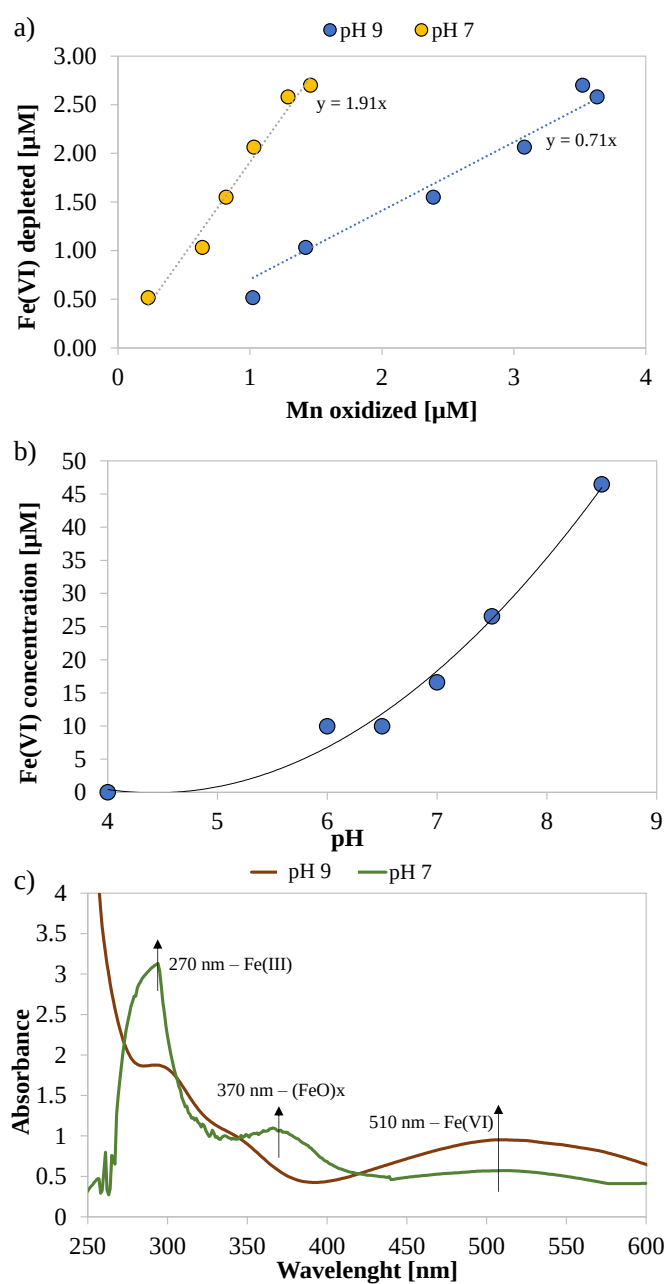


Figure 6.24. Relationship between the Fe(VI) and Mn(II) oxidized at pH 7 and 9 (a); Fe(VI) concentration in a Fe(VI) solution (10 mg/L in deionized water) under different pH (b); UV-vis absorption spectrum of the Fe(VI) solution at different pH (c)

6.3.1.2 Effect of Fe(III) on Mn(II) removal

Batch assays performed with potassium ferrate solution at neutral pH revealed that Fe(III) was the main iron compound derived from Fe(VI) decay/reduction. Basen on the literature review, any studies reported the possible role of Fe(III) in Mn(II) removal. To assess this, a specific assay in deionized water without oxidant demand (except of manganese) was performed. In this case, the initial Mn(II) concentration ranged between 2-14 μM , whereas Fe(III) dose was in the range 5-25 μM . Figure 6.25 shows the results for Mn(II) removal by Fe(III).

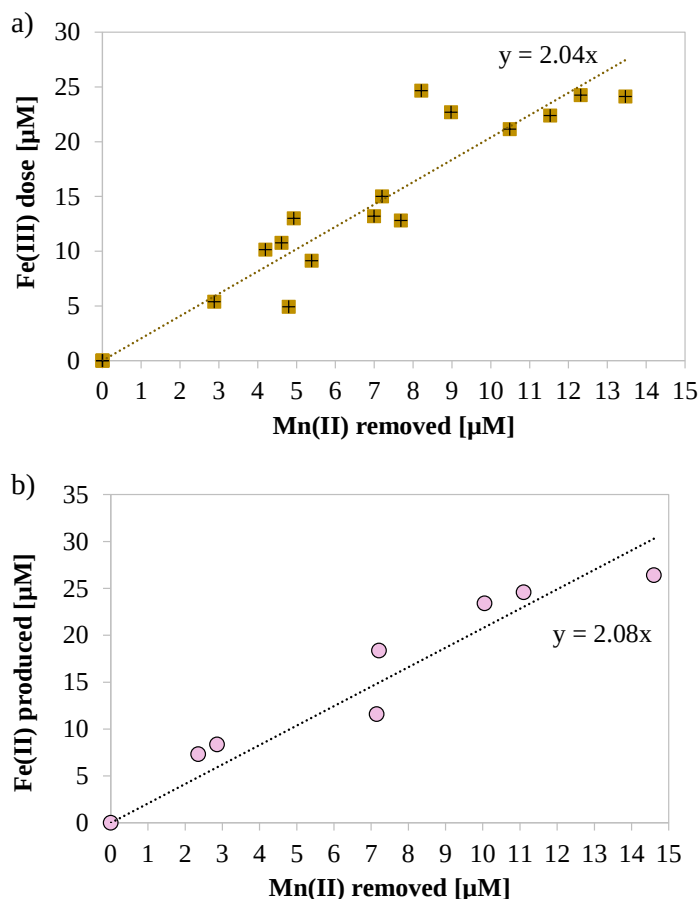
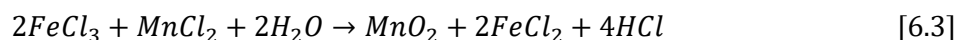


Figure 6.25. Linear regression between Fe(III) dose and Mn(II) removed (a); relationship between Fe(II) produced during Fe(III)-Mn(II) reaction and Mn(II) depleted (b)

The linear regression of the data indicated that the molar stoichiometry of the reaction between Fe(III) and Mn(II) was approximately 2:1. This value was similar to that achieved in the assay performed with potassium ferrate at neutral pH (1.90), thus suggesting that in that case the removal of Mn(II) was mainly attributable to Fe(III). It was interesting to note that at the end of the assay an increasing concentration of Fe(II) was observed, which resulted proportional to Mn(II) removed. This result indicated that Fe(III) underwent one electron transfer to Fe(II) and Mn(II) was oxidized to Mn(IV) as consequence. Based on the above results, the stoichiometry of Mn(II) removal by Fe(III) was hypothesized (Equation 6.3):



The implication of the above equation is that theoretically the oxidation reaction of Mn(II) by Fe(VI) could further proceed because the Fe(III) produced as a result of the reaction would be capable of further oxidizing Mn(II), although at a higher stoichiometric ratio compared to Fe(VI). However, in the assays carried out with Fe(VI), no contribution of Fe(III) to the overall oxidation reaction of Mn(II) was observed. In fact, if this had occurred, the demand for Fe(VI) in the oxidation of Mn(II) would have been lower, and the stoichiometric ratio would have been lower than 0.70. One possible explanation for this result could be attributed to the fact that the Mn oxidation assays with Fe(VI) were carried out with an excess of the latter. Indeed, as reported by Goodwill and co-authors (Goodwill et al., 2016b), the theoretical Fe(VI)/Mn(II) stoichiometric ratio is 0.67. Consequently, the presence of excess Fe(VI) implied that Mn(II) was preferentially oxidized by Fe(VI) rather than Fe(III), both due to the higher reactivity of the Fe(VI) molecule and its higher concentration in the solution.

6.3.1.3 Kinetics of Mn(II) oxidation by Fe(VI) and Fe(III)

To provide more insight into the Mn(II) oxidation reaction by Fe(VI) and the possible role of its reaction intermediates on the process, additional batch assays were carried out to investigate on manganese oxidation kinetics. Figure 6.26 depicts the results of Equation 6.1 and 6.3 kinetics.

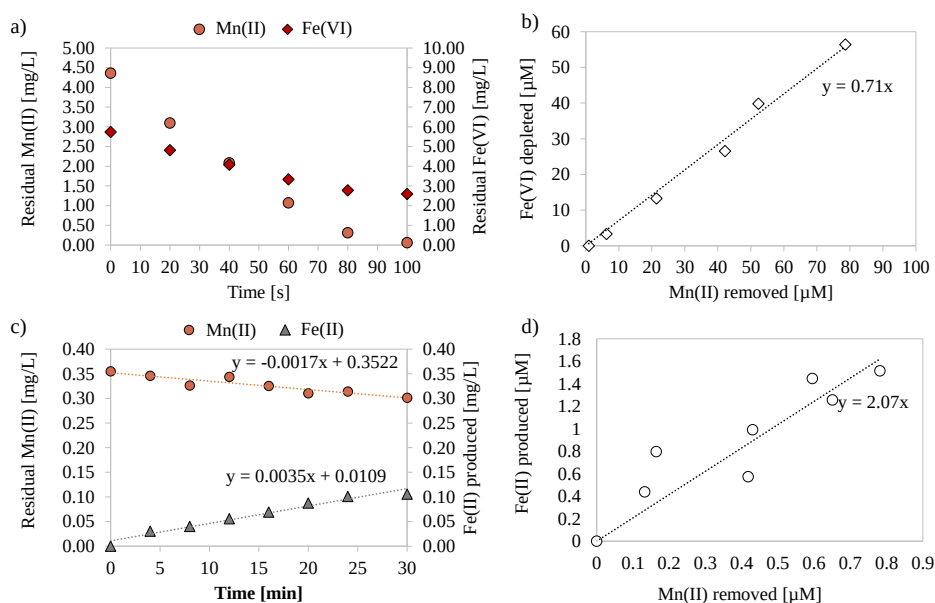


Figure 6.26. Kinetic of Mn(II) oxidation with Fe(VI) (a); relationship between Fe(VI) depleted and Mn(II) oxidized during the kinetic assay with Fe(VI) (b); Kinetic of Mn(II) oxidation with Fe(III) (c); relationship between Fe(II) produced and Mn(II) oxidized during the kinetic assay with ferric chloride (d)

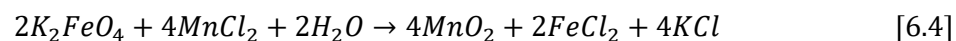
The oxidation reaction of Mn(II) by Fe(VI) exhibited a zero-order kinetic up to a concentration of approximately 0.30 mg_{Mn}(II)/L (Figure 6.26a). The Mn(II) oxidation rate resulted approximately 9.97×10^{-4} mM/s. At the end of the reaction, residual Fe(VI) was still measurable, indicating that the oxidation reaction of Mn(II) to Mn(IV) was entirely attributed to Fe(VI). To confirm this, the stoichiometric ratio between consumed Fe(VI) and removed Mn(II) showed a linear regression with a slope of approximately 0.70, consistent with previous results and with the theoretical molar ratio between Fe(VI) and Mn(II) of 2:3 (Figure 6.26b). The formation of Fe(II) was not observed at the end of this reaction, confirming that the produced Fe(III) did not react further.

The oxidation of Mn(II) by Fe(III) exhibited a zero-order kinetics similar to Fe(VI) but much slower (Figure 6.26c). In fact, the removal rate of Mn(II) by Fe(III) was found to be 5.5×10^{-7} mM/s, thus three orders of magnitude lower than that of Fe(VI). The simultaneous production of Fe(II) in a molar ratio with Mn(II) of approximately 2 indicated that the reaction proceeded according to Equation 6.3 (Figure 6.26d).

The aforementioned results confirmed the hypothesis regarding the contribution of Fe(VI) and Fe(III) to the oxidation of Mn(II). Since the oxidation reaction of Mn(II) with Fe(VI) is kinetically much faster than with Fe(III), in the presence of residual Fe(VI), it would rapidly oxidize the remaining Mn(II) compared to Fe(III). Consequently, although Fe(III) potentially produced from the reduction of Fe(VI) could remove Mn(II), this reaction cannot be observed when residual Fe(VI) is available because Mn(II) would be preferentially oxidized by Fe(VI).

6.3.1.4 Overall reaction of Mn(II) removal by Fe(VI)

Based on the results obtained from the kinetics of the oxidation reactions of Mn(II) with Fe(VI) and Fe(III), it has been observed that the reaction involving Fe(III) could be concurrent with that of Fe(VI). Consequently, this reaction can only occur if Fe(VI) is entirely depleted, i.e., if it is dosed at a stoichiometric deficit compared to Mn(II). From a theoretical standpoint, the resulting overall reaction from Equations 6.1 and 6.3 would be as follows (Equation 6.4):



To verify this hypothesis, further oxidation assays of Mn(II) with Fe(VI) were carried out, with different Fe(VI) dosages within the range of 0-14 μ M. The results are shown in Figure 6.27.

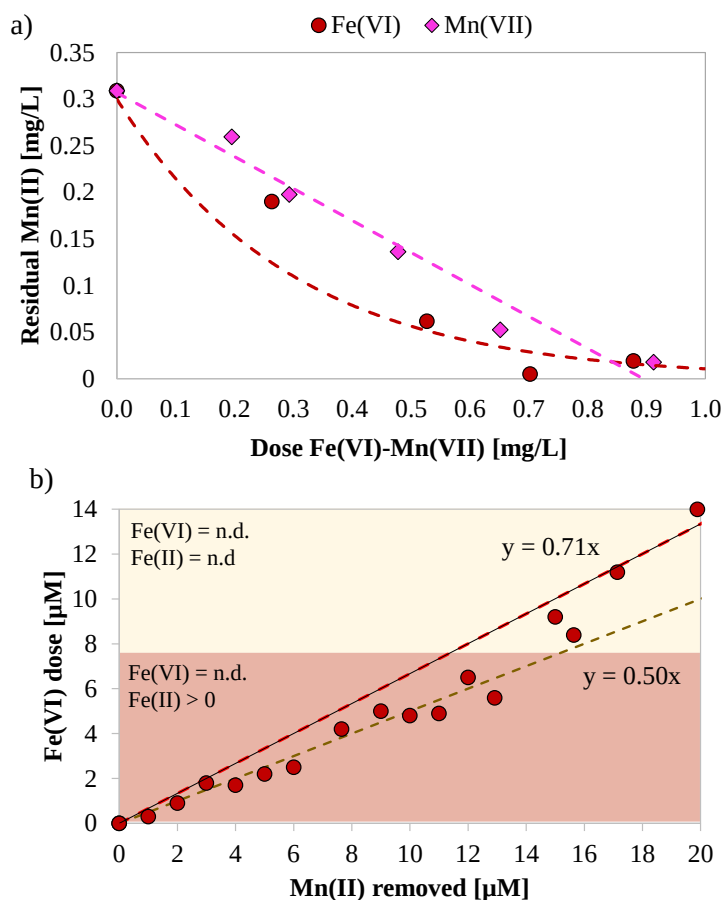


Figure 6.27. Relationship between the Fe(VI) dose and the Mn(II) removed

At low dosages of Fe(VI), the amount of removed Mn(II) was higher than the theoretical value predicted by Equation 6.1. Specifically, for Fe(VI) dosages below 8 μM , no residual Fe(VI) was detected, and the presence of Fe(II) was observed. In these tests, the average molar ratio between utilized Fe(VI) and removed Mn(II) was approximately 0.55, and the simultaneous presence of Fe(II) suggested that the Fe(III) produced from the reduction of Fe(VI) contributed to further oxidizing Mn(II). At Fe(VI) dosages greater than 8 μM , the average molar ratio between removed Fe(VI) and oxidized Mn(II) was approximately 0.71. In this case as well, no residual Fe(VI) was measured, but at the same time, no formation of Fe(II) was observed, suggesting that the formed Fe(III) did not react since all the available Mn(II) had already been oxidized by Fe(VI).

Therefore, in contrast to what reported in previous studies (Goodwill et al., 2016b), Fe(III) could contribute to remove Mn(II) from water, resulting in a decrease of the stoichiometric ratio between Fe(VI) and Mn(II).

In conclusion, it can be stated that the involvement of Fe(III) in the oxidation reaction of Mn(II) starting from Fe(VI) requires a slight deficit dosage of Fe(VI). However, considering the low reactivity of Fe(III) and the slow oxidation kinetics it is reasonable to assess that this process might not occur adequately within the pre-oxidation units of drinking water treatment plants due to the low hydraulic residence times. Nevertheless, Fe(III) could be effectively useful for metals and colloids removal, given its tendency to form hydroxides (Siéliéchi et al., 2008; Wu et al., 2010).

Overall, even not considering the contribution of Fe(III) to manganese oxidation, the dosage of K_2FeO_4 necessary was approximately 2.40 mg K_2FeO_4 per mg of Mn(II). Compared to other oxidants used for Mn(II) oxidation, the dose of Fe(VI) required was very similar. Indeed, in the absence of other oxidant demands chlorine dioxide oxidation of Mn(II) follows a stoichiometry of 2.45 mg ClO_2 per mg of Mn(II), permanganate (MnO_4^-) required approximately 1.95 mg $KMnO_4$ per mg of Mn(II), whereas ozone (O_3) oxidizes Mn(II) with a lower demand of 0.87 mg O_3 to 1.0 mg Mn(II) ratio although incurring very high production costs (Tobiason et al., 2016). Besides, while those oxidants can lead to downstream water quality problems like in situ formation of permanganate (ozone), formation of by-product chlorite (chlorine dioxide) or formation of additional particulate Mn(IV) that must be removed (permanganate), Fe(VI) by-products are not harmful and potentially useful to the water treatment process (Zhang et al., 2020).

6.3.2 Removal of NOM and turbidity

6.3.2.1 Removal of NOM with ferrate and permanganate

Removal of NOM by Fe(VI) was studied to focus on the degradation capacity of Fe(VI) toward organic pollution in drinking water. Figure 6.28 shows the trends of residual TOC as the dosage of Fe(VI) increases, with or without soluble manganese as Fe(VI) activator. Results were compared with potassium permanganate as conventional oxidant.

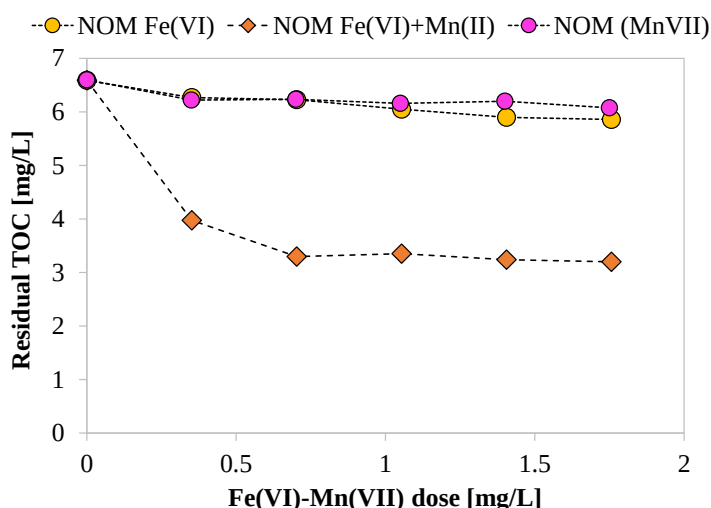


Figure 6.28. Trend of residual TOC at increasing dose of permanganate and ferrate with or without Mn(II) in the solution (pH = 8).

In the presence of NOM only in the water, the TOC removal efficiency was found to be very modest, and results were comparable with those obtained with Mn(VII). In fact, at the maximum Fe(VI) dosage of approximately 1.8 mg/L, removed TOC was only 10%, indicating a poor oxidative capacity of Fe(VI) under alkaline condition (pH = 8). These findings aligned with observations reported in other studies regarding the transformation and removal of NOM using Fe(VI) (Zhang et al., 2020). According to previous literature, at an alkaline condition the reduction potential of Fe(VI) is lower than at pH lower than 7, thus leading to poor NOM mineralization capacity (Lim and Kim, 2009; Zhang et al., 2020). In this context, Deng and co-authors suggested that NOM removal by ferrate increased as ferrate decomposition was improved (Deng et al., 2018). Therefore, as at high pH Fe(VI) is stable in its form, poor NOM removal was

observed. In a recent study, it was observed that the single use of ferrate for NOM removal was effective at pH of 5, thus suggesting that the more reactive forms towards NOM removal derived from Fe(VI) decomposition (Tien Khoi et al., 2023).

When soluble manganese was also added to the medium ($\text{Mn(II)} = 0.9 \text{ mg/L}$), the TOC removal efficiency increased significantly, reaching around 55%. In this case, in fact, although at low dose of Fe(VI) (0.7 mg/L), the residual TOC was 3.3 mg/L ; furthermore, as the Fe(VI) dose increased, the residual TOC remained nearly constant, thus suggesting that the maximum removal was already achieved at the lower doses. Previous studies demonstrated that the oxidation capacity of Fe(VI) depends on the involvement of intermediate iron species resulting from Fe(VI) reduction (Barışçı, 2017). In more detail, it has been demonstrated that generation of Fe(V) and Fe(IV) as intermediate of Fe(VI) reduction to Fe(III) is a crucial step for achieving high oxidation performances toward organic matter (Luo et al., 2022a, 2022b). Indeed, such molecules are reported to have up to 2-5 order of magnitude more reactive than Fe(VI) (Sun et al., 2019). In this sense, a recent study demonstrated that colloids manganese dioxide were able to accelerate the formation of Fe(V) and Fe(IV) from Fe(VI), leading to the formation of reactive intermediates very active toward NOM (Luo et al., 2022b). In this case, Mn(II) oxidation to Mn(IV) could likely contributed to activate Fe(VI) and promoted NOM removal. Nevertheless, it should be stressed that the absence of Mn or its concentration being insufficient to generate significant concentrations of Fe(VI) reduction intermediates could result in an ineffective reduction of organic substances in water. However, it should be noted that literature reports various compounds capable of serving as Fe(VI) activators, many of which are naturally present in river or reservoir waters (Sharma et al., 2022).

Moreover, it should be considered that when ferrate decomposition occur, Fe(III) is generated. In other literature studies, it was reported that ferrate pre-oxidation had positive effect on coagulation/flocculation of NOM (Jiang et al., 2016) because of Fe(III) production. Indeed, negatively charged compound of NOM are removed by iron ions by formation of colloidal hydroxides (Liao et al., 2017). Therefore, the simultaneous generation of Fe(III) deriving from Fe(VI) reduction is of significant importance as it may allow the removal of NOM from water and at the same time the use of lower coagulant doses due to the Fe(III) introduced by ferrate decomposition.

6.3.2.2 Removal of turbidity: using ferrate as enhancer coagulant/flocculant

Results on turbidity removal using conventional coagulant/flocculant and Fe(VI) as enhancer agent are presented in Figure 6.29. As the dose of PACl increased, the residual turbidity sharply decreased below 1 NTU and a minimum of 0.41 NTU was achieved at 20mgPACl/L dose. At higher dose, the residual turbidity increased, thus suggested that the excess of PACl caused by itself an increase of turbidity. Although very high removal of turbidity was obtained (93%), the lowest value obtained resulted higher than the limit introduced by the new Directive (EU) 2020/2184 already in force in many member states.

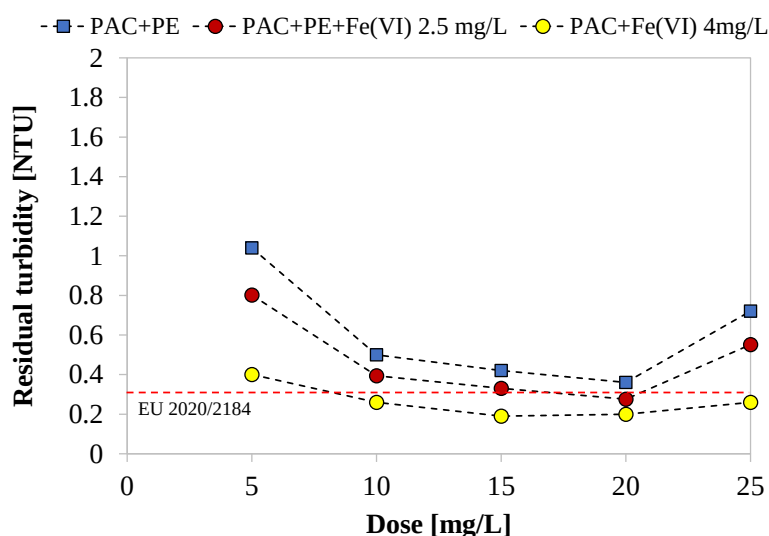


Figure 6.29. Residual turbidity of real surface water samples at different dose of PACl without (■) or with Fe(VI) at 2.5 mg/L (●) and 4 mg/L (●). The red dotted line indicates the limit imposed by Directive EU 2020/2184

Addition of a constant dose of Fe(VI) (2.5mg/L) improved turbidity removal. Indeed, while dosing Fe(VI) a residual turbidity lower than 0.30 NTU (0.27 NTU) was obtained at 20 mg_{PACl}/L. Therefore, compliance with the regulatory limit and approximately 25% of conventional chemicals saving was achieved using Fe(VI) as coagulant/flocculant enhancer. Nevertheless, a further increase of Fe(VI) dose to 4 mg/L significantly decreased the residual turbidity. A minimum of 0.19 NTU was obtained at a PACl dose of 15 mg/L, whereas the value of residual turbidity closer to the regulation limit (0.27 NTU) was achieved at 10 mg_{PACl}/L. Overall,

the obtained result were in line with previous studies, in which high turbidity removal (>80%) from reservoir water was achieved using Fe(VI) only (Zhang et al., 2020). Nevertheless, in that study, the residual turbidity using Fe(VI) only never resulted lower than 2 NTU, indicating that Fe(VI) should be used as a complementary treatment to conventional processes. The present study demonstrated that the addition of Fe(VI) to conventional coagulant/flocculant agent allowed a noticeable decrease of PACl dose (> 50%) to comply 0.30 NTU. A significantly smaller dose of PACl can significantly reduce the chemical requirements, providing the potential for significant cost savings in the treatment of drinking water. It is important to emphasize that Fe(VI) is used as an oxidant rather than a pure coagulant/flocculant agent. Hence, the operating cost associated with Fe(VI) use should not be considered an additional expense for the coagulation/flocculation process. As previously mentioned, the byproducts of Fe(VI) oxidation, such as ferric ion or ferric hydroxide, act as fundamental coagulant resources. (Jiang et al., 2018). Therefore, Fe(VI) can also perform coagulation after degrading organic matter and microorganisms or oxidizing inorganic substances (e.g., metals). Based on the achieved results, it can be stated that Fe(VI) allow complying more stringent regulations and at the same time providing additional removal capacity of turbidity and treatment robustness in the case that extreme event entailed increases in raw water turbidity.

6.3.3 Algae removal

6.3.3.1 Performance and mechanisms of algae removal

Potassium ferrate was tested to remove algae, and its efficiency was compared with another oxidating agent (i.e., potassium permanganate). Figure 6.30 reports the results of the assays carried out with the above reagents (Figure 6.30a), the removal efficiency achieved (Figure 6.30b) and the removal mechanisms hypothesized (Figure 6.30c).

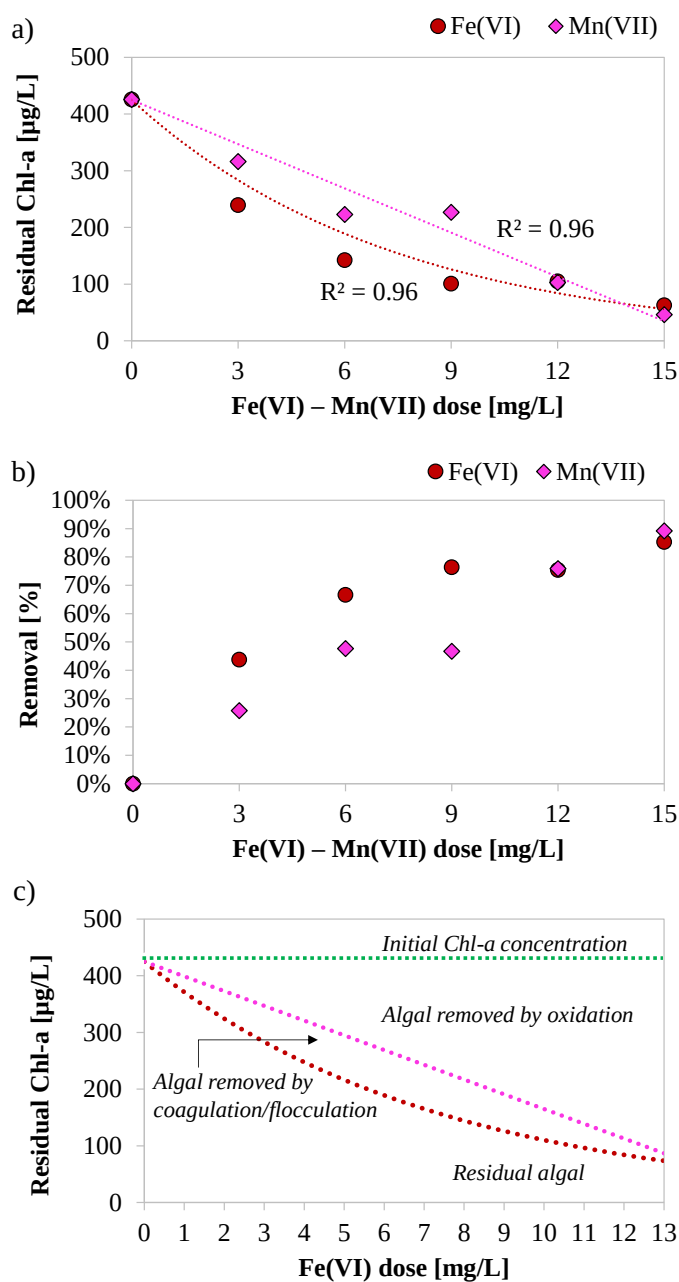


Figure 6.30. Removal of Chl-a with Fe(VI) and Mn(VII) at different dose (a); removal efficiency of Chl-a with increasing dosage of Fe(VI) and Mn(VII) (b); possible mechanisms of algal removal by ferrate and permanganate (c)

The concentration of Chl-a measured in the supernatant at the end of the jar test procedure gradually decreased with increasing doses of both Fe(VI) and Mn(VII) (Figure 6.30a). Specifically, the lowest Chl-a concentration of approximately 80 µg/L was achieved at the maximum dosage for both reagents (15 mg/L). However, it should be noted that the trend of Chl-a concentration removal with Fe(VI) was different from that of Mn(VII). While a nearly linear relationship was observed between the dosage of Mn(VII) and Chl-a removal (Chen and Yeh, 2005), the regression line for Fe(VI) followed a decreasing exponential trend. This implied that at the same reagent dosage, the residual Chl-a concentration was lower with Fe(VI) compared to that obtained with Mn(VII). However, this difference gradually diminished with increasing reagent doses, and at the maximum dosage, both reagents provided the same 90% removal efficiency (Figure 6.30b). Nevertheless, Fe(VI) allowed for removal efficiencies of around 80% even at lower dosages, approximately 30% lower than Mn(VII).

The exponential trend observed in the curve interpolating the data in Figure 6.30a indicated that besides Fe(VI), there were other compounds involved in the algae removal reaction, and their contribution decreased as the dosage of Fe(VI) increased. In previous study, it was stated that several process mechanisms are thought to be responsible for the efficient removal of algae through pre-oxidation with potassium ferrate (Kubiňáková et al., 2017). Specifically, the inactivation of algae and the subsequent formation of an intermediate form of iron, induced by Fe(VI) pre-oxidation, acted as a coagulant aid, ultimately resulting in the formation of algae agglomerates (Ma and Liu, 2002). Based on the obtained results, it was hypothesized that the Fe(III) generated from the reduction of Fe(VI) actively contributed to algae removal, albeit through a different mechanism than observed for manganese removal. In fact, the presence of Fe(II) was not detected in any of the analysed samples, indicating that the effect of Fe(III) on algae was not primarily oxidative but rather coagulation/flocculation (Figure 6.30c). As observed for manganese removal, it is possible that at low Fe(VI) dosages, being stoichiometrically deficient compared to the target pollutant (algae in this case), it may be depleted before complete removal of the pollutant. Consequently, slower concurrent reactions involving the oxidation byproducts (i.e., Fe(III)), can occur and contribute to reduce the residual algae concentration. On the other hand, at high Fe(VI) concentrations, the increased availability of Fe(VI) led to algae removal primarily through oxidation and mineralization mechanisms.

However, it should be noted that compared to conventional oxidizing agents, Fe(VI) allows for a significant improvement in algae removal efficiencies at lower dosages, while reducing the risk of potentially harmful byproduct formation.

6.3.3.2 Integration of ferrate with conventional flocculating agent for algal removal

The removal effect of algae by Fe(VI) was also evaluated synergistically with conventional coagulant/flocculant agents used in drinking water treatment plants. Figure 6.31 shows the trend of residual Chl-a concentration as a function of increasing coagulant dosage (PACl) without and with a constant dosage of Fe(VI) and Mn(VII). In particular, the results of the two assays with constant Fe(VI) and Mn(VII) concentrations shown in Figure 6.31 refer to the optimal dosage of ferrate (Figure 6.31a), which was 9 mg/L (as Fe(VI)), and permanganate dosage (Figure 6.31b) of 15 mg/L (as Mn(VII)), in accordance with the previous test.

PACl was capable of effectively removing algae, although at a high consumption ($> 25 \text{ mg}_{\text{PACl}}/\text{L}$). Certainly, the dosage of potassium permanganate on one hand and Fe(VI) on the other hand allowed for a reduction in the required flocculant quantity. Specifically, to achieve Chl-a concentrations on the order of 10 mg/L, approximately 20 mg/L of PACl had to be dosed in addition to 15 mg/L of potassium permanganate (as Mn(VII)), while for Fe(VI), the PACl dosage was approximately half (10 mg/L) and the Fe(VI) dosage was 9 mg/L. The above results were in line with previous studies in which a removal of algae close to 90% was achieved by supplying 5 mg/L of Fe(VI) with a 15 mg/L of alum (Ma and Liu, 2002).

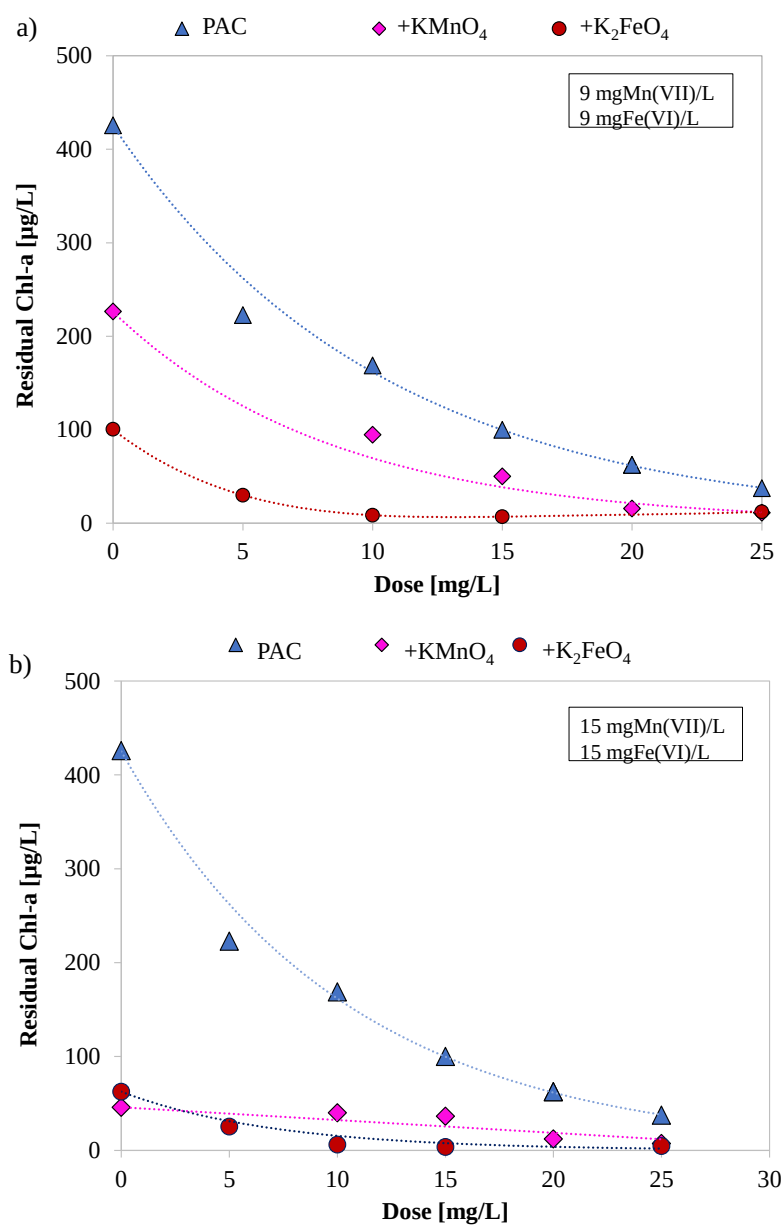


Figure 6.31. Chl-a removal using PACl at different dosage with the addition of 9 mg/L of Mn(VII) and Fe(VI) (a) and 15 mg/L of Mn(VII) and Fe(VI)

The use of Fe(VI) reduces the conventional coagulant dosage by almost 50% to lower the algae concentration. This result is important, especially in a context where the risk of algal blooms is very high due to climate change, and the frequency of such phenomena is more frequent. Consequently, Fe(VI) can be used as a reagent under normal conditions as well as in emergency situations, considering the possibility of on-site production when needed through electrochemical methods.

Conclusions

In the present study, the potential of Fe(VI) in removing three classes of pollutants (manganese, NOM, algae) was tested. The presence of these pollutants in surface waters intended for human consumption increased in recent years because of climate change, thus creating emergency situations to be faced. The obtained results confirmed that Fe(VI) can achieve high removal efficiencies for all the examined contaminants, often outperforming conventionally used reagents. Specifically, for manganese removal, the Fe(VI) dose can be lower than the stoichiometric dose (< 2 mol of Fe(VI) per 3 mol of Mn(II)), as the reaction by-products (Fe(III)) can contribute to further Mn(II) removal. Activation of Fe(VI) is required for NOM removal, which can be achieved through the simultaneous presence of soluble manganese in the water. Furthermore, the use of Fe(VI) allows for a reduction of approximately 50% in the quantity of oxidizing/coagulating agents required for algae and turbidity removal. Therefore, treating drinking water with Fe(VI) represents a promising process that can be used as an alternative or in conjunction with conventional methods to address the challenges posed by climate change, ensuring high quality standards and process sustainability.

6.4 Evaluation of Fe(VI) electrochemical production and stability

Ferrate(VI) electrochemical production tests conducted under different operating conditions showed different results.

As it is possible to observe from the graph in Figure 6.32, only tests number 3 and 6 resulted in a moderate production of ferrate(VI), exhibiting significant concentrations. These latter showed an asymptotic trend, characterized by an initial phase of linear growth in the first few minutes, until reaching a nearly steady value. In more detail test 3 reached the maximum Fe(VI) concentration, equal to 300 mg/L, after 15 minutes; instead, test 6 achieved a slightly higher concentration, close to 340 mg/L, after 10 minutes.

The significantly higher Fe(VI) concentration in tests 3 and 6, compared to other tests, is mainly due to the greater current intensity applied during the production process.

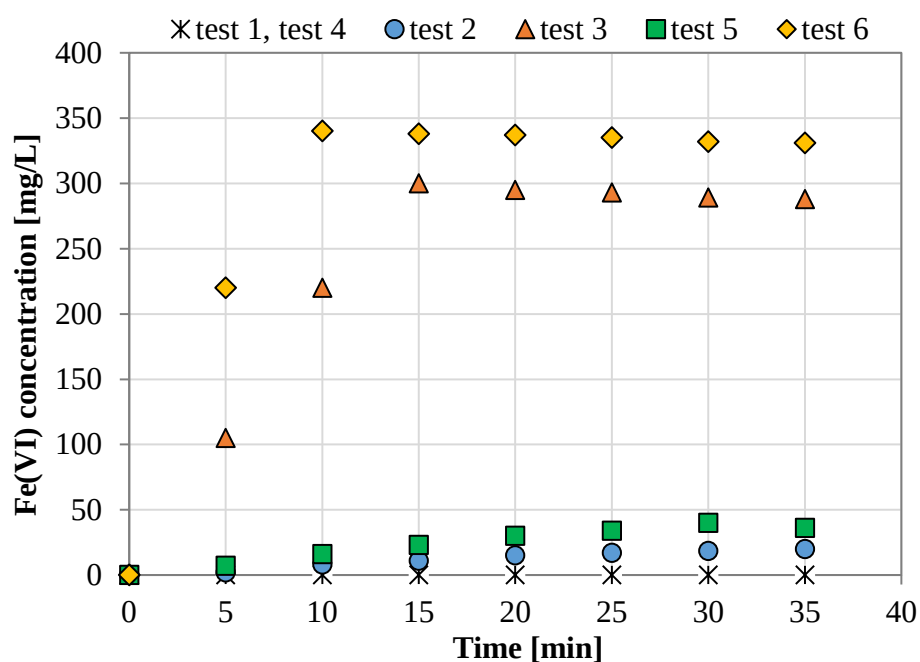


Figure 6.32. Fe(VI) concentration over time during electrochemical production tests

It should be noted that ferrate production stopped when a concentration far below the saturation level of ferrate in the electrochemical solution was reached. Consequently, it can be stated that the process interruption was not due to solution saturation. It is more likely, however, that the interruption was due to the isolation of the reaction electrode, caused by the formation of surface deposits that limited its contact with the electrochemical solution. Additionally, it cannot be ruled out that the configuration of the undivided cell reactor played a key role in this process. Indeed, undivided cell electrochemical reactors have several significant limitations. First, the lack of separation between the anode and cathode can lead to the recombination of oxidized and reduced products, reducing the efficiency of the desired reagent production and promoting unwanted side reactions. Moreover, formation of deposits on one or both electrodes could occur. In this respect, without separation, products can accumulate on the electrodes, isolating them from the electrochemical solution and halting the process, as above described. It could be also considered that since there is no barrier separating the anodic and cathodic compartments, part of the energy can be lost to side reactions, reducing the overall efficiency of the process. These limitations often make undivided cell reactors less suitable for processes that require high purity and product stability or for large-scale applications.

The specific production rate was calculated by considering the initial linear segment.

Results on ferrate(VI) production tests are summarized in Table 6.8.

Table 6.8. Results on ferrate(VI) electrochemical production

Tests	Electrolytic solutions	Molarity [M]	Current intensity [mA]	Max Fe(VI) concentration [mg/L]	Specific production rate [mg/L min cm ²]
1	NaOH	6	160	-	-
2	NaOH	10	160	20	0.07
3	NaOH	10	1000	300	2.50
4	KOH	6	160	-	-
5	KOH	10	160	40	0.17
6	KOH	10	1000	340	4.25

From the results obtained, it emerged that the principal problem for the electrochemical production of ferrate(VI) is the low current efficiency (or low concentration of ferrate(VI)), with consequent increase of the production costs.

With the aim of industrial application of the process, an additional problem is to reduce the cell voltage of electrolyzers, by reducing overvoltage for hydrogen production at the cathode (Diaz et al., 2021). Using of recycling iron or modifying the electrochemical reactor configuration (divided cells configuration) (Cai et al., 2021) could be suitable solutions to the above concerns, although more insights on these aspects are necessary.

It should also be considered that, given the high pH of the ferrate solution, dosing a certain mass of ferrate into a given volume of water to be treated would require a correspondingly large volume of solution. This would result in a significant increase in the water's pH, leading to notable alterations in its composition. Ideally, therefore, it would be necessary to maximize the ferrate concentration in the high-molarity solution so that dosing a known mass of ferrate would require only a modest volume, minimizing any significant alteration in the water's pH.

Therefore, the current systems for ferrate production are not sustainable from both an economical and industrial point of views, since the low production yield and technical drawbacks limit and reduce the benefits deriving from its use in place of other conventional chemicals.

In parallel to ferrate production tests, also stability assays of the produced ferrate were performed. Figure 6.33 depicts the results of the stability tests of ferrate(VI).

The graph reported in Figure 6.33a provides valuable insights into how the concentration of Fe(VI) changes over time under different conditions. All samples showed a decrease in Fe(VI) concentration and the rate of decrease varied between each of them, indicating differences in reaction kinetics. In more detail, samples A, B and D had a consistent reduction, and the concentration after 60 minutes were the lowest (close to 280 mg/L) among the other samples. Samples C and E exhibited a less pronounced reduction in concentration, reaching values slightly higher (~300 mg/L) than the previous ones. Sample F showed the least significant reduction, and the concentration remained almost constant over time and close to 325 mg/L.

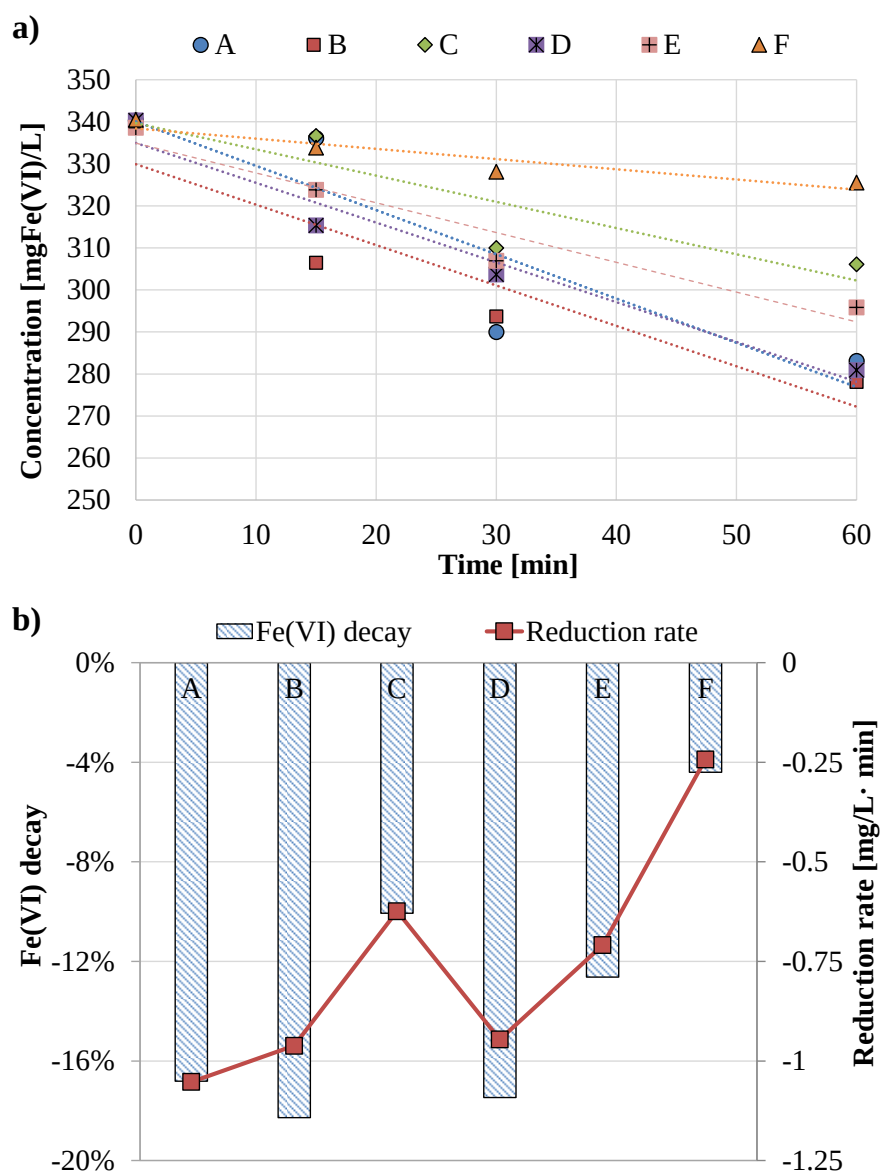


Figure 6.33. Reduction of ferrate(VI) concentration over time at different boundary conditions (a); ferrate decay and reduction rate after 1 hour (b).

Boundary conditions: A. sample exposed to light and kept at room temperature; B. sample kept in the dark and at room temperature; C. sample exposed to light and kept at 4°C; D. sample kept in the dark and at 4°C; E. oxygen saturated sample; F. deoxygenated sample.

From the observation of the graph in Figure 6.33b it resulted that:

- in samples A, B and D the Fe(VI) decay was approximately 17%, 18% and 17,5%, respectively and the reduction rate was equal to 1 mg/L h in sample A and 0.95 mg/L h in samples B and D;
- in sampled C and E both the Fe(VI) decay (10% and 12.5%, respectively) and the reduction rate (0.65 mg/L h and 0.7 mg/L h, respectively) were lower than the previous ones;
- sample F appeared to be the most consistent, maintaining the lower reduction rate (0.25 mg/L h) with minimal Fe(VI) decay (4.5%).

Therefore, results indicated that the stability/instability of ferrate(VI) is closely influenced by several factors, such as temperature, exposure to light and oxygenation conditions. In more detail, it emerged that ferrate(VI) is light-sensitive and its decomposition is accelerated by higher temperatures. Moreover, dissolved oxygen also contributes to the decay of Fe(VI); in fact, oxygen indirectly promotes its decomposition, creating an oxidant environment that can lead to the occurrence of side-effect oxidative reactions. Thus, deoxygenated conditions offer a significant advantage for ferrate(VI) stability, especially in combination with low temperatures and light protection.

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Overall Conclusions

Drinking water treatment plants (DWTPs) play a critical role in providing safe drinking water to communities. In recent years, climate change has exacerbated challenges by affecting the quality of raw water sources. According to a throughout literature review, it arose that the main effects of climate change in terms of water quality impacts are referred to three main concerns: (i) increase of soluble metals (Fe, Mn, Al) which are released from lake sediments under anoxic conditions, (ii) algal bloom due to the increase of water temperature in nutrients rich lakes, (iii) increase of natural organic matter (NOM) concentration and turbidity as a consequence of extreme precipitation events.

In addition, the recent entry into force of Directive (EU) 2020/2184, concerning the quality of water intended for human consumption, set stricter limits for turbidity and percentile statistics for continuous compliance, demanding greater robustness of the treatment processes.

These changes pose challenges to traditional water treatment plants, needing innovative approaches.

To address these issues, the thesis proposes a turbidity robustness index, TRI_{95B} , and a manganese robustness index, MRI_{95B} , to be used as a warning tool for detecting deviations from water quality standards and identifying process units that, by losing robustness, require alternative treatment solutions. In this light, Ferrate(VI) was explored as a potential solution to address climate change-related water emergencies, either alone or in combination with conventional reagents to producing safe potable water.

The first research topic showed that robustness indices represent a quantitative measure to assess how well a plant is performing in maintaining water quality standards while providing an early warning system by detecting deviations from desired water quality standards. The results reported in this study demonstrated that when considering the 95th percentile as a reference parameter for turbidity, the DWTP was not able to comply with the requirements of the new regulation. This suggested that a thorough and accurate analysis of the plant's robustness is required to provide high-quality water to consumers.

The TRIs already available in the literature and the one proposed in this study have demonstrated good reliability concerning the objectives set by the old regulations referring to water turbidity. Conversely, when considering a lower

threshold, the old TRIs showed poor adaptability, while the new robustness index was proven to be more reliable.

Overall, TRI_{95B} showed a greater capability of synthetically and effectively describing the variability of plant performance, allowing highlighting process failures more accurately than the other TRIs. More specifically, the greater sensitivity shown by the TRI_{95B} i.e., the ability to identify failures even if they are of short duration and low magnitude, complies with the purpose of the new regulation for drinking water. The generalizability of the proposed index should be further investigated in other contexts (e.g. different dataset, different processes, different regulations). In this sense, future studies are recommended to increase the reliability of TRI_{95B}.

Similarly, also MRI_{95B} showed significantly higher sensitivity and specificity, although it was found that the limited availability of data acquired during the single run has reduced the robustness of the index.

The use of these RIs could represent a useful evaluation tool for DWTP managers to identify and address potential issues especially if they are associated with certain conditions (e.g., units' overload, significant variability of influent turbidity). Such an approach can also be helpful in identifying process units that exhibit criticality and vulnerability to specific load conditions. In this sense, by monitoring RIs during time, operators could proactively manage risks associated with process upset, thus contributing to minimize process vulnerability.

Within this approach, using robustness indices could be helpful to predict how systems behave when subjected to different loads, environmental conditions, or operational disturbances. In this way, the application of the indices could highlight operational occurrences that stress specific process units, allowing the plant operator to mitigate or avoid process dysfunctions. In addition, the implementation of algorithms within the SCADA system for the real-time measurement of RIs and TLI would ensure a proactive approach and allow identifying failure units or processes and suggest preventive measures. In this sense, a real-time analysis of plant conditions could enable operators to forecast the long-term stability and reliability of a drinking water treatment plant, and act promptly before an issue arises, which is crucial for providing safe water to population.

Additionally, in a context of climate change, which leads to the occurrence of extreme and short-duration events, the index can be useful for assessing the

potential vulnerability of the plant. In this regard, a useful approach is to identify, through the index, a threshold value for a given event that leads to a robustness loss of the plant. The identification of such threshold can be useful for the operators to activate emergency protocols and systems capable of achieving the required quality standards.

In this regard, the second research topic demonstrated the effectiveness of ferrate (Fe(VI)) as a promising and potential solution in drinking water treatment, particularly in addressing challenges caused by climate change, such as the increasing presence of the key classes of pollutants (manganese, NOM, turbidity and algae). Since the presence of such pollutants in surface water can lead to water quality emergencies, requiring immediate attention and innovative treatment solutions, Fe(VI) offers a sustainable and effective alternative, ensuring that water treatment processes can maintain high-quality standards and remain robust while adapting to evolving environmental conditions.

Its ability to efficiently remove pollutants while reducing the need for additional chemicals makes it a strong candidate for use either as a standalone treatment or in combination with conventional methods.

However, further studies are needed to address potential gaps in the application of the indices and to better understand how to integrate Fe(VI) into the existing processes.