DEVELOPMENT OF AN ENVIRONMENTAL DECISION SUPPORT SYSTEM TO ENHANCE COAGULATION IN DRINKING WATER TREATMENT PLANTS

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Universitat de Girona

DOCTORAL THESIS

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Annex 1-4

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WE DECLARE:

That the thesis "Development of an environmental decision support system to enhance coagulation in drinking water treatment plants", presented by Jordi Suquet Masó to obtain a doctoral degree, has been completed under our supervision and meets the requirements to opt for Doctor degree.

For all intents and purposes, we hereby sign this document.

Dr. Hèctor Monclús Sales   Dr. Lluís Godo Pla

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List of publications

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- Suquet, J.; Godo-Pla, L.; Valentí, M.; Ferrandez, L.; Verdaguer, M.; Poch, M.; Martin, M.J.; Monclús, H., 2021. Assessing the effect of catchment characteristics to enhanced coagulation in drinking water treatment: RSM models and sensitivity analysis. Sci. Total Environ. 799, 149398. https://doi.org/10.1016/j.scitotenv.2021.149398

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- Valentí, M.; Suquet, J.; Godo-Pla, L.; Verdaguer, M.; Poch, M.; Monclús, H.; Martín, M.J. (2020). Hacia el desarrollo de un sistema de ayuda a la decisión para el tratamiento de aguaspotables: de la investigación básica a la óptima operación en planta real: Proyecto Watson. 003115 - RETEMA: revista técnica de medio ambiente. 220, pp. 112 - 117. ADC Media Ediciones Técnicas. https://webgrec.udg.edu/arxius/TPAREXFA/001701-1761.pdf

- Godo-Pla, L., Rodríguez, J.J., Suquet, J., Emiliano, P., Valero, F., Poch, M., Monclús, H. (2020). Control of primary disinfection in a drinking water treatment plant based on a fuzzy inference system. Process Saf. Environ. Prot. 145, 63–70. https://doi.org/10.1016/j.psep.2020.07.037

List of acronyms and symbols

AF	After flood
AI	Artificial Intelligence
ANN	Artificial neural network
ATL	Ens d'Abastament d'Aigua Ter-Llobregat
BDCM	Bromodichloromethane
BF	Before flood
CapEx	Capital expenditures
CCD	Central composite design
Cd	Coagulant dose
CFD	Computational fluid dynamics
DBCM	Dibromochloromethane
DBPs	Disinfection by-products
DOM	Dissolved organic matter
DWTP	Drinking water treatment plant
DWTP 1	Llobregat DWTP (Abrera)
DWTP 2	Ter DWTP (Cardedeu)
DWTP 3	Ter DWTP (Montfullà)
EDR	Electrodialysis reversal
EDSS	Environmental decision support system
Fd	Flocculant dose
FDS	Fraction of design space
GAC	Granular Activated Carbon
HF	Hollow fiber
HMW	High molecular weight
HPLC	High performance liquid chromatography
HRT	Hydraulic retention time
IoT	Internet of Things
K	Permeability
LMW	Low molecular weight
NOM	Natural organic matter

NTU	Nephelometric units
OFAT	One factor at a time
OpEx	Operational expenditures
PAC	Polyaluminium chloride
PO	Primary oxidation
PVDF	Polyvinylidene difluoride
RS	Response surface
RSM	Response surface methodology
SC	Sampling campaigns
SCADA	Supervisory control and data acquisition
SE	Standard error
SRs	Supervision rules
SUVA	Specific ultraviolet absorbance
TC	Total carbon
THMs	Trihalomethanes
TMP	Transmembrane pressure
TOC	Total organic carbon
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
UV_{254}	Ultraviolet absorbance at 254nm
WHO	World Health Organization

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Summary

Currently, the access to safe drinking water remains to be crucial for mankind development. Due to the geographical context, changes in demography and climate change perspectives, there are regions where water resources are being altered in terms of quantity and quality, compromising future generations availability. Within this context, drinking water treatment plants (DWTPs) are aimed to remove water pollutants through several processes to produce safe drinking water. For DWTPs, one of the main challenges is natural organic matter (NOM), a group of organic compounds which has the capacity to react during the water treatment to generate disinfection by-products (DBPs).

Inside the drinking water treatment train, coagulation is a conventional physicochemical treatment presenting high potential in terms of NOM removal. From here, the optimisation of coagulation for NOM removal at full-scale level can be achieved based on water quality. DWTPs digitalisation is increasing, providing a number of online measurements which allow to control NOM from the catchment to the final produced waters, including coagulation step.

The main objective of this thesis is the development of enhanced coagulation environmental decision support systems (EDSS) aimed to optimise coagulation for NOM removal at three surface water DWTPs located in the Mediterranean region.

To achieve that, an enhanced coagulation EDSS is developed and a three-level operation is proposed: data acquisition, control and supervision levels (Chapter 4). The EDSS was designed to propose the optimal values of coagulant dose (Cd) and pH based on raw water characteristics. From this, enhanced coagulation empirical models based on response surface methodology (RSM) were developed to be integrated into the EDSS control level. These models were aimed to remove turbidity, total organic carbon (TOC) and ultraviolet absorbance at 254nm (UV_{254}). Then, several supervision rules (SRs) were incorporated at the supervision level. These were designed based on expert knowledge and results obtained from ultrafiltration membranes (UF) experiments, which highlighted UV_{254} as an important fouling indicator. From that, the final proposed EDSS was designed to achieve 62% of turbidity, 21% of TOC and 25% of UV_{254} removals during coagulation step.

From the methodology described in Chapter 4, enhanced coagulation models were developed for two DWTPs presenting different types of catchment: river and reservoir (Chapter 5). To evaluate raw waters NOM fluctuations, cluster analysis was performed for both DWTPs identifying baseline and peak NOM scenarios. The enhanced coagulation models were specifically developed for each catchment type and scenario, aimed to remove turbidity, TOC and UV_{254}. Subsequently, models predictors selection and sensitivity analysis allowed to identify the critical factors to achieve enhanced coagulation at each scenario. For both DWTPs, results indicated that Cd is a crucial factor to remove NOM in peak scenarios, while baseline scenarios optimisation require a multiparametric optimisation (considering pH, Cd and Fd).

Models from Chapter 5 were tested with historical data and later integrated in a EDSS control system aimed to minimise trihalomethanes (THMs) using enhanced coagulation (Chapter 6). Results from EDSS application for the historical datasets shown that peak scenarios presented high values of THMs. From here, the developed EDSS proposed a readjustment of Cd which reduced THMs values below the limit in 99.2% of cases.

This thesis describes a methodology that allows to plan, design and develop an enhanced coagulation EDSS for drinking water treatment. To achieve that, empirical enhanced coagulation models were developed and integrated into EDSS control systems. The proposed EDSS were designed to propose the best suitable operational conditions for enhanced coagulation at the three case study DWTPs.

Resum

Actualment, l'accés de la població a l'aigua potable segueix essent un bé crucial per mantenir/assegurar el desenvolupament humà cap una societat del benestar. A causa del context geogràfic/demogràfic i el canvi climàtic, hi ha regions on el volum i la qualitat dels recursos hídrics disponibles es pot veure compromès per les generacions futures. En aquest context, el procés de potabilització de l'aigua comprèn un seguit de processos i tractaments que té com objectiu eliminar contaminants i generar aigua apte pel consum humà, procés realitzat a les estacions de tractament d'aigua potable (DWTPs). D'entre aquests contaminants, en aigües superficials destaca la matèria orgànica natural (NOM), un seguit de compostos orgànics la seva presència dels quals suposa un repte per la gestió degut a la capacitat per generar subproductes derivats de la desinfecció (DBPs).

En el tractament de l'aigua potable, la coagulació és un tractament fisicoquímic convencional que presenta major potencial per l'eliminació de la NOM. A partir d'aquí, l'optimització de la coagulació e escala operacional es pot dur a terme en base la qualitat de l'aigua produïda. Contemplant el marc de digitalització, les DWTPs disposen d'un seguit de mesures en línia per monitoritzar paràmetres relacionats amb la NOM, des de la captació de l'aigua fins la finalització del tractament, incloent la coagulació.

L'objectiu principal d'aquesta tesi és el desenvolupament d'uns sistemes d'ajut a la decisió ambiental (EDSS) per la coagulació millorada destinats a eliminar la NOM a tres DWTPs de captació d'aigua superficial en la regió mediterrània.

Per assolir l'objectiu, en el primer estudi s'ha proposat un EDSS per la coagulació millorada, estructurat jeràrquicament en tres nivells: adquisició de dades, control i supervisió (Capítol 4). L'EDSS està dissenyat per adquirir dades de l'entrada de la DWTP i proposar els òptims operacionals de pH i dosi de coagulant (Cd). El nivell de control de l'EDSS s'ha generat a partir del desenvolupament de models empírics per la coagulació millorada basats en la metodologia de resposta en superfície (RSM). Aquests han estat dissenyats per l'eliminació de la terbolesa, el carboni orgànic total (TOC) i l'absorbància per l'ultraviolat a 254nm (UV_{254}). Seguidament, s'ha proposat un seguit de regles per la supervisió (SRs) pel l'EDSS basades en coneixement expert i resultats derivats dels experiments realitzats amb membranes

d'ultrafiltració (UF), els quals relacionen el valor d'UV_{254} amb el fouling de les membranes. Finalment, s'ha presentat l'esquema operatiu per la implementació de l'EDSS, proporcionant l'eliminació del 62% de terbolesa, 21% de TOC i 25% d'UV_{254} a l'etapa de coagulació.

A partir de la metodologia descrita al Capítol 4, s'ha desenvolupat models per la coagulació millorada per dues DWTPs que tracten aigua provinent de captacions de riu i de pantà (Capítol 5). En base a avaluar les dades de qualitat de l'aigua d'entrada per mitjà d'un anàlisi de clústers s'ha identificat escenaris que presenten concentracions baixes i altes de NOM en l'aigua de l'entrada de les respectives DWTPs. Els models empírics per la coagulació millorada s'han generat específicament per cada DWTP i escenari per l'eliminació de la terbolesa, TOC i UV_{254}. Seguidament, la selecció dels predictors el posterior anàlisi de de sensibilitat dels models ha permès determinar els factors determinants per la coagulació millorada en cada escenari. En ambdues DWTPs, els resultats indiquen que la dosi de coagulant (Cd) és el factor determinant pels casos que presenten altes concentracions de NOM, mentre que per baixes concentracions de NOM els models indiquen que la coagulació millorada s'assoleix per mitjà d'una optimització multiparamètrica (pH, Cd i Fd).

En base els models desenvolupats al capítol 5 i sota la finalitat de desenvolupar un EDSS per la coagulació, els models de coagulació millorada han estat avaluats per la sèrie històrica de dades i posteriorment s'han integrat dins d'una proposta d'estratègia d'implementació per un EDSS a escala real, el qual té com a objectiu minimitzar la formació de trihalometans (THMs) a través de la coagulació millorada (Capítol 6). La posterior aplicació de l'EDSS per la sèrie històrica ha demostrat que els casos d'alta concentració de NOM a l'aigua d'entrada són aquells que presenten valors alts de THMs. A partir d'aquí, en un 99.2% dels casos l'EDSS ha proposat un reajustament de la Cd assolint un valor de THMs per sota del valor límit establert.

Aquesta tesi descriu una metodologia que permet planificar, dissenyar i desenvolupar un EDSS per la coagulació millorada pel tractament d'aigua potable. Per fer-ho, s'ha presentat una metodologia específica pel desenvolupament de models empírics de la coagulació millorada, així com els respectius sistemes de control i les propostes operatives per la implementació dels EDSS a escala real en cada un dels casos d'estudi plantejats.

Resumen

En la actualidad, el acceso de la población al agua potable es un bien crucial para mantener/asegurar el desarrollo humano hacia una sociedad del bienestar. A causa del contexto geográfico/demográfico y del cambio climático, hay regiones donde la cantidad y la cualidad de los recursos hídricos disponibles pueden ser alterados, comprometiendo el abastecimiento para las generaciones futuras. La potabilización del agua comprende una serie de procesos y tratamientos con el objetivo de eliminar contaminantes y generar agua apta para el consumo humano, realizado en las estaciones de tratamiento de agua potable (DWTPs). Entre estos contaminantes, en las aguas superficiales destaca la materia orgánica natural (NOM), un conjunto de componentes orgánicos la presencia de los cuales supone un reto por la gestión debido a la capacidad de generar subproductos derivados de la desinfección (DBPs).

En el tratamiento del agua potable, la coagulación es un tratamiento convencional con gran potencial para la eliminación de la NOM. La optimización de la coagulación se puede realizar en base la calidad del agua producida. En el marco de la digitalización, las DWTPs controlan parámetros relacionados con la NOM, desde la captación del agua hasta la finalización del tratamiento, incluyendo la coagulación.

El objetivo principal de esta tesis es el desarrollo de unos sistemas de ayuda a la decisión ambiental (EDSS) para la coagulación mejorada y la eliminación de la NOM en tres DWTPs de captación de agua superficial de la región mediterránea.

Para lograrlo, en el primer estudio realizado se ha propuesto un EDSS para la coagulación mejorada, estructurado jerárquicamente en tres niveles: adquisición de datos, control y supervisión (Capítulo 4). El EDSS está diseñado para adquirir datos de la entrada de la DWTP y proponer los óptimos operacionales de pH y dosis de coagulante (Cd). El nivel de control del EDSS se ha generado a partir del desarrollo de modelos empíricos para la coagulación mejorada a partir de la metodología de respuesta en superficie (RSM). Estos han sido diseñados para la eliminación de la turbidez, el carbono orgánico total (TOC) y la absorbancia por el ultravioleta a 254nm (UV_{254}). Seguidamente, se ha propuesto una serie de reglas por la supervisión (SRs) para el EDSS basadas en conocimiento experto y resultados derivados de los experimentos realizados con membranas de ultrafiltración (UF), los cuales relacionan el valor de UV_{254} con el fouling de las membranas. Finalmente, se

ha presentado el esquema operativo para la implementación del EDSS, proporcionando una eliminación del 62% de turbidez, el 21% de TOC y el 25% de UV_{254} durante la etapa de coagulación.

A partir de la metodología descrita al Capítulo 4, se ha desarrollado modelos por la coagulación mejorada para dos DWTPs, las cuales tratan agua de río y de pantano (Capítulo 5). En base a evaluar los datos de calidad del agua de entrada por medio de un análisis de clústeres se ha identificado los escenarios que presentan concentraciones bajas y altas de NOM en el agua entrante de las DWTPs. Los modelos empíricos por la coagulación mejorada se han generado específicamente para cada DWTP y escenario para la eliminación de la turbidez, TOC y UV_{254}. Seguidamente, la selección de los predictores i el posterior análisis de sensibilidad de los modelos ha permitido determinar los factores determinantes para lograr la coagulación mejorada en cada escenario. En ambas DWTPs, los resultados indican que la dosis de coagulante (Cd) es el factor determinante por los casos que presentan altas concentraciones de NOM, mientras que por bajas concentraciones de NOM los modelos indican que la coagulación mejorada se logra con una optimización multiparamétrica (pH, Cd y Fd).

Los modelos desarrollados durante el capítulo 5 han sido evaluados por la serie histórica de datos y posteriormente integrados en una propuesta de implementación a escala real, la cual tiene como objetivo minimizar la formación de trihalometanos (THMs) a través de la coagulación mejorada (Capítulo 6). Posteriormente, la aplicación del EDSS para la serie histórica ha demostrado que los casos de alta concentración de NOM en el agua de entrada son aquellos que presentan valores altos de THMs. A partir de aquí, en un 99.2% de los casos el EDSS ha propuesto un reajuste de la Cd logrando un valor de THMs por debajo del valor límite establecido.

Esta tesis describe una metodología que permite planificar, diseñar y desarrollar un EDSS por la coagulación mejorada para el tratamiento de agua potable. Para hacerlo, se ha presentado una metodología específica por el desarrollo de modelos empíricos de la coagulación mejorada, así como los respectivos sistemas de control y propuestas operativas para la implementación de los EDSS a escala real para cada uno de los casos de estudio planteados.

1. Introduction

Water has been considered a valuable resource since humans stepped on the Earth. At present, among all water uses (agriculture, livestock, energy production, ecology…) water consumption still remains to be one of the most important pillar for mankind development. One of the biggest concern in the world is related to drinking water, circa 31% of population has no access to safely managed drinking water, and current policies have the main objective to achieve the universal coverage by 2030 (UNICEF and WHO, 2019). The history of water treatment goes back to the Primitive humans, which were capable to implement some rudimentary actions based on decantation to improve water properties like smell and taste. Then, the subsequent civilizations (Greeks and Egyptians) used advanced technologies for water consumption like carbon filters. The emergence of Roman Empire supposed a watershed in the history of water treatment because of technological and scientific progress. Among other advances, the distribution systems and the use of air for water treatment were implemented during this period. However, it was not until the initial stages of 19th century when the first water treatment plants became a reality. These facilities were places where the processes and advanced treatments were implemented sequentially, i.e. using sedimentation and filters based technologies (sand and carbon). The main goal of these treatment stations was to supply potable water to the big cities. But, which was the impact for population the access to safe drinking water? The history brings the answer… After the implementation of the first drinking water treatment plants (DWTPs), human life-expectancy in only 30 years experienced the largest historical jump. This was due to the water disinfection, which caused the removal of microorganisms and the major part of water-derived human diseases overcome (Angelakis et al., 2021; Gulis, 2000; Kabir, 2008). At present, an example derived from the current pandemic situation is that there is no evidence of SARS-CoV-2 on drinking water (WHO, 2020). From that, it seems that drinking water is an old friend of humans but… the first DWTP was built only over 100 years ago! So, there is a room for improvement in terms of technology and the development of strategies for process optimisation can shed light on decision-making tasks.

1.1. Water in a shifting context

Regional surface water availability is related to the geographical location, demographic issues and the climate, mostly seasonality and the frequency of extreme events. Regarding the latter issue, the climate change and the globally greenhouse effect are altering the weather and subsequently the water availability. Also, the different scenarios determined that water scarcity is raising and the quantity of the available hydric resource can be reduced for the next years/decades (Gosling and Arnell, 2016; Vairavamoorthy et al., 2008). Specially in regions like the Mediterranean area, where the precipitation will be decreased during the year in terms of accumulated volume and the whole water basins will be affected. However, the precipitation intensities tend to increase (Bates et al., 2008; Giorgi and Lionello, 2008). To cope with that, water sector has been evolving during the last years to develop specific strategies related to the alternative water resources, connected to water reuse with the objective to avoid the resources overexploitation (Maiolo et al., 2017). Within this context, anthropic infrastructures and water systems should be prepared for extreme seasonal events associated to periods of heavy rains and large droughts. The fact is that these context is affecting the watersheds from the perspective of water quantity and quality. Concerning water treatment, as a general trend, heavy rains produce runoff effects resulting in an increase of surface water contaminants (Delpla et al., 2011; Sipaúba-Tavares et al., 2007). On the other hand, periods of water scarcity are becoming usual and water treatment should be adjusted accordingly to the expected increase of pollutants concentration. As a result, water production is required to act as a flexible and resilient system, where strategic plans should be aimed to the implementation of tools aiding to deal with the new situations, where the water systems should be improved for water monitoring, processes control as well as the capacity to predict the weather forecast and the subsequent raw water quality.

As mentioned, water sanitation is directly linked to a growth in population due to the increase of life expectancy. The absolute increase in global population remains to be more or less stable during the last twenty years, but presents huge differences depending on the regions. The total population in terms of number remains quite similar since 2000s, however exist a non-uniform distribution related to regional growth (Gerland et al., 2014). There are countries with big surface area and low population density and other on the opposite side, presenting high levels of density on small places. Observing population mass fluctuation, the tendency of first world countries is changing to the abandonment of rural areas, which is reflected to an increase of big cities population (Parker et al., 2018). This fact presents a challenge for water treatment, where bigger cities require larger facilities and interconnected distribution networks for water collection, storage and production. From this, the quality, the quantity and the availability of water resources are a result of the synergy between the hydrological and the anthropic water cycles. On that basis, the proper water management strategies are necessary to be updated according to the current and future demographic trends.

1.2. Surface water

Surface waters are defined as any body of water which is located above the ground, which are involved into the hydrological water cycle being an active layer connecting the precipitation, transport and the evaporation processes. Additionally, these waters play an important role in human water cycle because are used for drinking water production. Connected with drinking water, surface waters can be classified into natural or artificial origin. Natural surface waters are composed by rivers, streams, wetlands and lakes; artificial are basically related to reservoirs (human-made lakes or dams). Considering future water perspectives, where the surface waters dilution factor for contaminants is expected to decrease (less water), it is crucial to ensure resilient water sanitation infrastructures as well to stablish robust management strategies (Abily et al., 2021). Surface waters are subjected to multiple human uses like agriculture, industries, leisure activities… and also the surface water treatment for water consumption. Hence, considering changes in demography, land uses will be affected and some alterations to the physicochemical and biological surface water characteristics should be considered (Ullah et al., 2018; Ye et al., 2009). As stated Yong and Chen (2002), the land use has an impact on surface water quality, especially after rainfall. After rains surface waters experienced an increase of pollutants due to the runoff. Regarding the latter, most of these pollutants arise from human activities (Adeola et al., 2019). The geographical location and the demographic context can determine the quantity and the quality of surface waters, thus representing a challenge for the entire water treatment.

Water "receipt" is composed by a specific conjunction of components which are defined by its natural and anthropic idiosyncrasy. However, there exist some general groups of water compounds present in all surface waters. These are inorganic and organic components, which can be natural or derived from human activities. Some of this water components are regulated and legislated to a minimum acceptable threshold due to its properties against human health (WHO, 2017). Additionally, there are other challenging pollutants, which are not yet regulated, classified as emerging contaminants (Houtman, 2010). All of these water contaminants are managed to be removed during the drinking water treatment process. Inorganic components precedence is basically subjected to the geological systems which is the case of salts and metals (Brusseau and Artiola, 2019). Then, the water organic components are sorted into the natural organic matter (NOM), which is considered to be the major concern for drinking water production (Baghoth et al., 2011; Matilainen et al., 2011).

NOM is a complex and changing matrix formed by a heterogenic mixture of organic compounds, presenting various degrees of reactivity and chemical/physical properties (molecular weight and affinity). NOM variations are reported to be defined by geographical location and its fluctuations are mainly attributed to seasonal changes derived from the meteorological agents such as rainfalls, floods and droughts (Sillanpää et al., 2018). Hence, spatiotemporal oscillations on NOM quantity and composition is a result of the interaction between Earth interfaces: atmosphere, lithosphere, hydrosphere, biosphere and anthroposphere (Figure 1). E.g. during periods of rainfall of floods events it is expected an increase of NOM in surface waters (Fahad et al., 2020). For all of this, NOM quantification and characterization is extremely challenging. At the moment, NOM is not directly linked to human health, however its presence impact on drinking water treatment performance affecting water treatment and alters the final waters organoleptic properties such as colour, odour and taste (Health Canada, 2019). NOM can be categorized into hydrophobic and hydrophilic NOM and low molecular weight (LMW) and high molecular weight (HMW) NOM. The NOM hydrophobic fraction is mainly associated to HMW compounds formed by aromatic and cyclic compounds presenting high colloidal charge. On the other hand, hydrophilic NOM fraction is basically related to compounds presenting LMW such as proteins, sugars and carbohydrates (Saxena et al., 2018). Regarding the latter, is the fraction presenting lower removal effectiveness during drinking water treatment using conventional processes.

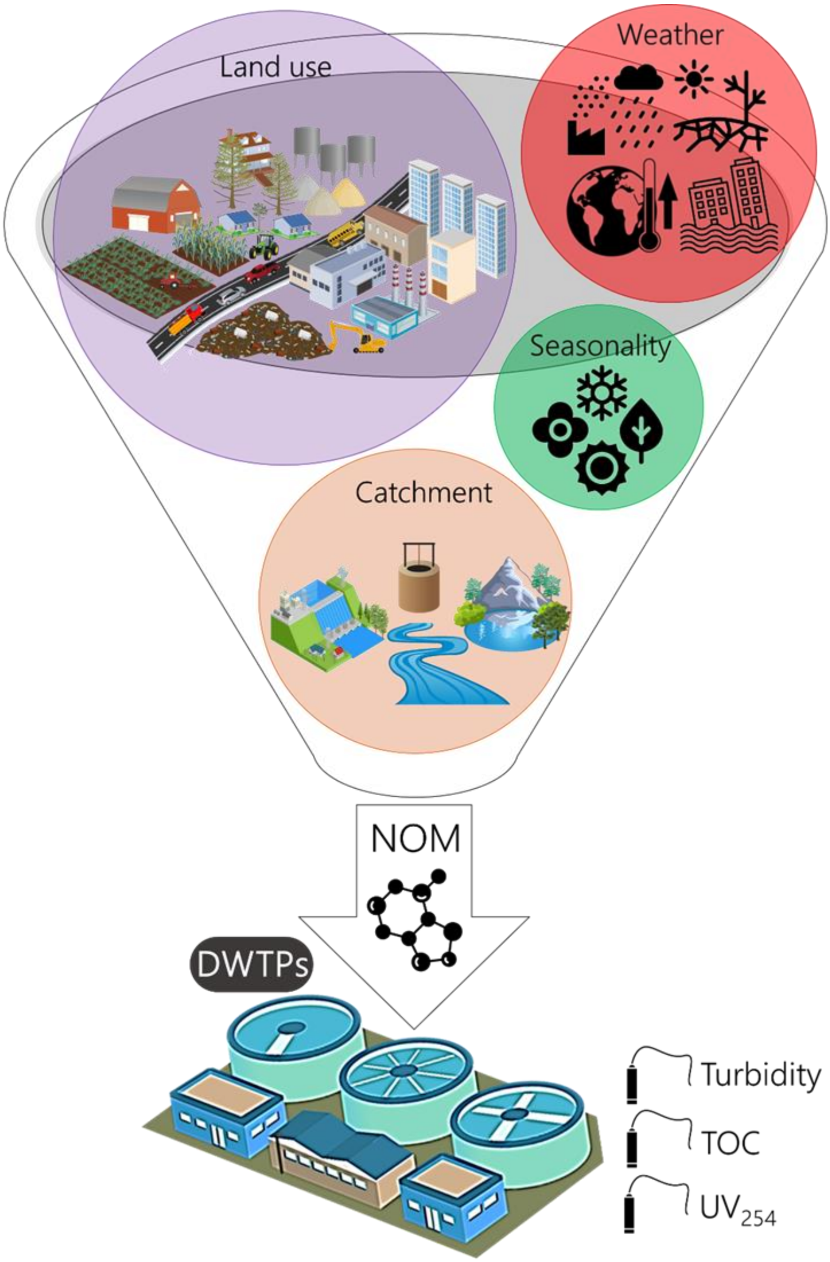

Figure 1: Factors influencing the surface waters accounting for the NOM quantity and quality and the subsequent treatment train implications.

There are several methods aimed to NOM quantification, characterization and fractionation. Some of them are based on high performance liquid chromatography (HPLC), fluorescence excitation emission matrices and UV absorbance, among others. All these methods are useful to identify NOM at lab scale but still present some limitations related to the cost, replicability, time and technical knowledge to be performed as routine analysis at full-scale plants. With the purpose of controlling NOM in real facilities, some parameters have been stablished as NOM indicators. These parameters are easily monitored (through proves or analysers) and provide information accounting for NOM, named as NOM surrogate parameters. The commonly used parameters for NOM are: Turbidity, total organic carbon/dissolved organic matter (TOC or DOM), ultraviolet absorbance at 254nm or UV_{254} and the specific ultraviolet absorbance or SUVA (Golea et al., 2017; Pifer et al., 2014). Turbidity is typically used as water quality indicator for full-scale application because of provides information related to a broad range of compounds: mainly particulate and some related to the colloidal fraction (Figure 2). NOM is composed by carbon structures; thus TOC represents the dissolved NOM fraction (carbon-based compounds <0.45µm). Then, UV_{254} enables to quantify specific NOM reactive compounds (mainly aromatics), usually linked to high molecular weight NOM compounds (Sadiq and Rodriguez, 2004; Pifer and Fairey, 2014).

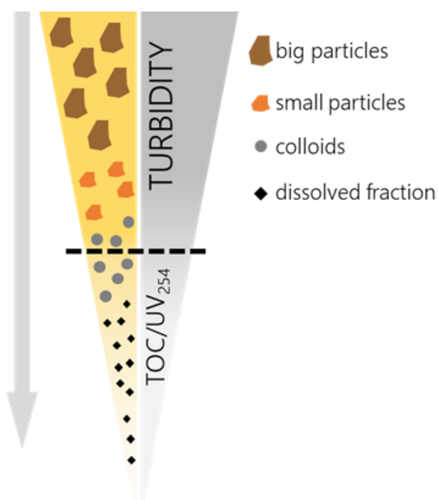

Figure 2: Drinking water quality parameters related to the water components size.

Table 1 summarises the information provided by each one of these water quality parameters. In sum, the continuous/online measurement of NOM surrogated parameters and its posterior evaluation (expert knowledge) can contribute to NOM understanding as well as water treatment optimisation.

Table 1: Information extracted from water quality parameters.

	Turbidity	TOC	UV_{254}
NOM fraction	Hydrophilic Hydrophobic	Hydrophilic Hydrophobic	Hydrophobic
Specific compounds	inorganic/organic suspended particles & colloidal fraction (Liu et al., 2019)	NOM (Sillanpää, 2015)	Unsaturated bonds and aromatic rings (Liu et al., 2022)

1.3. Water treatment

Water treatment consists on the implementation of several complementary processes placed in series aimed to remove some water components, which are directly related to water pollutants, for the production of safety drinking water. The typology and the characteristics of the water source and the drinking water requirements determine the number and the typology of unit operations/processes implemented for drinking water production. Regarding the water catchment, several studies describe that waters collected from big water masses are stable in terms of quality compared to those coming from rivers, streams and creeks (Chung et al., 2008; Straskraba et al., 1993). The final produced waters must fulfil the regulated water standards. The list of water contaminants is frequently updated where some of the current considered emergent water contaminants can be included on the list of the official regulated standards. The World Health Organisation stablishes the basic principles for drinking water uses and the quality required for its consumption (WHO, 2017). At the moment, there exist some general water frameworks (98/83/EC, 1998) that are implemented through regional/national regulations (RD 140/2003). Among others, these regulations have accelerated the DWTPs digital transformation improving water sensing, online monitoring and the subsequent generation of full-scale databases. This digitalization is aided to improve process control to face present and future water quality requirements.

DWTPs are usually larger facilities (high surface area), considered essential critical infrastructures for humans. DWTPs geographical location is typically placed near a surface water mass. However, there exist DWTPs which collect water from a source located in a considerable distance (through piping). Thus, DWTPs involve high costs in terms of capital (CapEx) and operational (OpEx) expenditures. CapEx is basically spent for the ground acquisition, the building cost and the equipment. Price and Heberling (2018) stated that the quality of water source determined the derived treatment costs. OpEx is related to the reagents, electricity and maintenance, which can be reduced through the process evaluation and its optimisation. Regarding water organics, NOM is reduced consecutively over the treatment train, where HMW compounds such as humic matter and biopolymers are removed during the first stages (coagulation/sedimentation/sand filtration) and LMW compounds are less removed (only using advanced technologies) becoming dominant in the produced waters (Krzeminski et al., 2019). Thus, according to Nissinen et al. (2001), the LMW are less removed during coagulation due to its intrinsic properties (hydrophilic fraction). At the moment, NOM remains to be the water component which compromises water treatment processes efficiency (Sillanpää, 2015). DWTPs unit operations are divided into physical, chemical and physicochemical processes. The typical DWTPs configuration is presented in the Figure 3. There are some of this processes which precise chemical reagents addition, representing the major portion of DWTPs OpEx. As coagulation is a physicochemical process implemented in worldwide facilities, if coagulation is optimised, more than 60% of NOM (mainly HMW compounds) can be removed (Krzeminski et al., 2019; Sharp et al., 2006; Volk et al., 2000).

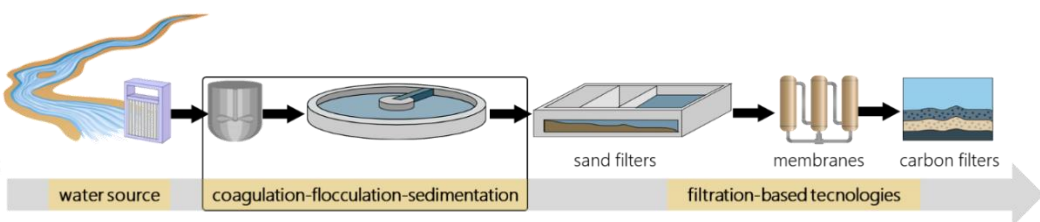

Figure 3: Treatments applied for drinking water production.

1.4. NOM as a DBPs precursor

NOM is ubiquitous in surface waters, has a different composition depending on geographical location (geological context and climate) and fluctuates due to seasonal changes and anthropic management purposes (Saxena et al., 2018). Seasonal changes are basically related to the meteorological agents: rains (storm events) and temperature. As is abovementioned, catchment context and anthropogenic activities can modify water composition. For example, in the Mediterranean region water transfer from rural regions (mostly located in mountains) is transferred to urban regions presenting high level of water demand. Especially on water catchments subjected to multiple water sources, where the daily water composition is subjected to decision-making.

NOM represents a challenge for drinking water producers because reacts with water disinfectants generating disinfection by-products (DBPs), some of them described as hazardous compounds (Tak and Vellanki, 2018). If DWTPs are not optimized for NOM removal, residual NOM can react with chlorine-based disinfectants to produce DBPs later in the distribution system. In other words, the more NOM in water, the higher will be the disinfectant demand and the subsequent formation of DBPs (Yu et al., 2015).

Disinfection can be found at different points on water treatment line (primary and final disinfection). Pre-oxidation (PO) is located as the first step in water treatment and basically contributes to act as a barrier for pathogen load and to avoid the proliferation of microorganisms and algae during the water production (Godo-Pla et al., 2020b). PO is the first chemical barrier against organics and pathogen load and coagulation helps to remove water particles, colloids and dissolved NOM. Potassium permanganate ($KMnO_4$) and chlorine dioxide (ClO_2) are strong oxidants used in the water treatment. PO should be carefully adjusted to avoid residual manganese (Mn) and the occurrence of pink waters caused by an overdose. Manganese is restricted in drinking water to 50µg·L-1, and for this reason its addition is located as the first stage in water treatment, ensuring its removal during the subsequent unit operations. Compared to ClO_2, Hall et al. (2016) reported that $KMnO_4$ requires higher doses to obtain similar removals. However, the permanganate is cheaper and easier to preserve, prepare and use. Subsequently, the coagulation-flocculation-sedimentation treatment is located (see Figure 3).

Disinfection is applied to produced waters with the objective to prevent microbial growth during the distribution system. Spanish drinking water national directive states as mandatory for the final waters the presence of residual chlorine to ensure water disinfection through the distribution system (RD 140/2003). One of the firsts discovered and regulated DBPs in water distribution systems, which are considered harmful for humans due to its carcinogenic properties, were the trihalomethanes (THMs). Since chlorine has been used as a disinfectant, the efforts have been focused the control of THMs (Sadiq and Rodriguez, 2004). THMs have been used as indicator accounting for DBPs due to its regulation and well-known standardized analytical measurement (Li and Mitch, 2018). Concerning Spain, the THMs threshold is fixed at 100 $\mu g \cdot L^{-1}$ in the final distributed waters.

THMs is a group of DBPs composed by bromoform, bromodichloromethane (BDCM), chloroform and dibromochloromethane (DBCM). These compounds were suggested as water pollutants for the first time by WHO (2006) due to their human associated risks, stating some guideline values: 300µg·L-1 for chloroform, 100µg·L-1 for bromoform and DBCM, and 60µg·L-1 for BDCM. Despite that, total THMs concentration does not exceed 100µg·L-1 for finished and chlorinated waters.

Hence, THMs minimisation is challenging for DWTPs because THMs concentration is influenced by multiple factors. THMs concentration is subjected to chlorine and NOM concentrations, temperature, pH and the presence of bromide ion (WHO, 2017). Regarding the latter, Chowdhury et al. (2010) indicated that bromide acts as a catalyser for the total THMs formation, increasing BDCM and DBCM concentrations. Furthermore, there are other factors influencing THMs formation such as hydraulic retention time (HRT), which is related with the formation of THMs affecting NOM-chlorite contact time (Brown et al., 2011; Zhong et al., 2012). On this basis, drinking water directives emphasize the importance of ensure the feasible minimum value for THMs concentration during the production of drinking water.

Despite the regulated DBPs, the general trend of water requirements is to include more pollutants being more restrictive with the actual limits. E.g. the US Environmental Protection Agency (US EPA) fixes the maximum THMs level (all species) at 80 $\mu g \cdot L^{-1}$ (USEPA, 2010). From this context, arises the need to optimise water processes for NOM removal, minimizing DBPs formation.

1.5. Coagulation

Coagulation is a unit operation widely implemented in DWTPs due to the high ratio efficiency/cost and it is usually located at the initial part of the treatment. Coagulation is a general term used to refer coagulation-flocculation-sedimentation step into the water treatment (Sun et al., 2019). Coagulation is a physicochemical process consisting on the addition of reagent/s promoting water particles agglomeration (Figure 4). Coagulation process is mainly attributed to adsorption, entrapment, charge neutralization and complexation mechanisms (Sillanpää et al., 2018). Then, these destabilized colloids and particles present in water are unified into larger flocs (Henderson et al., 2006). As organic molecules and compounds have negatively charged functional groups at neutral pH, charge neutralization occurs when positively charged ions of coagulant interact with NOM (Jeong et al., 2014; Zhao et al., 2011). For the coagulation, alum based coagulants are widely used for the reason that aluminium hydroxides have the capacity to precipitate promoting the NOM destabilization (Gregory and Duan, 2001). Then, it is demonstrated that working at enhanced coagulation conditions metal-based coagulants reduce NOM from natural waters in a range between 20 up to 60% (Saxena et al., 2018; Wang et al., 2021). Hence, during the coagulation the particles present in surface water, colloids and NOM can be removed. At the same time, coagulation is reported as the water treatment presenting highest cost-effectiveness ratio (Sun et al., 2019). Moreover, as it is said, coagulant selection plays a key role for process optimization where different waters can present different optimum regions.

The typical DWTPs configuration for coagulation is the coagulation-flocculation-sedimentation scheme. First, coagulant chamber is a reactor where water is rapidly mixed with the coagulant. Next, water is conducted to the clarifiers where floc formation and sedimentation occurs. In many cases, other type of coagulant, called flocculant, is added prior to clarification in order to aid floc formation (see Figure 4). Hence, coagulants are classified depending on its composition in organic and inorganic coagulants. Regarding the latter, within the inorganic coagulants, synthetic metal salts (mainly alum and iron based) are particularly used in drinking water treatment due to its capacity to form complexes with NOM, promoting floc formation and the posterior sedimentation. On the other hand, organic coagulants (polyelectrolytes) can be applied as primary coagulants or flocculants depending on if they are synthetic or natural, respectively (Matilainen et al., 2010). Sometimes coagulants are expensive and flocculants are used to reduce the coagulant demand. Additionally, it is reported that the synergy of various coagulants can improve NOM removal (Islam et al., 2011; Katrivesis et al., 2019; Saritha et al., 2017). Several studies related to wastewater treatment revealed the possibility to work using composite coagulants, taking advantage in the combination of inorganic and organic properties (Ng et al., 2012; Tzoupanos and Zouboulis, 2010). Similarly, research field is focussed on the development of novel coagulants, aimed to generate new reagents aimed to improve metal based coagulants properties for NOM removal (Sillanpää, 2015). Even today, Wang et al. (2021) reports that there is no evidence of which is the best coagulants combination ensuring enhanced coagulation. The reason of this relies on the NOM fluctuations and the characteristics of the water source. The study conducted by Saxena et al. (2018) reported that coagulant demand is more influenced by NOM fraction than the other particles present in surface waters due to the charge neutralization effects of coagulant-NOM.

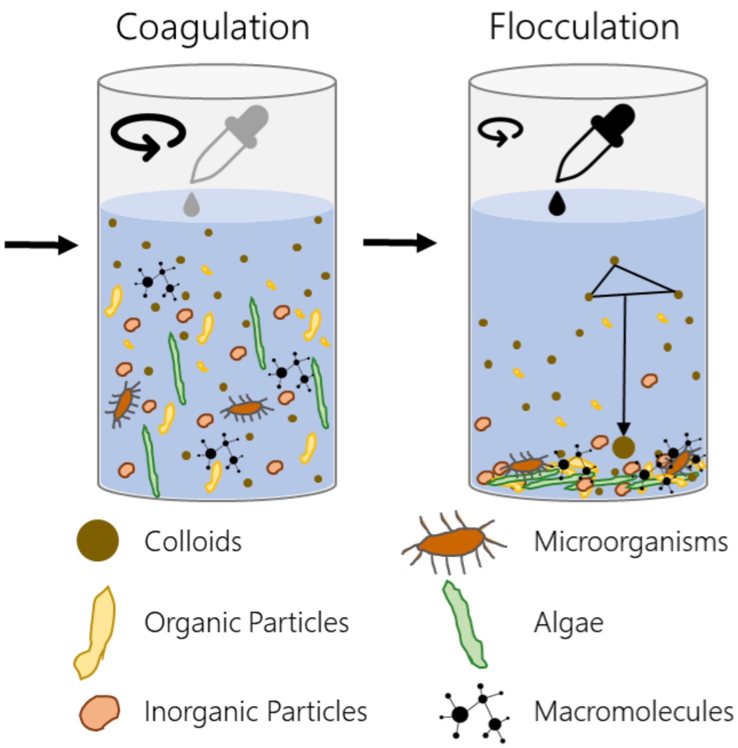

Figure 4: Coagulation scheme for drinking water treatment.

In water treatment, there are many cases where a filtration technology is located after the coagulation unit operation. Filtration technologies can be classified into different categories depending on the material used: sand, membranes and activated carbon filters. Basically, filtration is a physical process where particles higher than the pore size remain entrapped when pass through the filter media. Then, depending on the diameter of the pore size, filters are located on different stages of water treatment (Schäfer, 2001). Sand filters are placed after coagulation process aiding to retain the formed flocs. However, the bottleneck of this technology remains to be the pore blockage, which causes filters replacement or the need to plan some maintenance tasks with periodic backwashes. Then, granular activated carbon (GAC) filters or membranes-based technologies usually are located at the final stages due to its capacity to retain small water compounds. It is reported that the presence of NOM is the major cause of membrane fouling (Cheng et al., 2017). The affectation of enhanced coagulation to these advanced treatments is clear, the fact to optimise coagulation for the NOM removal induce to increase the filter media useful life. In other terms, enhanced coagulation helps in reducing maintenance derived costs and in delaying filters material replacement.

1.5.1. Operational practices to improve coagulation

From the early times of water treatment, traditional coagulation is aimed to optimise coagulation for turbidity removal, where plant operators used jar test methodology to determine the best suitable coagulation conditions. This method is called one factor at a time (OFAT), which consists to stablish the coagulation factors (pH and coagulants dose) for a specific water quality parameter. In some cases, turbidity was the operational parameter used to optimise coagulation with OFAT method using online turbidimeters for the measurement. The OFAT main limitation relies on that only one factor can be modified at each experiment. Thus, traditional coagulation present low to medium rates of NOM removal, reflected in a minimum reduction of DBPs during the water treatment and the posterior distribution system. In the context of coagulation optimisation, it is depicted that the best suitable conditions for NOM removal are not the same than these achieved optimising the process only for turbidity removal (Sillanpää et al., 2018). Furthermore, it is reported that coagulant demand is more influenced by NOM quantity/quality than turbidity value (Pernitsky and Edzwald, 2006). Concerning turbidity, is a parameter which consists on the quantification of water opaqueness and provides general information about the water quality, basically related to suspended solids and particle water fraction (Tuan Vo et al., 2020). Therefore, when coagulation is optimised for NOM removal is named as enhanced coagulation.

Enhanced coagulation aims to maximise NOM removal to minimise DBPs formation during the water treatment. Typically, coagulation is placed after PO. The operation (ragents, doses…) for an enhanced coagulation is determined by the quality requirements and the source water characteristics (Sun et al., 2019). Regarding the latter, NOM fractions are classified depending on its properties and physicochemical characteristics (mainly molecular weight and hydrophobicity). Functional groups composed with larger molecules such as humic acids (hydrophobic compounds) are removed during enhanced coagulation (HMW compounds). However, there are other NOM compounds (hydrophilic fraction) which are less removed during coagulation linked to the proportion of untreatable NOM (Sharp et al., 2006). Enhanced coagulation can positively influence the removal of this compounds. USEPA states enhanced coagulation as the better practise for DWTPs to remove NOM due to the low investment required and the possibility to use the original infrastructures (Sun et al., 2019).

Coagulation is a process influenced by multiple factors, which can be classified into environmental and operational factors. Environmental factors are those parameters which are external to the process. Although its control is not possible for full-scale drinking water production purposes, its affectation should be considered when the process wants to be optimised for NOM removal. Ergo, operational factors are these ones which can be adjusted in a DWTP for enhanced coagulation performance. Several studies reported that pH and coagulants dose are crucial factors for coagulation (Trinh and Kang, 2011; Zainal-Abideen et al., 2012). Operational factors specific impact will be discussed later on this introduction. For all these reasons, enhanced coagulation should be considered a multifactorial optimisation, where the selection of the optimal operation region relies on the specificities of each case (type of water and reagents used).

1.5.2. Optimisation of coagulation process

Regarding drinking water treatment and the development of models aimed to improve coagulation, several studies developed predictive models focussed to determine the optimal coagulation operation for coagulants doses (Cd), mainly based on artificial neural networks (ANNs) (Griffiths and Andrews, 2011; Jayaweera and Aziz, 2022). These type of models are usually codified with the historical coagulation datasets and some of them are aimed to remove turbidity at the effluent of coagulation (Zangooei et al., 2016). Then, van Leeuwen et al. (2005) used some mathematical models, aimed to describe Cd effects on DOM removal, to predict alum doses in two DWTPs in the Australian region. Others works were focussed specifically on the development on enhanced coagulation by determining the optimal coagulation conditions to achieve a specific water quality at the effluent of coagulation (Wang et al., 2021; Xie et al., 2012). On these studies, response surface methodology (RSM) was described as a useful methodology to develop models for NOM removal (Zhao et al., 2019; Zularisam et al., 2009).

From this, RSM is a useful methodology with the capacity to standardize and proportionate a rapid and complete overview of coagulation process. RSM permits to plan the minimum number of experiments for process optimisation, being widely implemented for the case of enhanced coagulation (Adesina et al., 2019; Moghaddam et al., 2010). RSM offers a multivariate response optimization useful to describe the importance of individual factors as well as their interactive influences (Arruda et al., 2018; Ghafari et al., 2009; Liu et al., 2019). From here, RSM consists on the statistical approach selection, the number of process factors and experiments performed. Central composite design (CCD) has been described as useful statistical approach for coagulation due to its high efficiency describing processes with less than six factors, providing second order models (Nair et al., 2014). For RSM, factors' selection and codification (ranges) is required to specify model boundaries. Also, to control process efficiency, it is crucial to select the output variables in order to control process efficiency (responses). Then, when RSM is designed and the experiments are evaluated, the quadratic equations are used to describe the responses (see Eq.1). After the correct evaluation and after a structural validation, these equations can be used to make predictions.

$$Y = \beta_0 + \beta_1 \cdot F_1 + \beta_2 \cdot F_2 + \beta_n \cdot F_n \ldots + \beta_3 \cdot F_1 \cdot F_2 + \beta_n \cdot F_n \cdot F_{n+1} \ldots + \beta_4 \cdot {F_1}^2 + \beta_n \cdot {F_n}^2 \quad (1)$$

Where β_x are model coefficients. β_1 and β_2 describe individual effects; β_3 interactions and β_4 measures quadratic effects. F_X are the model factors. Adapted from (Montgomery, 2009).

Nair et al. (2014) defined the steps to develop a mathematical model using RSM, summarized in Figure 5. The adaptation for the enhanced coagulation is as follows: i) RSM design and factors/responses selection; ii) Sampling campaigns planning, jar test experiments execution and responses evaluation (model development); iii) empirical model analysis (structural validation) and iv) Enhanced coagulation determination.

Enhanced coagulation not only has a direct impact on the coagulation itself but also has influence on other treatment aspects. For some cases, enhanced coagulation leads to a reduction in coagulants dosage, implying less reagents and the reduction of OpEx. Then, if coagulant is decreased, the amount of metal-based residual coagulant in the generated sludge (chemical sludge) is reduced. Therefore, for some facilities, the coagulation optimisation can result in some changes on HRTs, occasionally reducing HRT. Related to the NOM removal and the minimization of DBPs formation, waters from enhanced coagulation can be treated with less disinfectant dose. In DWTPs, filtration based technologies are typically located after coagulation unit operation, being its efficiency and maintenance costs highly dependent on coagulation performance (Cui and Choo, 2014). If there is an enhanced coagulation prior to sand filtration or carbon filters, then the associated cost can be significantly reduced.

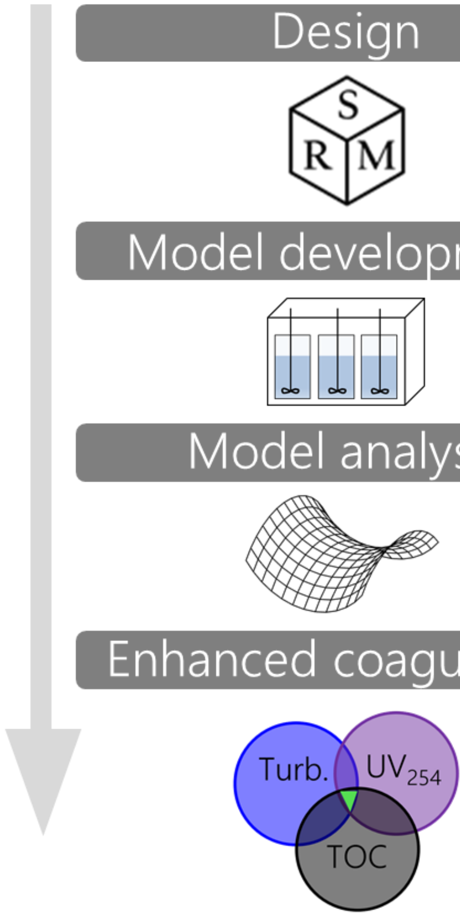

Figure 5: Steps for enhanced coagulation RSM model development.

1.5.3. Water inorganics affecting coagulation

Basically, water constituents can be classified into organic or inorganic fraction. Regarding the effect of inorganics in the coagulation step, some studies depict that inorganic fraction tend to increase coagulant demand (Yan et al., 2008). The watershed geology determines the inorganic water fraction, considering that the presence of ions is from rocks and minerals dissolution. Alkalinity is the parameter used accounting for the inorganic water composition. Thus, the organic part (carbon molecules) are those excreted compounds directly or indirectly derived from organisms. Regarding coagulation, the water composition has a direct effect on process performance.

Water inorganics are not isolated and interact with other water compounds affecting NOM removal in coagulation process (Ye et al., 2007). Water alkalinity main effect is its affectation on coagulant demand, competing with metal based coagulants for NOM neutralization. From this, Naceradska et al. (2019) reported that turbidity caused by the inorganic water fraction is removed during enhanced coagulation. Inorganic water content is monitored at full-scale level through several laboratory analyses. However, these parameters are not yet implemented as online sensors to control and optimise coagulation process.

1.5.4. Other factors affecting coagulation performance

Further factors are considered from the hydrodynamic perspective such us agitation performance, reactors and clarifiers structural design or water temperature. Regarding the latter, Zhang et al. (2018) reported that temperature affectation for coagulation is related to coagulants solubility and floc formation settleability. Then, the study and the implementation of the best suitable hydraulic conditions aids to improve the quality of produced waters. Several studies based on computational fluid dynamics (CFD) and impellers type (mostly in wastewater) shift light on which are the most favourable conditions (shapes, speeds…) to ensure the proper coagulant solubilisation and enhanced coagulation (Choudhary and Mathur, 2017; Lin et al., 2013). However, sometimes DWTPs are aged facilities, where it is easier for the managers to implement optimisation strategies by modifying operational set-points than to invest in new infrastructure.

From the water treatment perspective, operational factors are used to describe those variables which can be daily adjusted to run a specific process. For coagulation, pH and Cd are considered to be the most influence factors for process performance (Sillanpää et al., 2018). In several studies, pH has been reported to be the factor which has the larger impact on coagulation, particularly in those with the addition of metal-based coagulants. In this cases where metallic salts are added for coagulation, low pH level (acidic region) is reported to improve NOM removal. There are studies reporting that the optimum levelled pH range for metal-based coagulants oscillate between 4 to 7 (Saxena et al., 2018). When pH is optimised the Cd plays a key role on the coagulation efficiency. From this, research outcomes revealed that the optimum for NOM removal is located at intermedium Cd. Despite that, there are some general trends for enhanced coagulation, the scientific literature shows that every water mixture requires a specific assessment to determine the optimum operation region.

1.5.5. Restrictions for full-scale operations

To achieve enhanced coagulation, it should be taken into consideration some full-scale restrictions. First, the fact that there exist drinking water regulations which stablish limits for water consumption. In that list, parameters such as pH, aluminium or iron are ranged and the respective limits are stablished. Hence, pH is regulated from 6.5 to 8.5, then alum and iron concentrations are limited to 0.1 and 0.2 $mg{\cdot}L^{-1}$, respectively (WHO, 2017). Enhanced coagulation, if the final objective is to study full-scale processes, should be understand as this coagulation conditions which ensures de maximum NOM removal and at the same time fit with the water quality requirements. In other words, pH should be levelled between 6.5-8.5. If not, some implications like neutralization or remineralisation should be considered. Then, an underdosing/overdosing of coagulants can cause some implications for the subsequent water treatment. An overdose of coagulant can cause high levels of residual coagulant on the final waters and high amounts of chemical sludge (Ibrahim and Aziz, 2014; Wang et al., 2021), e.g. If an alum-based coagulant is used, residual alum should be controlled. Alum in water is associated to Alzheimer disease and depending on the concentration can be harmful for consumers. For all of this, when coagulation is pretended to be optimized, some restrictions should be considered to design the experiments or within models development.

1.6. Digital Water

Contemporary society is evolving through technological transformation towards the digitalisation of industrial and manufacturing processes. This digitalisation strikes factories and enterprises, where the internet of things (IoT) is essential for productivity and future mankind development strategies. Water sector is not an exception, which is submerged in a changing context where the technological transformation emerges as a way to improve water treatment processes efficiency and at the same time enables to achieve a resilient and flexible treatment (Mondejar et al., 2021; Poch et al., 2020). According to Salam (2020), this paradigm shift was catalysed by the appearance of online sensors/analysers as well as tools like the supervisory control and data acquisition (SCADA). DWTPs digitalisation supposed a progress in the water sector, allowing to generate and storage a huge quantity of data for the treatment control and monitoring. Is at this point where the water 4.0 arisen, where all this knowledge and technologies are applied to the water sector to treat water as a natural resource in a sustainable way. This approach is focused on the development of strategies for risk assessment and water quality improvement through processes optimisation.

Related to the water quality and pollutants removal, DBPs are considered a priority in terms of drinking water production, for this reason risk assessment studies are focussed on the minimisation of this compounds during the water treatment, storage and distribution. To achieve DBPs tracking, it is essential that DWTPs establish several analytical techniques for NOM characterization. In terms of unit operations performance, NOM is the major cause that determines Cd during the coagulation in the water treatment (Sharp et al., 2006; Sillanpää, 2014; Ritson et al., 2014). Ergo, if NOM is removed through enhanced coagulation, the potential concentration of DBPs during the distribution system as well as the human exposure associated risk will be minimised.

The previous works for the application of artificial intelligence (AI) techniques on drinking water were focussed on water treatment processes optimisation and water quality tracking during the distribution system. Regarding the latter, chlorine decay and the formation of DBPs are processes typically described by empirical models (Godo-Pla et al., 2021; Monteiro et al., 2014; Ricca et al., 2019; Xu et al., 2018). According to this, water temperature was also modelled to control the tap water quality (Blokker and Pieterse-Quirijns, 2013; García-Ávila et al., 2020). In the water treatment, many attempts have been focussed to develop models aimed to predict the oxidant dose for full-scale oxidation processes (Audenaert et al., 2010; Godo-Pla et al., 2019).

Coagulation models

Coagulation effectiveness is highly dependent on the correct adjustment of operating conditions. To control that, DWTPs invest on equipment to monitor the different variables. All these sensors and analysers are used to control process efficiency and the quality of the produced waters, generating huge amounts of data, which can be evaluated to understand coagulation performance or to estimate which is the optimal region. This data contains valuable information, which can be codified through models aimed to optimise coagulation. Some of this models are intended to determine Cd based on the historical dataset. Others, are targeted to determine the best suitable coagulation conditions to obtain a specific water quality for the clarified water. Several studies developed predictive models for coagulation, some of them are data-driven models, knowledge-based or hybrid models. ANNs have been applied in water research to predict coagulation operational factors, e.g. to detect seasonal fluctuations in water quality and link that with coagulant demand (Griffiths and Andrews, 2011; Zhu et al., 2021). Baxter et al. (1999) applied an ANN for enhanced coagulation. Then, other predictive models for pH and Cd were based on fuzzy logic algorithms (Li et al., 2021). According to the state of the art, modelling in coagulation is mainly aimed to optimise coagulant demand for turbidity removal.

In the case of coagulation, RSM has been a widely used method to develop predictive empirical mathematical models. This predictive models are aimed to stablish statistical relationships between several operational factors (Sadiq and Rodriguez, 2004). Models are designed and generated through experimentation, defining some process factors (independent variables) and selecting the desired responses (dependant variables). RSM models provide information and are useful to make predictions due to its capacity to analyse the effects of the independent variables and its interaction on the responses, providing the possibility to achieve enhanced coagulation. RSM comprises statistical experimental design, linear regression methods and optimization analysis (Nair et al., 2014). Using RSM, empirical models adequacy is validated through a set of statistics and can be graphically represented to find out the optimisation region. As it is abovementioned, to achieve NOM removal, coagulation process should be optimised for several water quality parameters, not only turbidity. From here, arises the need to develop models which enable to predict operational conditions based on water quality requirements, considering the NOM quality/quantity fluctuations.

1.6.1. Implementation of models

As a result of modelling progress, Environmental Decision Support Systems (EDSS) have emerged to provide solutions for environmental systems such as water treatment. The EDSS are tools used to integrate models and implement them for full-scale processes optimisation, which are helpful for decision-making due to the response systematization and time reduction. In the water sector, EDSS can be used for management assistance aimed to support plant managers and operators during the daily decision-making. These systems can be integrated by multiple AI methods coupled to provide a specific/s response/s. They can include statistical techniques, geographical information, specific process knowledge and environmental concerns (Hamouda et al., 2009). Then, these systems can be updated online where the end-users can validate EDSS proposals through a user interface. There exists a specific methodology for a model development, reported in the literature (Poch et al., 2004), which comprises different steps. First, problem analysis followed by data and knowledge acquisition. Then, the model selection (AI method) and the subsequent integration and implementation. The last step is model validation, where model is continuously updated and fitted with end-users' suggestions to maximise its predictability and resilience for the real process application.

The implementation of EDSS requires an operational structure (Figure 6), which can be structured following a hierarchal architecture divided into different levels (Poch et al., 2012). Where data acquisition module is located at the baseline of the architecture, located under the diagnosis and supervision levels, respectively. In the first level tasks related to the acquisition of input data used to feed the system. If the EDSS works online, is in this level where online servers' connectivity and data from probes, sensors and analysers is obtained and filtered/processed. Subsequently, the diagnosis level is where models are located. Basically, represents the reasoning engine of the EDSS. Finally, the supervision level is located at the top of the architecture, mainly designated to integrate all the proposals obtained in the diagnosis level providing alternatives in those cases where knowledge based actions derived from decision-making can be applied. Is the level it is important to stablish an interaction with the end-user, being crucial the development of a friendly user interface.

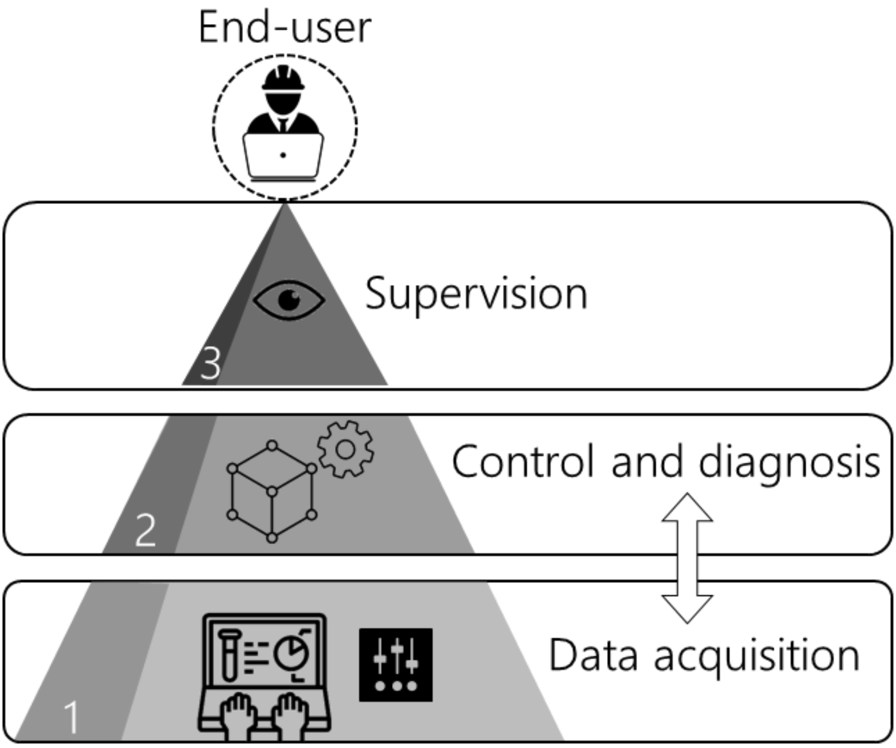

Figure 6: Theoretical architecture for EDSS operation.

1.7. Motivation

Drinking water supply will be increased worldwide at the same time that water regulations are becoming more restrictive. Inside the drinking water treatment, coagulation is a process widely implemented in DWTPs, since it has a key role for the removal of water pollutants. Enhanced coagulation is a pathway to optimise coagulation for NOM removal, which is the major precursor of DBPs. Hence, the coagulation optimisation for NOM removal is crucial to increase water treatment works performance and also to minimise the formation of DBPs. Based on that and the consolidation of water sector digitalisation, the development of specific AI tools aimed to achieve enhanced coagulation at full-scale level is still undergoing and could provide new insights for NOM removal and full-scale processes knowledge and management.

1.8. Hypothesis

Through a series of experiments (from different water catchments) and the development of empirical mathematical models it is possible to explore and determine the effect of operational factors for enhanced coagulation. The development of enhanced coagulation models and its integration in a EDSS for full-scale operation should provide systematically the best suitable operational conditions for NOM removal. These EDSS should be codified with different models according to the influent water quality scenarios, being a useful tool for the DWTPs.

2. Objectives

The main objective of this thesis is to design and develop an EDSS for enhanced coagulation at three Mediterranean surface water DWTPs located in Catalonia. The EDSS are aided to adjust coagulation for NOM removal and systematise decision-making. Methods for coagulation optimisation as well as the development of specific empirical models to determine the optimum operation is addressed in this thesis.

The EDSS presented in this work are tools developed to propose the optimal coagulation conditions for NOM removal based on the raw water characteristics. To achieve that, the available data, empirical determinations and process performance were specifically integrated for each case study to build the final EDSS. Through catchment assessment, several strategies for enhanced coagulation were proposed to achieve a flexible and resilient treatment, which provides solutions for enhanced coagulation in drinking water production. Within this framework, the proposed EDSS enable to adapt the water treatment to future climate scenarios and to more restrictive drinking water regulations. Subsequently, several specific objectives were defined:

- To stablish a specific methodology to study the determination of the optimum conditions for enhanced coagulation at different DWTPs.

- To develop mathematical models for enhanced coagulation based on the influent water at case-study DWTPs.

- To evaluate the operational factors involved in the de coagulation process, taking into account differences on each scenario and the water catchments: river and reservoir.

- To test enhanced coagulation models with full-scale data.

- To conceptualise a novel control strategy for THMs minimisation in drinking water production.

The scheme presented in Figure 7 shows the relationship between thesis chapters.

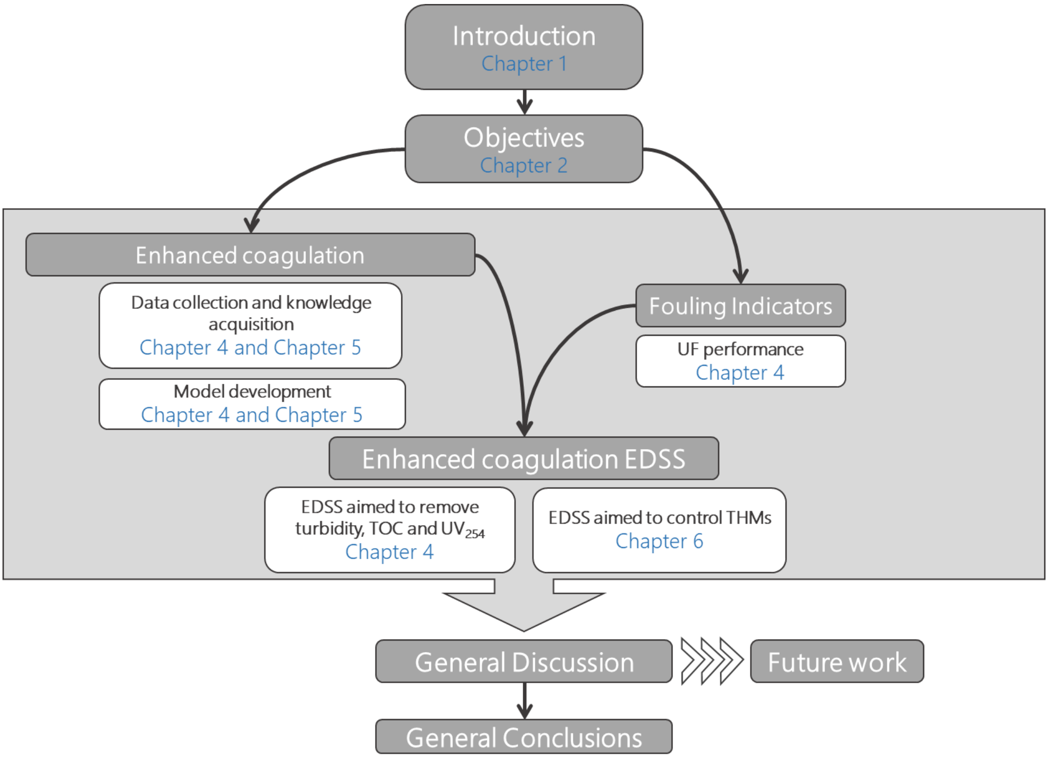

Figure 7: Thesis Road Map.

3. Methodology

3.1. Case Study

To develop the different works and the studies comprised in this thesis, three DWTPs were involved for sampling campaigns as well as the data acquisition/evaluation. These facilities are located in Catalonia (NE Spain), located in the Mediterranean region (Figure 8). The DWTPs are: Llobregat DWTP which is located in Abrera (Barcelona province), Ter DWTP placed in Cardedeu (Barcelona province) and Montfullà DWTP located close to Girona (Girona province). *Henceforth, Llobregat DWTP is named as DWTP 1, Ter DWTP as DWTP 2 and Montfullà DWTP as DWTP 3.*

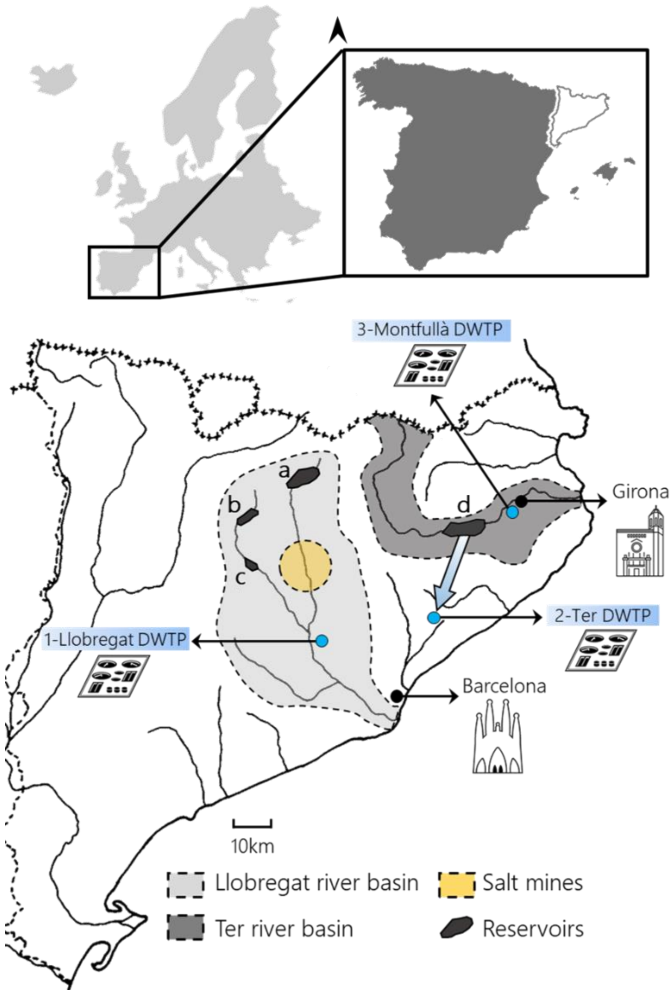

Figure 8: DWTPs location and the respective hydrological and demographic contexts.

The main differences among the DWTPs are based on their respective water source characterization. On the one hand, DWTP 1 takes water from the Llobregat river. This fact has some process implications which will be discussed during the Chapter 5 and Chapter 6 of this thesis. On the other hand, DWTPs 2 and 3 collect water from the Sau-Susqueda-Pasteral reservoirs system located in the Ter river course. Then, related to the demography, DWTPs 1 and 2 supply water to the Barcelona metropolitan area while DWTP 3 supply water to Girona. Thus, the geographic and demographic context is important and has an impact to the number of unit operations and the technologies applied for the water treatment.

3.1.1. DWTPs context

As it is abovementioned, the DWTPs environmental, hydrological, geological and demographic contexts have a series of implications affecting the water treatment. In the following section DWTPs some characteristics about the water catchment and applied technologies are detailed.

DWTP 1 – Llobregat DWTP (Abrera)

The DWPT is located in Abrera (Barcelona province, NE Spain) and is managed by Ens d'Abastament d'Aigua Ter-Llobregat (ATL). This facility was built in 1980 and takes water directly from Llobregat river. The Llobregat is one of the main rivers of the region and crosses Catalonia from the north to the south with the mouth into the Mediterranean Sea. Concerning the river hydrology, the Llobregat river basin and the river flow are controlled and managed through several reservoirs located upper basin. These are the Baells, Llosa del Cavall and Sant Ponç dams; with a capacity of 503, 80 and 24 hm^3, respectively (see Figure 8 a, b, c). Reservoirs function is basically related to store water for several uses (e.g. drinking water production) ensuring the ecological river flow. Concerning the geology and related to the Llobregat river water quality, the presence of salts in the upper part of the river induce riverbed minerals dissolution and in consequence an increase of the water pH and conductivity (Valero and Arbós, 2010; Postigo et al., 2018). On the other hand, many industrial activities and high density population centres are found close to the Llobregat river. Traditionally, textile factories used the water of the Llobregat river for the manufacturing processes. As a consequence, this area is an important pillar for the regional economy, becoming a place presenting a huge number of industries (mainly pharmaceutical and textile) using water for many processes involved in the production chain. Despite that the industries have its own water treatment plants, the final treated waters are returned to the river affecting the river water composition (Kuster et al., 2008). All of these factors directly affect water quality/quantity fluctuations. Currently, the constructed capacity for the water treatment is 3.2 $m^3 \cdot s^{-1}$ and supplies water to the Barcelona metropolitan area.

DWTP 2 – Ter DWTP (Cardedeu)

The DWTP is located in Cardedeu (Barcelona province, NE Spain) and is also managed by ATL. This facility started to work on 1966 and currently has the capacity to treat 8 $m^3 \cdot s^{-1}$ of water from Sau-Susqueda-Pasteral reservoirs system (Ter river). The Ter river is the third river in Catalonia in terms of water flow, originated in the Pyrenees ending in the Mediterranean Sea. In the middle part, the river is controlled by the abovementioned reservoirs, using the water potential energy for electricity production. These reservoirs are placed in series and have a total capacity of 400hm^3, with the following distribution: Sau is about 165hm^3, Susqueda has a capacity of 233hm^3 and then the Pasteral dam with 2hm^3. The water is collected through 56km of pipe (3m of diameter) ending directly to the DWTP inlet. The DWTP managers have the possibility to collect the water source from different reservoir depths depending on the expected water quality and its physicochemical properties controlled from the monitoring stations, which are installed in the reservoir. Together the DWTP 1 and 2 supply drinking water to the Barcelona metropolitan area, resulting in total of 4.5 million inhabitants.

DWTP 3 – Montfullà DWTP (Girona)

The DWTP is placed in the Montfullà (Girona province, NE Spain), upstream from Girona city. This fact allows to distribute the produced water gravitationally. The facility is managed by Aigües de Girona, Salt i Sarrià de Ter. The DWTP was built on 1976 and in 2012 its capacity was increased to cope with the population growth demand. The treatment capacity of the plant is 1.4 $m^3 \cdot s^{-1}$ supplying water to Girona province (Girona region and Costa Brava). Water is collected from the Sau-Susqueda-Pasteral reservouirs system (Ter river) through a pipe of 15km. The water is supplied to a total population ascending to 300k inhabitants.

3.1.2. DWTPs unit operations

As it is said in the introduction, water composition is determined by multiple factors. These composition has some implications for the water treatment processes. There are other factors which can influence the type and the number of processes implemented in a DWTP, which are related to the DWTP budget or the available surface area. The DWTPs implemented treatment processes (unit operations) are presented in Table 2.

Table 2: DWTPs main characteristics and technologies applied for the water treatment.

DWTP	Capacity ($m^3 \cdot s^{-1}$)	Water Source	Unit operation					
			PO	Coagulation	Settling	Sand Filters	GAC filters	Membranes
1	3.2	Llobregat river	X	X	X	X	X	X
2	8	Sau-Susqueda-Pasteral reservoirs	X	X	X	-	X	-
3	1.4	Sau-Susqueda-Pasteral reservoirs	X	X	X	X	X	-

In reference to Table 2, the DWTPs present some differences in terms of applied treatments and technologies. The three facilities have implemented the same configuration for the conventional water treatment: pre-oxidation (PO) followed by coagulation-sedimentation. From Table 2, it is shown that DWTP 1 is the facility where membrane-filtration technologies are applied. This fact basically relies on the need to remove DBPs precursors and improve the water organoleptic properties (Godo-Pla et al., 2021). Further information related to the technologies applied at each DWTP will be detailed in the following sections.

3.1.3. DWTPs data

With the aim to monitor water treatment process efficiency and control the operational factors for each unit operation, the DWTPs have implemented several analysers, online sensors and probes. Additionally, the DWTPs analyse the water samples routinely. Laboratory staff is responsible to check the final waters quality as well as to determine the water efficiency though the water treatment and unit operations performance. From this, databases for each case study DWTP were generated. These datasets were categorized depending on its precedence in operational data from online measurements and laboratory analyses carried out by the laboratory technicians.

Operational parameters database is composed by two main categories: process factors and water quality parameters. Regarding the former, involve all these standards related to the hydraulic conditions like water temperature and the different flows in the water treatment (influent, sludge, effluent…). Furthermore, all the dosages regarding the different processes are included in this category. Then, the water quality is monitored through several standards which are mainly used as surrogated parameters accounting for water organic compounds (e.g. TOC and UV_{254}) or are parameters aided to describe the general water characteristics (e.g. turbidity). From this, a summary of the water quality standards registered daily during one year at each DWTP is presented in Table 3.

Table 3: Influent water characterization at the three case study DWTPs. Data were obtained from the implemented operational sensors and values presented correspond to 365 days. Turbidity was measured in nephelometric units (NTU).

Parameter	DWTP 1			DWTP 2			DWTP 3		
	$\bar{X}$±Std	P10	P90	$\bar{X}$±Std	P10	P90	$\bar{X}$±Std	P10	P90
Temp. (ºC)	17.3±6.3	8.8	25.7	12.7±2.6	9.7	16.2	11.7±1.2	10.2	13.4
pH	8.1±0.2	7.9	8.3	8.1±3.9	7.8	8	7.8±0.1	7.6	7.9
Flow ($m^3 \cdot s^{-1}$)	1.4±0.5	0.7	2.2	4.8±1.5	3.1	6.9	0.6±0.1	0.5	0.8
Turb. (NTU)	44.8±15.7	5	55.5	4.7±4.2	0.6	10.2	1±0.9	0.4	1.6
TOC ($mgC \cdot L^{-1}$)	3±0.7	2.3	3.7	2.7±0.3	2.4	3.1	2.4±0.4	2	2.9
UV_{254} (m^{-1})	6.5±2.4	4.9	8.2	6.2±0.8	5	7.4	_	_	_

The presented values correspond to the average for each influent parameter. Table 3 shows significant differences between the DWTPs influent water quality, mainly attributed to the type of water catchment. Values are expressed by mean and standard deviation. The mean value provides information about the general influent water characteristics and the standard deviation determines the fluctuation of the different parameters during the year.

3.1.4. DWTPs processes

DWTPs hydraulic scheme is presented in Figure 9. As it is said, there are common treatments for the three DWTPs. Influent waters are treated through PO followed by coagulation-flocculation-sedimentation. Then, filtration-based technologies are applied. These can be conventional treatments like sand filtration (DWTP 1 and 3) or advanced treatments such as activated carbon filters (DWTPs 1, 2 and 3) or electrodialysis reversal (EDR) in the case of DWTP 1. Starting with PO, the reagent used as oxidant is different in DWTP 1 (potassium permanganate - $KMnO_4$) compared to DWTP 2 and 3 (chlorine dioxide - ClO_2).

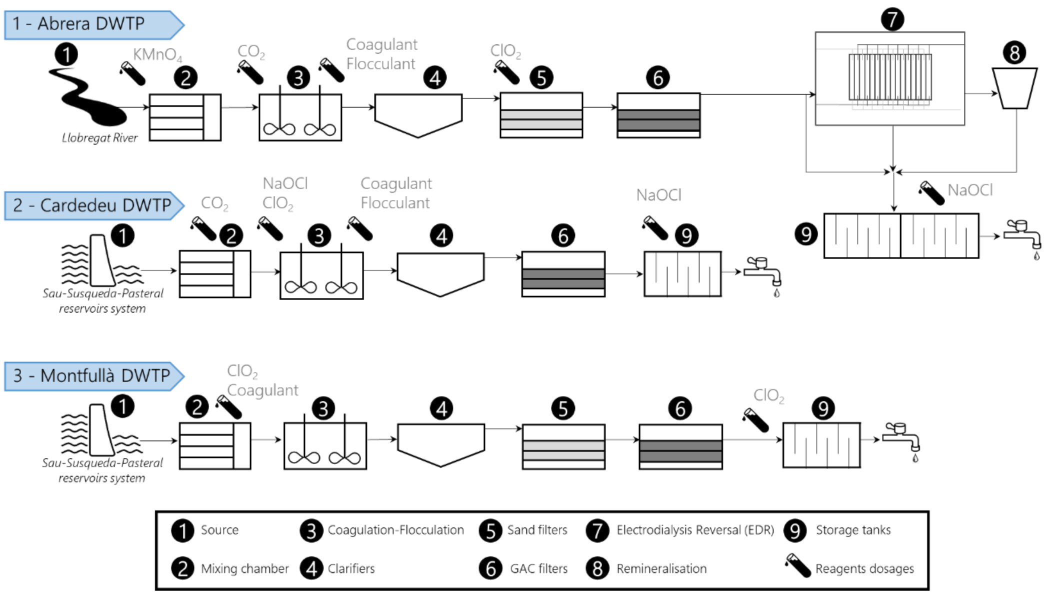

Figure 9: DWTPs unit operations scheme and reagents dosage from influent water to the final distributed tap water.

Following the treatment train, coagulation-flocculation-sedimentation step is located just after PO. In the DWTP 1 and DWTP 2 two different coagulants are added (acting as coagulant and flocculant) while in DWTP 3 only one reagent is added for coagulation. The reason behind adding only one coagulant is due to the water source characteristics, the coagulant nature and the treatment performance.

During the last decade, competitive online sensors and analysers have emerged to provide online data, aiding to DWTPs management. Currently, almost all plant managers and operators have the capacity to check the water characteristics and the hydraulic information about the process performance (flows, volumes...) at real time. All of this data is integrated and structured in a SCADA system. In some cases, the operational set points can be visualised. The system is continuously generating new data, which is stored in the DWTP database. Based on this, the list of the available data for each DWTP unit operation is presented in Figure 10.

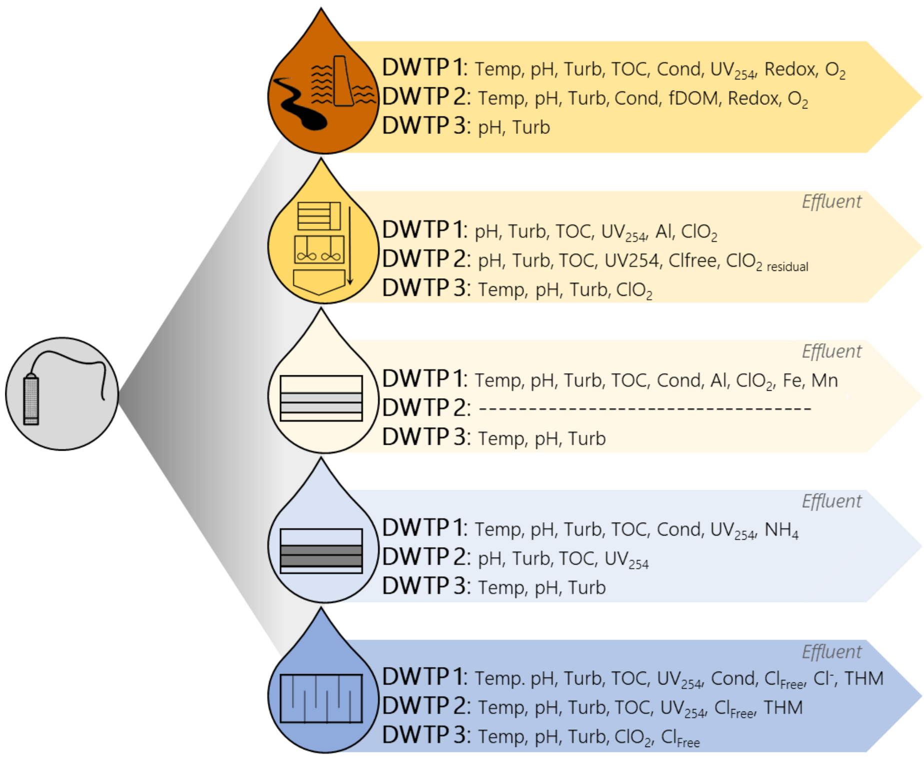

Figure 10: Parameters monitored through online sensors and analysers at the case study DWTPs. Parameters registered at the effluent of each unit operation.

From this information, databases were developed for each DWTP during the initial stages of this work, including data collected from operational sensors and the laboratory routine analyses. These databases were used to perform the different studies developed in this thesis.

3.1.5. Sampling campaigns and completed work

Several sampling campaigns and visits to the DWTPs were occurred during the development of the different studies. During the initial stages, works were focussed on the water samples characterization and the process knowledge acquisition through interviews and meetings with plant managers and operators.

3.2. Laboratory experiments

The different analyses were performed with real samples collected at the three DWTPs. Samples were obtained all over the years attempting to describe the seasonal fluctuations in terms of water quality.

3.2.1. Water storage and characterization

All water samples were collected and storage following the recommendations stated by the standardized water quality ISO for the preservation and handling of water samples (ISO 5667-3:2018). Then, depending on the nature of the analytics samples were collected with polypropylene bottles or glass vessels.

Water was characterized using the surrogated NOM parameters described in the introduction section. The available and updated versions of the standard methods for the examination of water samples were applied. The specific equipment and methodologies used for parameters determination are described in each thesis chapter.

3.2.2. Jar test

The jar test is a well-known and widely used methodology in the field of water treatment. From this, specific protocols for each DWTP were adapted for the development of RSM. Previous to the RSM, other jar test experiments were performed to stablish the desired analytical procedure with the aim to replicate the real full scale conditions for coagulation. To achieve that, water samples were collected from the case study DWTPs and rapidly transported to the university laboratories. Subsequently, the methodological procedure as well as the analytical characterization were done according to the goal of each study. This information will be provided in the respective thesis chapters.

Jar test consists in the replication of real DWTPs coagulation but at laboratory scale. Basically, as it was said in the introduction section, the key factors to control are pH and the Cd. Figure 11 shows a general schematic diagram for jar test in water treatment, consisting on pH and Cd adjustment under specific contact time and mixing velocities. Firstly, the same water samples (collected from the DWTPs) are placed on different vessels. Each one of this vessels will be adjusted under specific values of pH and Cd. Then the pH is adjusted and the coagulant is added under rapid mixing conditions. Subsequently, once it is ensured that the coagulant is completely mixed with the sample with the stablished contact time it is the turn of flocculant dose (Fd), if is required. Flocculation is the stage characterized by a slow mixing, which aids the flocculant to interact with colloidal NOM to form flocs (Pallier et al., 2010; Xia et al., 2018). To conclude, some minutes of sedimentation are required waiting for flocs precipitation. At the end, water samples are collected at the middle of water column for the analysis, avoiding the resuspension and the interference of the deep precipitates. The coagulation conditions as well as the nature of the coagulants used to perform the analyses are detailed in the respective thesis chapters.

3.2.3. Ultrafiltration experiments

Ultrafiltration (UF) membrane experiments were performed with different samples. The methodology as well the results obtained from the UF tests are presented and discussed in Chapter 4 of this thesis.

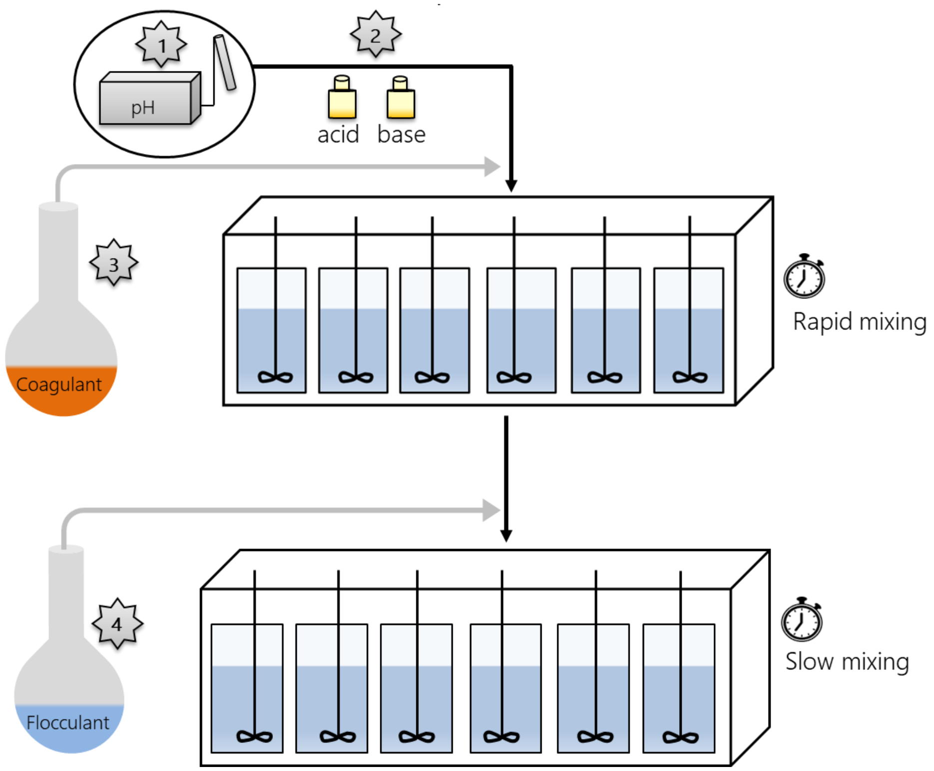

Figure 11: Schematic procedure for the application of jar test methodology for the optimization of coagulation unit operation in drinking water treatment.

3.3. Programming tools

With the aim to develop an EDSS for the enhanced coagulation in drinking water treatment, several tools were used to evaluate the data, for planning the experiments and for building the enhanced coagulation models.

3.3.1. Coagulation experiments design

Design-Expert® (Stat-Ease, Inc., Minneapolis, MN, USA) software version 11.0 was used as tool for planning RSM. This program allows to design the desired plan of experiments specifying the RSM boundaries and its internal structure selecting the statistical approach. Basically, the task consists in determining which are the factors and the responses affecting the coagulation process, defining the number of the experiments and the statistical approach selected for this purpose. Hence, the different RSMs were planned and executed following the software interface, with an individual design for each DWTP scenario. Then, Design-Expert offers some statistical metrics to evaluate the models and its structural validation (model analysis). Additionally, with this software is it possible to optimise the process based on the selection of the responses optimum range and then obtaining the corresponding factors' values. Further information about the specificities related to the factors and responses selection, factors' ranges and results obtained from the optimisation are detailed on each thesis chapter.

3.3.2. MATLAB

MATLAB software (Mathworks®, Natick, MA, USA) was used to systematise and optimise some tasks in this work. In Chapter 5, the study of model predictors and the subsequent sensitivity analysis were performed with MATLAB. Then, the models validation as well as the codification of the THMs models based on enhanced coagulation (Chapter 6) was executed with MATLAB. A part from that, other tasks related to the DWTPs databases evaluation were done using this software because the capacity to work with full-scale databases. More detailed information about this works is discussed in deep in each one of the thesis chapters.

3.3.3. Python

Python programming language (Python Software Foundation, Wilmington, DE, USA) was used to codify the cluster analysis accounting for the influent waters characterization in Chapter 5.

4. Results I

Development of an Environmental Decision Support System for Enhanced Coagulation in Drinking Water Production.

Redrafted from:

Suquet, J., Godo-Pla, L., Valentí, M., Verdaguer, M., Martin, M.J., Poch, M., Monclús, H. (2020). Development of an Environmental Decision Support System for enhanced coagulation in drinking water production. Water (Switzerland) 12 (8), 2115. https://doi.org/10.3390/w12082115

4.1. Background

To avoid DBPs formation throughout the distribution network, Spanish legislation requires a chlorine-based oxidation process at the end of treatment (RD 140/2003). It is at this point where NOM removal becomes significant, given that NOM is the largest precursor of these compounds (Crozes et al., 1995; Godo-Pla et al., 2021; Liang and Singer, 2003; Wang et al., 2017). An increase of NOM removal in coagulation reduces DBPs formation along water treatment and distribution.

The most typical configuration is coagulation/flocculation coupled to filtration-based processes. Considering processes following coagulation, UF membranes are emerging as promising and robust water quality treatments (Fiksdal and Leiknes, 2006; Liu et al., 2017) that can even work as hybrid systems (Meng et al., 2019; Sillanpää, 2015). In this sense, parameters monitored to control membrane fouling can be used to complement NOM characterization (Pollice et al., 2004). Hence, the integration of enhanced coagulation models coupled with the expert rules derived from membrane experiments can improve DWTPs performance.

In an integrated treatment, the efficacy of enhanced coagulation has an impact on the following unit operations and, as such, the type of coagulant, dosages, dosing methodologies (continuous or intermittent), dosing points, and mixing methods (Matilainen et al., 2010; Zularisam et al., 2007) must be controlled in order to avoid membrane fouling, if the next unit operation in the treatment chain is a membrane-based treatment (Bu et al., 2019; Kimura et al., 2014). Several water properties (hydrophobicity, charge density, molecular weight, and molecular size) and impurities (colloidal or dissolved, protein-like substances, organic or inorganic) contribute to the fouling phenomena (Chen et al., 2014; Shamsuddin et al., 2015). Considering all of this, UF fouling indicators can be used to characterize NOM, adding information to that already provided by the enhanced coagulation models.

To track and remove NOM content, DWTPs have developed a set of analytical techniques and have improved the quantity of the sensors implemented to monitor NOM, in an attempt to adapt the treatment to the environmental conditions (Bridgeman et al., 2011). This data can be codified and incorporated into an EDSS. EDSS operation requires a structure to work with a fast and easily updated version of the system and to include any new requirements (legislation updates and modifications), new models, or new DWTP treatments. In that sense, the EDSS operation can be structured hierarchically with the three-level architecture (see Figure 6).

The present study was carried out within the framework of developing an EDSS for a water treatment facility in the Mediterranean (DWTP 3), which would help to improve the whole plant's performance. The general objective was to develop an EDSS module for enhanced coagulation in order to determine the optimum operation conditions for this unit operation by achieving the following three specific objectives: (i) develop an enhanced coagulation models using RSM, (ii) evaluate the models for the case study, and (iii) to propose EDSS operational architecture.

The chapter is structured as follows: First, in the methodology section DWTP case study, laboratory experiments, and RSM coagulation models design are described; then, the results and discussion are divided into two subsections, the enhanced coagulation models development and the EDSS architecture, where models were analysed and structurally validated. Then, the three-level architecture of the EDSS is proposed and specified with expert supervision rules (SRs).

4.2. Methodology

4.2.1. Case study

The enhanced coagulation EDSS was developed at DWTP 3, previously described in the methodology section. This facility catches water from reservoirs located in the Ter river basin, conducted through 16 km pipeline. The effect the reservoirs have on the quality of the water along the Ter river has been studied since the 1990s, and the water before and after the reservoirs' experience has been determined as having differences in NOM quantity and quality due to the settling effect and also the degradation of the organic compounds (Espadaler et al., 1997). The treatment chain at the DWTP 3 is comprised of the following: PO process with chlorine dioxide (ClO_2) in the mixing chamber; followed by coagulation and flocculation with the addition of powdered polyaluminium chloride (PAC) before slow sedimentation settling; then, gravity filtration through sand filters and GAC beds. At the end of the treatment, the disinfection phase occurs to ensure the free chlorine concentration required as the water is moved through the supply distribution network (RD 140/2003), detailed in Figure 9.

A group of parameters are monitored to characterize the influent coming into the facility and adapt the treatment to the changing conditions (Table 3). Some of these parameters, such as turbidity and TOC are used as NOM content indicators.

Influent raw water parameter selection

First, for the EDSS data acquisition level, it was necessary to identify the source and the availability of data. The aim was to propose a database for EDSS data acquisition. Different types of information were included in this database: water quality from influent and treatment, operational reagent dosages and laboratory analytics. To proceed with this analysis objectively, data were classified into databases A, B, and C based on their source, typology, and nature. Database A contained the manually introduced data from the DWTP 3 laboratory analyses; Database B contained the data collected from the sensors, probes, and online analysers; and Database C contained the values of the operational reagent dosages and other working parameters (flow, pH, HRTs, etc.).

Then, data from the DWTP influent were evaluated statistically representing the temporal evolution of the variables to detect behavioural patterns (seasonality) and cases of changing conditions, as well as normal distribution diagrams and other statistical values (average, median and percentile values, box diagrams, and so forth). Furthermore, Pearson correlations were analysed to determine the influences between parameters. Data processing tools Excel 2016 (Microsoft®, USA, Santa Rosa, CA) and MATLAB 2015a (Mathworks®, USA, Natick, MA) were used to perform these analyses.

All these statistics, graphs, and correlations were assessed to identify the key influent parameters which needed to be considered to achieve an enhanced coagulation RSM model (EDSS control level). To compare the effect of raw water characterization and PO (ClO_{2DOSE}) against the coagulation parameters from the DWTP 3, the data provided for Databases A, B, and C were correlated with the Cd. Table 4 shows the results from these correlations.

Table 4: Pearson's correlations between the influent water quality parameters and Cd at DWTP 3 (1/1/2014-31/12/2018).

	$Turbidity_{RAW}$	TOC_{RAW}	pH_{RAW}	ClO_{2DOSE}
Cd	0.46	0.20	0.16	0.03

Observing Table 4, the highest correlations with the Cd were $Turbidity_{RAW}$ and TOC_{RAW}. Based on these results and the pre-existing scientific bibliography, these two raw water parameters were selected as enhanced coagulation model responses. Besides these, UV_{254} was included in the models and was proposed as a good indicator for NOM (Ates et al., 2007). The objective of enhanced coagulation is to consider more responses (water parameters) than the OFAT approach does. For that reason, and to increase RSM robustness, three factors were selected as the most representative for DWTP coagulation performance: Turbidity, TOC and UV_{254}.

4.2.2. Jar test experiments

Coagulant supplied by the DWTP was used in this study. The coagulant was alum-based (PAC), and the pH was adjusted with HCl 0.1M and NaOH 0.1M before the addition of the coagulant reagent. A Phipps & Bird (7790-910, Richmond, VA, USA) programmable jar tester was employed for the experiments (6 × 2 L rectangular jars). Mixing conditions were divided into three sequential steps as follows: rapid mix phase (1 min at 250 rpm), slow mix phase (30 min at 30 rpm), and a settling time of

30 min. The coagulant was added at T_0 of the rapid mix phase. NOM parameters (turbidity, TOC, and UV_{254}) were measured before and after the jar test experiments. Supernatants were collected from the middle of the water column to avoid collecting unstable superficial flocs.

4.2.3. Experimental methodology for UF membranes

To quantify the fouling phenomena, a bench-scale membrane filtration system with the ability to filter, in parallel, different water samples was constructed (Figure 12). As NOM is considered to be one of the most critical fouling factors, different operational and quality parameters were monitored, including transmembrane pressure (TMP) values, flux, and permeability (K).

To assemble the hollow fiber (HF) UF membrane modules, a protocol to ensure that their characteristics were similar had to be developed. Each module was composed of two new polyvinylidene difluoride (PVDF) fibers of equal length, (approximately 30 cm), thus, providing a useful filtration area of around 0.004 m^2. The fibers used for the modules were provided by Polymem® and had a cut-off of 0.1 μm. All the modules were validated with an integrity test (5 min at 1 bar of pressure) and then the liquid permeability was assessed at 20 °C. Next, the continuous filtration experiments for estimating potential fouling were planned by maintaining a theoretical constant flux (monitored during the experiments) and evaluating the permeability as a key parameter in order to analyse the fouling potential (Le Clech et al., 2003; Monclús et al., 2011).

The experimental UF tests, presented in this study, were evaluated by filtering the supernatant jar samples obtained after the coagulation experiments and the real DWTP coagulated sample. NOM-related parameters were measured before the UF experiments were run and at the same time as permeability was recorded. The study of permeability enabled the comparison between samples to be made because it integrated small changes into surface filtration areas which were calculated using online flux and transmembrane pressure (TMP) values (Eq.2). The loss of permeability over the experiment was also calculated (Eq.3).

$$\text{Permeability (K)} = \frac{\text{Flux (LMH)}}{\text{TMP (Bar)}} \tag{2}$$

where flux is expressed by $\mathrm{L \cdot m^{-2} \cdot H^{-1}}$ and TMP in Bar.

$$\% \text{ Permeability lost } (K_{LOST}) = \frac{K_{ti} - K_{tf}}{K_{ti}} \text{ x } 100 \quad (3)$$

where K_{ti} and K_{tf} are permeability values at time = 0 and time = final, respectively.

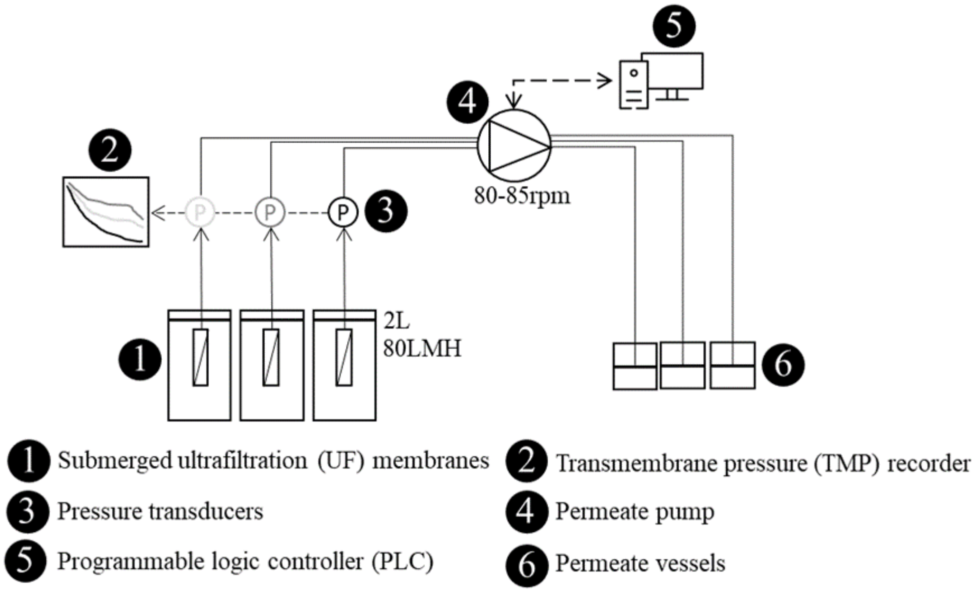

Figure 12: Membrane filtration bench scale setup.

The UF experiments were carried out before (BF) and after (AF) a heavy flood event. This kind of extreme phenomena is typical in Mediterranean regions, causing alterations in reservoirs' water quality in terms of particulate and dissolved organic loads (Romero and Imberger, 2003). As the DWTP catchment is a reservoir system, the aim of the UF experiments was to correlate enhanced coagulation performance and UF membrane operation. In addition, all the samples were chemically analysed.

4.2.4. Chemical analysis

Water samples were characterized by monitoring specific parameters, including pH, turbidity, total carbon (TC), TOC, UV_{254}, at the case study DWTP. For the turbidity measurements, a Hach TU5200 turbidimeter was used and the results were recorded in NTU. TC/TOC and UV_{254} (cm^{-1}) were analyzed with a Sievers M9 portable analyzer and a Cary 3500 UV-Vis Agilent Tech spectrophotometer with a quartz cell (1 cm of path length), respectively. The TC and TOC values were analyzed with the ICR function activated, thus, ensuring an inorganic carbon (IC) loss between 90 to 99%. Meanwhile, the pH was determined with a Crison micro pH 2000. SUVA value was calculated resulting from the division of UV_{254} by TOC (USEPA, 2009).

The ISO 5667-3:2018 requirements were followed to transport, store, and pretreat the samples. Samples were collected (without adding chemical reagents), directly from the DWTP influent through a pipe or from the river catchment, and were stored in amber bottles, in darkness at 4 °C. Once in the laboratory, to determine the TOC and UV_{254}, the samples were filtered through 0.45 μm nylon filters prior to analysis. UV_{254} was measured according to Standard Methods: 5910 (Eaton et al., 1995).

4.2.5. RSM design

The pH and Cd were considered to be the key factors (A and B, respectively) in developing RSM design. RSM has been reported as a useful approach to model multifactorial processes such as coagulation. According to the methodology reported by Trinh and Kang (2010), CCD was used for RSM design. Design response parameters were turbidity (%), TOC (%), and UV_{254} (%) removal. Design-Expert® was used to design, analyse and evaluate the RSM and also for planning the experiments.

The RSM was designed for a wider range of factors than those encountered in real DWTP operation, because the aim was to describe a total surface output model for the selected response parameters. The DWTP 3 design was factorized with a pH range from 5.5 to 8.5, but in a real plant the operation fluctuates between 7.5 and 8. The Cd was defined in the range from 10 to 40 $mg \cdot L^{-1}$, which was considered to be feasible and representative.

Once the CCD-RSM was developed, the model's outputs were used to identify the best pH and coagulant conditions for enhanced coagulation. The removal percentages of the response variables (turbidity, TOC, and UV_{254}) were configured as an output of the model by following equations (4) – (6). The raw water samples correspond to the DWTP influent water quality parameters, without reagents.

Sampling campaigns are planned to be carried out throughout the year, including seasonality events and different quantity/quality NOM fluctuations, in order to enhance the robustness and accuracy of the proposed design.

$$\%\mathrm{Turbidity}_{\mathrm{REMOVED}} = \frac{\mathrm{Turbidity}_{\mathrm{RAW}} - \mathrm{Turbidity}_{\mathrm{SUPERNATANT}}}{\mathrm{Turbidity}_{\mathrm{RAW}}} \times 100\% \tag{4}$$

$$\%\mathrm{TOC}_{\mathrm{REMOVED}} = \frac{\mathrm{TOC}_{\mathrm{RAW}} - \mathrm{TOC}_{\mathrm{SUPERNATANT}}}{\mathrm{TOC}_{\mathrm{RAW}}} \times 100\% \tag{5}$$

$$\%\mathrm{UV254}_{\mathrm{REMOVED}} = \frac{\mathrm{UV254}_{\mathrm{RAW}} - \mathrm{UV254}_{\mathrm{SUPERNATANT}}}{\mathrm{UV254}_{\mathrm{RAW}}} \times 100\% \tag{6}$$

4.3. Results and discussion

In this section, the enhanced coagulation model and the UF membrane experiments are presented. Then, the data and knowledge are incorporated into the EDSS architecture.

4.3.1. Development and evaluation of the enhanced coagulation models

The enhanced coagulation models based on the RSM-CCD developed at the case study DWTP is presented here. The factors for the model were pH (A) and Cd (B), while percentages of turbidity, TOC, and UV_{254} removal were the responses. The summary of run factors provided by the model's output and responses obtained from the analysis of the supernatants are presented in Table 5.

Table 5: Summary of runs, factors, and responses of RSM design.

$Water_{RAW}$: Turbidity = 1.41 NTU, TOC = 3.16 mg·L^{-1}, UV_{254} = 0.104 cm^{-1}						
Run	Factors		Responses (% of Removal)			
	pH	Cd	Turbidity	TOC	UV_{254}	$\bar{X}$
Units		(mg·L^{-1})	(NTU)	(mg·L^{-1})	(cm^{-1})	(%)
1	7	25	51	10.2	27.2	29.5
2	7	25	62.2	10.8	37.8	36.9
3	7	25	64.9	7.3	34	35.4
4	8.5	40	65.1	6.8	34.6	35.5
5	5.5	10	56.3	8	23.4	29.2
6	5.5	10	66.6	17	36.2	39.9
7	8.5	10	47.1	ns	1.2	-
8	5.5	40	70.9	36.3	41.8	49.7
9	8.5	10	55.4	ns	1.9	-
10	5.5	40	67.3	29.8	42.3	46.5
11	8.5	40	65.5	10.6	14.4	30.2

12	7	25	68.4	17	20.8	35.4
13	7	25	67.5	21.8	16	35.1
14	9.5	25	ns	11.2	19.5	-
15	4.5	25	77.5	23.2	49.3	50
16	7	0	47.6	ns	ns	-
17	7	50.1	62.1	35.3	22.7	40
18	7	25	67.7	20,4	22.1	36.7

ns: % of removal<0.5.

Some of the runs presented response values without significant percentages of removal (less than 0.5%) and, as such, were not considered. These results can be explained by the high pH effect (in Runs 7, 9, and 14) and the absence of coagulant dosage (Run 16).

Model analysis and diagnosis

In this section, the results from model fitting and process analyses are presented. For three responses, statistics provided by ANOVA exhibited that model terms were significant (p-value < 0.05). Models did not exhibit lack of fit (p-value > 0.05), thus, indicating a significant level of confidence (lack of fit was not significant relative to the pure error). Therefore, the normal plot of residuals did not show significant deviations with respect to the linear distribution (Figure 13 - A). Points which differed from a linear distribution were checked and significant relevance was not detected (Figure 13 - B).

The coded equation can be used to predict responses for a given level of each factor and to identify the relative impact of the factors by comparing the factor coefficients. In addition, it is useful to know what the most relevant factor for each response is (A, B, AB, A^2, and B^2) and which of these are significant model terms. In that sense, the quadratic equations suggest that the Cd represents the highest influence factor for turbidity and UV_{254} removal (Table 6).

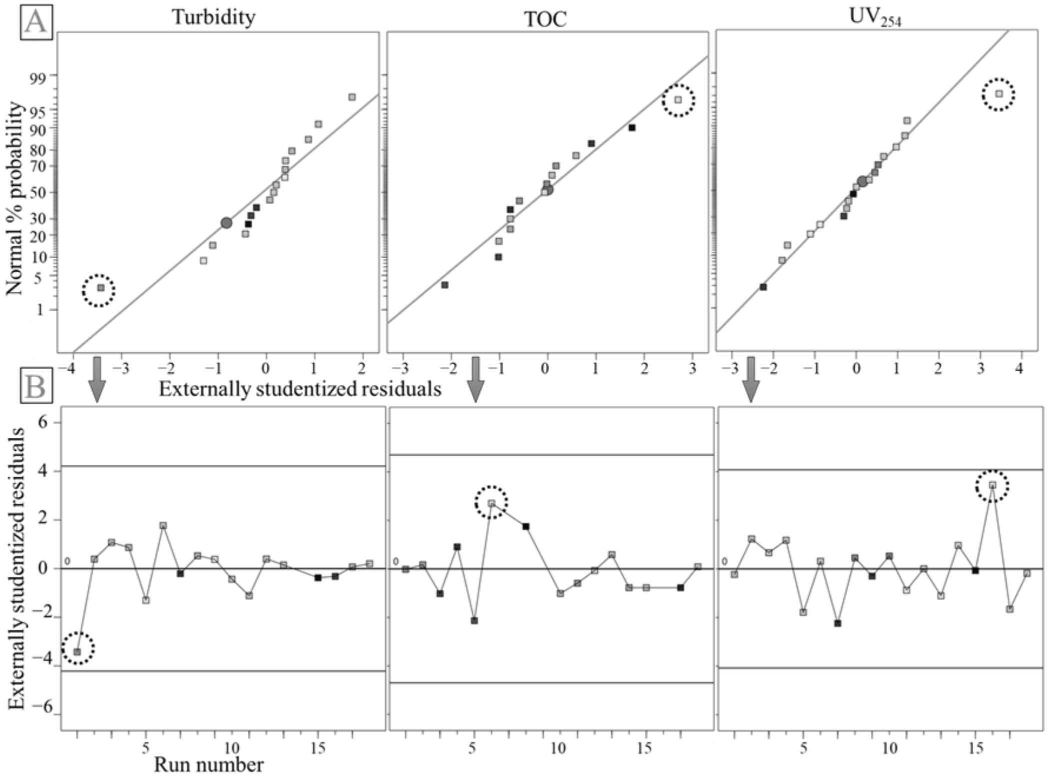

Figure 13: Normal distribution of residuals (A) and residuals per run (B).

Table 6: Enhanced coagulation models fitting at the DWTP 3.

Removal (%)	Coded Equation	N	R^2
Turbidity=	$+64.77 - 3.35A + 4.05B^* + 3.19AB + 2.02A^2 - 4.2B^{2*}$	17	0.79
TOC=	$+15.86 - 3.77A^* + 0.08B - 6.54AB - 0.88A^2 + 5.69B^{2*}$	15	0.89
UV_{254}=	$+24.39 - 10.4A^* + 7.06B^* + 0.62AB + 3.14A^2 - 2.03B^2$	18	0.76

A: pH and B: Cd. * Significant factors for each response.

To evaluate the designed response surface (RS), the standard error (SE) was plotted in the fraction of design space using a fraction of design space (FDS) graph, thus, providing information about the maximum predictor variability of any given factor the RS represented by the models (Anderson and Whitcomb, 2014). In this case, 80 percent of the described RS falls at or below 0.44 units of SE (Figure 14 - A). The representation of SE in our RS is useful in order to determine the prediction power. In this case, the RS predictability present less SE at intermediate values of pH and Cd (Figure 14 - B) because the CCD is a design composed of six centre points, and therefore more robust in the middle of the represented space. However, in the corners, close to our design limits, the RS is affected by the lack of predictability, i.e., regions where the response cannot be precisely predicted.

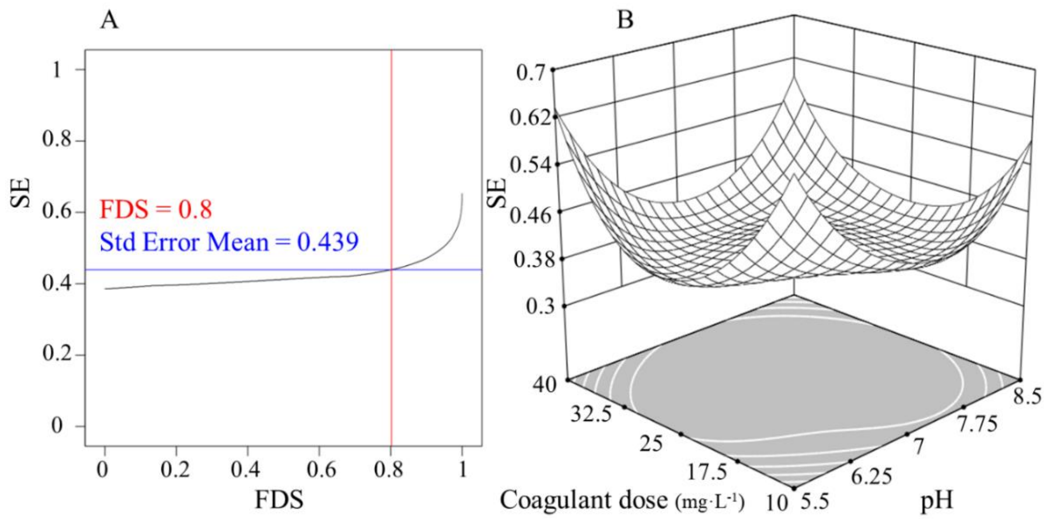

Figure 14: Model design evaluation. (A) FDS graph; (B) 3D SE representation.

Model optimisation

Once evaluated the accuracy and robustness of the performed models, the next step was to optimize the coagulation and to generate predictive models for the three responses, i.e., turbidity, TOC, and UV_{254} removal as a function of two factors, i.e., pH and Cd.

The numerical optimization is presented through the two-dimensional (2D) and three-dimensional (3D) RS plots shown in Figure 15. As a general trend, best removals were obtained at a lower pH for the three responses. For turbidity removal, the acceptable range (≥60%) was at a medium Cd and all ranges of pH, (see Figure

15). At neutral pH values and a high Cd, TOC removal was higher than 30%. At a feasible DWTP, (pH varying from 7 to 8), the highest removals were obtained at pH 7 and with a medium Cd (between 30 and 40 mg·L^{-1}), i.e., 65% of turbidity, 30% of TOC, and UV_{254} removal. RS plots are presented with the ranges fixed by model runs (0 – 50 mg·L^{-1}) for Cd and 4.5 – 9.5 for pH, (see Table 5) in order to observe the full gradient through the whole RS.

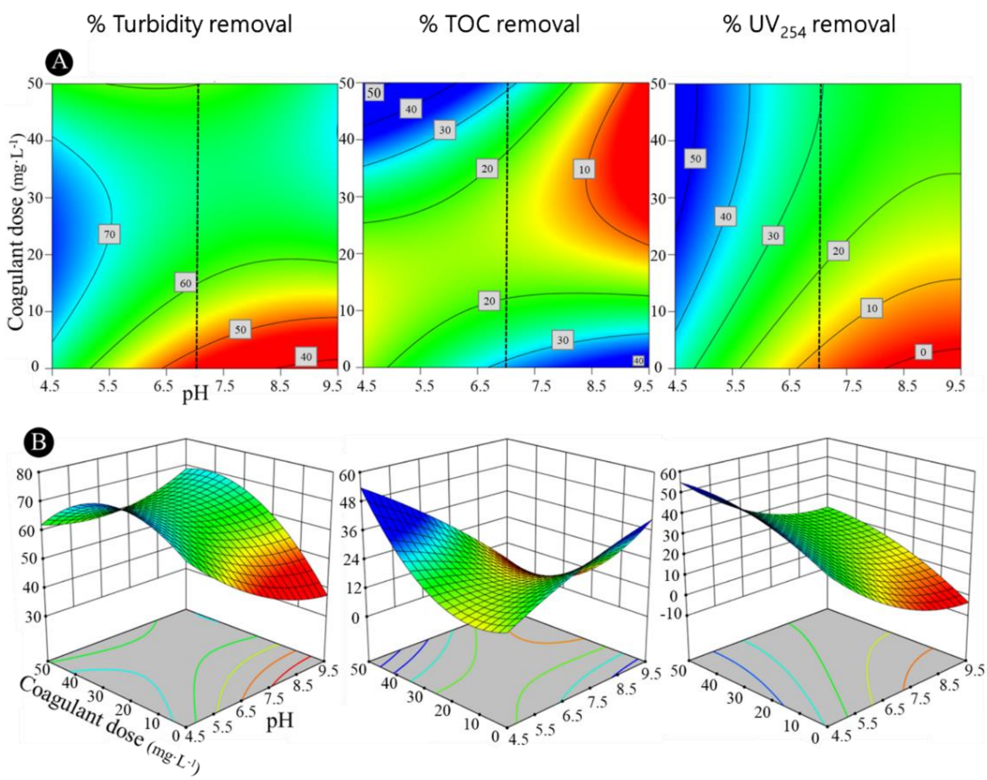

Figure 15: (A) 2D RS plots and (B) 3D RS plots of turbidity, total organic carbon (TOC), and UV_{254} removal for the model factors, Cd and pH. Dotted line in 5A corresponds to pH = 7.

Subsequently, the model was numerically optimized with the aim of determining a common RS in order to achieve satisfactory levels of removal for the three aforementioned responses. The optimization criteria were fixed by evaluating the minimum and maximum removals per run and response (see Table 5). For turbidity, the minimum removal was 47.1% and the maximum 77.5%, for TOC 6.8% and 36.3%, and for UV_{254} 1.2% and 49.3%. The suitable low range was calculated following Eq.7, thus, ensuring, at least, the mid-upper percentage of removal in the obtained response range. The upper range of response removal was the maximum obtained after the jar test experiments. Hence, selected ranges were superposed in a common surface, and the overlay graph was obtained (Figure 16). In Figure 16, the area shaded grey illustrates the surface area where the optimization criteria were achieved: 62.3 – 77.5% removal for turbidity, 21.55 – 36.3% for TOC, and 25.25 – 49.3% for UV_{254}. As in the discussion above, pH 7 was determined to be the best value for a feasible level in a real DWTP operation. For the model developed here, the yellow circle (pH=7 and Cd=40 $mg \cdot L^{-1}$) represents the optimized proposal for coagulation.

The results obtained by the model (the yellow circle) were compared with those from the real DWTP operation (the blue circle). For the real DWTP, the sampling campaign using the jar test took place in April 2019. The values were calculated from April's monthly average, with a pH result of 7.8 and Cd of 21.9 $mg \cdot L^{-1}$. The improvements obtained in terms of coagulation removals (Eq.8) were +4% for turbidity, +33% for TOC, and +28% for UV_{254} removal as compared with the DWTP's monthly operation mean. The lower impact on turbidity removal is fundamentally because of the low turbidity value of the influent water. However, it has been demonstrated that coagulants do increase the amount of turbidity removal with high turbid waters (as a consequence of more particulate NOM fraction), and their capacity for turbidity removal is likewise reduced in low turbidity waters (Asrafuzzaman et al., 2011; Pernitsky and Edzwald, 2006).

$$\text{Low Range (\%)} = \frac{\text{Response}_{\text{max}} - \text{Response}_{\text{min}}}{2} + \text{Response}_{\text{min}} \tag{7}$$

$$\text{Removal increase (\%)} = \frac{\text{Response}_{\text{RSM}} - \text{Response}_{\text{DWTP}}}{\text{Response}_{\text{RSM}}} \times 100 \tag{8}$$

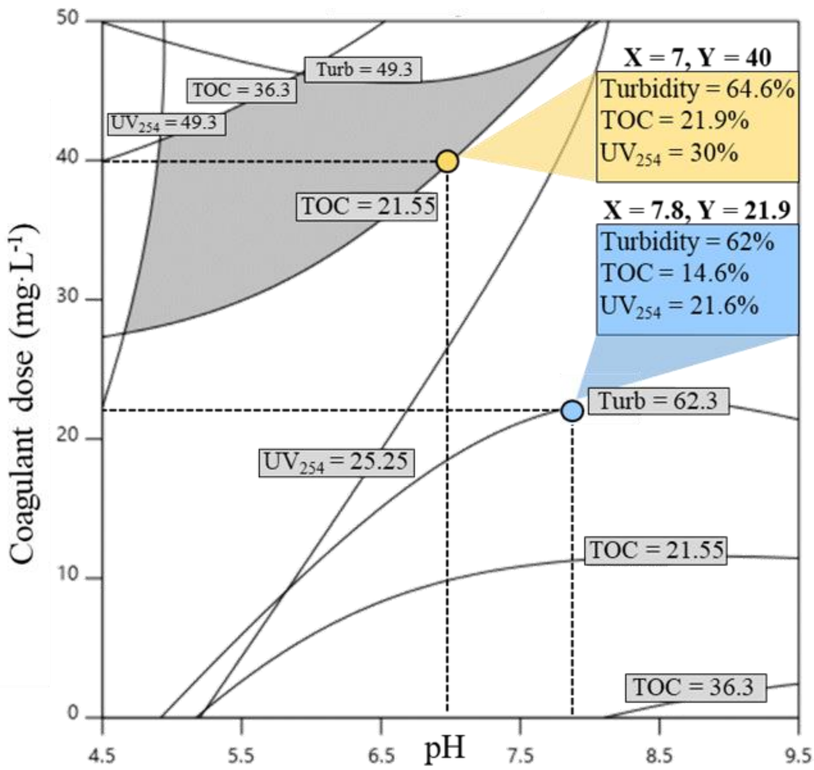

Figure 16: Responses overlay plots for turbidity, TOC, and UV254 % of removal at the DWTP 3. Regions that fit with fixed optimization criteria appear shaded in grey. The yellow circle represents optimum feasible conditions to achieve NOM enhanced coagulation and the blue circle shows real DWTP operation removals.

4.3.2. Enhanced coagulation — membrane filtration knowledge-based rules

In this section, the results from enhanced coagulation coupled to UF experiments are presented. After evaluating the supernatants obtained in the jar test experiments, runs 8 and 17 were chosen for continuous UF assays (Table 5). The election criteria followed the highest removal values for three responses (49.7%, Run 8) and the best run in a feasible operation at the DWTP (pH = 7, Run 17). Although Run 15 had high values, it was not selected because it was outside the initial model boundaries.

Permeability evolution over time was monitored. The reduction of permeability was related to fouling properties (Lee et al., 1984). The results shown in BF, dry period (Figure 17 - A), revealed that the decrease in permeability was higher in the DWTP sample than Runs 8 and 17, although the initial value being the largest. The UF membrane with the DWTP sample was the most fouled and experienced a 30% permeability loss. A comparison of these results with the AF event experiment (Figure 17- B) seems to indicate that there is no apparent relationship. After the flood, run 17 presented the most fouled sample, with a decrease in permeability of over 40%.

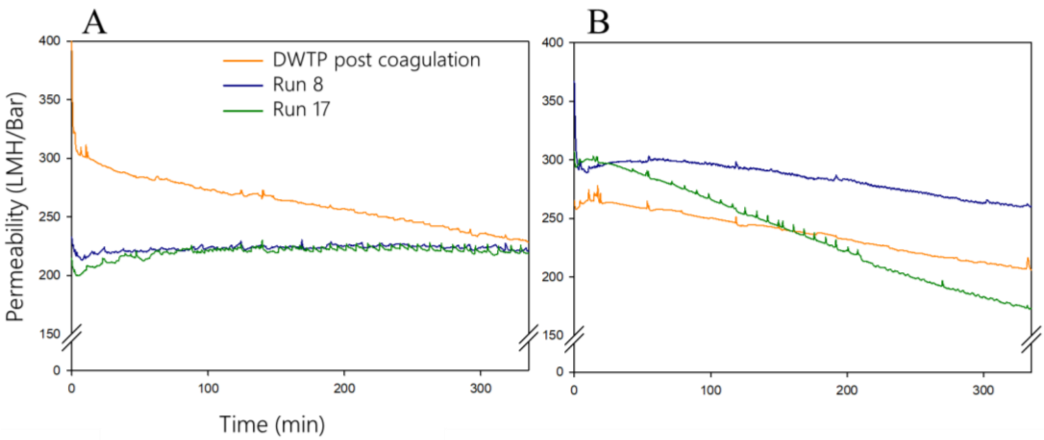

Figure 17: Evolution of permeability during UF experiments BF (A) and AF (B).

To understand these behaviours, the chemical parameters values (Table 7) had to be checked to comprehend the permeability decreases. As we expected, the waters from the AF event had more organic charge, reflected by the increase of turbidity and the UV_{254} values in the raw water samples collected. However, this trend was not observed for TOC. This can be explained by the fact that TOC content in large mass waters such as lakes or reservoirs is not related to precipitation or runoff (Hessen et al., 1997).

The results for samples with higher permeability loss are well associated with high values of UV_{254}. These results are in accordance with previous studies (Lowe and Hossain, 2008), supporting that UF membranes working with waters with a high level of aromatic compounds have a greater capacity to retain compounds associated with UV_{254} than those corresponding to the TOC fraction. The UV_{254} NOM fraction cannot pass through the membrane, consequently causing fouling and decreasing permeability capabilities.

Table 7: Chemical analysed parameters for each UF experiment.

Flood	Sample	Turbidity (NTU)	TOC ($mg \cdot L^{-1}$)	UV_{254} (cm^{-1})	K_{Lost}
BF	Raw water	1.97	3.72	0.075	ns
	DWTP post C.	0.85	3.28	0.046	30.3
	Run 8	1.3	3.15	0.031	ns
	Run 17	0.9	3.43	0.039	ns
AF	Raw water	74	3.6	0.264	ns
	DWTP post C.	0.85	3.28	0.046	19.2
	Run 8	1.3	3.15	0.031	21.5
	Run 17	0.9	3.43	0.039	42.3

ns, not significant and KLost value<5.

4.3.3. EDSS operational architecture

The information and knowledge acquired in this study allowed to establish a hierarchical structure and to propose the EDSS operational architecture (Figure 18). In the following section each EDSS level is described, including the proposed decision tree for the supervision level (Figure 19).

Data acquisition level

Data dumped directly from DWTP databases provide the input for the control and supervisory levels. The values used in the algorithms correspond to instantaneous readings from online sensors and analysers coupled with laboratory analytics.

Control level

Coagulation at DWTP 3 is controlled by fixing the Cd (PAC_{Dose}) and the pH set point at the clarifiers (pH_{clar}). The three parameters related to NOM content that were studied were considered for the EDSS design.

Turbidity, TOC, and UV_{254} are the raw water quality parameters monitored in DWTPs for NOM control. Regarding operational factors, in the case of DWTP 3 pH and Cd are the main variables that can be modified in order to optimize coagulation. Influent water quality accounts for the principal environmental conditions which, apart from the seasonal variations, also depends on the reservoir water quality (at the dam different heights can be selected to collect water) (Dragon et al., 2018). In order to include these fluctuations, it is important to complete the EDSS with updated versions that should include all this variability.

The model acts by recognizing the typology of influent water when it receives the three input variables (turbidity, TOC, and UV_{254}), and then considers all this information to propose an optimized pH and Cd for coagulation optimization. Based on the developed models foe enhanced coagulation, the EDSS was designed to propose operational consigns to ensure at least 62%, 21%, and 25% removal for turbidity, TOC, and UV_{254}, respectively.

Supervision level

Supervision level is placed at the top hierarchical EDSS architecture, where the expert knowledge is incorporated and supervises the control action module. The SRs developed to specify some process operation factors are also introduced at this stage. The main task of this level is to ensure NOM removal through enhanced coagulation (adjusting pH and Cd) under some active operational DWTP management considerations. SRs were established to build this EDSS, i.e., SR_1 is related to UV_{254}, SR_2 to cost-environmental assessment (Cd), and SR_3 in case of flood events. SRs are detailed as follows:

SR_1 intensifies the enhanced coagulation (pH and Cd) to achieve 50% UV_{254} removal (modify RSM optimization criteria) to ensure a high quality post-coagulated water prior to filtration. This SR works when an influent $UV254_{RAW}$ value is higher than 0.1 cm^{-1} so as to avoid sand filters pore blocking and increase their useful life. SR_1 acts with a fixed optimum pH = 7 and modifies the Cd of the control level optimization criteria (Figure 19). In addition, this SR decreases the costs associated with sand filters and CAG replacement, which represent more than 50% of total DWTP 3 OpEx.

SR_2 is related to economic cost of the PAC, in cases where control level proposes Cd >40 $mg{\cdot}L^{-1}$. In these cases, the priority is to adjust the pH instead of surpassing a Cd of 40 $mg{\cdot}L^{-1}$ (Figure 19). Pernitsky and Edzwald (2006) reported that polyaluminum coagulants are more expensive than other alum-based coagulants and for this reason, and also to reduce the formation of chemical sludge, SR_2 is important for managing tasks and indirectly contributes to generating lower impact from an environmental viewpoint.

SR_3 is designed to be activated when facing flood events. When the $Turbidity_{RAW}$ is >10 NTU, the percentage of turbidity removal is automatically increased to ensure 75%. As with SR_1, the intervention of this SR occurs at the optimization criteria of enhanced coagulation control level, readjusting the Cd to ensure the required quality (Figure 19). Ensuring this percentage of removal in cases of high turbidity at the influent of DWTP is crucial for plant managers, because turbidity is considered to be a critical factor in the performance of filtration-based treatments (sand filters and CAG).

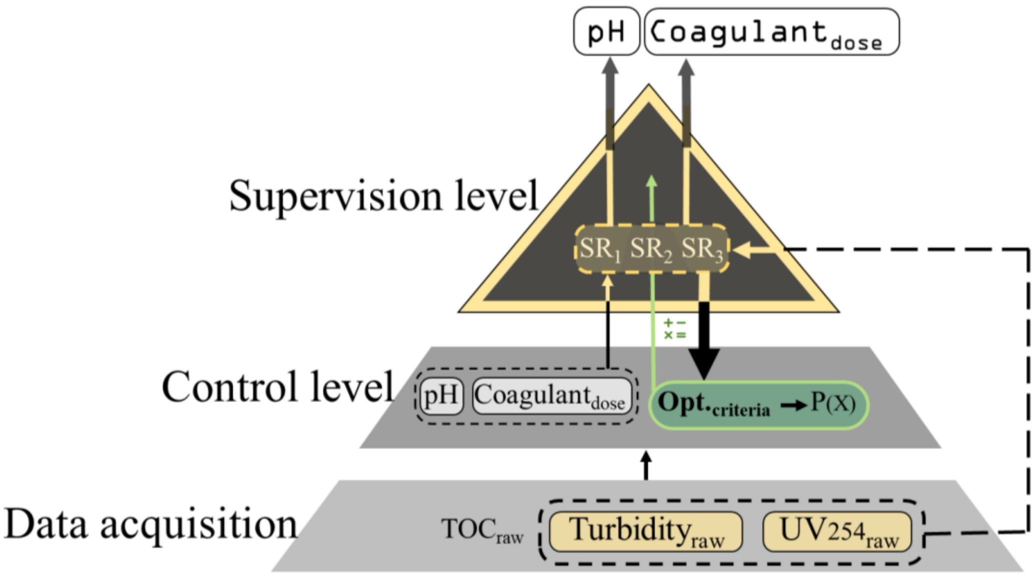

Figure 18: Proposed operational architecture for the enhanced coagulation EDSS.

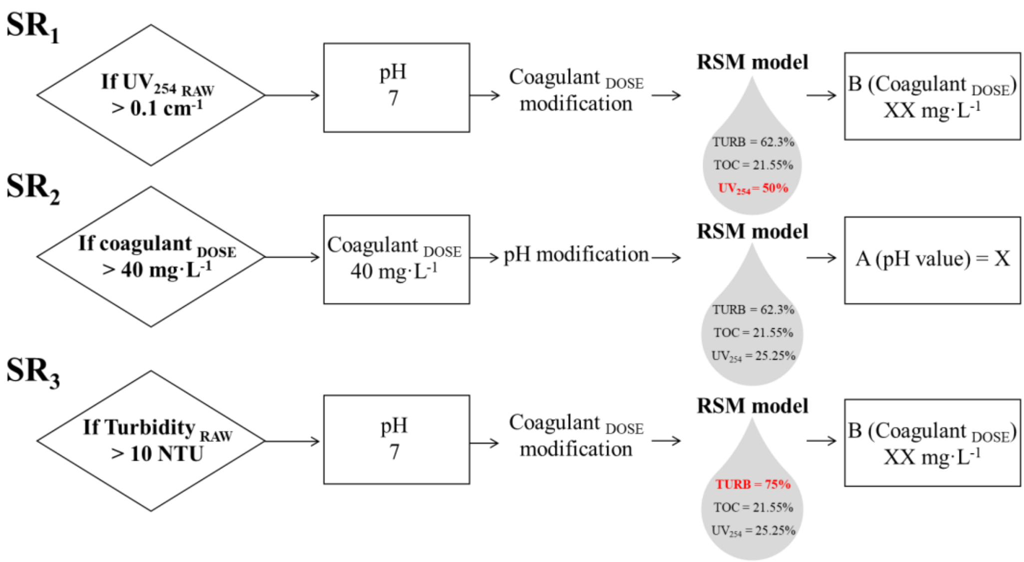

Figure 19: Decision trees for the proposed SRs (SR1, SR2, and SR3), located at the supervision level.

4.4. Conclusions

The study presents the development of an enhanced coagulation EDSS for drinking water production, with the aim to support daily decision-making. To accomplish this, the EDSS was structured onto a three-level hierarchical architecture, i.e., data acquisition, control, and supervision. Regarding the control level, the models developed for coagulation are designed based on RSM and proposes the optimum pH and Cd under specific removal quality requirements (optimization criteria). Under normal conditions, the control level of the EDSS is designed to achieve 62%, 21%, and 25% removal for turbidity, TOC, and UV_{254}, respectively, thus, helping to reduce the risk of DBPs formation. Membrane fouling indicators and expert knowledge allowed to establish a several SRs to set up at the top of the hierarchical architecture. Hence, the supervision level merges operational performance and expert decision-making knowledge. Three supervision rules (SR1, SR2, and SR3) were proposed to work as a feed-back supervisory system to readjust the RSM criteria for an integrated control. These SR's were designed to intensify treatment by modifying Cd in the case of detecting high influent water values of turbidity and UV_{254}, and readjusting pH when the proposed Cd exceed the maximum desired value.

The EDSS designed offers an innovative approach in terms of NOM tracking and integrating data and knowledge for an enhanced coagulation EDSS, aiding to decision-making. Because of the capacity to feed the EDSS with the online data acquired from the abovementioned full-scale DWTP facility, this proposal can be implemented as an open-loop system in the plant itself.

5. Results II

Assessing the effect of catchment characteristics to enhanced coagulation in drinking water treatment: RSM models and sensitivity analysis.

Redrafted from:

Suquet, J.; Godo-Pla, L.; Valentí, M.; Ferrandez, L.; Verdaguer, M.; Poch, M.; Martin, M.J.; Monclús, H. (2021). Assessing the effect of catchment characteristics to enhanced coagulation in drinking water treatment: RSM models and sensitivity analysis. Sci. Total Environ. 799, 149398.
https://doi.org/10.1016/j.scitotenv.2021.149398

5.1. Background

In the Mediterranean, present and future scenarios related to climate predict an increase of the number of extreme weather episodes, which could induce some variations in surface water NOM characteristics (Delpla et al., 2009; Sun et al., 2020). Thus, drinking water sector should be adapted to this changes, and some strategies for water treatment should be planned to face oncoming situations.

NOM react to generate DBPs and some of these compounds are regulated in both European (98/83/EC, 1998) and national directives (RD 140/2003). As enhanced coagulation aims to use coagulation for NOM removal, the objective is to reduce the residual organic water compounds (Sillanpää et al., 2018). To avoid high concentrations of DBPs at the end of large distribution networks (i.e., just before consumption), the minimization of NOM compounds should be the main strategy in the initial stages of water treatment, especially during the coagulation process (Liu et al., 2012; Williams et al., 2019).

Coagulation can be optimised through several pathways although there are various factors affecting coagulation performance. Because there are organic, inorganic, composite, hybrid coagulants and biocoagulants (Adesina et al., 2019; Harfouchi et al., 2016; Xia et al., 2018), the most efficient coagulation performance depends on the characteristics of the raw water. The optimal chemical dosages at full-scale are usually determined from laboratory jar test experiments. Even though, coagulation operation is usually suboptimal due to other limitations related to full-scale operation and influent water quality fluctuations. To deal with that, several modelling approaches to optimise coagulation in water production, particularly based on RSM, have been described in the literature.

For DWTPs, it is essential to adjust coagulation to cope with the different influent water quality scenarios. This is especially relevant in Mediterranean regions where water provisioning is decreasing, surface water masses are being stressed and seasonal changes and extreme events, such as heavy rains and droughts, are increasing in frequency (Jorda-Capdevila et al., 2019). Consequently, to achieve an optimal NOM removal, coagulation modelling requires process knowledge and also a broad range of available data.

Within this framework, the motivation of this study arose from the assumption that the optimisation of coagulation based on the influent water characterization contributes to the minimization of NOM at the effluent of DWTPs. The main objective of this study is to understand how coagulation process is affected by different surface water catchments and their intrinsic fluctuations. In order to achieve that, this work proposes enhanced coagulation models based on RSM and influent DWTP characterization for the optimisation of coagulation process at two Mediterranean DWTPs. This study has been conducted with the following specific objectives: i) to identify influent water quality classifications using clustering techniques, ii) to develop RSM models for enhanced coagulation and iii) to analyse the effect of operational parameters in enhanced coagulation through sensitivity analysis for the different water catchments.

5.2. Methodology

5.2.1. Case study

The study was carried out at DWTP 1 and DWTP 2. DWTP 1 catches water from Llobregat River, which is the second longest river in Catalonia presenting water quality fluctuations due to the human activities (Kuster et al., 2008). DWTP 2 catches water from reservoirs, which change river regimes and, consequently, water characterization. Thus, in both facilities, aimed to control the influent water quality fluctuations, the first step of the conventional treatment chain is PO, followed by the coagulation process (Methodology, Figure 9). PO represents the first chemical barrier, located at the beginning of the treatment, attempting to oxidise a wide range of compounds present in raw waters (Godo-Pla et al., 2020a). For this purpose, potassium permanganate is added at the DWTP 1, while chlorine-based oxidants are applied at the DWTP 2 before coagulation.

5.2.2. Cluster analysis

Influent water characteristics were evaluated using cluster analysis. In previous scientific literature, clustering has been stated as a suitable technique for water classification when detecting temporal changes in water characterizations (Celestino et al., 2018; Fathi et al., 2018; Gibert et al., 2012; Hou et al., 2018). For this purpose, k-means clustering was applied in this work, with the aim to establish influent water quality classifications. An unsupervised cluster algorithm was selected to identify differences in influent water NOM concentrations. These methods are described as useful tools to describe relationships in data presenting intracluster homogeneity and contrast between clusters (Gibert et al., 2014). Hence, K-means clustering is a partition method based on centroids aimed to classify large datasets into a pre-specified number of clusters. The first iteration of the cluster algorithm states randomly k-clusters along dataset and calculates the centroid of each cluster. Then, in the second iteration, each data point is assigned to the closest centroid. Centroids and their associated data constitute a cluster.

Historical datasets were obtained from case-study DWTPs daily laboratory analytics corresponding to the period 2017-2020. For cluster analysis and the subsequent profiles identification, the following influent water quality parameters were considered as features of the clustering algorithm: TOC, turbidity, UV_{254}, colour and SUVA. Based on the study of these parameters, a k-means clustering algorithm with k=2 was performed to classify the quality of the raw waters into two different profiles with the aim to identify cases presenting differences in raw waters composition through the seasons/year. programming language (Python Software Foundation, Wilmington, DE, USA) using Scikit-learn library (Pedregosa et al., 2011) was used to design and execute clustering algorithms. Afterwards, the nature of the discovered profiles was identified for the historical datasets, allowing to interpret and describe influent water fluctuations (different behaviours) all over the time series.

5.2.3. Enhanced coagulation models

First, RSM was designed. Then, experimental laboratory jar tests were conducted to develop enhanced coagulation models. Subsequently, sensitivity analysis was performed.

Enhanced coagulation models design

Central composite design (CCD) was selected as the RSM design. In this case, CCD was performed for three study variables (factors) that influence the coagulation process: pH, Cd and Fd. These variables have been used to optimise coagulation as the most influential factors in the coagulation performance (Trinh and Kang, 2010; Trinh and Kang, 2011). Responses were selected based on its nature and also the capacity to be monitored online at the full-scale facilities. As models developed for this work are aimed to aid decision-making, turbidity, TOC and UV_{254} were the chosen RSM responses. The total number of runs for CCD were 20, combining the conditions of various factors (Annex I). The Design-Expert® was used to perform RSMs.

The range of the factors for the RSMs in the two case-study DWTPs was 5.5 to 8.5 for pH level, 10 up to 70 $mg \cdot L^{-1}$ and 5.25 up to 70 $mg \cdot L^{-1}$ for the Cd at DWTP 1 and DWTP 2, respectively. Then, Fd varied from 0.2 up to 1.5 $mg \cdot L^{-1}$ at DWTP 1 and 0.15 up to 1.74 at DWTP 2. All RSM designs were planned by expanding operational full-scale ranges to cover the entire range of response (regions of interest). Two RSM were performed at each case study DWTP.

Experimental jar tests

Water samples were collected at each case-study DWTP to execute jar tests to develop the RSM models. Two different RSM were conducted in both DWTPs. Table 8 summarises the water characterization for the different sampling campaigns (SC).

For the laboratory analyses, turbidity, TOC and UV_{254} were measured with a Hach TU5200 turbidimeter, a Sievers M9 portable analyser and a Cary 3500 UV-Vis Agilent Tech spectrophotometer, respectively. For TOC and UV_{254} measurements, samples were filtered at 0.4μm to ensure the analysis of dissolved NOM. For UV_{254}, a quartz cell with a 1cm path length was used. Next, pH was determined using a Crison micro pH 2000 apparatus. ISO 5667-3:2018 requirements were ensured for the collection, storage, transport and pre-treatment of all the samples.

A summary of the jar tests phases (times and speeds) is presented in Annex II. Jar tests were carried out using a Phipps & Bird (7790-910, Richmond, VA, USA) six paddle programmable jar tester and the chemical reagents employed were obtained from the DWTPs supporting this study. The case-study DWTPs use alum-based coagulant (Polyaluminium Chloride) to perform coagulation unit operation. There is a difference concerning flocculant type in that the DWTP 1 adds a cationic quaternary ammonium-based polymer (PolyDADMAC), while the DWTP 2 doses with a starch-based flocculant.

Predictors selection

From RSM experiments, water characterization (turbidity, TOC and UV_{254}) was obtained for the fixed coagulation conditions, detailed in Annex I. Based on the selected factors (pH, Cd and Fd), the full quadratic equation is presented (Eq.9).

$$Y = \beta_0 + \beta_1 pH + \beta_2 C_d + \beta_3 F_d + \beta_4 pHC_d + \beta_5 pHF_d + \beta_6 C_d F_d + \beta_7 pH^2 + \beta_8 {C_d}^2 + \beta_9 {F_d}^2 \quad (9)$$

where Y is the percentage of removal for responses, β_x are numerical model coefficients and pH, C_d and F_d the model factors. Related to the equation elements β_1, β_2 and β_3 are the one factor interactions; β_4, β_5 and β_6 are the two factor interactions and β_7, β_8 and β_9 are the quadratic effects.

Among all models' factors, it is necessary to state a procedure with the capacity to systematize the selection of the best features for each model. Hence, the *best subset selection method* was applied to the models obtained from jar test experimental data, allowing to determine the optimal number of predictors to ensure the best features under a sufficient level of predictability. This method consists of fitting models considering each possible combination of the predictors candidates (*p*). In this case, the total number of *p* is listed in Eq.9 (*p*=9), being 2^p (2^9) the maximum number of combinations (Godo-Pla et al., 2020a). In this work, the identification of the best model was based on the determination of the following statistics: sum of squares error (SSE), R^2 and adjusted R^2 ($R^2_{adj.}$) values. From this, models can be selected by minimizing the prediction error or maximizing the $R^2 - R^2_{adj.}$ R^2 enables to identify the predictive accuracy while the $R^2_{adj.}$ value provides the coefficient of determination for each model pondered according to the number of predictors. Models coefficients significance were ensured (p-value < 0.05) after the application of the best subset selection method. Plots of R^2 considering 2^p are presented in Annex III. This method is useful for a limited number of predictors due to computational limitations. The software used in this study was MATLAB 2019a (Mathworks®, Natick, MA, USA).

Sensitivity analysis

To study the enhanced coagulation models designed by RSM and performed by the best subset selection method, a sensitivity analysis was conducted to explore and to determine the impact of factors (pH, Cd and Fd) on the quality parameters (turbidity, TOC and UV_{254} removal efficiency). Equations were analysed through delta mean-squared sensitivity analysis to determine the contribution of the relative factors. The delta mean-squared (δ_i^{msqr}) non-dimensional sensitivity function was chosen to determine the significance of model factors as well as their interactions. Sensitivity analysis was used to verify the robustness of the models and their reliability for the different scenarios at each DWTP. Further details on the methodology can be found elsewhere (Godo-Pla et al., 2021; Sin and Gernaey, 2016). MATLAB 2019a (Mathworks®, Natick, MA, USA) was used to perform the sensitivity analyses.

Table 8: DWTPs influent water characterization for the SC.

SC	DWTP	Date	Turbidity (NTU)	TOC ($mgC \cdot L^{-1}$)	UV_{254} (m^{-1})
SC 1*	1	03.2019	9.1	4.1	12.7
SC 2	1	03.2020	3.7	2.6	11
SC 3	1	08.2020	26.2	1.8	11.5
SC 4*	1	11.2020	63.3	3	12.9
SC 5*	2	02.2020	5.3	3.6	15.1
SC 6	2	03.2020	5.2	3.7	14.4
SC 7	2	07.2020	0.9	3.2	12.7
SC 8*	2	11.2020	4.8	2.8	11.9

*sampling campaigns performed for RSM

5.3. Results and discussion

5.3.1. Cluster analysis

K-means clustering was developed to classify in two clusters influent water quality datasets (2017-2020 period) for DWTP 1 and DWTP 2. Accounting for water characterization, the following parameters were selected: turbidity, TOC, UV_{254}, colour and SUVA value. Water colour is directly related to NOM content originated from wood and soil (Christman and Ghassemi, 1966; Dragon et al., 2018), turbidity accounts for particulate, colloidal and soluble water components (Gregor et al., 1997) while TOC and UV_{254} and SUVA values contribute to specific NOM fractions.

The study of the historical datasets coupled to the expert knowledge provided by plant managers indicated that raw water quality is changing over the year, detecting cases presenting high values of influent water quality parameters and other cases where these values are more less stable. With this information, the initial hypothesis of this study was to perform a cluster analysis with the aim to identify two types of influent waters related to NOM characterization. To validate that, k-means cluster analysis with k=2 was performed. After the application of the clustering algorithm for the historical datasets, two different profiles were identified and linked to the corresponding influent values for the entire time series Figure 20. From here, clusters description were useful to recognise two types of influent waters NOM composition, validating the initial hypothesis. Thus, clusters' profiles were identified as influent NOM baseline and peak scenarios. Based on that, Figure 20 is aimed to summarise cluster analysis into the entire dataset, identifying each one of the selected variables and the corresponding cluster based on the influent NOM content. Hence, this paper is focussed on enhanced coagulation models development, not to define the optimum number of clusters for the historical datasets. From here, results obtained at the DWTP 1 and DWTP 2 from the cluster analysis are presented in this section. In Figure 20, there are five plots for each facility (left column DWTP 1 and right DWTP 2) which classifies water quality for the chosen influent parameters in two groups. These groups were related to as baseline and peak water quality. In general, the DWTP 1 parameters fluctuations are higher than those of the DWTP 2.

Observing the output from the cluster analysis performed at both DWTPs, basic differences between the plots could be attributed to the catchment characteristics. To explain this, it is necessary to examine the influent water quality fluctuations in depth (see Figure 20). First, it is important to remark on the basic difference between the types of catchment the two case studies have. Reservoir system work as a massive water clarifier which, in turn, helps to maintain low fluctuations in the quality of the influent water. However, extreme events (heavy rains) could destabilize that system, leading to high changes in reservoir water quality. On the other hand, river catchment quality is more unstable, highly dependent on water flow (pollutants concentration) linked to weather (runoff effect) and other external factors related to human activities (Fernández-Turiel et al., 2003; Gallart et al., 2011; Navarro et al., 2002).

The main difference between DWTP 1 and DWTP 2 was the frequency of peak events: the river catchment water quality presented seasonal fluctuations, whereas water from the reservoir showed a lower frequency of peak events that were not strictly related to seasonal changes. At the DWTP 2, data which comprises a major part of dataset corresponds to the baseline group and the punctual anomalies to peak scenario. These peak events can be visually identified in October 2018 and January 2020 (see Figure 20, DWTP 2). Both series of data are directly related to historical heavy storms events, rains with more than 180 L·m-2 (13th-15th October 2018) and more than 400 L·m-2; the latter was Storm Gloria, which provoked a great deal of damage and multiple issues in this part of Europe (19-23 January, 2020) (Amores et al., 2020). Typical cases in the Mediterranean region, characterised by flash floods with local heavy rains in small surface regions (Cramer et al., 2018). These events consisting in heavy rains caused alterations in reservoirs stratifications and the quality of the influent of the DWTP 2 was affected by an increase of the water quality parameters. According to Casamitjana et al. (2003), this change in water composition is due to the resuspension of the organic content present in deep sediments towards epilimnetic waters (superficial waters). In summary, the time series show that the Ter river system of reservoirs act as a massive clarifier, thus maintaining the water quality in the influent of the DWTP 2. However, there are some exceptional situations where reservoir stability is altered and then water quality recovery (reservoir stratification) is slow compared to the river regime fluctuations. In DWTP 1, changes are strongly linked to seasonal events, and water content has fluctuations throughout the year. These results are aligned to previous local catchment studies (Fernández-Turiel et al., 2003a; Fernández-Turiel et al., 2003b). From this basis, DWTPs should adapt coagulation performance to this influent water quality changes.

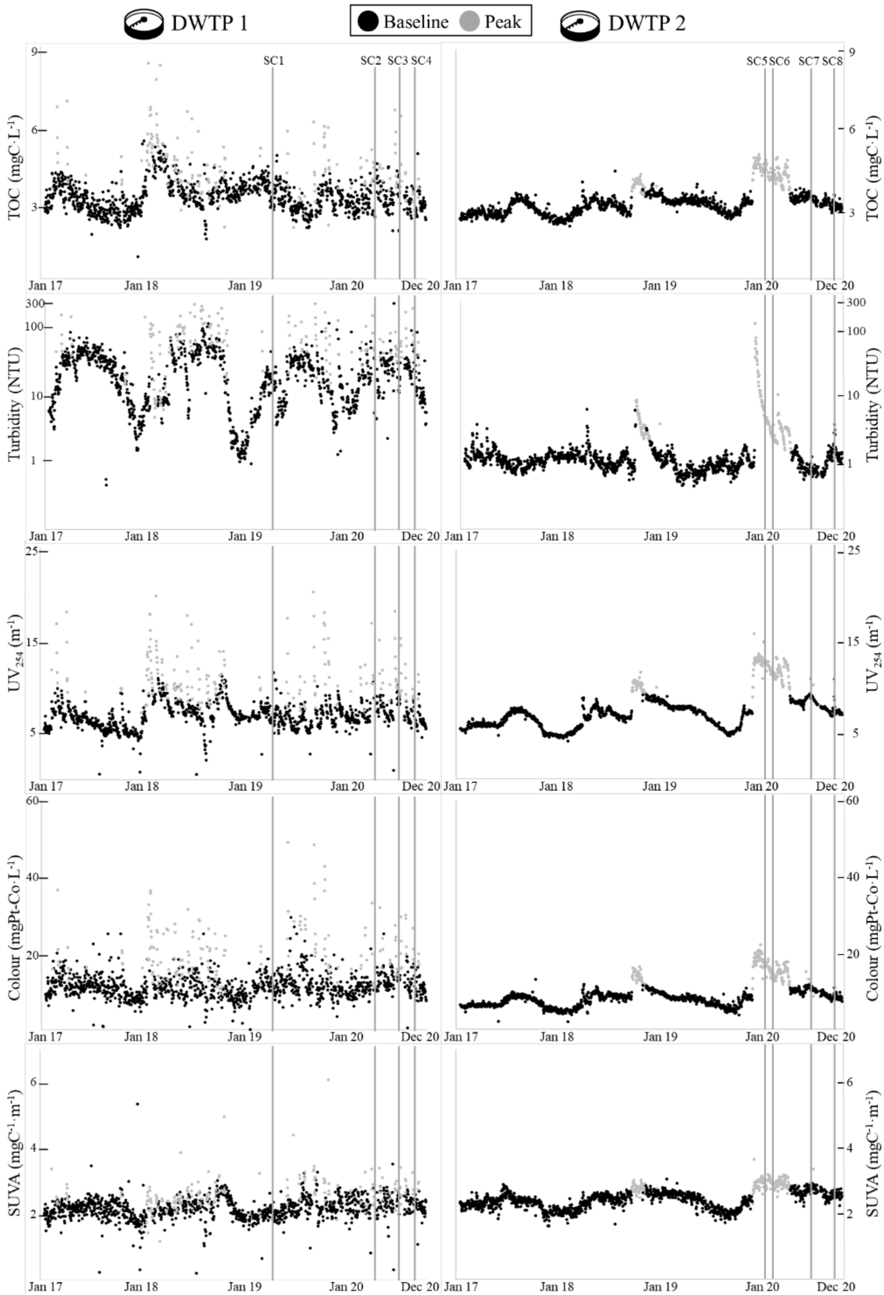

Figure 20: Influent water classifications resulting from cluster analysis at the DWTP 1 (left column) and DWTP 2 (right column) during the period 2017-2020. Y axis are the selected water quality parameters: turbidity, TOC, UV_{254}, colour and SUVA values. Black and grey colours indicate clusters: baseline and peak, respectively. The SCs are represented by vertical grey bars.

Influent water quality was classified depending on baseline and peak organic content for the two case-study DWTPs. Linking the information presented in Table 9 with cluster analysis, two SC were conducted at each DWTP (baseline and peak cases). For both DWTPs, a SC for each influent water classification was selected to develop RSM models (detailed in Figure 20). SC 1 and SC 8 (see Table 9) belong to the baseline cluster. Then, SC 4 and SC 5 are related to the peak cluster. SC and their respective classification is indicated in Figure 20. To link the SC with clustering analysis from here the SC 1, 4, 5, 8 are named Llobregat baseline (LB), Llobregat peak (LP), Ter peak (TP) and Ter baseline (TB), respectively.

5.3.2. Evaluation of enhanced coagulation models

The RSM experiments were conducted and supernatants from the jar test experiments were analysed. Model factors were pH, C_d and F_d, while responses were introduced as percentage of removal of turbidity, TOC and UV_{254}. All runs and different standards for each RSM are presented in Annex I.

Models were obtained from the RSM experiments and after the predictors selection. Prior to determine the optimum number of predictors an evaluation task was carried out to pre-validate models. Several analyses were checked such as diagnostics related to normalized plots (models residual for experimental runs, predicted and actual values, among others) to ensure models' fitting and detect outliers. Also, 3D surface plots were analysed in both facilities under the two scenarios to interpret models, which are presented in Annex IV. These plots are useful to interpret visually (colour legend) factors interactions and responses variations inside the RS. The final equations for each DWTP scenario with the number of predictors selected, coefficients and $R^2_{adj.}$ values are presented in Table 9.

Results from laboratory experiments (Annex I) revealed that turbidity experimented the highest mean removals in all enhanced coagulation models. The unified mean turbidity removals for all models was 85%. This effect can be explained by considering that turbidity accounts for the whole spectrum of water compounds: organic, inorganic, particulate, colloidal and dissolved. Concerning TOC and UV_{254}, which are related to water dissolved organic fractions, were less removed during coagulation. From this results, it is appreciable that turbidity removal is achieved in coagulation for the performed scenarios. The general trend in all RSMs were that the percentage of removal was higher in UV_{254} with respect to TOC. Examining all the RSMs, the average of removal for TOC and UV_{254} were 23% and 38%, respectively. TOC and UV_{254} removals were low compared to turbidity, indicating that the optimum conditions needs to be ensured in accordance to these parameters to achieve an optimal removal of dissolved pollutants during coagulation process.

Going into greater detail for both DWTPs, the maximum removals (three responses combined) were obtained at neutral pH and medium C_d and F_d. Otherwise, minimum removals were shown at high pH values above 8 and low C_d combined with high F_d. Regarding the latter, this is due to the fact that a flocculant overdose induces a decrease of sedimentation coagulation effect and, consequently, less efficiency in the process (Katrivesis et al., 2019). The highest turbidity removals >80% were observed at neutral pH and medium C_d and F_d, while the higher removals for TOC were obtained at depressed pH levels. According to Bell-Ajy et al. (2000) and Edwards (1997), this is attributed to the increase of floc precipitation originated by the entrapment of sorbable TOC fraction combined with alum hydroxide from the coagulant. The highest removals of UV_{254} were shown at low to neutral pH levels, linked with the removal of the organic compounds in these conditions (Altmann et al., 2016). The C_d and F_d affected the removals in a different way for each RSM. More information about the individual experiments, including the RSM models' runs and responses analyses is provided in Annex I.

At the DWTP 1, mean RSMs percentage of removals were 86%±23%, 21%±9%, 32%±13% for turbidity, TOC and UV_{254}, respectively. On the other hand, the results obtained reflected that the DWTP 2 responses mean percentage of removal were 84%±15% for turbidity, 27%±20% for TOC and 45%±13% for UV_{254}. For baseline clusters (LB and TB), in both facilities RSM outputs presented similar percentage of removals, especially for turbidity and UV_{254} removal. However, influent values of turbidity at the DWTP 1 were higher than those at DWTP 2. The reason for this is because Llobregat River water is affected by weather (periods of rains/droughts), runoff and some anthropogenic discharges of industrial origins, while reservoir remains stable. Turbidity removals >90% at DWTP 2 were difficult to observe during RSMs due to the water quality from reservoir, expressed in low turbidity values at the influent of the DWTP (5.23 and 4.76 NTU, respectively).

Peak scenarios at DWTP 1 (LP) presented turbidity removals ≥ 90% for all RSM experiments. This is due to the high initial value (63 NTUs), propitiating elevated removal values for this parameter. At the DWTP 2, TP showed high influent values of TOC and UV_{254}, indicating that during peak scenarios the dissolved NOM fraction needs to be removed for the optimal coagulation at this facility. The percentage of removal of TOC and UV_{254} comparing TB and TP is significant, where TOC has a mean removal of 11% in TB and 43% in TP and UV_{254} has a mean removal of 37% for TB and 53% for TP.

All enhanced coagulation models are presented in Table 9. Related to predictors selection, no single model with p=9 was selected after the application of the best subset selection method. The maximum number of predictors was located at p=5. Despite the total number of predictors, it is important to identify which are the selected ones in order to proceed with the sensitivity analysis. R^2 predictors selection for all DWTPs scenarios and coefficients combination (2^p) are presented in Annex III. Enhanced coagulation models considering turbidity, TOC and UV_{254} were performed with a mean R^2 of 0.85. The mean responses R^2 were 0.87, 0.83 and 0.86 for turbidity, TOC and UV_{254} removals. The equation coefficients are not normalized, therefore some of them are negative. As a consequence, the following step is to perform a sensitivity analysis to identify the relative weight of each individual factor/predictor to understand the enhanced coagulation. Predictors selection based on R^2, $R^2_{adj.}$ aid to ensure predictability. Also, the fact to consider SSE (residuals) to choose the best model works as a prevention barrier for avoiding biased models (James et al., 2013).

Hence, depending on the nature of the influent waters, coagulation can be optimised following models developed with RSM in a baseline or peak scenario. These model outputs suggest that during LP an increase of particulate water fraction at the influent is detected (high values of turbidity) while for TP high values of dissolved NOM fraction are detected at the influent (high TOC and UV_{254}).

Table 9: Enhanced coagulation models for each DWTP. The number of predictors selected based on best subset selection method, coefficients for each factor and the coefficient of determination (R^2) are presented.

	Y	P	β_0	β_1	β_2	β_3	β_4	β_5	β_6	β_7	β_8	β_9	R^2
LB	Turbidity	4	34.5	-	1.4	18.1	-	-	-0.3	-	-0.01	-	0.9
	TOC	3	6.8	-	0.3	21.3	-	-2.3	-	-	-	-	0.9
	UV_{254}	5	223.3	-60.4	0.6	-	-	3.9	-0.4	4.03	-	-	0.7
LP	Turbidity	4	77.7	1.6	0.5	-	-0.02	-	-	-	-0.01	-	0.8
	TOC	3	9.5	-	1.2	-	-0.1	-	-	-	-0.01	-	0.8
	UV_{254}	2	33.5	-	0.3	-	-	-	-	-0.3	-	-	0.9
TB	Turbidity	5	-16.1	7.9	2	43.1	-	-6.3	-	-	-0.02	-	0.9
	TOC	5	30.2	-2.9	0.6	-19	-	-	-	-	-0.01	9.4	0.7
	UV_{254}	3	23.9	-	1.1	-	-	-	-	-0.2	-0.01	-	0.9
TP	Turbidity	4	86.1	-	0.4	-	-	-0.8	0.1	-	-0.01	-	0.8
	TOC	4	-246	93.3	-	-	0.17	-	-	-7.6	-0.02	-	0.8
	UV_{254}	4	74.5	-	-0.8	-	0.3	-	-	-0.7	-0.01	-	0.9

Y: model responses; P: number of predictors.

5.3.3. Sensitivity analysis

Sensitivity analysis was performed to discuss the individual factors influence for each response, based on the equations resulting from RSM experiments and the best subset selection method. For this purpose, delta mean-squared analysis was applied to the models with the aim to identify the relative weights of model factors. For each scenario three enhanced coagulation models were obtained, one for each selected response: turbidity, TOC and UV_{254}; giving a total number of twelve equations (Table 9, β coefficients).

Delta mean-squared values for individual factors (β_1, β_2, β_3), combined interactions (β_4, β_5, β_6) and quadratic effects (β_7, β_8, β_9) are presented in Table 10. To proceed with the discussion, the relative impact of individual factors was included to Table 10, considering only the single individual factors contribution. Despite this simplification, factors interactions expressed by β_4, β_5, β_6 are significant for some of the enhanced coagulation models. For almost all scenarios (LB, LP, TB and TP) pH and C_d emerged as important factors. According to Bell-Ajy et al. (2000), pH is the most important factor for NOM removal during coagulation process. When coagulation is adjusted at the optimum pH, removals are improved because of major alum-NOM complexation and less coagulant demand. At this point, it is important to note that pH is legislated for water consumption and it is not feasible to optimize the process in the range of optimum pH, because this can be located outside of the threshold limits. From this, Cd and Fd adjustment play a key role to achieve enhanced coagulation in drinking water production.

Prior to comparing the models, it is important to remark that results from sensitivity analysis comparison is applicable for models developed at the same DWTP, because each RSM was designed under a specific treatment train and operational ranges. Furthermore, nature and regime of the sources as well as water characterization differs from the Llobregat river in comparison to the Ter river reservoirs system, details of which can be found in the cluster analysis section.

Starting with the comparison between baseline and peak events, there are similar behaviours at the two DWTPs. Regarding LP and TP, an increase of organic load is expected at the influent, and the sensitivity analysis reveals that pH and C_d are the key factors to ensure enhanced coagulation (Table 10). For these cases, when influent waters belong to peak scenarios, the optimum pH range is wider and the Cd needs to be carefully adjusted to ensure NOM adsorption and chemical bridging (Gaikwad and Munavalli, 2019). However, during LB and TB, it is necessary to carefully adjust pH, Cd and Fd to achieve high levels of pollutants removals during coagulation. In this cases Fd is also considered a key parameter, presenting high delta mean-squared, hence its importance on process performance.

Accounting for individual responses, Cd has a great influence on turbidity and UV_{254} removals efficiency and was selected as a predictor for all models accounting for these responses, ensuring high levels of removals when Cd is correctly optimised (Rocha et al., 2020). Regarding TOC value, there are different relevant factors depending on the scenario. This basically can be explained from the assumption that TOC value represents a great variety of dissolved compounds, depending on the predominant group of water pollutants the key conditions for coagulation can be modified.

Stablishing the comparison from the different water catchments, as a result of clustering analysis section DWTP 1 peak events (LP) are linked clearly to an increase of turbidity. This is mainly associated to rains and its derived runoff effect. Based on that, a major part of water pollutants present in water are linked to particles accounting for turbidity more than the dissolved fraction (TOC and UV_{254}). According to Aboubaraka et al. (2017), turbidity is representative for coloured organic compounds, changing water colour. Within this context and according to the sensitivity analysis, during LP Cd requires to be carefully optimised to ensure the particles aggregation and its sedimentation during coagulation process.

Table 10: Delta mean-squared (δ^{msqr}) values for individual factors' coefficients for each enhanced coagulation model. Factors' relative impact was simplified for pH, Cd and Fd. Hyphenated cells correspond to the coefficients dismissed after predictors selection.

	Y	δ^{msqr} β_1	δ^{msqr} β_2	δ^{msqr} β_3	δ^{msqr} β_4	δ^{msqr} β_5	δ^{msqr} β_6	δ^{msqr} β_7	δ^{msqr} β_8	δ^{msqr} β_9	relative weight
	Turbidity	-	0.5	1.3	-	-	0.6	-	0.1	-	Fd>Cd
LB	TOC	-	0.02	0.3	-	0.7	-	-	-	-	Fd>Cd*
	UV_{254}	0.3	0.002	-	-	0.09	0.01	0.4	-	-	pH>Cd*
	Turbidity	0.4	0.1	-	0.1	-	-	-	0.03	-	pH>Cd
LP	TOC	-	0.2	-	0.5	-	-	-	0.04	-	Cd*
	UV_{254}	-	0.01	-	-	-	-	0.5		-	pH>Cd*
	Turbidity	0.5	0.1	0.7	-	1.6	-	-	0.02	-	Fd>pH>Cd
TB	TOC	0.5	0.02	0.9	-	-	-	-	0.01	1.8	Fd>pH>Cd*
	UV_{254}	-	0.4	-	-	-	-	0.9	0.1	-	pH>Cd*
	Turbidity	-	0.1	-	-	0.2	0.1	-	0.01	-	Cd
TP	TOC	7.4	-	-	0.2	-	-	2.2	0.1	-	pH>Cd*
	UV_{254}	-	0.2	-	0.2	-	-	0.2	0.1	-	pH≈Cd*

* Scenarios selected for profile plots visualization.

Profile plots for enhanced coagulation were performed to complement the information provided by the sensitivity analysis (Figure 21). According to Table 9, turbidity was a parameter with the highest percentage of removals in all the scenarios. Based on that, these profile plots were evaluated for TOC and UV_{254}, as parameters accounting for the water dissolved organic fraction selected to achieve the enhanced coagulation. Figure 21 presents the profile plots for the enhanced coagulation models for TOC and UV_{254} removals at each DWTP under the different scenarios. In each plot, the entire range of pH, C_d or F_d is presented for the low, medium or high values of the other factors. The pH was ranged in a feasible full-scale values of operation from 6 to 8. The selected profile plots (see Figure 21) were the cases where TOC or UV_{254} emerge as significant factors (see Table 10). Profile plots (see Figure 21) for each response (turbidity, TOC and UV_{254}) were levelled according to the other significant factors detailed in Table 10.

According to Figure 21, in LB the pH should be adjusted at a neutral levels and Fd has a positive relation with turbidity, TOC and UV_{254} removals. In the case of turbidity removal, high Fd increases significantly turbidity removal with low Cd, being the medium dose of Cd and Fd the best for an optimal operation. Regarding TOC, pH is not critical (≈7) and Fd and Cd have a strong positive impact in the percentage of removal. For LB-UV_{254}, pH is significant for the model (sensitivity analysis results) but not critical between 6 to 8. However, Cd has clear positive impact to remove UV_{254}. In summary, for LB at a neutral pH, high Cd and Fd TOC and UV_{254} removals improve. Compared to LP, medium level of Cd and low-neutral pH are required for turbidity, TOC and UV_{254} removals. In accordance to sensitivity analysis, Fd is not relevant for enhanced coagulation in LP case. Regarding TB, the optimal adjustment of Fd is located at medium pH and Cd. Concerning the TP scenarios, the optimum removals for dissolved NOM are located at medium pH and Cd levels (Fd is not a significant factor). In those cases, the medium range of pH-Cd is highlighted as a proper option for coagulation removals. Profile plots are useful to complement the information obtained through the sensitivity analysis, increasing model understanding for each specific scenario.

Results from sensitivity analysis indicate that enhanced coagulation for river catchment in baseline scenario is subjected to the optimal adjustment of the three factors influencing enhanced coagulation while during peaks, which are related to the increase of particulate compounds in water resulting from rain runoff effects, pH and Cd are crucial for enhanced coagulation. On the other hand, reservoir catchment is stable all over the time series where enhance coagulation is controlled by high Cd and Fd, but during peaks (extreme events) an increase of dissolved NOM is expected at the influent, resulting from the resuspension of reservoir deep sediments. In these cases, coagulation pH should be carefully levelled to ensure the optimum TOC removal and Cd emerges as a crucial factor for turbidity and UV_{254}.

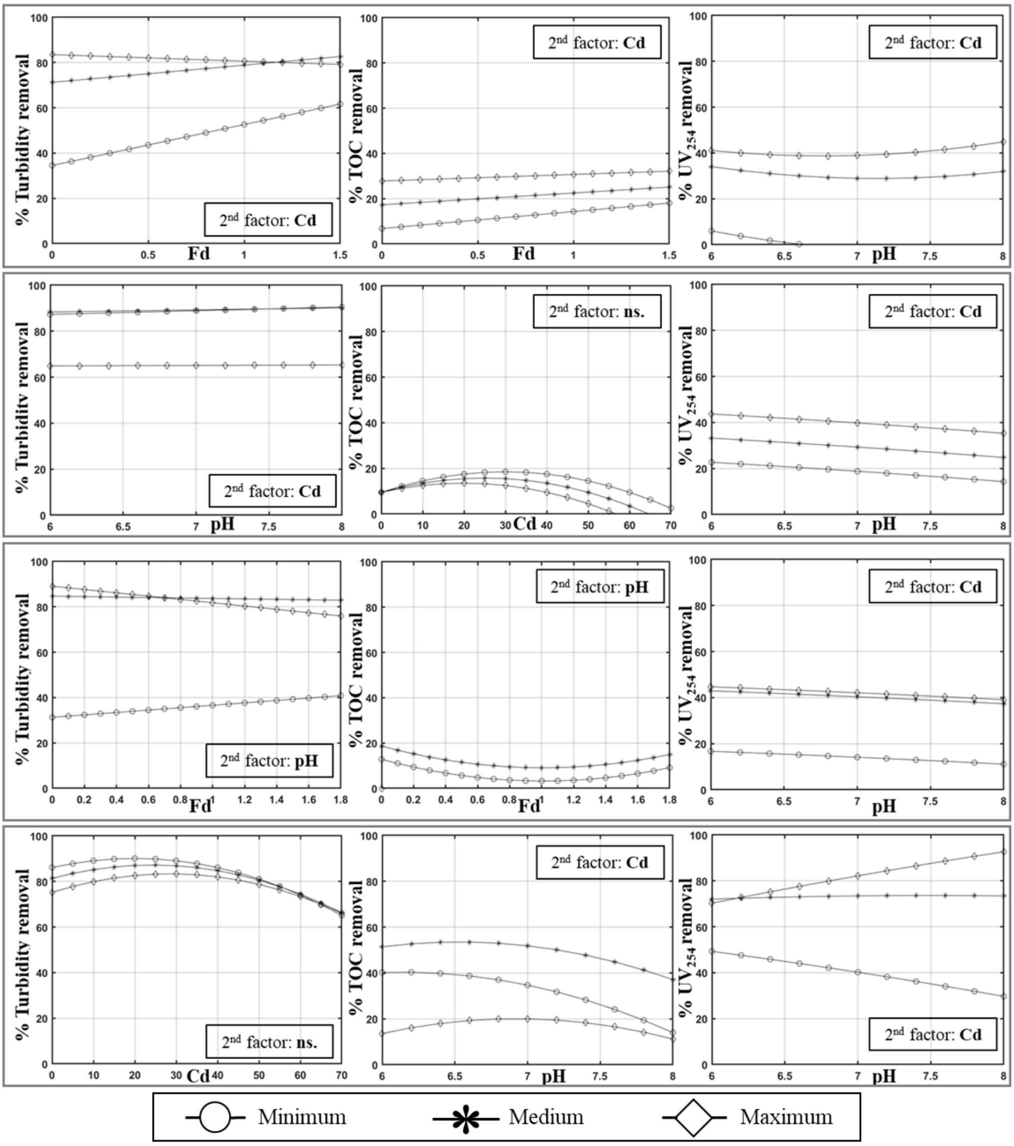

Figure 21: Profile plots for TOC and UV_{254} percentage of removals for LB, LP, TB and TP (for factors presenting the highest δ^{msqr}). The X axis are this factors presenting the highest δ^{msqr} (pH, Cd and Fd) for each response DWTP scenario, located at Y axis as % of removal. Then, the other factors presenting lower relative impact were levelled for the minimum, medium and maximum values according to the operational DWTP ranges.

5.3.4. Practical implications

In this section, practical implications as well as the limitations for models implementation are stated. Enhanced coagulation models implementation is based on influent waters classification, thus determining which model to propose for coagulation. Then, depending on the fixed enhanced coagulation optimisation criteria for the selected quality standards (responses removal), a specific pH, Cd and Fd can be proposed by models for the desired operation (Figure 22).

This study, which has been developed within the context of two water treatment facilities, is adaptable to other full scale DWTPs, but some requirements should be taken in consideration. Firstly, the type of catchment. Results demonstrate that influent water quality is subjected to the type of surface water catchment (river or reservoir) and these has an effect on the optimisation of coagulation process. The water regimes differ between them and this affects water quality, quantity, as well as the frequency of these fluctuations. Then, the installation and the capacity to monitor and track influent water quality is crucial when implementing the models. To characterise waters, a number of minimum parameters should be analysed, i.e., at least the three basics for enhanced coagulation models: turbidity, TOC and UV_{254}. This step, in some cases, could imply capital investment and derived operational costs (sensor maintenance and replacement). Also, all these data generated by influent water sensors should be upload to SCADA within a control system architecture with the capacity to register and display data. Moreover, a flexible operation for coagulation would be required, allowing water treatment to be adapted to the proposed model outputs (operational factors). In other words, DWTPs should have the capacity to easily change pH, Cd and Fd. It is important to considerer coagulation location in water treatment train, at the two case studies raw water parameters were used because no other process was affecting the water characterization. Should there be other steps before coagulation, the quality of influent waters would not be representative for the optimisation.

There are some practical operational implications which could be taken in consideration. In the case of extreme events, detecting high levels of turbidity in the influent (>40NTUs), coagulation optimisation criteria should be readjusted by, at least, >95% to ensure the removal during coagulation and avoid pore blockage in the subsequent processes if there are some filtration-based technologies involved.

Also, taking in consideration the results obtained in this study, in these cases the correct adjustment of Cd becomes crucial for enhanced coagulation because pH level should be maintained within the legislated ranges. This means that can exist cases where model-propose pH levels that are not applicable to full-scale operations. For example, if pH=5.5 or 8.5 are suggested to ensure optimum conditions for a specific removal criterion, this may will be the ideal for enhanced coagulation, but is not feasible for drinking water production and the later consumption. Then, some restrictions can be applied to the models by considering a readjustment of Cd and Fd instead of the decrease in pH by fixing some limiting thresholds (e.g., pH>7 and pH < 8). During baseline scenarios, where water quality at the influent is not considered poor and water characterization levels is low, enhanced coagulation depends on the correct adjustment of pH, Cd and Fd, being the latter a determinant parameter for process performance.

The mathematical models developed here have some design limitations and it is important to state them for the future applications. First, RSM experiments and models should be performed for individual catchments. Moreover, to develop RSM model replicates (jar test experiments) during the year within specific catchment/weather situations would bring additional information for the existing models and increase their reliability in all scenarios. Under the supervision of an experienced user, the proposed models also have the potential to act as decision-making support tools with which to check the viability of any proposed values (see Figure 22). That said, a user interface for that task would need to be developed.

As a point of insight into (and related to) prevention tasks, increasing the capacity to be able to monitor and predict weather forecast in the drinking water sector by controlling hydraulic regimes, retention times and catchment basins, is important. As present and near-future predictions anticipate, the frequency of extreme weather events will be reduced in time and therefore, regular floods will have to be taken in consideration for decision-making purposes. This study highlights the importance of meteorology to water production/management sector. In the case of river (seasonality) and reservoir (extreme events) catchments the relationship between influent water quality and rains/storms was highlighted. These exceptional circumstances will become habitual and adapting water treatment to them will be required to safeguard the water supply during these stages.

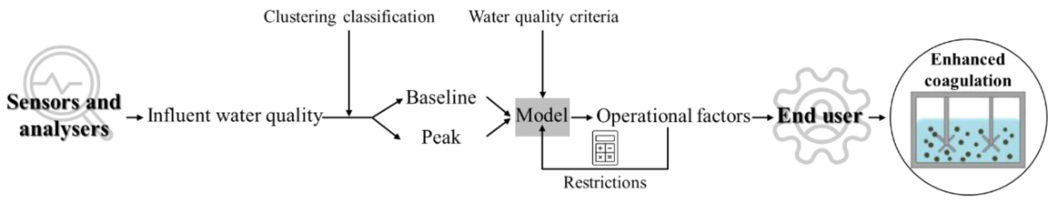

Figure 22: Roadmap for the implementation of enhanced coagulation models at a full-scale DWTP.

5.4. Conclusions

Enhanced coagulation models were developed to optimise coagulation processes at two Mediterranean DWTPs. Specifically, these models were designed to remove turbidity, TOC and UV_{254}, which are stated as water quality parameters and NOM surrogates. Cluster analysis based on K-means algorithm was applied to influent water characterization databases to classify waters into baseline and peak organic content. For each cluster, a coagulation RSM accounting for turbidity, TOC and UV_{254} percentage of removals was designed and developed. Then, after the predictors selection the models outputs (equations) were validated with a sensitivity analysis based on delta mean-squared (δ^{msqr}) to quantify model factors relative impact for the previously-mentioned scenarios. The models mean R^2 value for the three responses at DWTP 1 were 0.85 and 0.86 while in DWTP 2 were 0.85 and 0.84, in both cases for baseline and peak scenarios, respectively.

The study of these models was conducted to determine that the differences between water catchments alter the quality of the influent water at the DWTPs, thus affecting the optimum for enhanced coagulation. Results from clusters analysis revealed that the water catchment determines drinking water quality because of the temporal fluctuations of influent organic load. Clustering analysis provided information about the intensity, the frequency and the water characterization during baseline and peak scenarios. Then, sensitivity analysis allowed to find out which are the key factors for enhanced coagulation depending on the scenario.

The Llobregat river, which is the DWTP 1 catchment, is a challenging case due to seasonal fluctuations and the sudden high organic loads in the waters caused by anthropogenic pressure and rains runoff. On the other hand, rather than the seasonal change, the influent waters at the DWTP 2 (reservoir catchment) are altered through extreme weather events. Results of cluster analysis determined that peak events at DWTP 1 are seasonal and related to an increase of particles and coloured compounds, expressed by high levels of turbidity at the influent. On the other hand, DWTP 2 peak scenarios are linked to extreme weather events and are challenging due to the increase of dissolved NOM, which is expressed by higher values of TOC and UV_{254} more than turbidity. From this and considering the sensitivity analysis, in baseline scenarios it is important to adjust at the optimum levels (which are not the highest) the three influential factors (pH, Cd and Fd) in order to ensure enhanced coagulation, resulting obvious if low pollutants load is located at the influent waters. However, during peak scenarios pH and Cd are the factors to be considered for enhanced coagulation and Fd is not relevant for the process itself due to reduce the high levels of pollutants present at the influent. In this cases, Cd is highlighted as a key factor to ensure enhanced coagulation and desired NOM removals.

6. Results III:

Strategy to minimise THMs formation using enhanced coagulation models

Suquet, J.; Godo-Pla, L.; Galizia, A.; Poch, M.; Monclús, H. Strategy to minimise THMs formation using enhanced coagulation models. (In preparation).

6.1. Background

Enhanced coagulation has been extensively studied for DBPs mitigation. As coagulation is a powerful process for NOM removal, several studies were aimed to evaluate DBPs removal using enhanced coagulation (Ghernaout et al., 2009; Zhao et al., 2013). Through coagulation, Wang et al. (2021) reported that DBPs can be reduced from 20% up to 60%. To control DBPs formation potential, some specific water quality parameters are used to track NOM composition at full-scale facilities, being TOC and UV_{254} the most widely used. From this basis, the enhanced coagulation models are usually developed to remove TOC or/and UV_{254} (Awad et al., 2018; Liu et al., 2019; Tafvizi and Husain, 2022). As it exists a correlation between NOM removal during coagulation and DBPs minimisation, enhanced coagulation models could systematise DBPs reduction during drinking water treatment.

In the Chapter 5 of this thesis, enhanced coagulation mathematical models were developed for NOM removal (TOC and UV_{254}) accounting for different influent water quality NOM scenarios for river and reservoir catchment. The aim of this chapter is to develop an implementation strategy for a full-scale control system targeting DBPs minimisation using enhanced coagulation. Is at this point were the following specific objectives are described: first, i) to evaluate enhanced coagulation models application for full-scale historical datasets for the different water catchments (river and reservoir) and influent NOM scenarios (baseline and peak). Then, ii) to develop a control strategy to minimise THMs using the enhanced coagulation. Finally, iii) to evaluate the control system for the historical full-scale datasets at DWTP 1.

6.2. Methodology

6.2.1. Enhanced coagulation models

Enhanced coagulation models for TOC and UV_{254} developed in Chapter 5 at DWTP 1 and DWTP 2 were used for the historical datasets evaluation, presented in Table 9 for LB, LP, TB and TP scenarios.

6.2.2. Determination of Cd for enhanced coagulation

A mathematical algorithm, using MATLAB 2015a (Mathworks®, USA) software, was performed to obtain the daily historical Cd values presenting the highest TOC and UV_{254} removals at DWTP 1 and DWTP 2. Cd was ranged according to full-scale operation from 0 to 70 $mg \cdot L^{-1}$. Then, the enhanced coagulation models were used to calculate TOC and UV_{254} depending on the case study and the influent water NOM scenario. From here, the developed algorithm calculated the daily TOC and UV_{254} removals for the entire Cd range. Those Cd presenting the highest removal values for TOC and UV_{254} were selected and named hereafter $Cd_{Adjusted}$. Results obtained were classified in the low, medium or high Cd ranges. From 0 to 30 $mg \cdot L^{-1}$ was considered low Cd, then from 30 to 50 $mg \cdot L^{-1}$ was medium Cd and 50 to 70 $mg \cdot L^{-1}$ high Cd.

6.2.3. THMs empirical model

THMs empirical model used to design and test the proposal of implementation at DWTP 1 was developed in the study conducted by (Godo-Pla et al., 2021). In that study, an empirical model aimed to determine the formation of THMs at DWTP 1 was developed based on a multi linear regression (MLR) model and was later validated with full-scale datasets, presenting a R^2 value of 0.88.

$$\begin{aligned} \mathrm{THMs} &= \mathrm{a} \cdot (\mathrm{UV254}+1)^{\mathrm{b}} \cdot \mathrm{TOC}^{\mathrm{c}} \cdot \mathrm{D_{Cl}}^{\mathrm{d}} \cdot (\mathrm{Br}+1)^{\mathrm{e}} \cdot \mathrm{T}^{\mathrm{f}} \cdot \mathrm{pH}^{\mathrm{g}} \cdot \mathrm{HRT}^{\mathrm{h}} \\ &= 6.18 \cdot (\mathrm{UV254}+1)^{3.64} \cdot \mathrm{TOC}^{0.462} \cdot \mathrm{D_{Cl}}^{0.42} \cdot (\mathrm{Br}+1)^{0.471} \cdot \mathrm{T}^{0.169} \cdot \mathrm{pH}^{0.048} \cdot \mathrm{HRT}^{0.298} \end{aligned} \tag{10}$$

Where UV_{254} is ultraviolet absorbance at 254 nm (m^{-1}), TOC is total organic carbon ($mg \cdot L^{-1}$), D_{cl} is chlorine dose ($mg \cdot L^{-1}$), Br is bromide concentration ($\mu g \cdot L^{-1}$), T is the water temperature (ºC), pH and HRT is the hydraulic retention time (hours).

6.3. Results and discussion

6.3.1. Enhanced coagulation models performance

Water catchment implications

The enhanced coagulation models were evaluated for TOC and UV_{254} removals at DWTP 1 and DWTP 2. In each DWTP, the removal of TOC and UV_{254} was predicted using the enhanced coagulation models developed in Chapter 5, using daily historical operational conditions (Cd, pH and Fd). Additionally, the Cd values presenting the daily highest removal for TOC and UV_{254} ($Cd_{Adjusted}$) were calculated. Results comparing the predicted values for TOC and UV_{254} using the historical Cd value and using $Cd_{Adjusted}$ are presented in Figure 23 and Figure 24, respectively. In these figures daily influent NOM is presented through TOC and UV_{254} values (grey markers). Hence, historical influent TOC and UV_{254} values were plotted to display influent water quality fluctuations.

For both DWTPs results shown that $Cd_{Adjusted}$ can improve coagulation efficiency. In general, TOC removal presented lower values than UV_{254} removal. These results are aligned with the findings reported by Pei et al., (2007), where the higher reduction of UV_{254} relies on the NOM fraction. UV_{254} is composed by hydrophobic organic carbon compounds which are easily removed by adsorption during coagulation. On the other hand, TOC comprises hydrophobic and hydrophilic NOM fractions, being the latter fraction less removed by coagulation.

Regarding DWTP 1, influent TOC and UV_{254} values presented high fluctuations during the time series (Figure 23, grey markers). The expected NOM values for DWTP conditions (Figure 23, black markers) showed average removals of 17.3±3.2% for TOC and 30.6±6.1% for UV_{254}. Then, with $Cd_{Adjusted}$ (Figure 23, green markers) NOM removal increased, being 32.7±10.2% and 43.6±11.8% for TOC and UV_{254} removal, respectively. Sudden changes in surface water composition have a direct impact on the coagulation optimal operation. Concerning DWTP 2, TOC and UV_{254} values remained stable all over the time series. TOC and UV_{254} were removed in 10.6±3.5% and 36,9±14,7% for simulated historical DWTP conditions (Figure 24, black markers). With the Cd adjustment (Figure 24, green markers), an increase of

NOM removal was observed: 16,9±11,1% and 48,8±15,8% for TOC and UV_{254} removals, respectively.

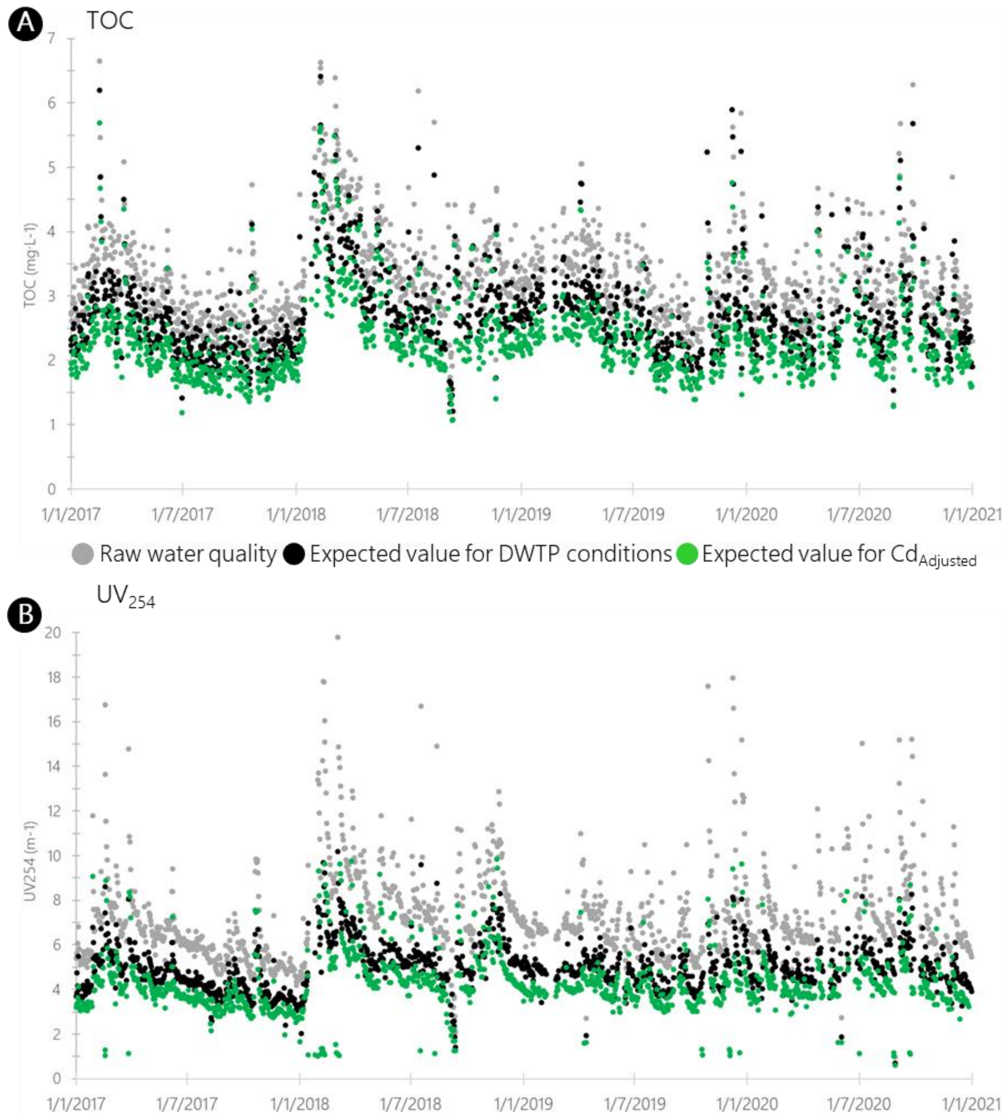

Figure 23: Enhanced coagulation models performance at DWTP 1 for TOC (A) and UV_{254} (B). Grey markers are the historical influent values for TOC and UV_{254}. Black and green markers are model outputs (values after coagulation) under different Cd; black are the expected values of TOC and UV_{254} with the historical DWTP operation and green are the expected values for the $Cd_{Adjusted}$. Period 2017-2020, n= 1232.

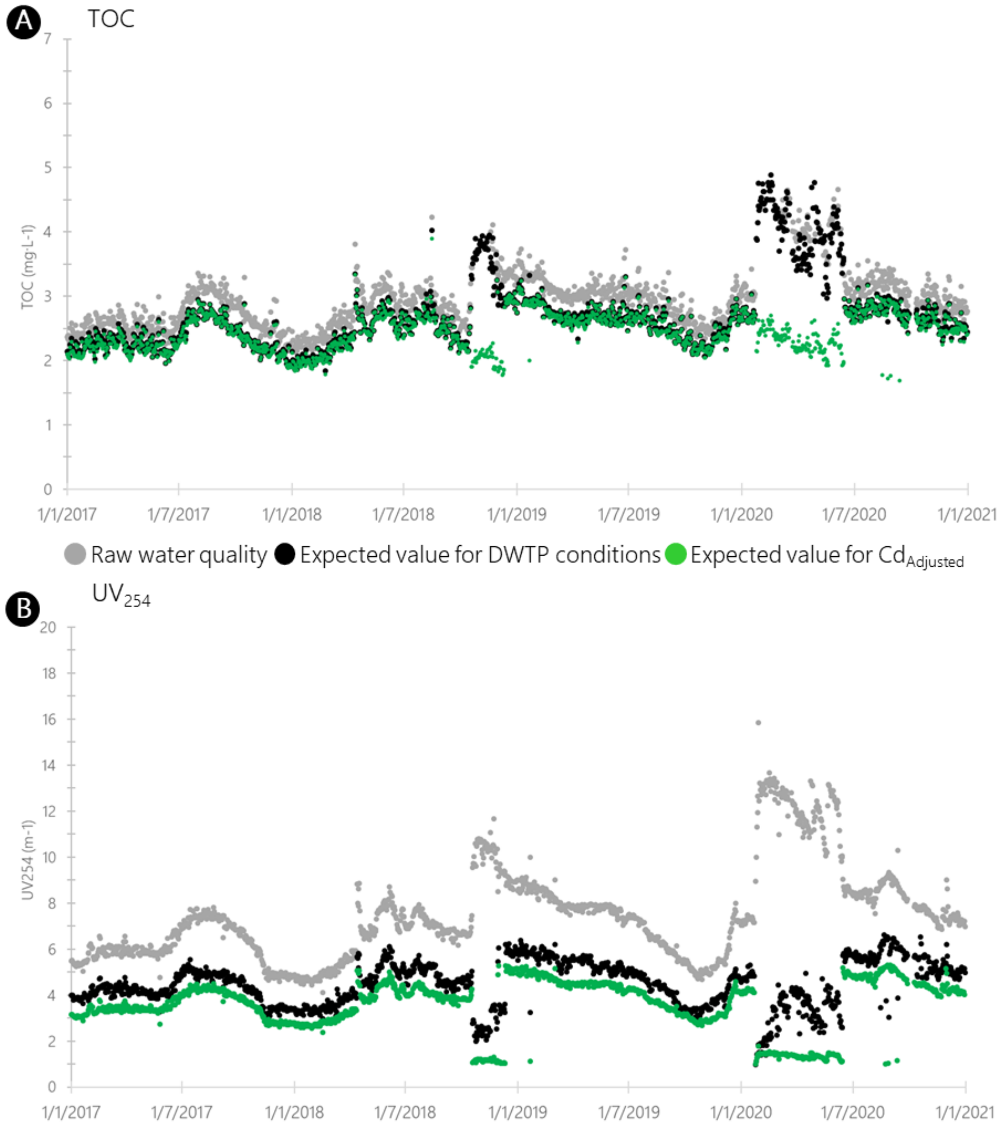

Figure 24: Enhanced coagulation models performance at DWTP 2 for TOC (A) and UV_{254} (B). Grey markers are the historical influent values for TOC and UV_{254}. Black and green markers are model outputs (values after coagulation) under different Cd; black are the expected values of TOC and UV_{254} with the historical DWTP operation and green are the expected values for the $Cd_{Adjusted}$. Period 2017-2020, n= 1428.

In summary, the application of enhanced coagulation models for the entire datasets outlined some differences related to the impact of surface water catchments in drinking water treatment. The predicted values of TOC and UV_{254} showed that there is still a room for improvement in terms of coagulation and $Cd_{Adjusted}$ results highlighted that Cd is important to remove NOM in drinking water production.

Influent water quality scenarios implications

The aim of this section was to determine the implications of the influent water quality scenarios on the performance of enhanced coagulation. To accomplish with that task, $Cd_{Adjusted}$ was calculated at each DWTP for baseline and peak cases. Results from DWTP 1 and DWPT 2 are presented in Figure 25 and Figure 26.

Related to TOC (Figure 25), enhanced coagulation models with $Cd_{Adjusted}$ showed different predicted removals for each DWTP and scenario. For DWTP 1, TOC removals under baseline (30.6±6.8%) were lower compared to peak (46.8±16.8%) cases. The same trend is observed for DWTP 2, where the predicted values for baseline TOC removals using $Cd_{Adjusted}$ presented lower values than in peak cases with 12.5±1.5% and 44.8±1% in average, respectively. Differences in coagulation performance between baseline cases in DWTP 1 and DWTP 2 are linked to the catchment type. $Cd_{Adjusted}$ do not show high removals for reservoir baseline cases because TOC is not a critical parameter (low values at the influent). However, predicted results from $Cd_{Adjusted}$ determine that TOC removal could be enhanced up to 40% during peak cases for both DWTPs.

Related to UV_{254} (Figure 26), same trends were observed from $Cd_{Adjusted}$ predicted removals. The percentage of UV_{254} removed during peak cases (59.8±15%) at DWTP 1 was higher than in baseline (41.2±9%). For DWTP 2 these differences were expanded, resulting in 42.7±2.3% for baseline cases compared to 87.9±6.3% for peak scenarios.

From the comparison between predicted TOC and UV_{254} removals for $Cd_{Adjusted}$ some differences in terms of TOC and UV_{254} removals during peak cases are observed. In all cases $Cd_{Adjusted}$ impact is higher for UV_{254}, denoting that this kind of compounds are easily removed during coagulation.

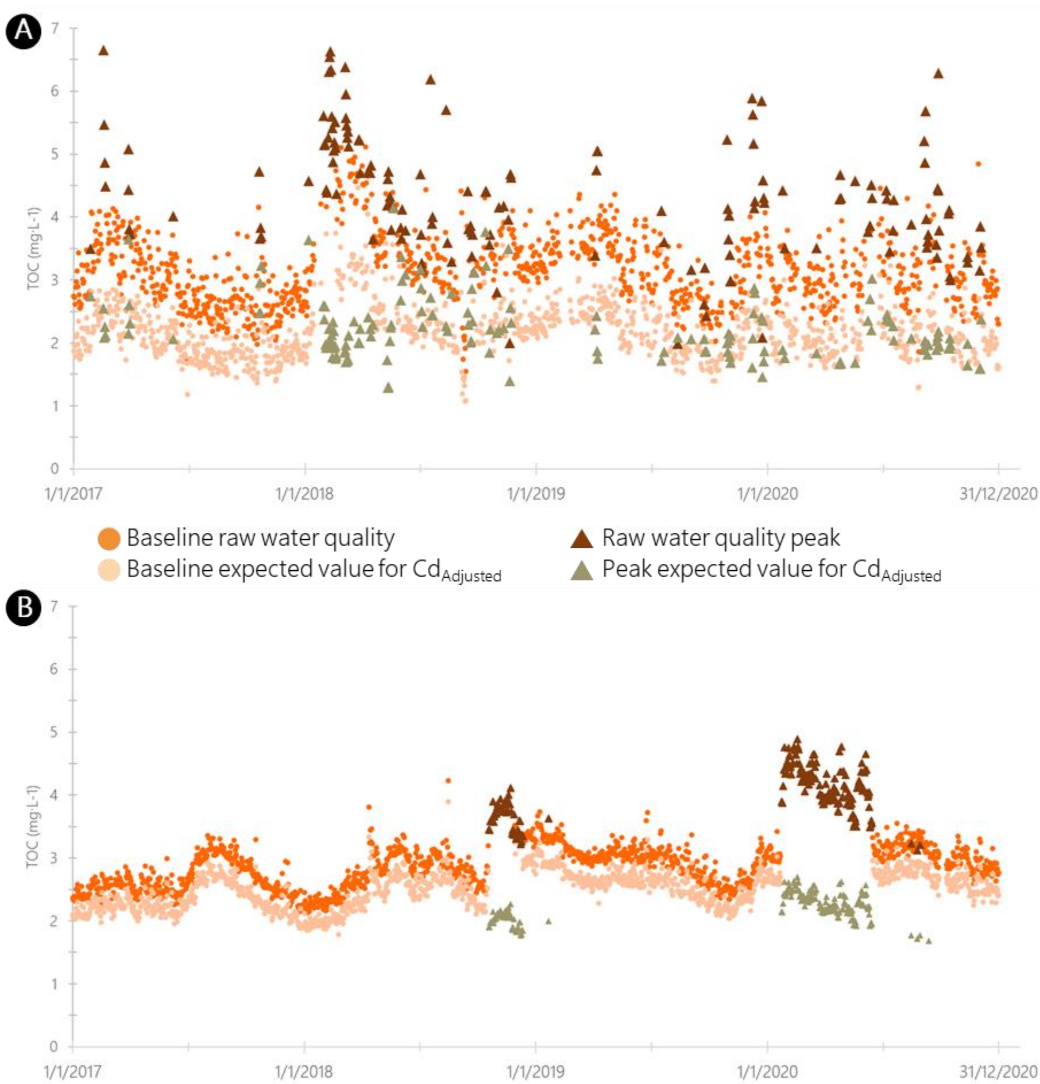

Figure 25: Influent TOC values and TOC values with $Cd_{Adjusted}$ are presented for baseline and peak scenarios in river (DWTP 1, A) and reservoir catchment (DWTP 2, B). Period 2017-2020. DWTP 1: n_T=1232, $n_{baseline}$=1076 and n_{peak}=156; DWTP 2: n_T=1428, $n_{baseline}$=1235 and n_{peak}=193.

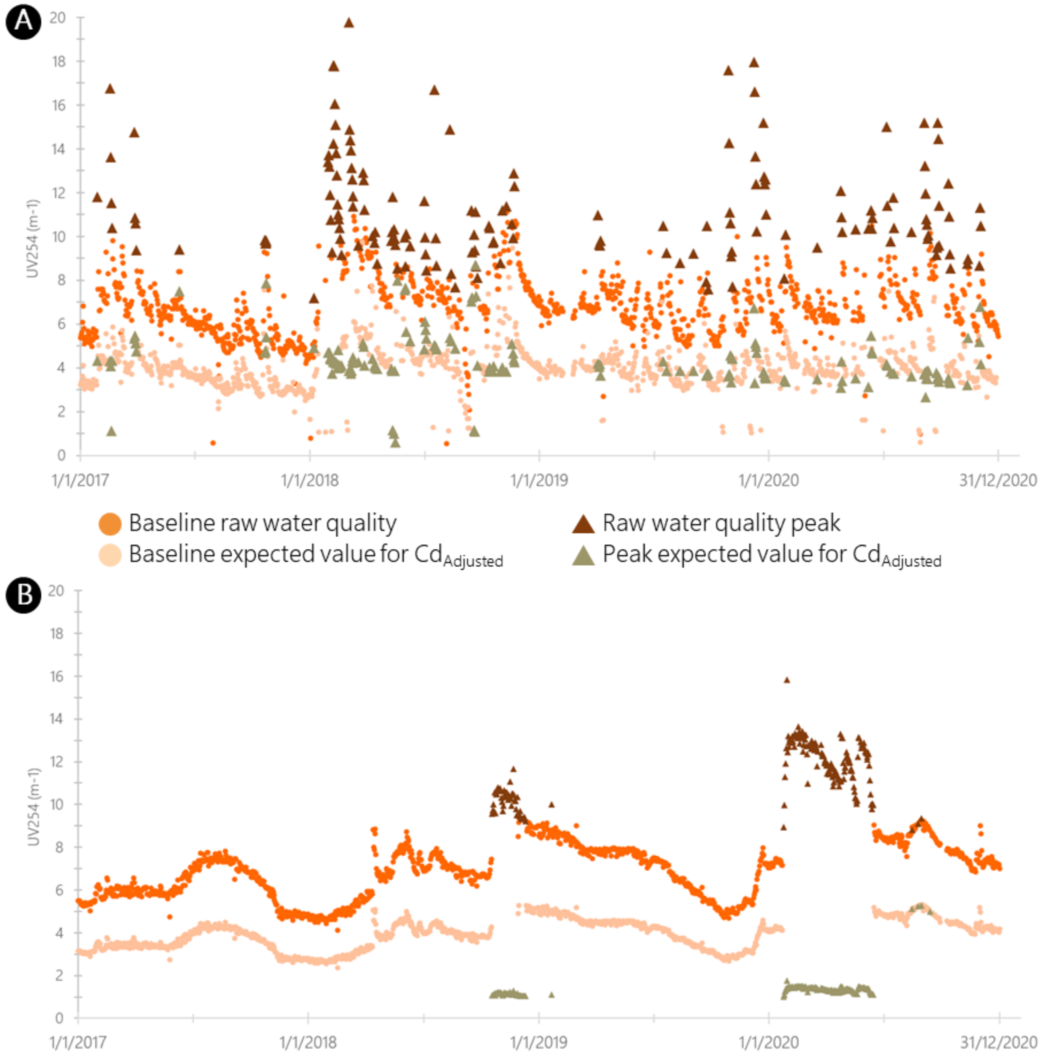

Figure 26: Influent UV_{254} values and UV_{254} values with $Cd_{Adjusted}$ are presented for baseline and peak scenarios in river (DWTP 1, A) and reservoir catchment (DWTP 2, B). Period 2017-2020. DWTP 1: n_T=1232, $n_{baseline}$=1076 and n_{peak}=156; DWTP 2: n_T=1428, $n_{baseline}$=1235 and n_{peak}=193.

A summary of the predicted removals as well as the $Cd_{Adjusted}$ values is presented in Table 11: Summary of the removal efficiencies with $Cd_{Adjusted}$ for each DWTP and scenario. Regarding DWTP 1, higher removals for TOC and UV_{254} were found with high values of Cd in all scenarios excepting for the removal of TOC during peak events. Thus, results suggest that high Cd (50-70mg·L-1) is proposed for baseline cases, while medium Cd (≈30mg·L^{-1}) presented higher removals accounting for TOC and UV_{254} during peak conditions. Concerning DWTP 2, higher NOM removals were found at medium Cd values (30-50 mg·L^{-1}).

Table 11: Summary of the removal efficiencies with $Cd_{Adjusted}$

DWTP	Scenario	$\bar{X}$ Influent mgC·L^{-1}/m^{-1}	$Cd_{Adjusted}$ mg·L^{-1}	$\bar{X}$ Removal %	$\bar{X}$ SUVA	ANOVA p-value
1 (river)	Baseline TOC	3.1±0.6	High (50-70)	30.6±6.8	2.16±0.32	<0.05
	Baseline UV_{254}	6.8±1.3	High (50-70)	41.2±9		
	Peak TOC	4.4±1.1	Low (15-30)	46.8±16.8	2.61±0.52	
	Peak UV_{254}	11.2±2.4	High (50-70)	59.8±15		
2 (reservoir)	Baseline TOC	2.8±0.3	Med. (20-40)	12.5±1.5	2.39±0.24	<0.05
	Baseline UV_{254}	6.8±1.2	Med. (40-60)	42.7±2.3		
	Peak TOC	4±0.4	Med. (20-40)	44.8±1	2.88±0.16	
	Peak UV_{254}	11.5±1.3	High (50-70)	87.9±6.3		

Saxena et al. (2018) stated that high SUVA values (>2.5) indicate waters with dominance of hydrophobic compounds. These kind of compounds are those which are easily removed through coagulation (adsorption) with the correct coagulant adjustment. Waters presenting low SUVA (<2.5) values are mainly composed by hydrophilic compounds and its removal can be increased through enhanced coagulation (Yan et al., 2006). Also, Boyer and Singer (2006) determined that SUVA value is an important indicator for predicting NOM removal during coagulation. In the following section, the influent SUVA values for both DWTPs and scenarios are further discussed.

Regarding DWTP 1 influent characterization, influent mean SUVA value was 2.16±0.32 for baseline cases and 2.61±0.52 for peak scenarios, denoting that the hydrophilic NOM fraction in baseline waters was higher than in peak cases. According to this, Parsa et al. (2020) reported that TOC removal is highly influenced by Cd, hence the removal of hydrophobic NOM occurs when high Cd is applied during coagulation. For these reason, for baseline scenarios higher removals were obtained with high Cd. Then, peak cases were dominated by hydrophobic NOM (high SUVA and UV_{254}) requiring high Cd to ensure hydrophobic NOM adsorption an entrapment. In these cases, UV_{254} is the key parameter to achieve enhanced coagulation. Peak events were characterized by an increase of turbidity and hydrophobic NOM at the influent of DWTP 1.

For DWTP 2, similar results were obtained for the influent water characterization. Influent baseline waters presented low SUVA values compared to peak cases. SUVA value for baseline cases was 2.39±0.24, while in peak scenarios was 2.88±0.16. In this case, enhanced coagulation in baseline cases is achieved through medium-to-high Cd. TOC value increase was not significant for peak scenarios. Peak cases were clearly dominated by UV_{254} increase and higher SUVA values at the influent.

These results are in line with the study conducted by (Volk et al., 2002), where NOM was characterized and monitored for several surface and drinking waters concluding that after rainfall events TOC and UV_{254} can be increased by a factor of 3.5 and 12, respectively. Regarding the analysis of variance, a single factor ANOVA was performed for baseline and peak scenarios SUVA values. From here, significant differences were described between SUVA baseline and SUVA peak for both DWTPs influent waters (see Table 11). Then, removal percentages were higher in peak scenarios compared to baseline, which was basically due to the higher SUVA values. From this results UV_{254} is highlighted as a crucial parameter to be removed during coagulation in peak cases.

6.3.2. Full-scale control strategy for THMs minimisation based on enhanced coagulation

The scheme of the conceptual framework of the control system for enhanced coagulation and the minimisation of DBPs is presented in Figure 27. To achieve that, enhanced coagulation models are planned to be implemented to determine the optimal operational conditions for DWTP coagulation based on the influent water characterization. First, the influent water quality is monitored through sensors and analysers located at the influent of the DWTP (step 1). Then, baseline or peak scenario can be identified based on the influent NOM quality parameters (step 2). Afterwards, enhanced coagulation models are executed to propose the optimal conditions (pH, Cd and Fd) for the desired water quality at the effluent of coagulation (step 3 and 4). DBPs formation is predicted using a predictive model (se Eq.10) as a soft sensor (step 5). THMs model is executed and coagulation is adjusted according to the THMs threshold (step 6). Therefore, if the THMs value is higher or lower than the fixed threshold, then coagulation will be adjusted.

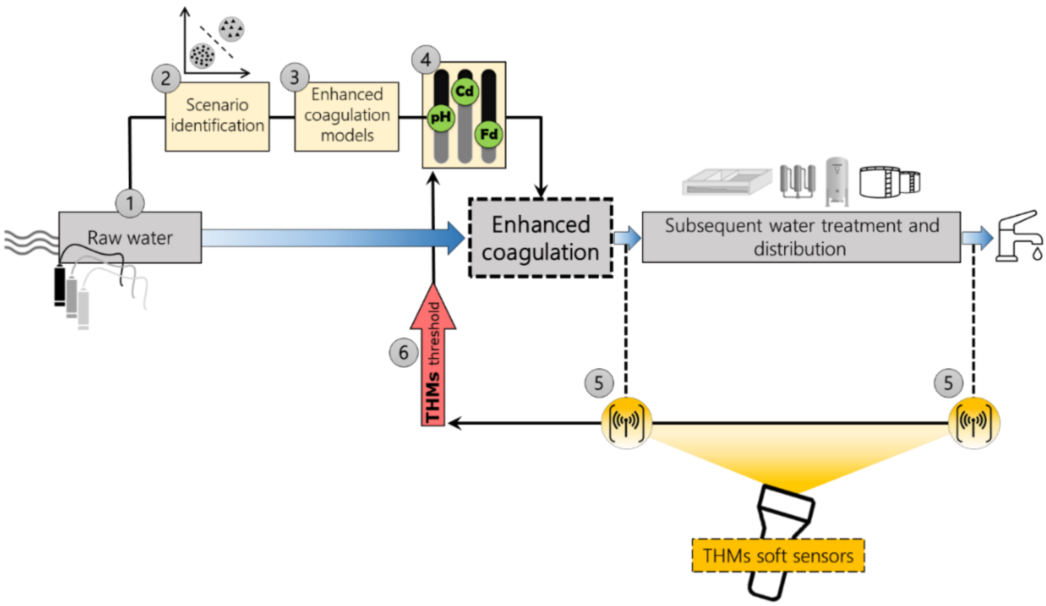

Figure 27: Full-scale scheme for the proposed strategy based on enhanced coagulation – THMs minimisation.

The case of DWTP 1: Proposal for the control strategy implementation

Strategy for THMs minimisation using enhanced coagulation was tested with the historical full-scale database at DWTP 1. For that, some assumptions were stated to present enhanced coagulation and THMs outputs. The implementation proposed was done with the assessment of the historical datasets, where each case and scenario was evaluated for $Cd_{Adjusted}$ and THMs formation using empirical models (Table 9 and Eq.10).

The effluent of enhanced coagulation was modelled for the THMs values based on the historical DWTP conditions and for $Cd_{Adjusted}$ to achieve enhanced coagulation. THMs threshold for produced waters was set at $80\mu g{\cdot}L^{-1}$ assuming that the Spanish legislation establishes the maximum THMs concentration for tap water in $100\mu g{\cdot}L^{-1}$. Considering that THMs value can be increased during the distribution system this threshold can be modified according to the water quality/management purposes. At a full-scale level, there exist complementary treatments aimed to remove residual NOM, all of them are detailed in Figure 9.

In Figure 28, THMs formation predicted using historical DWTP conditions and these calculated from the $Cd_{Adjusted}$ for enhanced coagulation are presented for the period 2017-2020 at DWTP 1. To predict THMs formation, it was considered 30 hours of HRT. From the results shown in this figure, it was shown that enhanced coagulation can significantly reduce THMs along the study period.

Using DWTP operational conditions, predicted THMs average was $68.2\pm9.7\mu g{\cdot}L^{-1}$ compared to these obtained with $Cd_{Adjusted}$ for enhanced coagulation, which was $59.3\pm6.8\mu g{\cdot}L^{-1}$. This supposed a mean THMs reduction of 13%. From the total studied cases, 87.3% were baseline and 12.7% were peak cases. However, peak scenarios accounted for the 68.5% of the days presenting an exceeded THMs value (n=85). On the other hand, baseline cases were the remaining 31.5% (n=39). Thus, peak cases present higher chances of surpassing the established THMs threshold. Nonetheless, with $Cd_{Adjusted}$ for enhanced coagulation, the 99.2% of total cases predicting THMs exceeded values were corrected (n_{total}=124).

To achieve lower values for predicted THMs, pH and Fd should be considered according to the models presented in Table 9. Considering that DWTPs has implemented multiple unit operations, this chapter states a flexible approach for THMs minimisation where some complementary water treatments can be added, each of them contributing to a certain degree in NOM removal and therefore, to THMs formation minimisation (see Figure 28). In particular, DWTP 1 has several technologies implemented as advanced treatments and each one has some contribution to NOM removal.

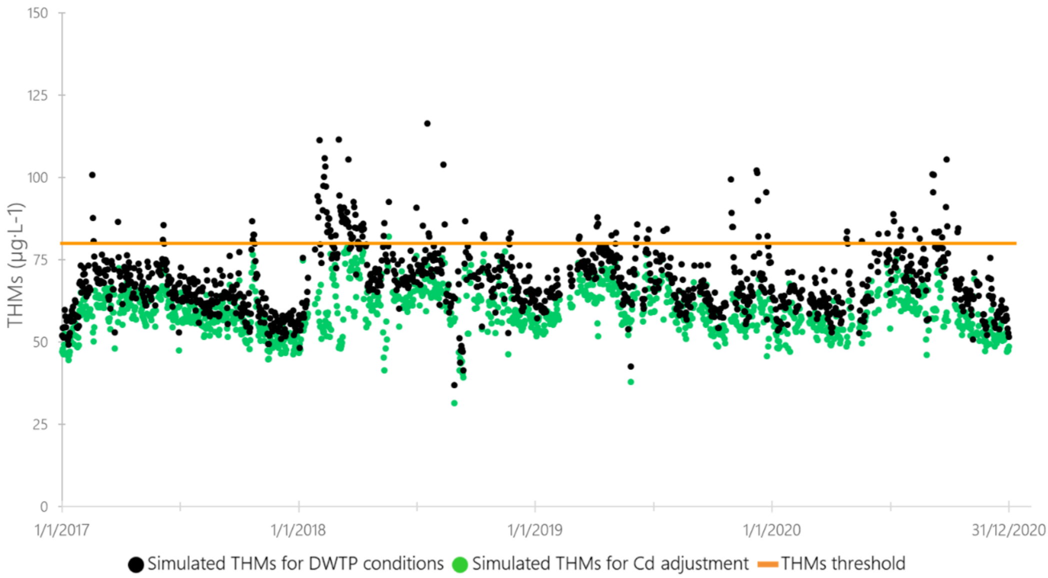

Figure 28: Simulated THMs formation at post-coagulated water at DWTP 1 accounting for historical DWTP conditions and the $Cd_{Adjusted}$ to achieve enhanced coagulation.

6.4. Conclusions

The nature and the quality of influent waters determines coagulation efficiency, which should be adjusted according to the water composition to achieve enhanced coagulation. In this chapter, historical data for two DWTPs were evaluated to test the enhanced coagulation models developed in chapter 5 of this thesis. Coagulation efficiencies for the two water catchments (river and reservoir) under different influent NOM scenarios (baseline and peak) were discussed presenting the following findings:

- In both DWTPs, the application of enhanced coagulation models predicted lower coagulation TOC removal compared to UV_{254}. This is due basically to NOM fractionation and the reason that UV_{254} is linked to the hydrophobic NOM fraction, which is removed during coagulation by adsorption.

- NOM removal through enhanced coagulation models was simulated for the historical DWTP operational values and $Cd_{Adjusted}$ aimed to achieve NOM removal. Regarding DWTP 1, $Cd_{Adjusted}$ improved coagulation NOM removals compared to the historical values, supposing an increase of 15.4% and 13% for TOC and UV_{254} removals, respectively. In this sense, similar results were observed in DWTP 2, where TOC and UV_{254} removals increased with 6.3% and 11.9%, respectively. These results indicated that $Cd_{Adjusted}$ improves coagulation NOM removal in both DWTPs and scenarios.

- Significant differences were determined between SUVA values for baseline and peak scenarios for both DWTPs. From here, high SUVA values during peak cases highlighted UV_{254} as a crucial parameter to be removed in peak cases. Also, enhanced coagulation models showed that $Cd_{Adjusted}$ can considerably improve NOM removal during peak cases. These peak scenarios represented the 12.7% and 15.6% of the total evaluated cases for DWTP 1 and DWTP 2, respectively.

A control system for enhanced coagulation module aimed to minimise THMs is proposed/conceptualised for a potential full-scale implementation. The application of this control system for DWTP 1 highlighted peak scenarios as challenging cases for controlling THMs, which supposed the 68.5% of cases presenting high THMs predicted values. Results of THMs simulation at DWTP 1 showed that peak scenarios are those cases where special attention is required due to the higher risk for THMs formation. From here, $Cd_{Adjusted}$ was useful to reduce THMs predicted values for 99.2% of cases.

7. General discussion

This thesis presents enhanced coagulation EDSS for three Mediterranean DWTPs. These systems are aimed to minimise DBPs using enhanced coagulation.

From here, the most substantial contribution of this thesis in the research field is the development of enhanced coagulation models aimed to remove NOM minimising DBPs formation (THMs) for its integration in a full-scale system at three Mediterranean DWTPs. The enhanced coagulation models presented on this thesis were performed from laboratory experiments and were specifically designed and developed for different types of water, providing a novel framework of how the applied research can be performed in a full-scale level application. To achieve that, real DWTP samples and reagents as well as the standardised DWTPs protocols were used to obtain enhanced coagulation empirical models. The chapters presented in this thesis describe which are the most significant factors to achieve enhanced coagulation for different types of surface waters and NOM quantity/quality fluctuations (NOM scenarios). From here, enhanced coagulation models were tested providing insights on how NOM can be removed through enhanced coagulation. Furthermore, these models were integrated at the EDSS control level, aiding DWTPs decision-making systematization and also for water treatment optimisation.

EDSS were developed in several steps, which individually contributed to plan, design and build the proposed enhanced coagulation control systems presented in this thesis (Figure 29). Thus, the EDSS development comprised four steps: i) problem analysis, ii) data collection and knowledge acquisition, iii) cognitive analysis and model development and iv) models implementation and EDSS validation. From here, thesis specific contribution to achieve an enhanced coagulation EDSS for drinking water production is detailed.

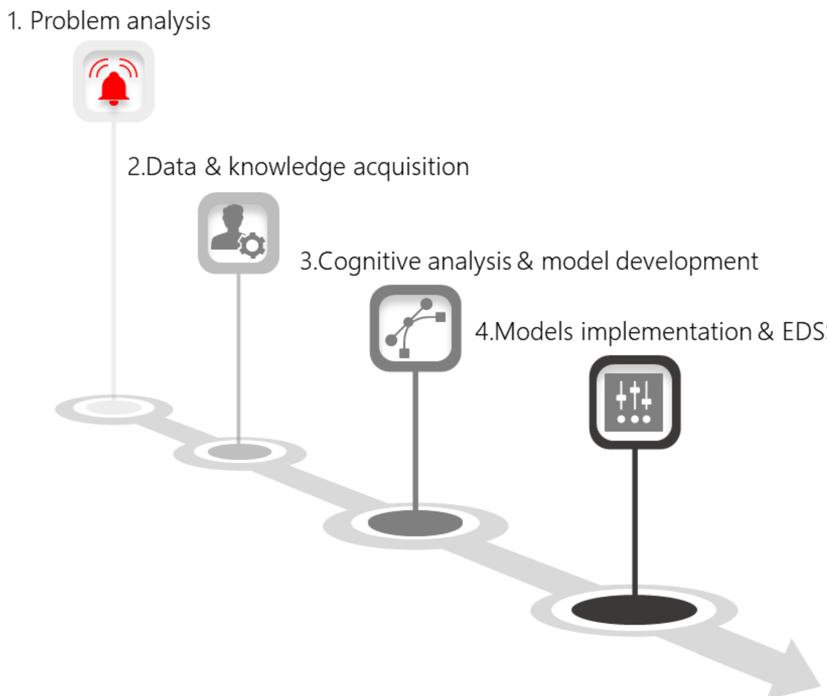

Figure 29: Steps followed for the development of a drinking water enhanced coagulation EDSS.

Problem analysis

From years ago, drinking water sector is focussed on the control and removal of NOM during the water treatment for the reduction of these DBPs (Lazaridis and Colbeck, 2010; Richardson and Postigo, 2015; Sadiq and Rodriguez, 2004). NOM characterization varies from water sources due to the catchment type, seasonality, extreme weather events and the demographic context. As coagulation is the first step in drinking water treatment, the proposed enhanced coagulation EDSS, specially the developed control systems, suppose an upgrade in terms of drinking water production, optimising coagulation and contributing to DBPs minimisation.

The control systems proposed for full-scale EDSS are planned to operate following the hierarchical architecture presented in the introduction section of this thesis. Located at the control level, the presented control systems for enhanced coagulation are the core of reasoning for the proposed enhanced coagulation EDSS.

Data collection and knowledge acquisition

Data was collected at DWTPs from routine laboratory experiments and online sensors/analysers. Specific databases for each DWTP were built aimed to be used by the enhanced coagulation EDSS.

Knowledge was acquired from different sources of information using theoretical, expert, empirical and full-scale sources of information. Knowledge acquired is detailed in Figure 30.

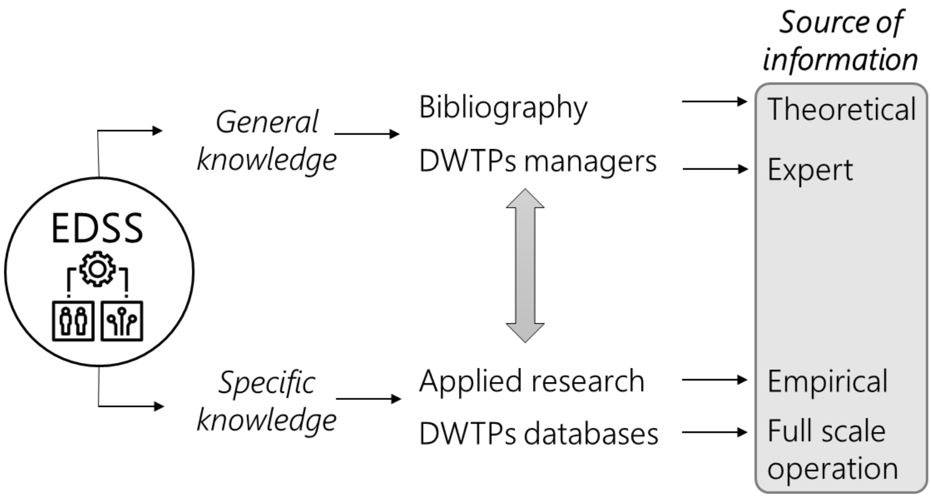

Figure 30: Knowledge acquisition diagram adopted for enhanced coagulation EDSS development.

Knowledge was divided into general and specific. General knowledge provided insights on the optimisation method, in this case RSM, used to design and develop enhanced coagulation models used for the EDSS.

Specific knowledge was obtained from laboratory analyses and DWTP databases evaluation (Chapter 4 and Chapter 5). Regarding the latter, clustering analysis was performed to the historical DWTP databases obtaining knowledge related to the influent NOM. This analysis allowed to detect differences between water catchments and influent NOM scenarios. Thus, enhanced coagulation models were performed according to the information provided by cluster analysis, classifying influent NOM waters concentration into baseline and peak scenarios. Empirical knowledge for the development of empirical enhanced coagulation models was obtained through jar test experiments, being the basis to codify the control systems for the proposed EDSS at each DWTP. Additionally, through laboratory experiments, tandem efficiency coagulation-UF experiments was evaluated in Chapter 4, highlighting UV_{254} as a significant membrane fouling factor. Information derived from full-scale operation was used to evaluate NOM removal during coagulation. This evaluation evidenced differences between turbidity removal and NOM removal (TOC, UV_{254} and SUVA) during the water treatment. All this information allowed to design specific EDSS control strategies at each case study. Hence, SRs were detailed in Chapter 4 for a coagulation EDSS aimed to remove NOM at DWTP 3. Also, the proposed EDSS for DWTP 1 and DWTP 2 were designed based on the type of water catchment and influent NOM scenario, with the integration of several enhanced coagulation models (for each scenario) integrated in the enhanced coagulation EDSS control system (Chapter 6).

Cognitive analysis and model development

Mentioned in the previous section, knowledge used to develop the EDSS was acquired from several sources of information. The enhanced coagulation models were designed and adapted to integrate all this information, contributing to plan a strategy for enhanced coagulation. Thus, the EDSS were developed considering the obtained general and specific knowledge. The EDSS control level were designed based on specific knowledge, using the enhanced coagulation models developed in Chapter 4 and Chapter 5 of this thesis. These models describe the effectiveness of coagulation conditions (pH, Cd and Fd) for NOM removal (turbidity, TOC and UV_{254}), which were analysed through a sensitivity analysis (Chapter 5) to be later evaluated for the historical databases (Chapter 6). Regarding DWTP 3, an EDSS was developed aimed to achieve some specific water quality standards. Concerning DWTP 1 and DWTP 2, a control strategy was presented based on THMs minimisation using enhanced coagulation, allowing to identify the best suitable strategies for enhanced coagulation accounting for the type of catchment (river and reservoir) and influent water NOM concentration (baseline or peak).

Model implementation and EDSS validation

From here, the conceptual framework and the proposal for a control system aimed to minimise DBPs through enhanced coagulation for drinking water production is detailed in this thesis. The enhanced coagulation EDSS are operationally structured under the three level architecture (Figure 31).

Present and future challenges in drinking water production in the Mediterranean region are related to climate change perspectives and to hydric stress scenarios (Romano and Akhmouch, 2019). Moreover, the big cities will increase in population and drinking water supply should be distributed according to the new demand. Within this context, the water sector should develop and implement strategies able to cope with the changing context and adapted to these situations. Hence, this work provides several pathways to minimise DBPs using enhanced coagulation. Thesis outcomes provide tools for a resilient treatment, adapted to influent water quality fluctuations and providing a flexible system for integrated management which allows to adjust enhanced coagulation for NOM removal and subsequently minimise DBPs.

Regarding full-scale EDSS implementation, the outputs proposed by the control system should be evaluated and validated. Also, the acceptance or not of the EDSS proposals and should be subjected to a cost-benefit analysis. For each particular case-study and scenario, an increase or a reduction of reagents dosages during coagulation can induce some implications in terms of the associated economic costs. Then, the frequency in which the enhanced coagulation EDSS is executed imply a reagent doses readjustment (pH, Cd and Fd) and this changes can be traduced into economic gains or savings, depending on the DWTP and scenario. From here, for the enhanced coagulation EDSS implementation, DWTPs managers should determine and assess which is the optimal NOM removal considering the reagents costs used to achieve enhanced coagulation at full-scale level, which sometimes are changing all over the year (between cold and hot seasons). To complete the EDSS, some of these reagents economic implications can be codified as SRs at the top of the EDSS hierarchical architecture (supervision level), controlling the relationship between reagents economical costs and proposing some changes depending on the EDSS proposed values. For example, in the case that the proposed EDSS output overpass a specific threshold ($mg \cdot L^{-1}$) of Cd, some specific prioritization criteria can be introduced to achieve enhanced coagulation using an increase/decrease of pH or Fd when Cd output is above this fixed limit. In other words, there are some cases where the enhanced coagulation EDSS proposes that the maximum NOM removal is achieved at high doses of Cd, summarized in Table 11. In those cases, a readjustment of the enhanced coagulation NOM removal criteria (% of removal for Turbidity, TOC and UV_{254}) through SRs should be essential for the EDSS full-scale implementation.

In an attempt to quantify, through a simplification, the derived economic implications for the DWTP 3 case study some values were calculated. Regarding Chapter 4 and specially Figure 16, a comparison between enhanced coagulation economic implications was determined. Information provided by plant managers stablished the price of polyaluminium chloride around 350€/T. In this case, the enhanced coagulation EDSS proposes to increase of Cd (from 21.9 to 40 $mg{\cdot}L^{-1}$) to achieve the maximum NOM removals. After the calculation and assuming a mean flow rate of $0.5m^3/s$ the economic costs are as following: 331€ of reagent per day if coagulation is operated using 21.9 $mg{\cdot}L^{-1}$ versus 605€ of Cd per day if the coagulation is operated at 40 $mg{\cdot}L^{-1}$. As it is previously mentioned, these economic implications should be considered to achieve enhanced coagulation. At this point it is important to highlight that the removal of NOM during coagulation affects disinfectants dosages, reducing costs associated to these chemicals.

In summary, an assessment of the full-scale conditions will be necessary to quantify and analyse model proposals economic implications related to the reagent dosages. EDSS outputs suggest that enhanced coagulation is achieve by increasing/reducing pH, Cd, Fd in respect to the historical applied values. As it is said, strategies based on the implementation attempting to control reagents cost using prioritization criteria could be useful in the task to reduce OpEX, in those cases where the EDSS propose to work at high levels of reagents dosages.

In that sense, this thesis provides some considerations for the EDSS full-scale implementation. Regarding river catchment, the detection of NOM fluctuations relies on controlling the industrial derived dejections (through flowmeters and NOM concentrations), crucial to predict the influent NOM concentration. To achieve that, the intensification of river headwaters analysis can give valuable information to anticipate coagulation adjustment and water treatment operation. On the other hand, for reservoir catchment, intensive weather forecasting coupled to the information provided by sensors and analysers located at the reservoir should be useful to identify and predict periods presenting peak NOM water quality scenarios and adjust coagulation accordingly. All the data provided by headwaters river analyses as well as the reservoir water quality can be integrated into the EDSS to adjust coagulation operation.

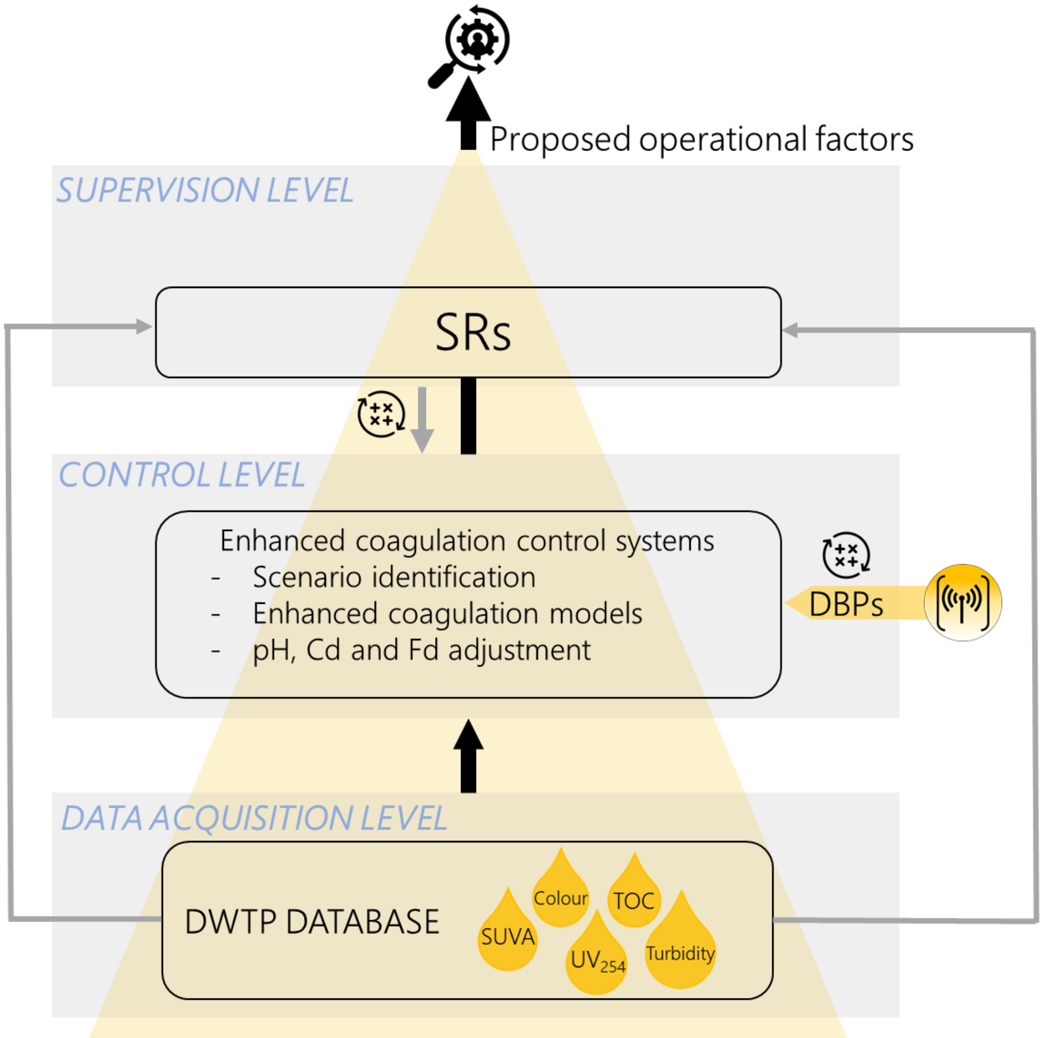

Figure 31: Proposed scheme for EDSS operation.

Future work

Model implementation tasks

- Scenario detection. From cluster analysis, the number of scenarios related to the influent NOM content can be increased providing a new classification for influent water quality. An example could be to identify baseline, peak and "low" scenarios, where NOM characterization does not exhibit low or high values. Furthermore, scenario identification can be achieved by complementing the existing parameters used for cluster analysis (Turbidity, colour, TOC, UV_{254} and SUVA values) with other representative parameters for NOM characterisation (e.g. photo-electrochemical measurement of chemical oxygen demand).
- Enhanced coagulation models. According to the scenarios, enhanced coagulation models can be improved and complemented with some specific sampling campaigns, jar tests experiments and RSM designs to obtain new enhanced coagulation models aimed to complete the previous models presented in Chapter 4 and Chapter 5 of this thesis.

EDSS validation tasks

- Active validation. EDSS full-scale implementation requires a validation period. Is at this point where routine water quality laboratory analysis for TOC and UV_{254} after coagulation is required to validate the proposed EDSS values. From here, enhanced coagulation removals should be validated with real data provided by the process itself.
- Multiobjective optimisation. To achieve enhanced coagulation through enhanced coagulation models it is necessary to develop an algorithm capable to optimise coagulation for pH, Cd and Fd (multiparametric optimisation). For each case and scenario, enhanced coagulation should be readjusted according to the desired values of TOC and UV_{254} at the effluent of coagulation-flocculation-sedimentation. The enhanced coagulation models are used to propose the operational pH, Cd and Fd according to the desired NOM removal (detailed in Chapter 4 and Chapter 5).
- User interface. Regarding the control systems implementation and validation, it is essential to develop a user-friendly interface. From there, DWTP operators and plant managers should be able to validate the proposed values for coagulation

collecting feedback in order to improve the platform itself or readjust some factors.

- Incorporation of emerging DBPs. Apart from THMs, the current drinking water legislation states haloacetic acids (HAAs) as regulated DBPs. In the following years, water regulations are expected to include some other DBPs, considered hazardous compounds. Although that the proposed control system presented in Chapter 6 are proposed for THMs, the incorporation of models related to the DBPs formation can be included to the current proposal.

Thesis impact

Optimising a process requires not only to improve the process performance but also to find out a specific strategy to achieve enhanced coagulation, in this case. This thesis provides insights on a relevant priority water cycle goal, which is related to the cost reduction along the urban water cycle, in this case by an enhance coagulation for drinking water treatment. At the time, by tackling drinking water DBPs, contributing to improve the human health and water quality.

From here, control systems for enhanced coagulation were planned and executed based on some considerations, summarised in Figure 32. Specific contributions of this thesis are based on the development of flexible tools aimed to improve coagulation efficiency in a sustainable way and minimising the risk of DBPs.

Three spheres were considered as the main contributions of the thesis outputs to the DWTPs: digitalisation, sustainability and systematised management. Full-scale drinking water *digitalisation* is raising, where a huge quantity of data is generated to treatment control. In this case, data from the influent waters is used to detect the influent water quality scenario and subsequently optimise coagulation for NOM removal. *Sustainability* applied to drinking water treatment, is the fact to achieve enhanced coagulation finding the best suitable and feasible solutions to optimise a process. In this thesis, some tools providing solutions for enhanced coagulation are presented, giving systematised responses to optimise coagulation for NOM removal. The final proposed EDSS are tools developed to provide an integrated management, aimed to merge all the knowledge extracted from the entire water treatment and propose outputs considering several individual functions. As it is said, the presented enhanced coagulation EDSS suppose an upgrade for decision-making, a single unit which provides outputs aimed to maximise treatment efficiency considering catchment type, each one of the influent water quality scenarios, enhanced coagulation operational conditions as well as the DBPs minimisation.

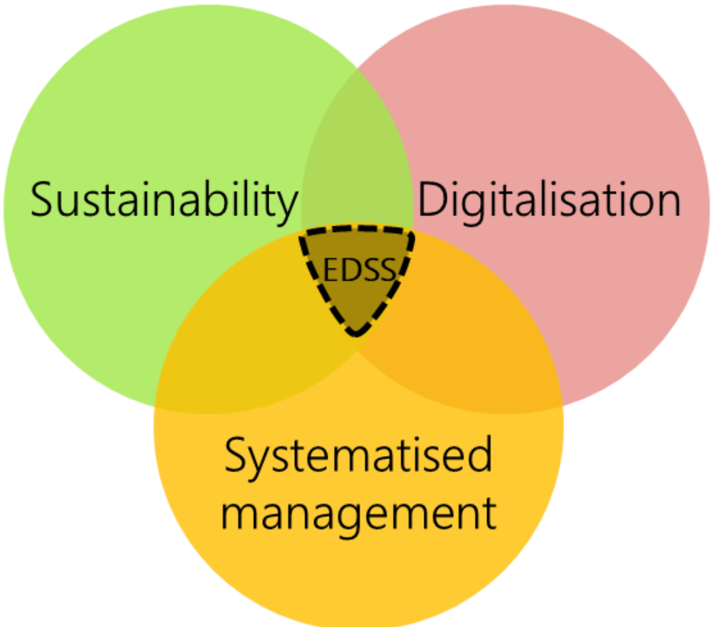

Figure 32: Contributions of the presented EDSS for drinking water treatment.

8. Conclusions

In this thesis, enhanced coagulation EDSS were designed, developed and proposed to be implemented at three Mediterranean DWTPs. To achieve that, NOM was studied for coagulation and empirical models were developed to be integrated in enhanced coagulation control systems aimed to be used for full-scale application. The following conclusions are underlined from the chapters presented in this thesis.

The optimum conditions for enhanced coagulation were determined for the three DWTPs. To do that, a specific methodology was developed to achieve NOM removal during coagulation. Enhanced coagulation control systems were built based on the development of enhanced coagulation models. These models were statistically designed and empirically performed using RSM and jar test experiments, aimed to describe the optimal coagulation conditions to achieve NOM removal through the determination of pH, Cd and Fd. Thus, NOM removal is achieved using the enhanced coagulation control systems for the three case-study DWTPs.

Enhanced coagulation models were developed at the three case study DWTPs, aimed to remove turbidity, TOC and UV_{254} during coagulation (Chapter 4 and Chapter 5). In Chapter 5, some of them were specifically performed based on influent waters NOM quality for baseline and peak scenarios. In this case, models were developed accounting for catchment type and influent NOM scenarios, presenting a mean R^2 value of 0.85.

The operational factors involved in coagulation optimisation were evaluated for the type of water catchment (river and reservoir) and influent NOM scenarios (baseline and peak), detailed in Chapter 5 and Chapter 6.

- Cluster analysis provided insights on the distribution of NOM scenarios for river and reservoir catchments. River catchment presents unpredictable fluctuations characterised by the presence of high turbidity at the influent during peak scenarios. Then, regarding reservoir catchment, peak events are clearly identified during extreme weather events, presenting high NOM concentrations at the influent.
- From here, sensitivity analysis determined the significant coagulation factors to achieve NOM removal for each catchment and scenario. In both water catchments, results reported that when baseline cases are detected a multi-objective optimisation is required for enhanced coagulation. However, Cd is crucial to control NOM adsorption during coagulation in peak cases.

Enhanced coagulation models were tested for the $Cd_{Adjustment}$ in river and reservoir catchment, Chapter 6.

- Results revealed that $Cd_{Adjustment}$ improve NOM removal due to the NOM fractionation, especially for peak scenarios,
- NOM fractionation was assessed based on SUVA values. Results determined that hydrophobic NOM dominates peak scenarios and for this reason Cd emerges as a key parameter to remove NOM with coagulation.

A novel strategy aimed to develop an EDSS for DBPs minimisation using enhanced coagulation is presented for drinking water production.

- An enhanced coagulation EDSS is proposed to achieve 62%, 21%, and 25% removal for turbidity, TOC, and UV_{254} (Chapter 4). A three-level hierarchical architecture is described for data acquisition, control and supervision levels.
- A control system aimed to minimise THMs using enhanced coagulation is proposed for river and reservoir catchment. From influent water characterisation, the proposed control system provides solutions for coagulation operation (pH, Cd and Fd) to control THMs.

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10. Annexes

10.1. RSM models' runs and responses analyses

Table A1: RSM experimental design runs and response removals (%) at the DWTP 1. Hyphenated cells are % of removals < 0.5. DWTP 1 - 26.03.2019. Cd and Fd units: $mg \cdot L^{-1}$.

	Factors			Responses		
run	pH	Cd	Fd	Turbidity	TOC	UV_{254}
1	5.5	70	1.5	85.8	44.4	46.7
2	8.5	70	0.2	90	36.5	35.5
3	5.5	10	0.2	52.3	10.6	22.3
4	7	40	0.85	84.6	21.8	24.9
5	8.5	10	1.5	72.7	14	58.8
6	7	40	0.85	84.5	21.2	35.4
7	8.5	70	1.5	85.4	31.7	39.6
8	7	40	0.85	83	22.7	22
9	5.5	70	0.2	82.5	35.8	48.5
10	7	40	0.85	82.6	24.3	7.9
11	8.5	10	0.2	48.8	-	13.4
12	5.5	10	1.5	76.1	22.9	-
13	7	90.4	0.85	90.4	40	44.1
14	9.5	40	0.85	-	19.1	56.2
15	7	40	0	81.8	15.6	45.1
16	7	40	1.9	80.8	28.7	32.5
17	4.5	40	0.85	76.8	29.4	54.1
18	7	40	0.85	83.6	28.3	50.1
19	7	40	0.85	80.9	27.7	51.5
20	7	0	0.85	42.7	13.5	13.4

Table A2: RSM experimental design runs and response removals (%) at the DWTP 1. Hyphenated cells are % of removals < 0.5. DWTP 1 - 12.11.2020. Cd and Fd units: mg·L^{-1}.

		Factors			Responses	
run	pH	Coagulant	Flocculant	Turbidity	TOC	UV_{254}
1	8.5	70	0.2	96.7	1.8	27.9
2	5.5	70	1.5	93.9	18.8	41.9
3	8.5	10	0.2	94.5	15.8	11.6
4	7	40	0.85	97.9	17.5	28.7
5	7	40	0.85	97.7	8.1	28.7
6	7	40	0.85	97.6	15.1	23.3
7	7	40	0.85	96.1	18.2	31.0
8	8.5	10	1.5	93.0	-	17.1
9	5.5	70	0.2	96.3	22.8	41.9
10	5.5	10	1.5	89.7	-	24.0
11	8.5	70	1.5	96.9	2.4	24.0
12	5.5	10	0.2	88.1	14.5	24.8
13	8.5	40	0.85	97.1	16.5	17.1
14	7	40	0.85	96.3	29.5	29.5
15	7	70	0.85	97.0	25.5	35.7
16	7	10	0.85	94.2	12.5	20.2
17	7	40	1.5	96.7	21.5	31.0
18	5.5	40	0.85	97.7	31.2	31.8
19	7	40	0.2	98.1	18.5	27.9
20	7	40	0.85	98.1	20.5	27.1

Table A3: RSM experimental design runs and response removals (%) at the DWTP 1. Hyphenated cells are % of removals < 0.5. DWTP 1 - 19.02.2020. Cd and Fd units: mg·L^{-1}.

	Factors			Responses		
run	pH	Cd	Fd	Turbidity	TOC	UV_{254}
1	5.5	5.25	0.2	85.9	40.1	51.0
2	8.5	37.6	0.88	91.8	42.6	57.6
3	8.5	5.25	1.74	75.9	-	31.1
4	5.5	70	0.2	-	17.9	29.8
5	7	70	0.88	93.3	51.5	61.6
6	7	37.6	0.2	93.5	51.5	56.3
7	8.5	5.25	0.2	86.5	0.6	27.2
8	8.5	70	0.2	93.9	33.3	59.6
9	7	5.25	0.88	88.4	40.6	48.3
10	7	37.6	0.88	93.2	59.1	61.6
11	7	37.6	0.88	94.6	53.5	61.6
12	8.5	70	1.74	90.7	6.7	57.6
13	7	37.6	0.88	85.8	52.7	61.6
14	7	37.6	0.88	93.3	61.1	60.3
15	7	37.6	0.88	90.8	58.8	60.3
16	7	37.6	0.88	93.4	60.5	60.3
17	5.5	5.25	1.74	79.0	41.2	57.0
18	7	37.6	1.74	94.3	54.6	60.9
19	5.5	70	1.74	-	39.2	37.1
20	5.5	37.6	0.88	-	51.0	60.3

Table A4: RSM experimental design runs and response removals (%) at the DWTP 1. Hyphenated cells are % of removals < 0.5. DWTP 2 - 03.11.2020. Cd and Fd units: mg·L^{-1}.

	Factors			Responses		
run	pH	Cd	Fd	Turbidity	TOC	UV_{254}
1	8.5	37.6	0.88	87.7	9.5	39.4
2	7	37.6	0.88	88.3	20.8	48.4
3	5.5	5.25	0.2	28.8	14.6	17.8
4	5.5	5.25	1.74	58.2	13.5	30.1
5	7	37.6	0.2	88.5	13.1	44.8
6	5.5	70	1.74	86.0	10.6	45.9
7	8.5	70	1.74	88.5	4.0	39.2
8	5.5	70	0.2	87.4	19.3	48.5
9	7	37.6	0.88	88.2	10.6	41.9
10	7	5.25	0.88	49.4	1.8	21.3
11	8.5	5.25	0.2	66.5	-	23.5
12	7	37.6	0.88	91.0	13.9	43.6
13	8.5	70	0.2	92.0	-	39.2
14	7	70	0.88	91.8	7.3	45.9
15	8.5	5.25	1.74	39.3	-	14.3
16	7	37.6	0.88	89.4	2.9	38.9
17	7	37.6	0.88	89.7	4.4	39.5
18	7	37.6	0.88	89.5	9.5	41.9
19	5.5	37.6	0.88	84.8	14.6	45.5
20	7	37.6	1.74	84.4	21.5	45.1

10.2. Jar test experimental phases

Table A5: Jar test experimental phases, speeds and times at each case-study DWTP.

Phase	DWTP 1	DWTP 2
Rapid mixing (rpm, min)	140,1	140,7
Slow mixing (rpm, min)	50,15	40,13
Sedimentation time (min)	15	20

10.3. Predictors selection: Adjusted R^2 values for each scenario (2^p)

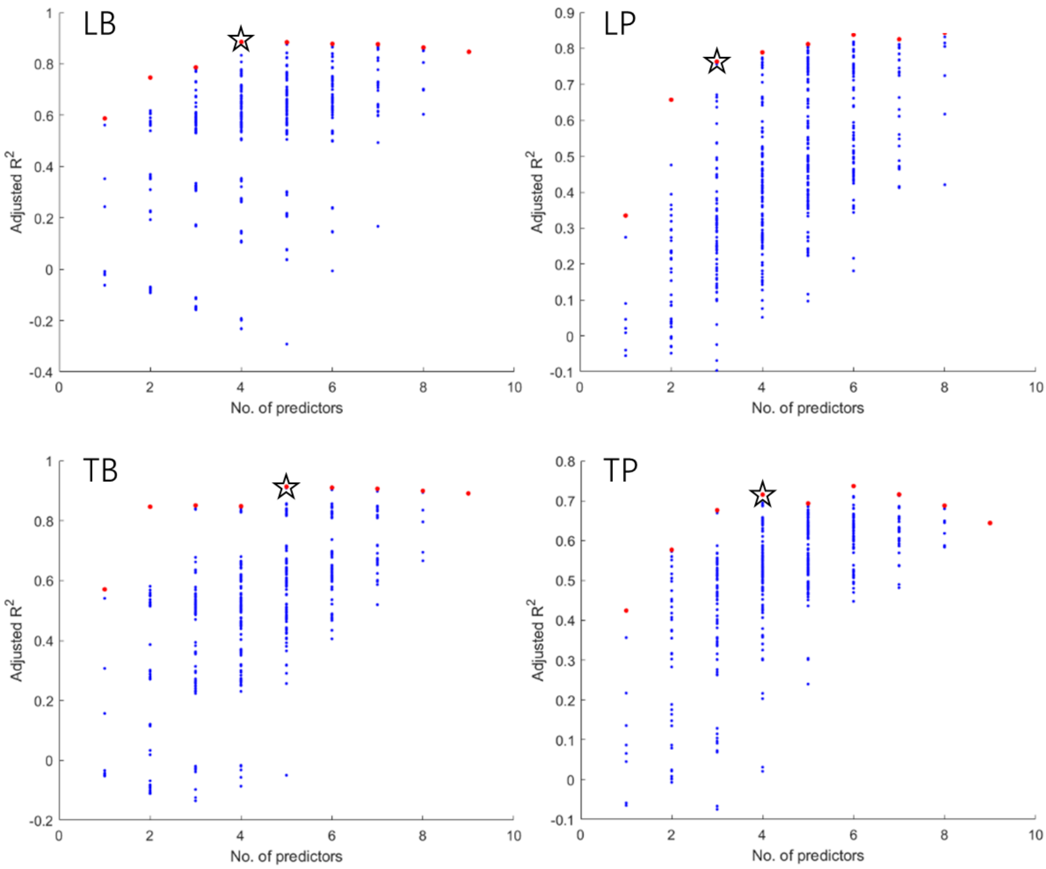

Figure A1: Adjusted R^2 values and number of predictors (2^p) at each DWTP scenario for turbidity. Red points indicate the best models for the different model sizes. Starry dots identify the final number of predictors selected for each DWTP scenario.

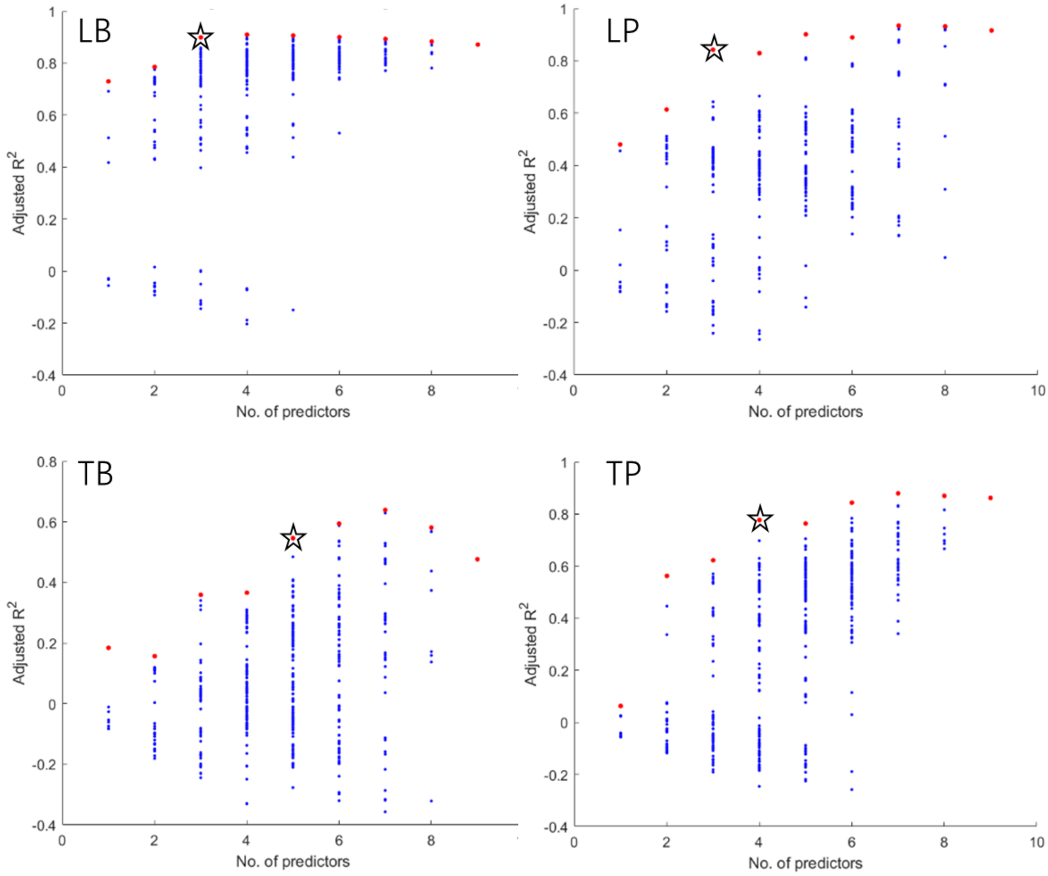

Figure A2: Adjusted R^2 values and number of predictors (2^p) at each DWTP scenario for TOC. Red points indicate the best models for the different model sizes. Starry dots identify the final number of predictors selected for each DWTP scenario.

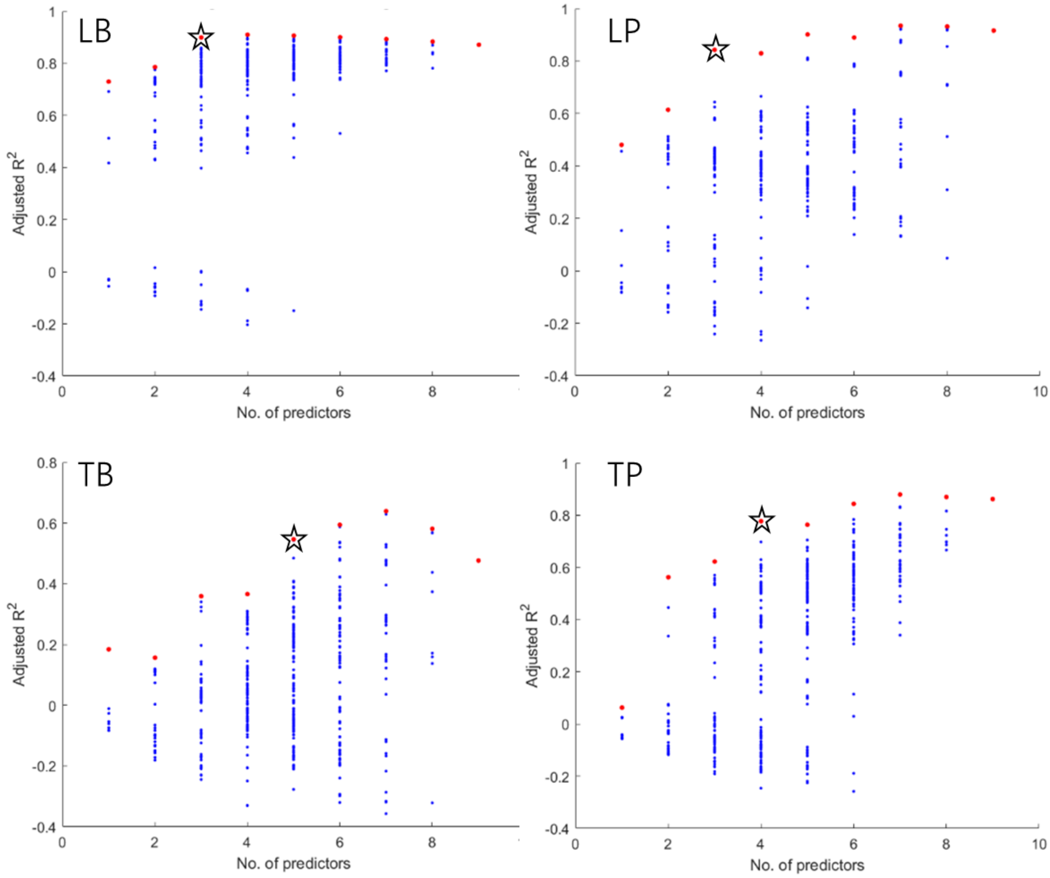

Figure A3: Adjusted R^2 values and number of predictors (2^p) at each DWTP scenario for UV_{254}. Red points indicate the best models for the different model sizes. Starry dots identify the final number of predictors selected for each DWTP scenario.

10.4. 3D surface plots for enhanced coagulation

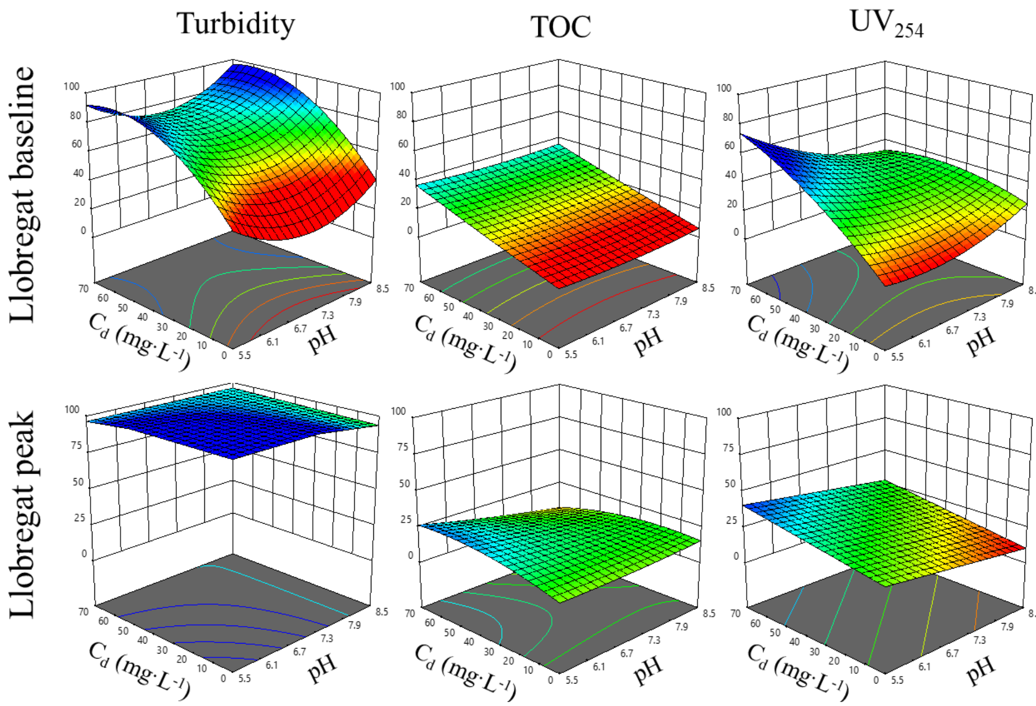

Figure A4: Responses surface plots for RSM models developed at Llobregat DWPT for baseline and peak scenarios. X_1 is pH level (5.5-8.5), X_2 coagulant dose (0-70 mg·L^{-1}) and Y axis is the response expressed in percentage of removal (0-100%). To represent these plots flocculant dose was fixed at the minimum operation level for coagulation at DWTP 1, F_d = 0.2 mg·L^{-1}.

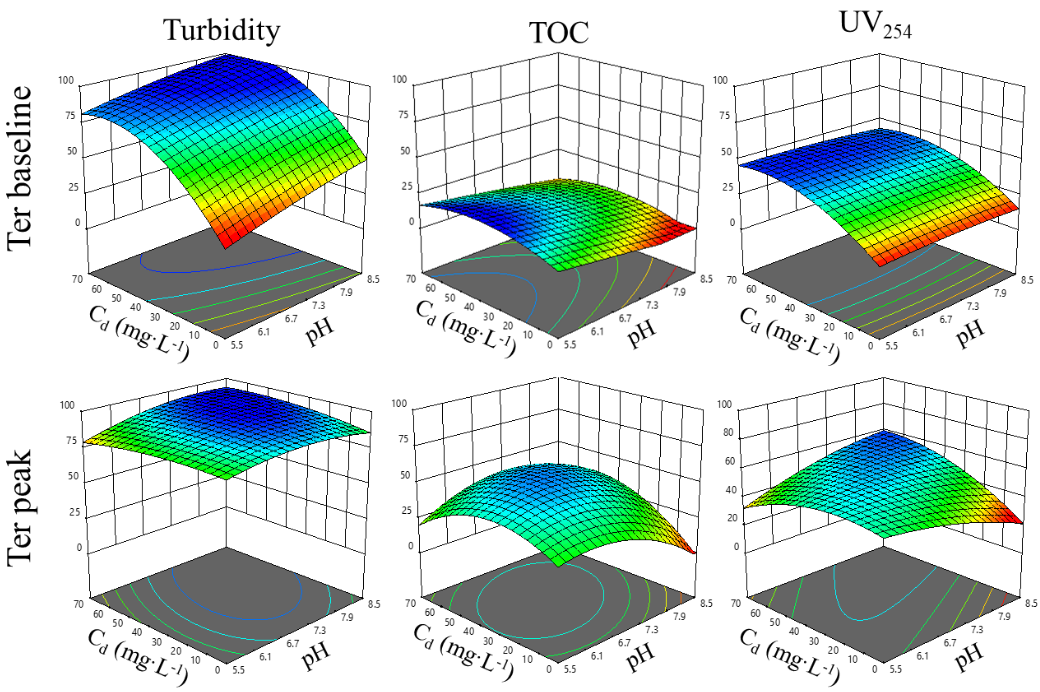

Figure A5: Responses surface plots for RSM models developed at Ter DWPT for baseline and peak scenarios content. X1 is pH level (5.5-8.5), X2 coagulant dose (0-70 mg·L-1) and Y axis is the response expressed in percentage of removal (0-100%). To represent these plots flocculant dose was fixed at the minimum operation level for coagulation at DWTP 2, F_d = 0.15 mg·L^{-1}.