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Industrial Process Water Treatment and Reuse: A Framework for Synthesis and Design

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S Supporting Information

ABSTRACT: Mathematical optimization has shown the potential to contribute to industrial water management, through the development of the solution methods needed for optimization-based design of wastewater treatment and reuse networks (also called water networks). Nevertheless, the application of this approach is still limited to motivating examples lacking the ability to handle problems with complexity of industrial relevance. To address this challenge, in this contribution, we focus on the integration of wastewater engineering concepts and models, together with optimization methods and solution algorithms. To this end, we propose a computer-aided framework for the design of water treatment and reuse networks. In the framework, optimization methods, problem analysis tools and wastewater engineering knowledge are integrated in a computer-aided environment, in order to facilitate the formulation and solution of the design problems with fair complexity representative of industrial applications. The framework is demonstrated through the solution of a case study dealing with the treatment and reuse of water effluent produced by an oil refinery. The problem is solved, and a win−win solution is identified, allowing a reduced water footprint, and the treatment costs are identified.

1. INTRODUCTION

Water is a valuable resource for the development and welfare of humanity. Although the total volume of water present on Earth amounts to 1.386 $\times 10^9$ km^3, only 2.5% is freshwater, 30% of which is embodied in glaciers. In 2010, the global freshwater withdrawal amounted to ~3.9 $\times 10^3$ km^3/yr, 60% of which is employed for agricultural use, 22% is committed for domestic use, and 18% is applied for industrial use.[1] Prior to discharge to the environment, a large part of the water withdrawn for domestic and industrial use must be treated in order to reduce its contamination level. Therefore, the design of water treatment and reuse systems is crucial to ensure cost-effective and sustainable use of water.

The goal of wastewater treatment processes is the removal of the pollutant load in a wastewater stream, to a level that either complies with discharge regulations or meets water quality requirements for reuse in industrial processes. Wastewater treatment processes are generally composed by three stages: a primary treatment, based on physical operations to remove nonsoluble suspended solids; a secondary treatment for removal of dissolved contaminants through chemical or biological action; and a tertiary treatment for removal of residual contaminants. In the scientific literature, a complete and descriptive overview of technologies and issues related to wastewater treatment operations can be found.[2,3]

The configuration of a wastewater treatment plant is largely determined by the type and characteristics of contaminants present in the wastewater (e.g., biodegradability of organic matter, nitrogen load, presence of heavy metals, alkalinity, salinity, etc.), the effluent discharge limits to be met and the environmental conditions (especially temperature).

In the industrial practice, the design of wastewater treatment plants is an expert-based procedure, which requires specific know-how and often involves laboratory and pilot-scale trials.[4,5] Because of the time and resource constraints typical to engineering projects, we argue that, in the design phase, only a small number of alternative design configurations (often based on the replication of previous experiences) can be explored. This may result, especially for complex case, in a suboptimal plant design, in which options for water recycle and/or recovery and valorization of contaminants may be disregarded.

Recent developments of process systems engineering (PSE) have focused on the design of water/wastewater networks, in particular through the development of optimization-based methods for water systems design. In those methods, the design problem is cast as a mathematical optimization through the definition of a superstructure (in which all possible configurations are contained) and of an objective function (typically the maximization of water recycle or the minimization of costs). The problem is then solved to determine the optimal network configuration, as well as the optimal flow through it.

Because of the relevance of the problem and of the scientific challenge that it represents, the problem of water network

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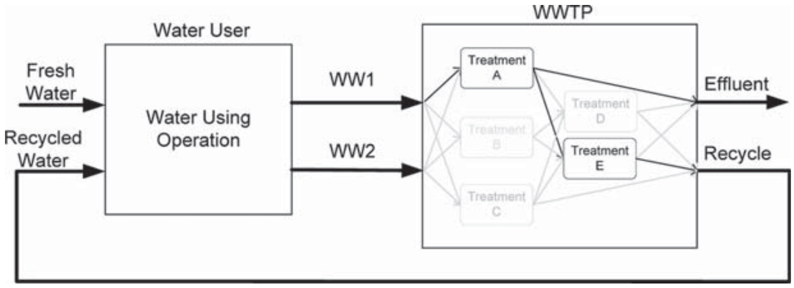

Figure 1. Schematic of the optimal wastewater treatment plant (WWTP) design problem.

design has attracted the attention of many authors in the scientific literature, starting from the seminal work of Takama and co-workers,[6] who solved a water network for a refinery including both water using processes and water treatment processes.

More recently, Tan and co-workers[7] developed a superstructure-based approach for the synthesis of a water network, based on partitioning regenerators, considering a single contaminant and 4 wastewater streams. Khor and co-workers[8,9] studied the optimal design of a membrane-based treatment for the treatment and reuse of water contaminated by a single contaminant, for a system of 28 wastewater sources, 15 water sinks, and 17 wastewater treatments.

Karuppiah and Grossmann[10,11] proposed a spatial branch-and-bound algorithm for the solution of water network problem, and they applied it to a case including both the water-using section and the water treatment section, considering three contaminants, five water users, and four treatment options.

Ahmetovic and Grossman[12] developed a general superstructure and global optimization strategy for the synthesis of water networks, and they applied it for the solution of several example problems characterized by only a few contaminants and treatment units, focusing on the establishing the optimal tradeoff between cost and complexity of the treatment network.

Bogataj and Bagajewicz[13] formulated and solved the problem of synthesis of heat-integrated water networks, in which the synthesis and the heat integration problem are solved simultaneously, for small multicontaminant systems.

Rojas-Torres and co-workers[14] investigated the design of a water network based on property integration, for a system of 6 wastewater flows and 15 treatment options, considering one contaminant and 4 temperature-dependent properties (pH, toxicity index, odor, and temperature).

Teles and co-workers[15] proposed an algorithm based on parametric disaggregation for the solution of nonconvex MINLP problems featuring bilinear terms, and they demonstrated it by solving several optimization problems, including water networks.

Through the important work of these and many other authors on the development of models, solution strategies, and formal approaches (not reported here, in the interest of space), the maturity of optimization-based techniques for the design of water network has been greatly advanced. Nevertheless, their penetration in the industrial practice is somewhat less than what might have been expected.[16] This suggests that further developments are still needed, in order to increase the acceptance of those methods by wastewater treatment design engineers, experts, and professionals and reach the full potential of optimization-based water networks design.

One of the reasons limiting the penetration of these optimization-based methods in the wastewater community can be traced in the fact that most of the authors focus on the mathematical dimension of the problem primarily (working on the development of solution strategies to obtain the solution to global optimality), rather than on the problem of integrating those methods with knowledge and models specific to wastewater engineering.

In fact, most of the problems solved as case studies are intended to demonstrate algorithmic developments and, consequently, are often based on extremely simple description of treatment processes and wastewater composition, or on a relatively small number of streams and treatment options, which often do not represent the complexity of a real industrial problem.

In this contribution, we propose a computer-aided framework for optimization-based design of complex water networks. The key novelty of the proposed framework is to integrate wastewater engineering expertise together with state-of-the art optimization methods, problem analysis tools, and solution strategies. Through this integration, implemented in a computer-aided tool, water network problems of industrial complexity can be formulated and solved in a simple and time-effective manner.

The paper is structured as follows: first, the framework is briefly described, underlining the principal components and the data and information needed for the problem formulation. Then, a case study dealing with the problem of treatment and reuse of industrial wastewater is formulated and solved under different scenarios, in order to demonstrate the features of the tool. Finally, some conclusions and recommendations for future works are exposed.

2. PROBLEM FORMULATION: OPTIMAL WASTEWATER TREATMENT AND REUSE PLANT DESIGN

From a general standpoint, the problem of optimal wastewater treatment plant (WWTP) design can be formulated as follows (see Figure 1): given (i) a water-using plant, consuming a certain amount of fresh water (at a required purity level) and producing a certain amount of wastewater (at a given contamination level), (ii) a list of treatment technologies, (iii) one or more effluent water discharge opportunities (at given contamination level), and (iv) an optimality criterion; the optimal WWTP design problem corresponds to the selection of the treatment train configuration (designed to treat the wastewater load and to meet purity level for the effluents), which maximizes the optimality criterion.

In this contribution, the problem of optimal WWTP design is cast as a mathematical programming optimization which, for a given optimality criterion, is solved in order to identify the optimal WWTP design.

3. THE COMPUTER-AIDED FRAMEWORK

In order to facilitate the formulation and solution of optimal WWTP design problems, a systematic framework has been developed, as an expansion of the integrated business and engineering framework for synthesis and design of processing network developed earlier.[17,18]

Through the integration of workflow, dataflow, analysis tools and state of art solution strategies in a computer-aided environment, the framework is designed to increase the productivity of water network design, simplifying the task of formulating and solving optimization-based design problems for cases of industrial complexity.

The workflow for optimal WWTP design (shown in Figure 2) is constituted by four main steps.

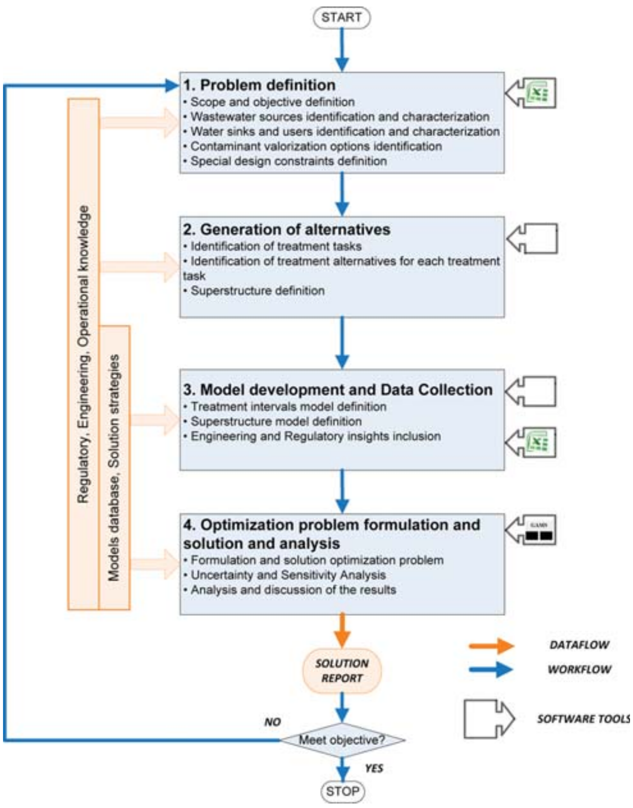

Figure 2. Workflow for optimal WWTP design.

In the first step, the problem is defined by setting its scope and objectives. The wastewater flows are listed and characterized in terms of flow and composition. All possible water sinks are identified; those include water discharge options (as effluent) and water reuse opportunities. For both, maximum acceptable contamination levels are defined, as a consequence of environmental regulations and engineering insights. Moreover, options for contaminants recovery and valorization (as byproducts or as feedstock for the production of value added chemicals) can be defined at this step.

In the second step, alternative WWTP configurations are generated and organized in a superstructure (Figure 3). The superstructure is built as follows: incoming wastewater streams are listed in the first column and water sinks (effluents recycle

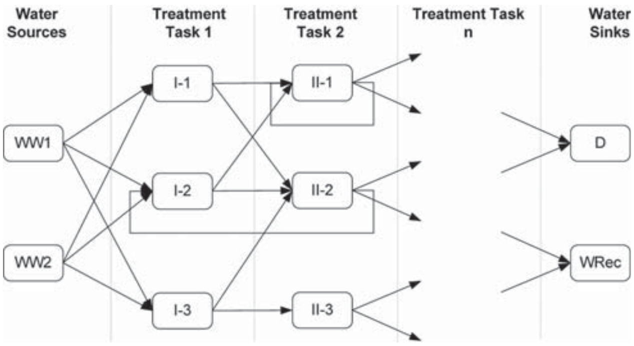

Figure 3. Example of a superstructure.

to water using processes and contaminant valorization opportunities) in the last one. In between, all treatment options are represented, organized in *treatment tasks* (columns of the superstructure) and *intervals* (rows).

A treatment task represents a section of a treatment train, in which the task of treatment/removal one or more pollutants is performed. A treatment interval represents a specific technological alternative for the execution of a given task. An example of task can be carbon and nitrogen removal; examples of process intervals for this task are activated sludge (AS) technology and membrane biological reactors (MBRs), among many others.

The superstructure is completed by adding the connections between treatment intervals, which represents potential material flows through the network. These include forward connections (in which the flow is in the same direction as the overall water flow), internal recycles (recycles around one treatment interval), and backward connections (when the flow is opposite to the overall water flow).

In the third step, data and models needed to formulate the design problem are collected. Those include models for the characterization of the wastewater composition, models to describe each treatment interval, models that describe the material flow through the network, and models to calculate the objective function and any other relevant indicators. More details on each of the above-mentioned models are reported in the next section.

Moreover, all available engineering and regulatory insights are converted to logical constraints and variable bounds, in order to exclude unwanted solutions from the search space.

In the fourth step, the design problem is formulated as a mixed-integer nonlinear programming (MILNP) optimization, which is solved to determine the optimal WWTP design. If any data has been found subject to a considerable uncertainty, uncertainty and sensitivity analysis can be executed at this step. The results are then analyzed and consolidated in a report, containing the optimal configuration, together with more additional information (stream table, utility table, cost breakdown over the different treatment section, etc.).

3.1. Models and Tools.

3.1.1. Contaminant Characterization. A wastewater stream normally contains a very large number of chemical species, which are considered contaminants. Because of their number, it is often impractical to track the composition of each of the contaminant species, and an aggregation in pseudo-components is performed.

In wastewater practice, different wastewater characterization methods exist. The traditional aggregation approach is based on the analytical method employed to characterize a given

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wastewater (chemical oxygen demand (COD), biochemical oxygen demand (BOD), total Kjeldahl nitrogen (TKN), etc.). Despite having been widely used, this characterization is often too simplistic and disregards important differences in wastewater composition, especially with regard to organic carbonaceous matter.[19,20] Moreover, since a given contaminant may be detected by more than one analytical test, those pseudo-components are not independent, which complicate the definition of mass conservation relations (e.g., mass balance).

A more-detailed alternative for wastewater characterization is constituted by the use of the Activated Sludge Model (ASM) components.[21] According to the ASM method, the wastewater is characterized by 13 independent pseudo-components (see Table 1). Our motivation for using this method can be described as follows. This wastewater characterization is considered a breakthrough achievement in the decades-long attempt to develop reliable mechanistic modeling of wastewater treatment systems, which was pioneered by the release of ASM1 (Activated Sludge Model No. 1) by Henze and co-workers[22] in 1987. Since then, this principle of wastewater characterization and the associated ASM1 modeling concept has been extended to cover many wastewater treatment technologies, which forms the basis of commercial process simulators used in wastewater treatment engineering (Biowing, GPSx, WEST, etc.) and commonly used by wastewater professionals.[23] Hence, it is very important that optimization-based approaches employ the common standard achieved in wastewater engineering to facilitate the transfer of this approach.

Table 1. ASM1 Compounds[a]

symbol	description of compound
X_i	inert particulate organic matter
X_s	slowly biodegradable substrate
X_H	heterotrophic biomass
X_A	autotrophic biomass
X_p	inert particulate from biomass death
S_i	inert soluble organic matter
S_s	readily biodegradable substrate
S_O	dissolved oxygen
S_{NO}	nitrate
S_{NH}	ammonia
S_{ND}	soluble biodegradable organic nitrogen
X_{ND}	particulate degradable organic nitrogen
S_{ALK}	alkalinity

[a]Data taken from ref 19.

An example of the relationship between traditional and ASM component characterization is reported in Figure 4, with respect to the classification of carbonaceous species. According to the ASM classification, the total COD load is broken down into four different pseudo-components, namely X_i, X_s, S_i, and S_s. The biodegradable fraction of the COD (called bCOD, or BOD) is constituted by the sum of not readily available (particulate) biodegradable matter (S_s), and readily available (soluble) matter (X_s). The same characterization is also done for nitrogen species.[19]

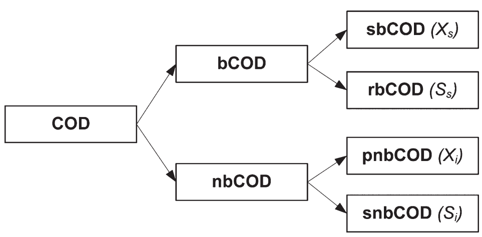

Figure 4. Classification of carbonaceous organic matter in wastewater.

Even though the ASM contaminant characterization is widely adopted in wastewater engineering, cases may arise in which a different characterization is more convenient. In some cases, in fact, the representation of the full spectrum of ASM components may result in a too-complicated problem formulation, and some of the components may be merged or disregarded.

In other cases (e.g., industrial wastewater problems), the ASM characterization may not contain all the components which must be tracked. In these cases, the contaminant list is expanded to consider other pollutants, such as, for example, metals (Cr^{6+}, Cr^{3+}, Fe^{2+}, Fe^{3+}), gases (H_2S, CO, CH_4), etc.

3.1.2. Water Treatment Models. In this contribution, treatment intervals are modeled according to a generic functional model, adapted from the model proposed by Zondervan and co-workers.[24] In the generic model, each treatment interval is described as a sequence of process tasks, namely, mixing, utilities and chemicals addition, dissolution of nonaqueous utilities and chemicals in water, reaction, waste separation, separation and pumping (see Figure 5). Each of these tasks is described through simple short-cut models presented in eqs 1−9.

In particular, the consumption of utilities and chemicals (R) is calculated as a function of the component influent flow as

$$R_{u,k} = \sum_i (\mu_{u,i,k} \cdot F_{i,k}^{\mathrm{IN}}) \tag{1}$$

where i is the index of the utility compounds; u is a subset of i containing the utility components; k and kk are indexes representing the treatment intervals as source and destination of a flow, respectively; and μ is the specific consumption of utility u, with respect to the incoming flow of component i in interval k.

The mixing utilities and chemicals to the process stream is calculated as

$$F_{i,kk}^{M} = \sum_k (F_{i,k,kk}) = \alpha_{u,kk} \cdot R_{u,kk} \tag{2}$$

where α is the fraction of utility stream mixed with the process stream.

The reaction of aqueous dissolution of utilities and chemicals is given as

$$F_{i,kk}^{\mathrm{AQ}} = F_{i,kk}^{M} + \sum_{\mathrm{rr,react}} (\gamma_{i,kk,\mathrm{rr}}^{\mathrm{AQ}} \cdot \theta_{\mathrm{react},kk,\mathrm{rr}}^{\mathrm{AQ}} \cdot F_{\mathrm{react},kk}^{M}) \tag{3}$$

where γ^{AQ} and θ^{AQ} are the stoichiometry and conversion of the reaction, respectively.

The reaction is given as

$$F_{i,kk}^{R} = F_{i,kk}^{\mathrm{AQ}} + \sum_{\mathrm{rr,react}} (\gamma_{i,kk,\mathrm{rr}} \cdot \theta_{\mathrm{react},kk,\mathrm{rr}} \cdot F_{\mathrm{react},kk}) \tag{4}$$

where γ and θ are the stoichiometry and conversion of the aqueous dissociation reaction, respectively.

The separation of wastes is given as

$$F_{i,kk}^{\mathrm{out}} = F_{i,kk}^{R} \cdot (1 - \mathrm{SW}_{i,kk}) \tag{5}$$

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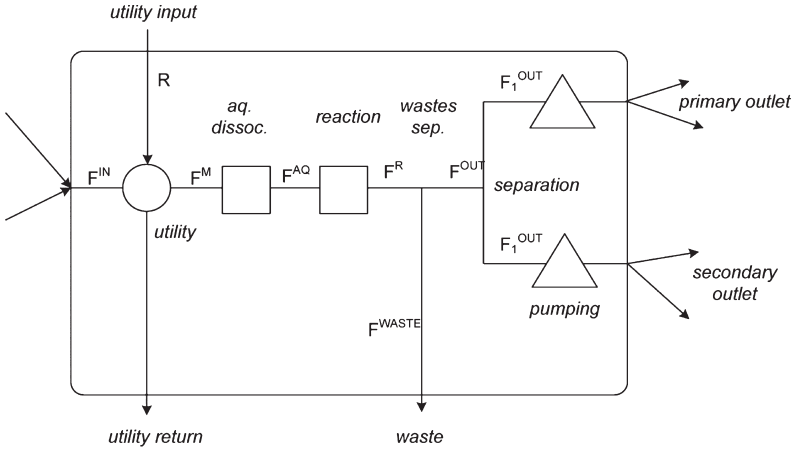

Figure 5. Generic treatment interval model structure.

where SW is the fraction of component flow separated as waste.

The primary outlet of the separation is given as

$$F_{i,kk}^{\mathrm{out1}} = F_{i,k}^{\mathrm{out}} \cdot \mathrm{Split}_{i,k} \tag{6}$$

where Split is the fraction of component flow separated in the primary outlet. Similarly, the secondary outlet is given as

$$F_{i,kk}^{\mathrm{out2}} = F_{i,k}^{\mathrm{out}} - F_{i,k}^{\mathrm{out1}} \tag{7}$$

The cost associated with water pumping (PC) is calculated as

$$\mathrm{PC}_{k,kk} = \sum_{i} (F_{i,k,kk}) \cdot \Delta P_{k,kk} \tag{8}$$

where ΔP is the pressure drop between intervals k and kk.

Finally, the capital cost required for the construction of the treatment interval is estimated as a function of the throughput as

$$\mathrm{INV}_{kk} = (a_{kk} \cdot F_{i,kk}^{M})^{n_{kk}} \tag{9}$$

where α_{kk} and n_{kk} are coefficients for the capital cost calculation.

Through the above-described generic treatment model, a wide range of treatment processes can be described.

The use of the generic treatment interval models has several advantages, in particular at early stages of design. First of all, being based on a common structure, the generic model relies on a compact set of model equations written in matrix form, and facilitate data systematization and handling in a database form. This provides a structure for knowledge and information representation and storage, and it allows for automation of the problem formulation workflow.[25]

Moreover, despite its simplicity, the generic treatment model allows the explicit definition of the different process tasks executed in each treatment interval. Consequently, engineering and financial-relevant quantities (utility consumption, emission of wastes, etc.) are explicitly tracked.

Finally, the model provides a structure that, if needed, can be incrementally refined in order to obtain a more-detailed description of the treatment process. For example, single value data such as reaction conversions can be substituted with more-detailed constitutive kinetic models.[17]

3.1.3. Network Model. The network model describes the material flow through the network of treatment intervals. In the most general formulation, this is

$$F_{i,k,kk} = F_{i,k}^{\mathrm{OUT1}} \cdot \mathrm{SM}_{k,kk}^{\mathrm{OUT1}} \cdot S_{k,kk}^{\mathrm{p}} + F_{i,k}^{\mathrm{OUT2}} \cdot \mathrm{SM}_{k,kk}^{\mathrm{OUT2}} \cdot S_{k,kk}^{\mathrm{s}} \tag{10}$$

where $F_{i,k,kk}$ is the flow of component i between treatment k and treatment kk; the indexes "1" and "2" are used to identify primary and secondary flows (with respect to a binary separation), respectively; $S_{k,kk}^{\mathrm{p}}$ and $S_{k,kk}^{\mathrm{s}}$ define the primary and secondary connections existing in the superstructure, respectively; and $\mathrm{SM}_{k,kk}^{\mathrm{OUT1}}$ and $\mathrm{SM}_{k,kk}^{\mathrm{OUT2}}$ are the fractions of outflow from interval k, which is fed to interval kk (split factor), which are subject to the following consistency condition:

$$\sum_{k} \mathrm{SM}_{k,kk}^{\mathrm{OUT1}} = \sum_{k} \mathrm{SM}_{k,kk}^{\mathrm{OUT2}} = y_k \tag{11}$$

where y_k is a binary variable that is equal to 1 if treatment k is selected and is equal to 0 otherwise.

In the most general case, when the split factors $\mathrm{SM}_{k,kk}^{\mathrm{OUT1}}$ and $\mathrm{SM}_{k,kk}^{\mathrm{OUT2}}$ are optimization variables, eq 10 is a nonlinear nonconvex constraint. This type of problem, which is inherently nonlinear, is termed a *multistream problem* here.

A simplified case is obtained for problems that admit the selection of maximum one treatment interval per treatment task. Given those types of problems, which are termed *single-stream problems* here, the network model can be reformulated in a linear way through eqs 12–14:

$$F_{i,k,kk} < F_{i,k}^{\mathrm{OUT1}} \cdot S_{k,kk}^{\mathrm{p}} + F_{i,k}^{\mathrm{OUT2}} \cdot S_{k,kk}^{\mathrm{s}} \tag{12}$$

$$\sum_{kk} F_{i,k,kk} = F_{i,k}^{\mathrm{OUT1}} + F_{i,k}^{\mathrm{OUT2}} \tag{13}$$

$$\sum_{k \in \mathrm{St}_j} y_k \leq 1 \tag{14}$$

Provided that the other constraints are linear, a single-stream problem can be therefore formulated as a MILP.

3.2. Solution Strategies. The framework integrates different state-of-the art solution strategies, which are employed based on the problem formulation.

3.2.1. Direct Solution. Direct solution is employed for simple problems, which include single-stream linear problems and small size (indicatively containing <30 bilinear constraints) multistream problems. Single-stream linear problems are solved through the solver CPLEX,[26] while the multistream problem solution is obtained through Baron.[27]

3.2.2. Bilevel Decomposition. Large multistream problems, which cannot be solved directly with Baron, are solved through a bilevel decomposition algorithm. This solution strategy is based on the decomposition of the problem into an lower bound (obtained through relaxation of the original problem) and an upper bound (obtained through the local solution of the original problem), which are solved iteratively until the convergence criteria are met. As commonly done in water network problems, the bilinear term are relaxed through McCormick relaxation (eqs 15−18).[28]

$$F_{i,k}\cdot\mathrm{SM}_{k,kk} \geq F_{i,k}^{\mathrm{LO}}\cdot\mathrm{SM}_{k,kk} + F_{i,k}\cdot\mathrm{SM}_{k,kk}^{\mathrm{LO}} - F_{i,k}^{\mathrm{LO}}\cdot\mathrm{SM}_{k,kk}^{\mathrm{LO}} \tag{15}$$

$$F_{i,k}\cdot\mathrm{SM}_{k,kk} \geq F_{i,k}^{\mathrm{UP}}\cdot\mathrm{SM}_{k,kk} + F_{i,k}\cdot\mathrm{SM}_{k,kk}^{\mathrm{UP}} - F_{i,k}^{\mathrm{UP}}\cdot\mathrm{SM}_{k,kk}^{\mathrm{UP}} \tag{16}$$

$$F_{i,k}\cdot\mathrm{SM}_{k,kk} \leq F_{i,k}^{\mathrm{LO}}\cdot\mathrm{SM}_{k,kk} + F_{i,k}\cdot\mathrm{SM}_{k,kk}^{\mathrm{UP}} - F_{i,k}^{\mathrm{LO}}\cdot\mathrm{SM}_{k,kk}^{\mathrm{UP}} \tag{17}$$

$$F_{i,k}\cdot\mathrm{SM}_{k,kk} \leq F_{i,k}^{\mathrm{UP}}\cdot\mathrm{SM}_{k,kk} + F_{i,k}\cdot\mathrm{SM}_{k,kk}^{\mathrm{LO}} - F_{i,k}^{\mathrm{UP}}\cdot\mathrm{SM}_{k,kk}^{\mathrm{LO}} \tag{18}$$

where $F_{i,k}^{\mathrm{LO}}$, $F_{i,k}^{\mathrm{UP}}$, $\mathrm{SM}_{k,kk}^{\mathrm{LO}}$, and $\mathrm{SM}_{k,kk}^{\mathrm{UP}}$ are upper and lower bounds for the variables F and SM, respectively.

The efficiency of bilevel decompositions schemes is strongly dependent on the tightness of the relaxation operated to obtain the lower bound problem. In order to tighten the McCormick relaxation, the framework integrates some of the strategies proposed in the literature for these types of problems, such as *variable bounding*, *domain partitioning*, and *strengthening cuts*.

The *variable bounding strategy* consists in establishing tight bounds for the variables appearing in the bilinear term, in order to improve the tightness of the McCormick relaxation over the variable domain, while at the same time not eliminating any feasible solution from the search space.

In the proposed problem formulation, variables SM is, by definition, bounded between 0 and 1, while the flow variable $F_{i,kk}^{\mathrm{out1}}$ does not have a clearly defined upper bound. Our framework integrates problem data analysis tools, which are designed to identify meaningful variable bounds in a systematic manner. In the case of a superstructure without internal or external recycle flows, for example, it can be easily seen that the maximum value of $F_{i,kk}^{\mathrm{out1}}$ is obtained when the sources containing the highest amount of contaminant i flows through the sequence of treatment which has the minimum removal potential with respect to i. As a consequence, the upper bound for the flow variable $(F_{i,k}^{\mathrm{out1}})^{\mathrm{UP}}$ can be calculated according to eq 19 for interval representing wastewater sources, and via eq 20 for treatment intervals.

$$(F_{i,k}^{\mathrm{out1}})^{\mathrm{UP}} = \varnothing_{i,k} \qquad \forall\ k \in \text{sources} \tag{19}$$

$$\begin{aligned}(F_{i,kk}^{\mathrm{out1}})^{\mathrm{UP}} &= \sum_{k}[(F_{i,kk}^{\mathrm{out1}})^{\mathrm{UP}}\cdot\mathrm{SP}_{k,kk} + (F_{i,kk}^{\mathrm{out2}})^{\mathrm{UP}}\cdot\mathrm{SS}_{k,kk}]\cdot\\ &\quad[(1+\alpha_{i,kk}\cdot\mu_{i,kk})\cdot(1+\sum_{rr,\mathrm{react}}\gamma_{i,kk,\mathrm{rr}}\cdot\theta_{\mathrm{react},kk,\mathrm{rr}})\cdot\\ &\quad(1-\mathrm{SW}_{i,kk})\cdot\mathrm{Split}_{i,kk}] \qquad \forall\ kk \notin \text{sources}\end{aligned} \tag{20}$$

Similarly, for $(F_{i,k}^{\mathrm{out2}})^{\mathrm{UP}}$:

$$(F_{i,k}^{\mathrm{out2}})^{\mathrm{UP}} = 0 \qquad \forall\ k \in \text{sources} \tag{21}$$

$$\begin{aligned}(F_{i,kk}^{\mathrm{out2}})^{\mathrm{UP}} &= \sum_{k}[(F_{i,k}^{\mathrm{out1}})^{\mathrm{UP}}\cdot\mathrm{SP}_{k,kk} + (F_{i,k}^{\mathrm{out2}})^{\mathrm{UP}}\cdot\mathrm{SS}_{k,kk}]\cdot\\ &\quad[(1+\alpha_{i,kk}\cdot\mu_{i,kk})\cdot(1+\sum_{\mathrm{rr,react}}(\gamma_{i,kk,\mathrm{rr}}\cdot\theta_{\mathrm{react},kk,\mathrm{rr}}))\cdot\\ &\quad(1-\mathrm{SW}_{i,kk})\cdot(1-\mathrm{Split}_{i,kk})] \qquad \forall\ kk \notin \text{sources}\end{aligned} \tag{22}$$

It should be emphasized that the proposed analysis is based on simple function evaluations based exclusively on problem data, and can therefore be executed prior to the optimization, without any additional computational burden for the optimizer.

Moreover, in case the above-mentioned analysis returns an upper bound equal to zero for a flow variable, the variable can be fixed to zero and the corresponding bilinear constraint eliminated from the model, allowing reducing the mathematical complexity of the problem. Being based on a systematic analysis of the problems data, this simplification is an exact method and does not cause any consequence on the quality of the obtained solution.

The *domain partitioning* strategy consists in partitioning the domain of the variables appearing in the bilinear term, and use piecewise linear underestimators and overestimators over each partition. The domain partitioning can be monodimensional (when one of the variables appearing in the bilinear term is partitioned) or bidimensional (when both are partitioned).[29] While providing a tighter relaxation, this strategy causes an increase in the number of binary variables due to the piecewise linearization. Typically, it has been observed that a partitioning over 2−3 intervals represents the best tradeoff, in terms of computational time.[10]

In order to mitigate this problem, recent studies suggested the use of multilevel domain partitioning strategy, in which progressive tightening of the lower bound over the progression of the algorithm is obtained, by solving multiple time the lower bound problem and refining the domain partitioning grid according to the results.[30]

As an alternative, the use of a parametric disaggregation strategy to limit the number of additional binary variables resulting from the piecewise relaxation has been recently proposed.[15] At the current status, parametric disaggregation is not implemented in the framework, but it could be integrated as a further development.

Strengthening cuts are linear constraints that were redundant in the original MINLP formulation. Because of the relaxation of the nonconvex constraints, those cuts become nonredundant for the lower bound subproblem, and may therefore be included in order to tighten the relaxation and reduce the computational time.[29] Those are, for example, overall mass balances and contaminant mass balances for each treatment interval, such as eq 13.

For a detailed explanation of those methods, the reader is invited to refer to the above-mentioned sources.

4. CASE STUDY: OIL REFINERY WASTEWATER TREATMENT AND REUSE

In this section, the above-presented computer-aided framework for synthesis and design of wastewater treatment and recycle systems is applied to a case study, dealing with the problem of treatment and reuse of oil refinery wastewater. The case study is based on data available in the open literature, and aims at representing a problem of industrial complexity, with respect to the number and type of contaminants, the number of treatment options, and environmental regulations.

Oil refineries are characterized by an intensive use of water (between 1.55 and 2.14 m^3 of water per m^3 of crude oil in U.S. refineries,[31] and they are often located in water-scarce geographies. In addition, refineries are very different from each other, in terms of water flow rates involved and the level of contaminant present in their wastewaters, making the replication of a standard water network design often disadvantageous or impossible.

In refineries (as in every processing plant), water is used as cooling water, boiler feedwater, and for washing operations. In addition, water is heavily employed in the form of steam in many units, such as crude distillation, steam stripping, coking, etc.; water is also used in the desalter to remove solids and salts from the crude prior to sending it to the crude distillation units.

The wastewater produced by oil refining processes is highly variable in flow rate and composition. Wastewater typically contains hydrocarbons, dissolved materials, suspended solids, phenols, ammonia, sulfides, and other compounds. More-detailed information on oil refineries water and wastewater figures can be found in the scientific literature.[2,3,31]

In the following sections, the formulation and solution of the design problem according with the support of the proposed framework will be briefly described.

4.1. Step 1: Problem Formulation. The goal of the study is the design of an optimal integrated wastewater treatment plant (IWWTP) to treat the refinery wastewater, with the objective of minimizing the total annualized cost (TAC) of the treatment 23, over an investment horizon of 10 years. The design should include all options for water recycle that have an economical justification.

$$\mathrm{TAC} = \mathrm{cost}_{\mathrm{utility}} + \mathrm{cost}_{\mathrm{wastes}} - \mathrm{savings}_{\mathrm{water\ recycle}} + \frac{\mathrm{capital}}{\mathrm{time}} \tag{23}$$

where "$\mathrm{cost}_{\mathrm{utility}}$" represents the yearly cost for utility consumption, "$\mathrm{cost}_{\mathrm{wastes}}$" is the yearly cost associated with the disposal of the wastes produced, "$\mathrm{savings}_{\mathrm{water\ recycle}}$" represents the yearly savings associated with the recycle of water, "capital" is the investment cost required for the construction of the treatment plant, and "time" is the time horizon for the investment (given in years).

Incoming wastewater streams have been characterized in terms of flow and composition based on literature data. As stated earlier, those data are highly dependent from the configuration of the process. For this study, the wastewater data reported from Khor et al.[8] and Eckenfelder et al.[2] have been considered. Three wastewater streams have been identified:

(1) Caustic wastewater: representative of spent caustic from isomerization, alkylation and drying, and sweetening.
(2) Sour wastewater: representative of all sour wastewater sources (distillation, cracking, etc.).
(3) Oily wastewater: representative of oily wastewater sources (not sour or caustic).

Each of the streams has been characterized in terms of flow and composition (see Table 2).

Four water sinks options have been identified: discharge as surface water effluent, recycle as process water in the oil desalter, recycle as cooling towers makeup, and recycle as boiler feedwater. Each of the identified options has been characterized in terms of maximum flow and contaminants concentration, on the basis of environmental regulation and technical specifications (see Table 3). No opportunity for contaminant valorization has been identified for this case.

Table 2. Refinery Wastewater Characterization[a]

	caustic WW	sour WW	oily WW
flow (t/h)	0.2	100.0	558.8
C (mg/L)	80 491.4	869.0	1333.4
NH_4^+ (mg/L)	551.4	1462.9	79.4
H_2S (mg/L)	14 512.9	1,553.0	55.2
Cr^{6+} (mg/L)	5.8	0.0	28.0
oil and grease (mg/L)	5.0	281.4	1475.8
FSS (mg/L)	0.0	0.0	470.0
BOD5 (mg/L)	2176.5	660.0	712.7
TSS (mg/L)	0.0	0.0	940.1

[a]Data taken from refs 2 and 8.

Table 3. Water Sink Limits[a]

limit	surface discharge (D)	recycle BFW (BFW)	recycle CW (CTW)	recycle desalter (Des)
flow (t/h)		198.5	104.6	50.00
C (mg/L)	105.3	3.5	52.6	
NH_4^+ (mg/L)	4.9	0.1		50
H_2S (mg/L)	1.1			10
PO_4^{3+} (mg/L)				
Cr^{6+} (mg/L)	0.1			
Cr^{3+} (mg/L)	0.4			-
Ca^{2+} (mg/L)		0.4	50.0	
SO_4^{2+} (mg/L)			200.0	
Fe^{2+} (mg/L)		0.3	0.5	
Fe^{3+} (mg/L)		0.3	0.5	
Cl^- (mg/L)			500.0	
CO_3^{2+} (mg/L)		120.0	24.0	
oil and grease (mg/L)	10.0	25.0	25.0	
FSS (mg/L)	15.0	5.0	100.0	
BOD5 (mg/L)	30.0	3.5	52.6	
TSS (mg/L)	30.0	5.0	100.0	

[a]Data taken from refs 3 and 32.

In order to evaluate the impact of the water recycling on the treatment plant, the problem is solved for two scenarios:

- *No recycle:* recycle opportunities are disabled and all water is discharged as effluent.
- *Water recycle:* water recycle opportunities are enabled.

As explained in the previous chapter, scenario 1 can be formulated as a single-stream problem, while scenario 2 requires the formulation of a multistream problem.

For the single-stream problem, the impact of wastewater composition uncertainty is studied.

4.2. Step 2: Generation of Alternatives. The open literature has been searched to identify known treatment configurations, which have been decomposed as sequences of treatment intervals (see Table 4) and organized in a superstructure for oil refinery wastewater treatment and reuse, in which more than 50 000 possible treatment configurations are represented (Figure 3).

For the sake of simplicity, the sludge treatment line has not been explicitly considered in the scope of the design problem; the costs related to sludge treatment (e.g., through anaerobic or

Table 4. Treatment Intervals

ID	description
WAO	wet air oxidation
ChOx	chlorine oxidation
SWS	sour water stripper
SS	H_2S stripper
NS	NH_3 stripper
AirS	air stripper
API	API separator
PI/PPI	CPI/PPI separator
DAF	dissolved air flotation
IAF	induced air flotation
TF	trickling filter
RBC	rotating biological contactor
AS	activated sludge
PACT	powdered activated carbon treatment
MBR	membrane biological reactor
GAC	adsorption on granular active carbon
PhPrec	phosphorus precipitation
MePrec	metal precipitation
CrPrec	chromium precipitation
IE	ion exchange
ED	electrodialysis
MF/UF	microfiltration/ultrafiltration
NF/RO	nanofiltration/reverse osmosis

aerobic digestion and ultimate disposal to landfill) are considered through the definition of a sludge disposal price.

4.3. Step 3: Data and Model Collection. Each treatment unit has been modeled using the generic process interval model described in the previous section. Extensive description of the data collection and the calculation of the model parameters is given as Supporting Information.

The component list has been defined by adapting the ASM list to the problem. Many extra contaminants not included in ASM (Cr^{6+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, H_2S, CO, CH_4, etc.) have been added, together with all utility components required by the treatment intervals identified in the previous step (low-pressure steam, H_3PO_4, NaOH, electricity, etc.).

Moreover, some of the list of ASM components have been modified, either by disregarding some components that were not relevant for this case (such as S_{alk} and X_0), or by merging some of them (e.g., X_s and S_s, considered together as BOD (see Figure 4)).

As a result, a component list containing 44 components has been identified. Components for which mass balance do not apply (such as electricity) have been identified and excluded from the mass balance relations.

4.4. Step 4: Optimization Problem Formulation and Solution. Through the framework, the problem has been formulated in GAMS both for the single-stream case and the multistream case.

4.4.1. Single-Stream Problem Solution. The single-stream case resulted in the formulation of a MILP problem containing 51 567 equations and 10 562 variables (41 of which binary), which have been solved using CPLEX within 2.6 s on a standard laptop computer with CPU Intel Core i5 2.53 GHz.

The solution identifies a water treatment network with an annualized cost of 17.454 M$/yr. The selected water treatment configuration (see Figure 6) is composed by SWS as pretreatment, CPI/PPI and IAF as primary treatment, AS technology as secondary treatment and MF/UF and NF/RO as tertiary treatment. After this treatment sequence, the water meets the purity requirements and is discharged as effluent.

4.4.2. Uncertainty Analysis. As mentioned in the Introduction, the composition of oil refinery wastewater is function of process configuration, crude oil quality, as well as external factors such as temperature. Consequently, oil refinery wastewater composition data are subject to large variations, as showed in Table 5, and therefore during the design phase, those data are associated with a large degree of uncertainty.

In order to evaluate the consequences of the above-described data uncertainty on the WWTP design, uncertainty analysis has been performed, based on the methodology described in an earlier work.[17]

To this goal, the composition of the incoming wastewater with respect to the six contaminants reported in Table 5 has been described in terms of uniform probability distribution. The defined domain of uncertainty has been sampled, obtaining a list of 150 possible future scenarios with equal probability of realization with respect to wastewater composition. The Latin Hypercube Sampling (LHS) technique has been employed in order to guarantee uniform coverage of the uncertainty domain.[32]

In order to estimate the consequence of the uncertainty on the design problem, the performances of the obtained treatment configuration have been evaluated against the defined domain of uncertainty.

The result shows that, when the uncertainty in the wastewater composition is considered, the selected treatment configuration is unable to guarantee robust compliance with the discharge regulation. In particular, as shown in Figure 7, the probability of discharging a water effluent violating the concentration limit of Cr^{6+} (0.1 mg/L) is over 70%.

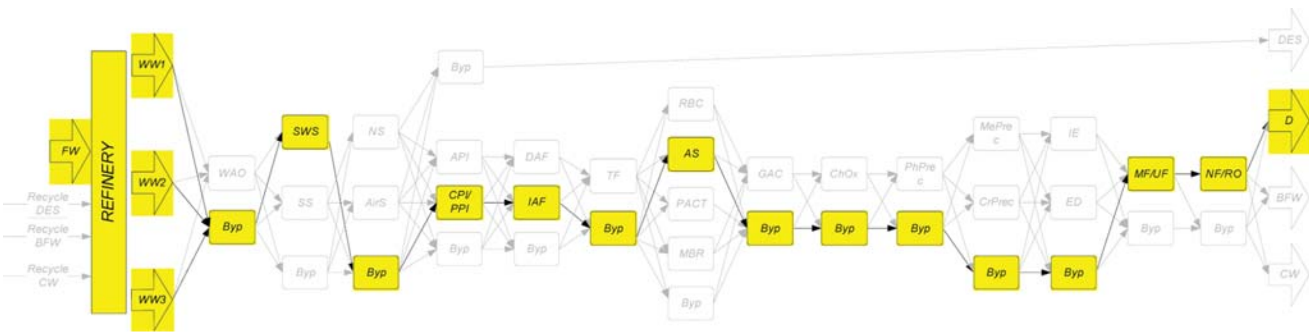

Figure 6. Treatment of oil refinery wastewater, optimal solution for single-stream formulation.

Table 5. Range of Variation for Composition of Oil Refinery Wastewater Contaminants Reported in Scientific Literature[a]

contaminant (mg/L)	WW1 Min	WW1 Max	WW2 Min	WW2 Max	WW3 Min	WW3 Max
H_2S	0.2	48500.0	19.0	4320.0	1.5	121.6
NH_4^+	2.8	1100.0	36.1	3342.5	2.9	205.9
COD	302.0	364100.0	935.0	1530.0	450.0	4774.0
oil and grease	0.0	0.0	12.7	550.0	22.6	9357.5
Cr^{6+}	0.0	0.0	0.0	0.0	0.3	121.6
TSS	0.0	0.0	0.0	0.0	200.5	4781.5

[a]Data taken from refs 2 and 8.

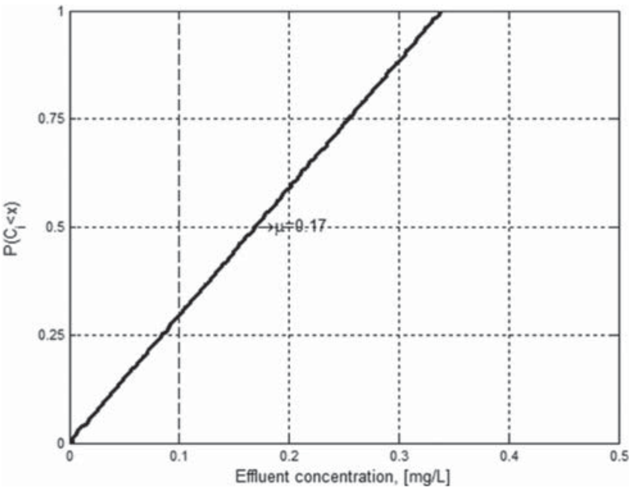

Figure 7. Cumulative distribution function for the discharge concentration of Cr^{6+}.

This result suggests the opportunity of incorporating the uncertainty in the design problem. To this goal, the design problem is formulated under data uncertainty and solved, aiming at the identification of a treatment network that is feasible over all uncertainty domains and whose expected TAC is minimal. The solution is reported in Figure 8.

With respect to the solution obtained under deterministic condition, ion exchange is added as tertiary treatment, in order to ensure compliance with the regulation, with respect to Cr^{6+} emissions.

As highlighted in Table 6, robustness against wastewater composition uncertainty is obtained at the price of a relevant decrease in financial performances for the treatment, with the TAC increasing by more than 36%.

Table 6. Comparison between Deterministic Solution and Solution under Uncertainty

item	Financial Indexes: single-stream deterministic solution	Financial Indexes: single-stream solution under uncertainty	% diff
total annualized cost, TAC (M $/yr)	17.454	23.762	+36.10%
Capex (M$)	22.800	25.217	+10.60%
Opex (M$/yr)	15.934	22.081	+38.60%
utility cost (M$/yr)	11.049	11.535	+4.40%
waste cost (M$/yr)	4.886	10.546	+115.90%

The root cause of such a dramatic performance erosion can be identified in the wide range of variation for wastewater composition identified in Table 5, which the treatment plant must be able to manage. Consequently, the analysis suggests focusing on the reduction of such a data uncertainty through further investigation of wastewater composition.

4.4.3. Multistream Problem. The multistream formulation resulted in a problem of the same size as the above-described single-stream case, but in the form of nonconvex MINLP containing 4326 bilinear terms. Because of the size of the problem and the number of bilinear terms, direct solution is not possible, and the bilevel decomposition strategy has been used.

In order to facilitate the solution of the problem, the methods described in the previous chapter have been adopted. First, the upper bound values for the flow variable F^{out1} has been obtained through data analysis, using eqs 19 and 20. Through this analysis, the number of bilinear terms have been reduced to 2060 (corresponding to a reduction by 52%), by identifying the variables which can be fixed to zero and eliminating the corresponding constraints. Bidimensional domain partitioning has implemented, by dividing each of the variables appearing in the bilinear terms in a 2 × 2 grid. This

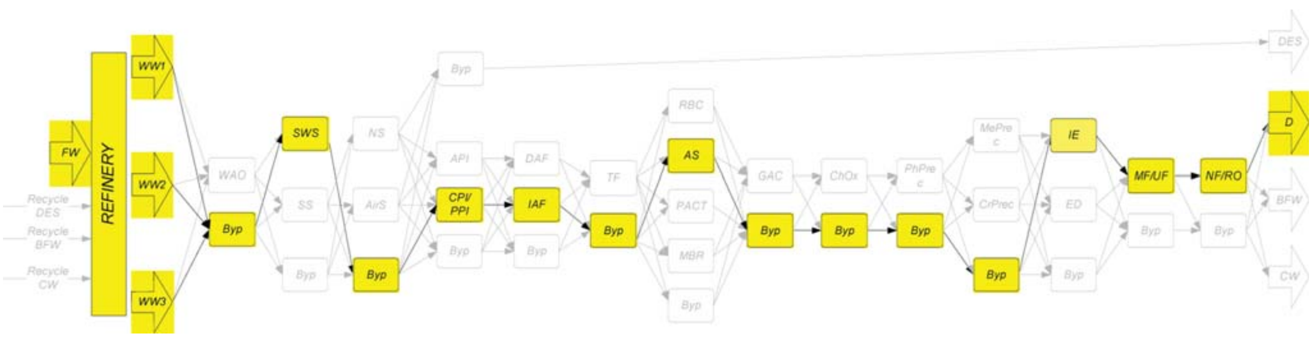

Figure 8. Solution under uncertainty.

resulted in the definition of additional 1806 binary variables. Finally, component mass balance for the flow splitters (6) has been added as a strengthening cut.

The problem has been solved via bilevel decomposition; a solution characterized by a TAC of 13.654 M$/yr, has been identified, with a relative optimality tolerance of 7.5%. The solution required 10 major iterations and a CPU time of 90 238 s (25 h) on a standard laptop computer with CPU Intel Core i5 2.53 GHz (see Table 7).

Table 7. Solution Statistics

problem	single-stream	single-stream under uncertainty	multistream
class	MILP	MILP	MINLP
number of binary variables	41	41	41
number of constraints	51 567	3 632 748	51 567
number of nonconvex constraints			2060
relative optimality tolerance	1×10^{-6}	1×10^{-6}	7.5%
CPU time (s)	2.5	460.2	90 238.2
solution algorithm	direct	direct	bilevel decomp.
number of outer iterations			10
average CPU time for 1 iteration (s)			9023.8

In the treatment configuration obtained (shown in Figure 9), the incoming wastewater is pretreated by the SWS. The purity of the pretreated water meets the desalter specification; therefore, part of the water (7.7% of the total load) is sent back to the refinery bypassing the remaining treatment sections. The remaining water is treated by the CPI/PPI and IAF, prior to be fed to the AS for biological treatment. Most of the ternary treatments are bypassed, with the exception of ion exchange, MF/UF, and NF/RO. Together with the optimal configuration, several additional information such as the utility table (Table 8) and cost breakdown analysis (Figure 10) are obtained.

The comparison of the results for the two scenarios (Table 9) shows that, when water recycle is considered, the proposed approach has been able to identify a win−win solution, meaning a solution in which both the economic objective (total cost) and a sustainability indicator (water footprint) are improved. In particular, a reduction of 21.8% of the total annualized cost and of 45.3% of the water footprint has been achieved.

The existence of a win−win solution when water recycle is considered is specific to the case study and cannot be generalized. In this case, the simultaneous improvement of both objectives is due to the reduced load to primary, secondary, and tertiary treatments (because of the water recycle to the desalter), which causes a reduction in capital and operational costs for these sections. However, the problem solution strategy is generic and can be applied to explore optimal networks alternatives for different oil refinery wastewater characteristics.

The optimal treatment configuration obtained as a result of the computer-aided analysis provides design targets for detailed engineering and dimensioning of unit operations involved in the network which can further be simulated and verified with the use of rigorous and detailed models using for example commercial process simulators (WEST(R), Biowin(R), etc.) and experimentally verified at pilot scale, if needed, in order to obtain the final design.

5. CONCLUSIONS AND FUTURE WORKS

In this work, a systematic framework for optimization-based design of water treatment and reuse networks is proposed. In the framework, state-of-the-art optimization methods and solution strategies are integrated together with wastewater engineering knowledge and tools in a computer-aided environment, designed to guide and assist the user through the formulation and solution of the problem. The computer-aided framework contributed to improving the efficiency of the workflow needed to formulate and solve the problem, allowing time-effective and simple formulation of problems of industrial complexity.

The framework is demonstrated through the formulation and solution of a problem of industrial relevance, related to the design of a wastewater treatment and reuse network for an oil refinery. The case study is solved for two scenarios: (a) disregarding options for water recycle, resulting in a simpler linear problem; and (b) including three possible water recycle opportunities, requiring different water purity, resulting in a nonlinear nonconvex problem.

The comparison between the solutions of the 2 scenarios showed that, when water recycle is considered, the proposed framework allowed the identification of a win−win scenario, allowing the improvement of both the economical objective and of the water footprint.

In conclusion, the framework allowed comparing a large number of alternative configurations, in order to identify the most promising candidates, allowing focusing the most expensive and time-consuming steps of process design.

Based on these results, future work should focus on the development of a comprehensive database of water treatment

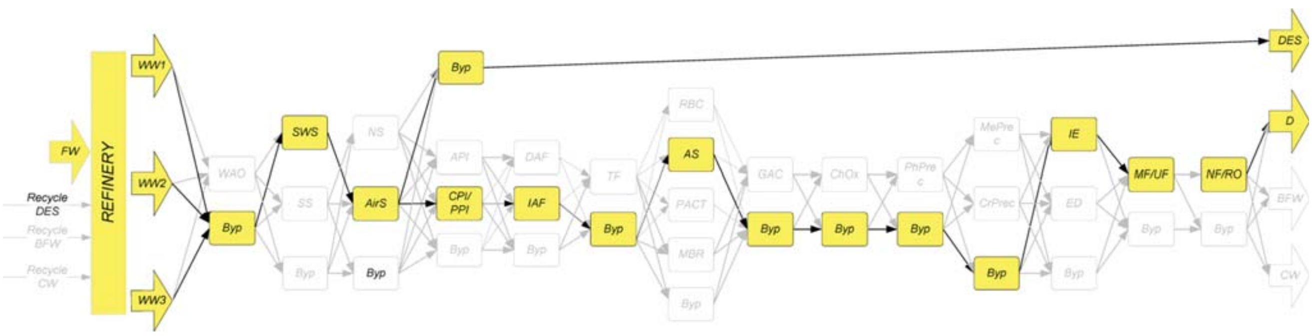

Figure 9. Treatment of oil refinery wastewater, and optimal solution for multistream formulation.

Table 8. Multistream Problem Results: Utility Table

	SWS	AirS	CPI/PPI	IAF	AS	IE	MF/UF	NF	total
N_2 (kg/h)		10257.45		22.142	1777.476				12057.07
O_2 (kg/h)		3063.913		6.614	530.934				3601.461
electricity (kW)	10354.81	1284.542	132.207	398.668	629.272	2258.468	3718.063	4481.956	23257.99
LPS (kg/h)	128.097	24.62							152.717
CW (kg/h)	921.903	294.08							1215.983
H_3PO_4 (kg/h)					2.465				2.465
H_2SO_4 (kg/h)						160.452	101.524	21.338	283.314
NaOH (kg/h)							9.365	1.968	11.333
Cl_2 (kg/h)							0.271	0.05	0.321

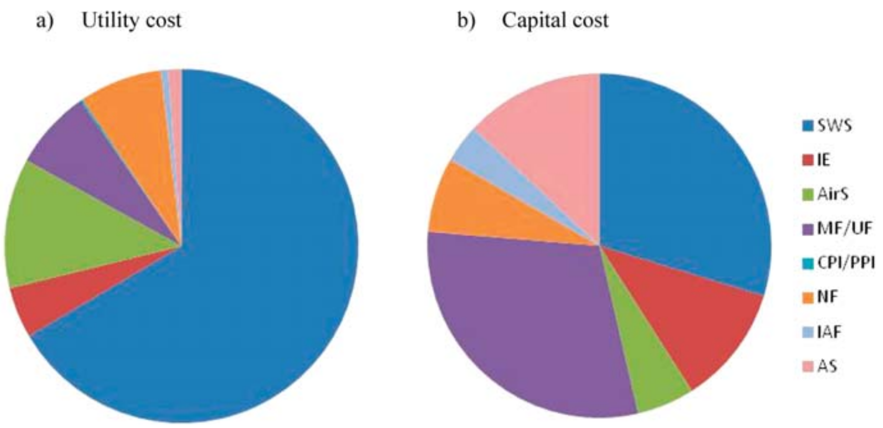

Figure 10. Multistream problem results. Cost breakdown: (a) utility cost and (b) capital cost.

Table 9. Comparison of Solutions

item	scenario 1: no recycle	scenario 2: recycle	% Diff
	Financial Indexes		
total annualized cost, TAC (M$/yr)	17.454	13.654	−21.8%
Capex (M$)	22.800	19.859	−12.9%
Opex (M$/yr)	15.934	12.340	−22.5%
utility cost (M$/yr)	11.049	8.644	−21.8%
waste cost (M$/yr)	4.886	3.696	−24.4%
savings (M$/yr)		0.074	
	Environmental Indexes		
refinery water footprint (t/h)	208.02	113.769	−45.3%
water recycled (t/h)		50	
water effluent (t/h)	449.53	493.735	+9.8%
water wasted (t/h)	208.02	113.769	−45.3%
water withdrawn (t/h)	657.504	607.504	−7.6%

processes and models and data. Moreover, recently developed optimization methods and solution approaches (such as parametric disaggregation) should be integrated in the framework, in order to allow time effective solution of complicated multistream problems. Furthermore, strategies for the solution of large scale multistream problem (such as the case study proposed in this work) under uncertainty should be developed and integrated within the framework.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A more-detailed description of the data collection step described in step 2 of the above-described methodology is reported as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ NOMENCLATURE

Indexes

i = component
k = process interval (origin)
kk = process interval (destination)
react = key reactant (subset of component)
rr = reaction
u = utility (subset of component)

Parameters

MW_i = molecular weight
$SW_{i,kk}$ = wastes fraction
$S^p_{k,kk}$ = if a primary connection may exist between interval k and interval kk, $S^p_{k,kk}$ = 1; otherwise, $S^p_{k,kk}$ = 0
$S^s_{k,kk}$ = if a secondary connection may exist between interval k and interval kk, $S^s_{k,kk}$ = 1; otherwise, $S^s_{k,kk}$ = 0
a_{kk} = coefficient for capital cost estimation
$\varnothing_{i,kk}$ = water source component flow
$\Delta P_{k,kk}$ = pressure drop
n_{kk} = coefficient for capital cost estimation
$\alpha_{i,kk}$ = fraction of utility flow mixed with process stream

$\gamma_{i,kk,rr}$ = reaction stoichiometry
$\mathrm{Split}_{i,kk}$ = separation split factor
$\theta_{\mathrm{react},kk,rr}$ = conversion of key reactant
$\mu_{u,i,kk}$ = specific utility consumption

Variables

$F_{i,k,kk}$ = flow of component i from process intervals k to process intervals kk
$\mathrm{SM}_{k,kk}^{\mathrm{OUT1}}$ = fraction of primary outlet from interval k fed to interval kk
$\mathrm{SM}_{k,kk}^{\mathrm{OUT2}}$ = fraction of secondary outlet from interval k fed to interval kk
$\mathrm{ff}_{i,kk}$ = component flow after mixing
$R_{i,kk}$ = utility flow
$F_{i,kk}^{M}$ = component flow after mixing
$F_{i,kk}^{\mathrm{out1}}$ = component flow leaving process intervals kk through the primary outlet
$F_{i,kk}^{\mathrm{out2}}$ = component flow leaving process intervals kk through a secondary outlet
$F_{i,kk}^{R}$ = component flow after reaction
$F_{i,kk}^{AQ}$ = component flow after aqueous dissociation
$\mathrm{F}_{i,kk}^{\mathrm{OUT}}$ = component flow after waste separation
$\mathrm{PC}_{k,kk}$ = pumping cost from interval k to kk
INV_{k} = investment cost for interval k
y_k = selection of process intervals k (binary)

Abbreviations

TAC = total annualized cost
UB = upper bound of the objective function
LB = lower bound of the objective function

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