AIChE

A Property-Based Optimization of Direct Recycle Networks and Wastewater Treatment Processes

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DOI 10.1002/aic.11828

This article presents a mathematical programming approach to optimize direct recycle-reuse networks together with wastewater treatment processes in order to satisfy a given set of environmental regulations. A disjunctive programming formulation is developed to optimize the recycle/reuse of process streams to units and the performance of wastewater treatment units. In addition to composition-based constraints, the formulation also incorporates in-plant property constraints as well as properties impacting the environment toxicity, ThOD, pH, color, and odor. The MINLP model is used to minimize the total annual cost of the system, which includes the cost for the fresh sources, the piping cost for the process integration and the waste stream treatment cost. An example problem is used to show the application of the proposed model. The results show that the simultaneous optimization of a recycle network and waste treatment process yields significant savings with respect to a commonly-used sequential optimization strategy. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 2329–2344, 2009

Keywords: direct recycle-reuse, property integration, mass integration, environmental constraints, wastewater treatment, optimization

Introduction

Mass integration strategies have been the subject of study of many research efforts because of the economical and environmental benefits they provide. In the area of sustainable design, mass integration can be used to lower the consumption of fresh sources and to reduce the waste materials discharged to the environment. A complete treatment on the basic concepts of mass integration can be found in literature.[1,2] A particular application that has attracted recent interest is in the minimization of fresh water usage and wastewater discharge through recycle/reuse strategies. The papers by Wang and Smith,[3,4] Dhole et al.,[5] El-Halwagi and Spriggs,[6] Sorin and Bedard,[7] Kuo and Smith,[8] Polley and Polley,[9] Hallale,[10] and El-Halwagi et al.[11] provide some conceptual approaches to solve the fresh water-wastewater

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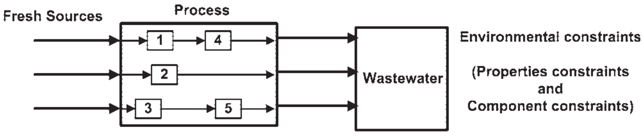


Figure 1. Traditional strategy for mass integration.

allocation problem. The papers by Takama et al.,[12] Doyle and Smith,[13] Alva-Argaez et al.,[14,15] Galan and Grossmann,[16] Huang et al.,[17] Benko et al.,[18] Savelski and Bagajewicz,[19,20] Hernandez-Suarez et al.,[21] Gabriel and El-Halwagi,[22] and Karuppiah and Grossmann[23] have shown the application of mathematical programming techniques to solve the water allocation problem. Gunaratnam et al.[24] proposed a method based on the composition of the streams to design total water systems considering simultaneously the water usage and wastewater treatment processes. They considered constraints on the waste composition, and included piping costs in the objective function. Kiperstok and Sharratt[25] presented a methodology for the simultaneous optimization of waste minimization and end-of-pipe treatments considering the decay capabilities of the receptors. Bagajewicz[26] has published a paper review on the procedures reported to design water networks.

The aforementioned works have provided major contributions to the synthesis of water recycle/reuse networks. However, they suffer from at least one of the following limitations:

(1) Focus has been given to in-plant recycle strategies with constraints limited to process units and without considering the effects of the resulting terminal wastewater streams and the environmental regulations (see Figure 1). To satisfy the environmental constraints, the wastewater stream needs to be treated prior to be discharged to the environment; this situation may increase the total cost associated to the recycle-reuse mass integration process. For example, when the solution that minimizes fresh sources consumption yields a high wastewater treatment cost, then such a solution may not correspond to the overall optimal solution. In this case, it may be preferable to use more fresh sources and lower the wastewater treatment cost. Therefore, it is important to consider simultaneously the optimization of the process integration together with the wastewater treatment process to take into account the trade offs between both factors.

(2) The impact of process discharges on the environment has been characterized in terms of the composition of pollutants. In many cases, there are important environmental regulations that are given in terms of properties (e.g., color, toxicity, pH, etc.).

(3) Process characterization and recycle constraints have been based on compositions. It is worth noting that there are many industrial cases when such constraints should be based on properties. Examples include applications when the performance of the process units is affected by the properties of its feed and the cases when environmental regulations impose limits for specific properties of waste streams such as toxicity, theoretical oxygen demand (ThOD), pH, temperature, color, odor, viscosity, and density. These properties are difficult to quantify as a function of composition because of the many components of the process streams. It is also difficult to track properties throughout the process because they are not conserved. To overcome this limitation, Shelley and El-Halwagi[27] introduced the concept of property-based componentless design by defining surrogate properties (called clusters) that enable the conserved tracking of properties. Later, El-Halwagi et al.[28] generalized it to the concept of property integration defined as "a functionality-based holistic approach for the allocation and manipulation of streams and processing units, which is based on functionality tracking, adjustment, and assignment throughout the process." For a network with up to three properties in concern, graphical tools may be used to guide the synthesis and analysis tasks.[27–29] When the number of properties is higher than three, algebraic tools are used.[30] Eden et al.,[31] Eljack et al.,[32] and Grooms et al.[33] incorporated the concept of property integration into the product design strategy. Kazantzi et al.[34] and Eljack et al.[35] presented graphical approaches for simultaneous process and molecular design.

This article presents a mathematical programming model to simultaneously optimize the direct recycle networks together with the wastewater treatment process in order to satisfy a set of process and environmental constraints. An optimization formulation is developed based on disjunctive programming (e.g., Raman and Grossmann[36]). The model is formulated to consider environmental-constrained properties such as toxicity, ThOD, pH, color, odor, and any other property that may cause pollution to the environment, in addition to the mass and composition constraints for hazardous compounds in the waste stream. The problem is formulated with proper constraints as an MINLP problem that minimizes the total annual cost of the system, which includes the cost for the fresh sources, the piping cost for the process integration and the wastewater treatment cost.

The following section presents an outline of the proposed model, followed by the mathematical description of the mathematical model for the simultaneous process integration and wastewater treatment process. The last sections deal with the application of the proposed model and the conclusions of the article.

Outline of the Proposed Model

The definition of the problem is as follows. Given is a set of process and fresh sources with known flowrates, compositions and properties. Also given is a set of sinks (process units) with constraints for the inlet flowrates and allowed compositions and properties. In addition, there is a set of constraints given by the environmental regulations for the waste streams discharged to the environment. The problem then consists of finding the optimal mass and property integration network that includes a direct recycle strategy that meets the environmental regulations for the waste streams and minimizes the total annual cost of the overall process.

The sets used in the model formulation are defined first. NSINKS contains the sinks for the streams within the process, whereas NSOURCES and NFRESH contain the process and fresh sources. NCOMP contains all the components that are considered in the process integration, and NPROP contains the properties constrained for the process sinks and the properties considered by the environmental regulations.

Figure 2 shows a representation of the problem that includes a direct recycle strategy, which takes into account

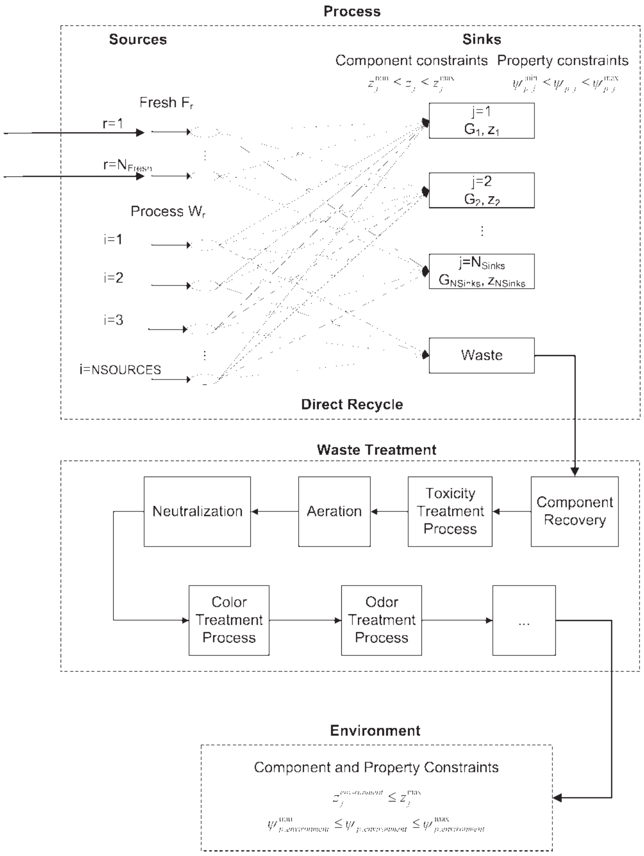


Figure 2. Source-sink representation for mass and property integration including waste treatment.

constraints for the components and properties of the sinks as well as a centralized waste treatment process needed for the waste to be discharged. It should be noted that a decentralized treatment facility could be used as another option for the waste streams. Figure 3 shows the differences between these options. Figure 3a shows a waste treatment network with a decentralized facility, while in Figure 3b waste streams are mixed before being fed to a centralized waste treatment facility, as assumed in this work.

Model formulation

The model formulation consists of the set of equations for the process constraints and the waste stream treatment constraints. The formulation is based on a direct recycle configuration, and the waste treatment constraints are based on a disjunctive programming formulation. First, the process constraints to model the direct recycle-mass integration, which includes component and properties constraints given by the process units, are given, followed by the constraints for the waste stream treatment process. The objective function is given at the end of the formulation.

Process constraints

Splitting of Process Source Streams. The flow rate from every process source i is segregated and directed to the sinks j and to the waste.

$$W_i = \sum_{j \in \text{NSINKS}} w_{i,j} + \text{waste}_i, \quad i \in \text{NSOURCES} \qquad (1)$$

Here, W_i is the total flowrate from source i, $w_{i,j}$ is the flowrate segregated from source i and directed to sink j, and waste_i is the flowrate segregated from source i and directed to the waste stream.

Splitting of Fresh Source Streams. Fresh sources are segregated and directed to the sinks.

$$F_r = \sum_{j \in \text{NSINKS}} f_{r,j}, \quad r \in \text{NFRESH} \qquad (2)$$

In Eq. 2, F_r is the total flowrate consumed from fresh source r and $f_{r,j}$ is the flowrate segregated from fresh source r and directed to sink j. Notice that the fresh sources are not allowed to be discharged into the waste stream.

Total Waste. The total waste is the sum of the waste streams from all sources.

$$\text{WASTE} = \sum_{i \in \text{NSOURCES}} \text{waste}_i \qquad (3)$$

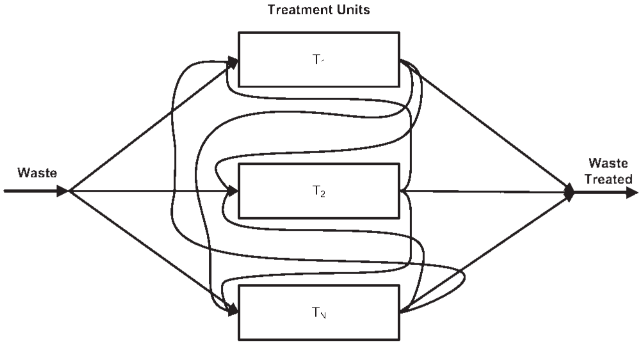
Mass Balances at the Mixing Point Before Each Sink. To find the inlet flowrate at each sink, the following mass balance is written.

$$G_j = \sum_{i \in \text{NSOURCES}} w_{i,j} + \sum_{r \in \text{NFRESH}} f_{r,j}, \quad j \in \text{NSINKS} \qquad (4)$$

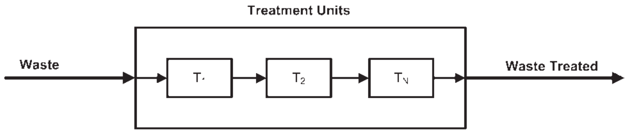
where G_j is the total inlet flowrate at sink j.

Component Balances at the Mixing Point Before Each Sink. To determine the composition of a stream inlet to any sink, the following component balance is used,

$$z_{j,c}^{\text{in}} G_j = \sum_{i \in \text{NSOURCES}} \left[z_{i,c} w_{i,j} \right] + \sum_{r \in \text{NFRESH}} \left[z_{r,c} f_{r,j} \right], \quad j \in \text{NSINKS}, c \in \text{NCOMP} \qquad (5)$$



3a. Distributed Treatment



3b. Centralized Treatment

Figure 3. Wastewater treatment alternatives.

where $z_{j,c}^{\text{in}}$ is the inlet composition for component c at the inlet of sink j, and $z_{i,c}$ and $z_{r,c}$ are the given compositions for the process and fresh sources, respectively.

Property Balance at the Mixing Point Before Each Sink. To determine the properties at the inlet of each sink, the following property balance is needed.

$$\psi_p(p_{j,p}^{\text{in}})G_j = \sum_{i \in \text{NSOURCES}} \left[\psi_p(p_{i,p})w_{i,j}\right] + \sum_{r \in \text{NFRESH}} \left[\psi_p(p_{r,p})f_{r,j}\right], \quad j \in \text{NSINKS}, p \in \text{NPROP} \quad (6)$$

Here, $\psi_p\ (p_{j,p}^{\text{in}})$ is the property operator at the inlet conditions of sink j for property p, and $\psi_p(p_{i,p})$ and $\psi_p(p_{r,p})$ are property operators for process and fresh sources i and r, respectively. As stated by Shelley and El-Halwagi,[27] the property operators follow a mixing rule that assumes to be proportional to each mass contribution, although the property operator may be linear or nonlinear depending on the specific property. The property operators can be calculated from first principles or estimated through empirical or semi-empirical methods. For properties such as composition, toxicity, chemical oxygen demand, and odor, the property operator is simply $\psi_P(P) = P$, but some transformations are convenient to be used for other properties. Some examples include the following properties: for pH, $\psi_{\text{pH}}(\text{pH}) = 10^{\text{pH}}$, for density, $\psi_\rho(\rho) = 1/\rho$, for viscosity $\psi_\mu(\mu) = \log\ (\mu)$, and for the Reid vapor pressure, $\psi_{\text{RVP}}\ (\text{RVP}) = \text{RVP}^{1.44}$.

Sinks Composition Constraints. Every sink is restricted to receive the inlet stream within composition limits as follows,

$$z_{j,c}^{\min} \leq z_{j,c}^{\text{in}} \leq z_{j,c}^{\max}, \quad j \in \text{NSINKS}, c \in \text{NCOMP} \quad (7)$$

Sinks Properties Constraints. It is frequently necessary to include limits for specific properties that are difficult to quantify with the component constraints when there is a large number of components in the stream. Therefore, the sinks property constraints are given as follows,

$$p_{p,j}^{\min} \leq p_{p,j}^{\text{in}} \leq p_{p,j}^{\max}, \quad j \in \text{NSINKS}, p \in \text{NPROP} \quad (8)$$

Waste stream treatment constraints

A waste stream needs to satisfy the environmental regulations before it is discharged to the environment. Constraints are formulated from the environmental regulations for hazardous materials. Whenever possible, they are based on component constraints, but for properties that are difficult to characterize because of the large number of components in some waste streams, they are formulated as property constraints.

The methodology proposed in this article is based on a direct recycle strategy. This formulation eliminates several nonlinear terms that would arise if treatment of streams were allowed before be sent to process sinks. In those cases, several bilinear product terms for the property balances would arise, which would affect the numerical solution of the problem. In addition, it should be noticed that if the waste is the only stream that needs to be treated, the order of the treatment units may be easily fixed based on industrial knowledge, experience, or the characteristics of streams for the particular process under consideration.

Ratio Waste Stream. The contribution of each source stream to the total waste is given by,

$$\text{Ratio}_i = \frac{\text{waste}_i}{\sum\limits_{i \in \text{SOURCES}} \text{waste}_i} \quad (9)$$

where Ratio_i is the fractional contribution of each process source i for the waste stream.

Density for the Waste Stream. The density for the waste stream (ρ_{waste}) is determined using the following mixing rule,

$$\frac{1}{\rho_{\text{waste}}} = \sum_{i \in \text{SOURCES}} \left[\frac{\text{Ratio}_i}{\rho_i}\right] \quad (10)$$

Recovery process

To satisfy the environmental regulation associated with the discharge of a specific hazardous compound, it is necessary to put a recovery process in the waste treatment process. This recovery process depends on the mass load and concentration of the specific components. Therefore, it is necessary to determine the composition and the mass load for the undesirable compounds before be discharged to the environment. In addition, for each compound u to be recovered, there exist specific technologies that can be used with a recovery efficiency EFF_u.

The mass flow inlet to the recovery process is given by,

$$\text{WINREC} = \text{WASTE} \quad (11)$$

The component balance inlet to the recovery process is,

$$\text{WINRECU}_u = \sum_{i \in \text{NSOURCES}} \left(\text{waste}_i\ z_{i,u}^{\text{inrecov}}\right) \quad (12)$$

and

$$z_u^{\text{inrecov}}\ \text{WINREC} = \text{WINRECU}_u \quad (13)$$

The recovery of component u is needed only if its concentration is higher than the maximum value allowed to be discharged to the environment. Otherwise, the recovery process is not applied. This situation is formulated through the following linear disjunction,

$$\begin{bmatrix} Y_u^{\text{Recov}} \\ z_u^{\text{inrecov}} \geq z_u^{\text{MaxEnv}} \\ W_u^{\text{Recovery}} = \text{WINRECU}_u\ \text{EFF}_u \\ \text{Cost}_u^{\text{Recoveryu}} = \text{Cost}_u^{\text{Recu}}\ W_u^{\text{Recovery}}\ H_Y \end{bmatrix} \vee \begin{bmatrix} \neg Y_u^{\text{Recov}} \\ z_u^{\text{inrecov}} \leq z_u^{\text{MaxEnv}} \\ W_u^{\text{Recovery}} = 0 \\ \text{Cost}_u^{\text{Recoveryu}} = 0 \end{bmatrix}$$

where Y_u^{Rccov} is a logical variable that is true when $z_u^{\text{inrecov}} \geq z_u^{\text{MaxEnv}}$; in this case it is necessary to include the recovery process, and the cost associated is a function of the recovery flowrate for component u. Otherwise, when $z_u^{\text{inrecov}} \leq z_u^{\text{MaxEnv}}$, the logical variable Y_u^{Recov} becomes false, and in this case the recovery process is not needed. The binary variable y_u^{Recov} is used to model the logical variable Y_u^{Recov}; therefore, y_u^{Recov} is equal to one when Y_u^{Recov} is true, and y_u^{Recov} is zero when Y_u^{Recov} is false.

Such a disjunction can be formulated as a linear model as follows,

$$z_u^{\text{inrecov}} = z_u^{\text{inrecov1}} + z_u^{\text{inrecov2}} \tag{14}$$

$$\text{WINRECU}_u = \text{WINRECU}_u^1 + \text{WINRECU}_u^2 \tag{15}$$

$$z_u^{\text{inrecov1}} \geq z_u^{\text{Max}} y_u^{\text{Recov}} \tag{16}$$

$$W_u^{\text{Recovery}} = \text{WINRECU}_u^1\ \text{EFF}_u \tag{17}$$

$$\text{Cost}_u^{\text{Recoveryu}} = \text{Cost}_u^{\text{Recu}}\ W_u^{\text{Recovery}}\ H_{\text{Y}} \tag{18}$$

$$z_u^{\text{inrecov2}} \leq z_u^{\text{Max}} \left(1 - y_u^{\text{Recov}}\right) \tag{19}$$

$$z_u^{\text{inrecov1}} \leq M_u^{y^{\text{inrecov}}}\ y_u^{\text{Recov}} \tag{20}$$

$$\text{WINRECOVU}_u^1 \leq M_u^{\text{WINRECOV}}\ y_u^{\text{Recov}} \tag{21}$$

$$\text{Cost}_u^{\text{Recoveryu}} \leq M_u^{\text{Cost}^{\text{Recov}}}\ y_u^{\text{Recov}} \tag{22}$$

$$W_u^{\text{Recovery}} \leq M_u^{W^{\text{Recovery}}}\ y_u^{\text{Recov}} \tag{23}$$

$$z_u^{\text{inrecov2}} \leq M_u^{y^{\text{inrecov}}} \left(1 - y_u^{\text{Recov}}\right) \tag{24}$$

$$\text{WINRECOVU}_u^2 \leq M_u^{\text{WINRECOV}} \left(1 - y_u^{\text{Recov}}\right) \tag{25}$$

Mass Balance at the Recovery Process. It is necessary to calculate the flowrate after the recovery process with a mass balance,

$$\text{W1} = \text{WINREC} - \sum_u W_u^{\text{Recovery}} \tag{26}$$

Component Balances. The composition after the recovery process is calculated as follows,

$$z1_u \text{W1} = \text{WINRECU}_u - W_u^{\text{Recovery}} \tag{27}$$

Toxicity treatment

Toxicity is a property that describes the effect of hazardous chemicals on biological organisms. Chemicals such as phenol, cyanides, ionic metals, among others, are considered as toxic because they may cause death to organisms exposed to them. To quantify the lethal response of a toxic chemical t, the toxicity is represented by the following equation,

$$Y_{\text{t}}(\%\text{Mortality}) = k_{1_{\text{t}}} + k_{2_{\text{t}}} \log(c_{\text{t}}) \tag{28}$$

where Y_{t} is the percentage of organisms that would die if exposed to a concentration c_{t} (in ppm) of chemical t. Regularly, the environmental regulations state maximum mass loads and compositions allowed to be discharged to the environment to yield a mortality of 0% for the organisms exposed to the toxic compounds. Therefore, the toxicity of a chemical compound can be characterized by the flowrate and composition of a toxic compound. For further discussion on toxicity modeling and a comparison of probit expressions for lethality predictions due to toxic exposure, see the paper by Schubach.[37]

The flowrates of the toxic compounds at the inlet of the toxicity treatment process are given by,

$$W_{\text{t}}^{\text{BT}} = \text{WINRECU}_{\text{t}} - W_{\text{t}}^{\text{Recovery}}, \quad \text{t} \in \text{TOX} \tag{29}$$

When there is a toxic compound in the waste stream, an environmental constraint must be satisfied. The environmental regulations are given in terms of the concentration and the mass flowrate of the toxic compounds discharged to the environment. Four scenarios can be considered for the toxicity treatment process of the waste stream, which can be modeled using the following disjunction,

$$\left[\begin{array}{c} Y_{A_{\text{t}}}^{\text{Tox}} \\ \left[\begin{array}{c} Y_{1_{\text{t}}}^{\text{Tox}} \\ z1_{\text{t}} \geq z_{\text{Tox}_{\text{t}}}^{\text{Max}} \\ W_{\text{t}}^{\text{BT}} \leq D_{\text{Tox}_{\text{t}}}^{\text{Max}} \\ W_{\text{t}}^{\text{Rem}} = W_{\text{t}}^{\text{BT}} - z_{\text{Tox}_{\text{t}}}^{\text{Max}} W1 \end{array}\right] \vee \left[\begin{array}{c} Y_{2_{\text{t}}}^{\text{Tox}} \\ z1_{\text{t}} \leq z_{\text{Tox}_{\text{t}}}^{\text{Max}} \\ W_{\text{t}}^{\text{BT}} \geq D_{\text{Tox}_{\text{t}}}^{\text{Max}} \\ W_{\text{t}}^{\text{Rem}} = W_{\text{t}}^{\text{BT}} - D_{\text{Tox}_{\text{t}}}^{\text{Max}} \end{array}\right] \vee \left[\begin{array}{c} Y_{3_{\text{t}}}^{\text{Tox}} \\ z1_{\text{t}} \geq z_{\text{Tox}_{\text{t}}}^{\text{Max}} \\ W_{\text{t}}^{\text{BT}} \geq D_{\text{Tox}_{\text{t}}}^{\text{Max}} \\ W_{\text{t}}^{\text{Rema}} = W_{\text{t}}^{\text{BT}} - z_{\text{Tox}_{\text{t}}}^{\text{Max}} \text{W1} \\ W_{\text{t}}^{\text{Remb}} = W_{\text{t}}^{\text{BT}} - D_{\text{Tox}_{\text{t}}}^{\text{Max}} \\ \left[\begin{array}{c} Y_{3\text{a}_{\text{t}}}^{\text{Tox}} \\ W_{\text{t}}^{\text{Rema}} \geq W_{\text{t}}^{\text{Remb}} \\ W_{\text{t}}^{\text{Rem}} = W_{\text{t}}^{\text{Rema}} \end{array}\right] \vee \left[\begin{array}{c} Y_{3\text{b}_{\text{t}}}^{\text{Tox}} \\ W_{\text{t}}^{\text{Rema}} \leq W_{\text{t}}^{\text{Remb}} \\ W_{\text{t}}^{\text{Rem}} = W_{\text{t}}^{\text{Rema}} \end{array}\right] \end{array}\right] \\ \text{Cost}_{\text{t}}^{\text{Toxicity}} = W_{\text{t}}^{\text{Rem}} \text{Cost}_{\text{t}}^{\text{Toxict}}\ H_{\text{Y}} \end{array}\right] \vee \left[\begin{array}{c} Y_{\text{B}_{\text{t}}}^{\text{Tox}} \\ z1_{\text{t}} \leq z_{\text{Tox}_{\text{t}}}^{\text{Max}} \\ W_{\text{t}}^{\text{BT}} \leq D_{\text{Tox}_{\text{t}}}^{\text{Max}} \\ W_{\text{t}}^{\text{Rem}} = 0 \\ \text{Cost}_{\text{t}}^{\text{Toxicity}} = 0 \end{array}\right], \quad \text{t} \in \text{TOX}$$

Here, $\boldsymbol{Y}_{\mathrm{A_t}}^{\mathrm{Tox}}$ and $\boldsymbol{Y}_{\mathrm{B_t}}^{\mathrm{Tox}}$ are logical variables that are used to model the existence or not existence of the toxicity treatment process. $\boldsymbol{Y}_{1_\mathrm{t}}^{\mathrm{Tox}}$, $\boldsymbol{Y}_{2_\mathrm{t}}^{\mathrm{Tox}}$ and $\boldsymbol{Y}_{3_\mathrm{t}}^{\mathrm{Tox}}$ are logical variables used to model three different scenarios when the toxicity treatment process is needed. The first scenario, $\boldsymbol{Y}_{1_\mathrm{t}}^{\mathrm{Tox}}$, applies when the mass flowrate of the toxic compound t in the waste stream is lower than the one given by the toxicity constraint, but its composition is higher than the maximum allowed value; in this case, the mass removed of the toxic compound is determined from its composition. The second scenario, $\boldsymbol{Y}_{2_\mathrm{t}}^{\mathrm{Tox}}$, models the situation when the composition satisfies the toxicity constraint but the mass flowrate does not; in this case, the mass removed of the toxic compound t is determined from its mass flow rate. The scenario $\boldsymbol{Y}_{3_\mathrm{t}}^{\mathrm{Tox}}$ considers the situation when both the composition and mass flowrate of t do not satisfy the toxicity constraints; in this case, we have two inner scenarios to determine the mass of t to be removed, modeled with the logical variables $\boldsymbol{Y}_{3\mathrm{a_t}}^{\mathrm{Tox}}$ and $\boldsymbol{Y}_{3\mathrm{b_t}}^{\mathrm{Tox}}$, which apply one when the composition and the other one when the mass flowrate of t is the dominant term with respect to the toxicity constraint. The problem is modeled in this form to yield linear terms inside the disjunctions, and the following set of linear equations can be written.

First, we have the following logical relations,

$$y_{A_\mathrm{t}}^{\mathrm{Tox}} + y_{\mathrm{B_t}}^{\mathrm{Tox}} = 1, \quad \mathrm{t} \in \mathrm{TOX} \tag{30}$$

$$y_{\mathrm{A_t}}^{\mathrm{Tox}} = y_{1_\mathrm{t}}^{\mathrm{Tox}} + y_{2_\mathrm{t}}^{\mathrm{Tox}} + y_{3_\mathrm{t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{31}$$

$$y_{3_\mathrm{t}}^{\mathrm{Tox}} = y_{3\mathrm{a_t}}^{\mathrm{Tox}} + y_{3\mathrm{b_t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{32}$$

The disaggregated variables are,

$$z1_\mathrm{t} = z1_\mathrm{t}^1 + z1_\mathrm{t}^2 + z1_\mathrm{t}^3 + z1_\mathrm{t}^4, \quad \mathrm{t} \in \mathrm{TOX} \tag{33}$$

$$W_\mathrm{t}^{\mathrm{BT}} = W_\mathrm{t}^{\mathrm{BT1}} + W_\mathrm{t}^{\mathrm{BT2}} + W_\mathrm{t}^{\mathrm{BT3}} + W_\mathrm{t}^{\mathrm{BT4}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{34}$$

$$\mathrm{W1} = \mathrm{W1}^1 + \mathrm{W1}^2 + \mathrm{W1}^3 + \mathrm{W1}^4, \quad \mathrm{t} \in \mathrm{TOX} \tag{35}$$

$$W_\mathrm{t}^{\mathrm{Rem}} = W_\mathrm{t}^{\mathrm{Rem1}} + W_\mathrm{t}^{\mathrm{Rem2}} + W_\mathrm{t}^{\mathrm{Rem3}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{36}$$

$$W_\mathrm{t}^{\mathrm{Rem3}} = W_\mathrm{t}^{\mathrm{Rem3a}} + W_\mathrm{t}^{\mathrm{Rem3b}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{37}$$

$$W_\mathrm{t}^{\mathrm{Rema3}} = W_\mathrm{t}^{\mathrm{Rema3a}} + W_\mathrm{t}^{\mathrm{Rema3b}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{38}$$

$$W_\mathrm{t}^{\mathrm{Remb3}} = W_\mathrm{t}^{\mathrm{Remb3a}} + W_\mathrm{t}^{\mathrm{Remb3b}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{39}$$

The equations for the first disjunction are,

$$z1_\mathrm{t}^1 \geq z_{\mathrm{Tox_t}}^{\mathrm{Max}}\, y_{1_\mathrm{t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{40}$$

$$W_\mathrm{t}^{\mathrm{BT1}} \leq D_{\mathrm{Tox_t}}^{\mathrm{Max}}\, y_{1_\mathrm{t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{41}$$

$$W_\mathrm{t}^{\mathrm{Rem1}} = W_\mathrm{t}^{\mathrm{BT1}} - z_{\mathrm{Tox_t}}^{\mathrm{Max}} W1^1, \quad \mathrm{t} \in \mathrm{TOX} \tag{42}$$

For the second disjunction, we have,

$$z1_\mathrm{t}^2 \leq z_{\mathrm{Tox_t}}^{\mathrm{Max}}\, y_{2_\mathrm{t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{43}$$

$$W_\mathrm{t}^{\mathrm{BT2}} \geq D_{\mathrm{Tox_t}}^{\mathrm{Max}}\, y_{2_\mathrm{t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{44}$$

$$W_\mathrm{t}^{\mathrm{Rem2}} = W_\mathrm{t}^{\mathrm{BT2}} - D_{\mathrm{Tox_t}}^{\mathrm{Max}}\, y_{2_\mathrm{t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{45}$$

For the third disjunction, the following model applies,

$$z1_\mathrm{t}^3 \geq z_{\mathrm{Tox_t}}^{\mathrm{Max}}\, y_{3_\mathrm{t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{46}$$

$$W_\mathrm{t}^{\mathrm{BT3}} \geq D_{\mathrm{Tox_t}}^{\mathrm{Max}}\, y_{3_\mathrm{t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{47}$$

$$W_\mathrm{t}^{\mathrm{Rema3}} = W_\mathrm{t}^{\mathrm{BT3}} - z_{\mathrm{Tox_t}}^{\mathrm{Max}}\ \mathrm{W1}^3, \quad \mathrm{t} \in \mathrm{TOX} \tag{48}$$

$$W_\mathrm{t}^{\mathrm{Remb3}} = W_\mathrm{t}^{\mathrm{BT3}} - D_{\mathrm{Tox_t}}^{\mathrm{Max}}\, y_{3_\mathrm{t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{49}$$

where for subsection 3a,

$$W_\mathrm{t}^{\mathrm{Rema3a}} \geq W_\mathrm{t}^{\mathrm{Remb3a}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{50}$$

$$W_\mathrm{t}^{\mathrm{Rem3a}} = W_\mathrm{t}^{\mathrm{Rema3a}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{51}$$

and for subsection 3b,

$$W_\mathrm{t}^{\mathrm{Rema3b}} \leq W_\mathrm{t}^{\mathrm{Remb3b}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{52}$$

$$W_\mathrm{t}^{\mathrm{Rem3b}} = W_\mathrm{t}^{\mathrm{Remb3b}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{53}$$

The total cost for the toxicity treatment is given by,

$$\mathrm{Cost}_\mathrm{t}^{\mathrm{Toxicity}} = W_\mathrm{t}^{\mathrm{Rem}}\ \mathrm{Cost}_\mathrm{t}^{\mathrm{Toxic}} H_\mathrm{Y}, \quad \mathrm{t} \in \mathrm{TOX} \tag{54}$$

For the fourth disjunction, we have,

$$z1_\mathrm{t}^4 \leq z_{\mathrm{Tox_t}}^{\mathrm{Max}}\, y_{\mathrm{B_t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{55}$$

$$W_\mathrm{t}^{\mathrm{BT4}} \leq D_{\mathrm{Tox_t}}^{\mathrm{Max}}\, y_{\mathrm{B_t}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{56}$$

Upper limits for the disaggregated variables are incorporated:

$$z1_t^1 \le M_t^{z_{\mathrm{Tox}}^{\mathrm{Max}}}\ y_{1_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{57}$$

$$\mathrm{W}_t^{\mathrm{BT1}} \le M_t^{W_{\mathrm{Tox}}^{\mathrm{Max}}}\ y_{1_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{58}$$

$$W1^1 \le M^{\mathrm{W1}^{\mathrm{Max}}}\ y_{1_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{59}$$

$$W_t^{\mathrm{Rem1}} \le M_t^{W^{\mathrm{Rem}}}\ y_{1_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{60}$$

$$z1_t^2 \le M_t^{z_{\mathrm{Tox}}^{\mathrm{Max}}}\ y_{2_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{61}$$

$$W_t^{\mathrm{BT2}} \le M_t^{W_{\mathrm{Tox}}^{\mathrm{Max}}}\ y_{2_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{62}$$

$$W1^2 \le M^{\mathrm{W1}^{\mathrm{Max}}\ y_{2_t}^{\mathrm{Tox}}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{63}$$

$$W_t^{\mathrm{Rem2}} \le M_t^{W^{\mathrm{Rem}}}\ y_{2_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{64}$$

$$z1_t^3 \le M_t^{z_{\mathrm{Tox}}^{\mathrm{Max}}}\ y_{3_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{65}$$

$$W_t^{\mathrm{BT3}} \le M_t^{W_{\mathrm{Tox}}^{\mathrm{Max}}}\ y_{3_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{66}$$

$$W1^3 \le M^{W1^{\mathrm{Max}}}\ y_{3_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{67}$$

$$W_t^{\mathrm{Rem3}} \le M_t^{W^{\mathrm{Rem}}}\ y_{3_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{68}$$

$$W_t^{\mathrm{Rem3a}} \le M_t^{W^{\mathrm{Rem}}}\ y_{3a_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{69}$$

$$W_t^{\mathrm{Rema3a}} \le M_t^{W^{\mathrm{Rem}}}\ y_{3a_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{70}$$

$$W_t^{\mathrm{Remb3a}} \le M_t^{W^{\mathrm{Rem}}}\ y_{3a_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{71}$$

$$W_t^{\mathrm{Rem3b}} \le M_t^{W^{\mathrm{Rem}}}\ y_{3b_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{72}$$

$$W_t^{\mathrm{Rema3b}} \le M_t^{W^{\mathrm{Rem}}}\ y_{3b_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{73}$$

$$W_t^{\mathrm{Remb3b}} \le M_t^{W^{\mathrm{Rem}}}\ y_{3b_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{74}$$

$$\mathrm{z}1_t^4 \le M_t^{z_{\mathrm{Tox}}^{\mathrm{Max}}}\ y_{\mathrm{B}_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{75}$$

$$W_t^{\mathrm{BT4}} \le M_t^{W_{\mathrm{Tox}}^{\mathrm{Max}}}\ y_{\mathrm{B}_t}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{76}$$

$$\mathrm{W}1^4 \le M^{\mathrm{W1}^{\mathrm{Max}}}\ y_{\mathrm{B}}^{\mathrm{Tox}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{77}$$

Mass Balance in the Unit for Toxicity Treatment. It is necessary to formulate a mass balance around the toxicity treatment unit to find the flowrate at the exit conditions,

$$\mathrm{W2} = \mathrm{W1} - \sum_{\mathrm{i} \in \mathrm{TOX}} W_t^{\mathrm{Rem}} \tag{78}$$

Component Balances. A component balance is used to determine the composition at the exit of the toxicity treatment unit,

$$\mathrm{W2}\ z2_t = \mathrm{W1}\ z1_t - W_t^{\mathrm{Rem}}, \quad \mathrm{t} \in \mathrm{TOX} \tag{79}$$

Aeration process

Theoretical oxygen demand (ThOD) is the theoretical amount of oxygen required to oxidize an organic compound to its final oxidation products. ThOD in wastewater streams has been strictly regulated since the discharge of high values of ThOD would reduce significantly the oxygen available and cause adverse effects on the aquatic flora and fauna. Because the ThOD in the waste stream depends on the many compounds present, it would be difficult to quantify it with the composition of the waste stream. In this case, the ThOD in the waste stream is calculated using a property balance, because the property ThOD for each process source discharged to the waste stream is known before the optimization process. Therefore, the theoretical oxygen demand for the waste stream can be calculated from the following equation,

$$\mathrm{ThOD}^{\mathrm{Total}} = \sum_{i \in \mathrm{SOURCES}} (\mathrm{Ratio}_i\ \mathrm{ThOD}_i) \tag{80}$$

where ThOD_i is the theoretical oxygen demand for the process source i, which is a parameter known before the optimization process.

To get linear disjunctions, we define the following variables,

$$W^{\mathrm{ThOD}} = \frac{\mathrm{ThOD}^{\mathrm{Total}}\ \mathrm{W2}}{\rho_{\mathrm{waste}}} \tag{81}$$

and

$$W^{\mathrm{ThOD}^{\mathrm{Reg}}} = \frac{\mathrm{ThOD}^{\mathrm{Reg}}\ \mathrm{W2}}{\rho_{\mathrm{waste}}} \tag{82}$$

The aeration process is needed only when the ThOD for a waste stream is higher than the value stated by the environmental regulation. Therefore, the following disjunction applies for the aeration process,

$$\begin{bmatrix} Y^{\text{ThOD}} \\ W^{\text{ThOD}} \geq W^{\text{ThOD}^{\text{Reg}}} \\ \text{Cost}^{\text{ThOD}} = \left(W^{\text{ThOD}} - W^{\text{ThOD}^{\text{Reg}}}\right)\left[\frac{29}{32^{*}0.21^{*}10^{3}}\right]\text{Cost}^{\text{Aeration}}\ H_{\text{Y}} \end{bmatrix} \vee \begin{bmatrix} \neg Y^{\text{ThOD}} \\ W^{\text{ThOD}} \leq W^{\text{ThOD}^{\text{Reg}}} \\ \text{Cost}^{\text{ThOD}} = 0 \end{bmatrix}$$

where Y^{ThOD} is a logical variable that is true when $W^{\text{ThOD}} \geq W^{\text{ThOD}^{\text{Reg}}}$; in that case, the cost of the aeration process is calculated (the factors in parenthesis are used to get proper units). Otherwise, when the ThOD for the waste stream is lower than the one given by the environmental regulation, the cost of the aeration process is zero. This disjunction can be modeled as follows. First, we use the disaggregated variables,

$$W^{\text{ThOD}} = W^{\text{ThOD}^{1}} + W^{\text{ThOD}^{2}} \tag{83}$$

$$W^{\text{ThOD}^{\text{Reg}}} = W^{\text{ThOD}^{\text{Reg}^{1}}} + W^{\text{ThOD}^{\text{Reg}^{2}}} \tag{84}$$

The constraints for the first disjunction are,

$$W^{\text{ThOD}^{1}} \geq W^{\text{ThOD}^{\text{Reg}^{1}}} \tag{85}$$

$$\text{Cost}^{\text{ThOD}} = \left(W^{\text{ThOD}^{1}} - W^{\text{ThOD}^{\text{Reg}^{1}}}\right) \times \left[\frac{29}{32^{*}0.21^{*}10^{3}}\right]\text{Cost}^{\text{Aeration}}\ H_{\text{Y}} \tag{86}$$

and for the second disjunction,

$$W^{\text{ThOD}^{2}} \leq W^{\text{ThOD}^{\text{Reg}^{2}}} \tag{87}$$

Finally, limits on the disaggregated variables are imposed,

$$W^{\text{ThOD}^{1}} \leq M^{W^{\text{ThOD}}}\ y^{\text{ThOD}} \tag{88}$$

$$W^{\text{ThOD}^{\text{Reg}^{1}}} \leq M^{W^{\text{ThOD}}}\ y^{\text{ThOD}} \tag{89}$$

$$\text{Cost}^{\text{ThOD}} \leq M^{\text{Cost}^{\text{ThOD}}}\ y^{\text{ThOD}} \tag{90}$$

$$W^{\text{ThOD}^{2}} \leq M^{W^{\text{ThOD}}}\left(1 - y^{\text{ThOD}}\right) \tag{91}$$

$$W^{\text{ThOD}^{\text{Reg}^{2}}} \leq M^{W^{\text{ThOD}}}\left(1 - y^{\text{ThOD}}\right) \tag{92}$$

Notice that in the previous disjunction all relationships are linear.

Neutralization process

pH is an important property to be regulated in waste discharges. High and low values of pH for the waste streams are considered extremely hazardous; therefore, waste streams sometimes need to be treated before be discharged to the environment to satisfy pH environmental regulations. The pH estimation for a waste stream with many compounds is a difficult task; in this case, we resort to the property integration formulation by El-Halwagi et al.[28] and use the following property contribution relationship,

$$10^{\text{pH}_{\text{mean}}} = \sum_{i \in \text{NSOURCES}} \left(\text{Ratio}_{i}\ 10^{\text{pH}_{i}}\right) \tag{93}$$

where pH_i is the individual pH for process source i that is known before the optimization process.

Then, the pOH for the waste stream is calculated as follows,

$$\text{pOH}_{\text{mean}} = 14 - \text{pH}_{\text{mean}} \tag{94}$$

We also have,

$$\text{W3} = \text{W2} \tag{95}$$

The concentration of ions H_3O^+ and OH^- in the waste stream are determined as follows,

$$(W_{\text{H3O}}) = 10^{-\text{pH}_{\text{mean}}} \tag{96}$$

$$(W_{\text{OH}}) = 10^{-\text{pOH}_{\text{mean}}} \tag{97}$$

Since the highest value for pH and pOH is 14, we can impose the following limits to avoid singularities,

$$W_{\text{H3O}} \geq 10^{-14} \tag{98}$$

$$W_{\text{OH}} \geq 10^{-14} \tag{99}$$

The total moles of H_3O^+ and OH^- discharged into the waste stream are,

$$\text{Total}^{\text{H3O}} = \frac{\text{W3}W_{\text{H3O}}}{\rho_{\text{waste}}} \tag{100}$$

$$\text{Total}^{\text{OH}} = \frac{W3W_{\text{OH}}}{\rho_{\text{waste}}} \tag{101}$$

Three cases may occur for the neutralization process. The pH of the waste stream can be lower than the value given by the environmental regulation; in this case, it is necessary to add an amount of base to be determined. The second case arises when the pH of the waste stream is higher than the one given by the environmental regulation; in this case, it is necessary to add an amount of acid. Finally, if the pH of the waste stream meets the environmental regulation, the neutralization process is not needed. Therefore, to calculate the cost of acid or base added to a waste stream, as needed to satisfy the environmental regulations, the following disjunction can be written,

$$\begin{bmatrix} Y_{\mathrm{B}}^{\mathrm{Neu}} \\ \mathrm{pH}_{\mathrm{mean}} \leq 5.5 \\ \mathrm{pH}_{\mathrm{discharged}} = 5.5 \\ \mathrm{Base} = \frac{\mathrm{Total}^{\mathrm{H3O}} - 10^{-5.5}\ \mathrm{Waste4}}{\mathrm{OH}_{\mathrm{conc}}} \\ \mathrm{Acid} = 0 \\ \mathrm{Cost}^{\mathrm{Neu}} = \mathrm{Base\ Cost}^{\mathrm{Base}}\ H_{\mathrm{Y}} \end{bmatrix}$$

$$\vee \begin{bmatrix} Y_{\mathrm{A}}^{\mathrm{Neu}} \\ \mathrm{pH}_{\mathrm{mean}} \geq 9 \\ \mathrm{pH}_{\mathrm{discharged}} = 9 \\ \mathrm{Base} = 0 \\ \mathrm{Acid} = \frac{\mathrm{Total}^{\mathrm{OH}} - 10^{-5}\ \mathrm{Waste4}}{\mathrm{H3O}_{\mathrm{conc}}} \\ \mathrm{Cost}^{\mathrm{Neu}} = \mathrm{Acid\ Cost}^{\mathrm{Acid}}\ H_{\mathrm{Y}} \end{bmatrix} \vee \begin{bmatrix} Y_{\mathrm{C}}^{\mathrm{Neu}} \\ \mathrm{pH}_{\mathrm{mean}} \geq 5.5 \\ \mathrm{pH}_{\mathrm{mean}} \leq 9 \\ \mathrm{pH}_{\mathrm{discharged}} = \mathrm{pH}_{\mathrm{mean}} \\ \mathrm{Base} = 0 \\ \mathrm{Acid} = 0 \\ \mathrm{Cost}^{\mathrm{Neu}} = 0 \end{bmatrix}$$

Here, $Y_{\mathrm{B}}^{\mathrm{Neu}}$, $Y_{\mathrm{A}}^{\mathrm{Neu}}$, and $Y_{\mathrm{C}}^{\mathrm{Neu}}$ are logical variables for the base treatment, acid treatment, and no neutralization treatment, respectively. $\mathrm{pH}_{\mathrm{discharged}}$ is the pH for the waste stream discharged to the environment, and Acid and Base are the amounts of acid and base added in the neutralization process to yield $\mathrm{pH}_{\mathrm{discharged}}$. This disjunction can be modeled as follows,

$$y_{\mathrm{B}}^{\mathrm{Neu}} + y_{\mathrm{A}}^{\mathrm{Neu}} + y_{\mathrm{C}}^{\mathrm{Neu}} = 1 \tag{102}$$

Then, it is necessary to define the following disaggregated variables,

$$\mathrm{pH}_{\mathrm{mean}} = \mathrm{pH}_{\mathrm{mean}}^{\mathrm{B}} + \mathrm{pH}_{\mathrm{mean}}^{\mathrm{A}} + \mathrm{pH}_{\mathrm{mean}}^{\mathrm{C}} \tag{103}$$

$$\mathrm{pH}_{\mathrm{discharged}} = \mathrm{pH}_{\mathrm{discharged}}^{\mathrm{B}} + \mathrm{pH}_{\mathrm{discharged}}^{\mathrm{A}} + \mathrm{pH}_{\mathrm{discharged}}^{\mathrm{C}} \tag{104}$$

$$\mathrm{Total}^{\mathrm{H3O}} = \mathrm{Total}^{\mathrm{H3O}^{\mathrm{B}}} + \mathrm{Total}^{\mathrm{H3O}^{\mathrm{A}}} + \mathrm{Total}^{\mathrm{H3O}^{\mathrm{C}}} \tag{105}$$

$$\mathrm{Total}^{\mathrm{OH}} = \mathrm{Total}^{\mathrm{OH}^{\mathrm{B}}} + \mathrm{Total}^{\mathrm{OH}^{\mathrm{A}}} + \mathrm{Total}^{\mathrm{OH}^{\mathrm{C}}} \tag{106}$$

$$\mathrm{Waste4} = \mathrm{Waste4}^{\mathrm{B}} + \mathrm{Waste4}^{\mathrm{A}} + \mathrm{Waste4}^{\mathrm{C}} \tag{107}$$

$$\mathrm{Cost}^{\mathrm{Neu}} = \mathrm{Cost}^{\mathrm{Neu}^{\mathrm{B}}} + \mathrm{Cost}^{\mathrm{Neu}^{\mathrm{A}}} \tag{108}$$

For the first disjunction we have,

$$\mathrm{pH}_{\mathrm{mean}}^{\mathrm{B}} \leq 5.5\, y_{\mathrm{B}}^{\mathrm{Neu}} \tag{109}$$

$$\mathrm{pH}_{\mathrm{discharged}}^{\mathrm{B}} = 5.5\, y_{\mathrm{B}}^{\mathrm{Neu}} \tag{110}$$

$$\mathrm{Base} = \frac{\mathrm{Total}^{\mathrm{H3O}^{\mathrm{B}}} - 10^{-5.5}\mathrm{Waste4}^{\mathrm{B}}}{\mathrm{OH}_{\mathrm{conc}}} \tag{111}$$

$$\mathrm{Cost}^{\mathrm{Neu}^{\mathrm{B}}} = \mathrm{Base\ Cost}^{\mathrm{Base}}\ H_{\mathrm{Y}} \tag{112}$$

For the second disjunction,

$$\mathrm{pH}_{\mathrm{mean}}^{\mathrm{A}} \geq 9\, y_{\mathrm{A}}^{\mathrm{Neu}} \tag{113}$$

$$\mathrm{pH}_{\mathrm{discharged}}^{\mathrm{A}} = 5.5\, y_{\mathrm{A}}^{\mathrm{Neu}} \tag{114}$$

$$\mathrm{Acid} = \frac{\mathrm{Total}^{\mathrm{OH}^{\mathrm{A}}} - 10^{-5}\ \mathrm{Waste4}^{\mathrm{A}}}{\mathrm{H3O}_{\mathrm{conc}}} \tag{115}$$

$$\mathrm{Cost}^{\mathrm{Neu}^{\mathrm{A}}} = \mathrm{Acid\ Cost}^{\mathrm{Acid}}\ H_{\mathrm{Y}} \tag{116}$$

And, for the third disjunction,

$$\mathrm{pH}_{\mathrm{mean}}^{\mathrm{C}} \leq 9\, y_{\mathrm{C}}^{\mathrm{Neu}} \tag{117}$$

$$\mathrm{pH}_{\mathrm{mean}}^{\mathrm{C}} \geq 5.5\, y_{\mathrm{C}}^{\mathrm{Neu}} \tag{118}$$

$$\mathrm{pH}_{\mathrm{discharged}}^{\mathrm{C}} = \mathrm{pH}_{\mathrm{mean}}^{\mathrm{C}} \tag{119}$$

Finally, we need the following upper limits for the disaggregated variables,

$$\mathrm{pH}_{\mathrm{mean}}^{\mathrm{B}} \leq M^{\mathrm{pH}}\ y_{\mathrm{B}}^{\mathrm{Neu}} \tag{120}$$

$$\mathrm{Total}^{\mathrm{H3O}^{\mathrm{B}}} \leq M^{\mathrm{Total}^{\mathrm{H3O}}}\ y_{\mathrm{B}}^{\mathrm{Neu}} \tag{121}$$

$$\mathrm{Total}^{\mathrm{OH}^{\mathrm{B}}} \leq M^{\mathrm{Total}^{\mathrm{OH}}}\ y_{\mathrm{B}}^{\mathrm{Neu}} \tag{122}$$

$$\mathrm{Waste4}^{\mathrm{B}} \leq M^{\mathrm{Waste4}}\ y_{\mathrm{B}}^{\mathrm{Neu}} \tag{123}$$

$$\mathrm{pH}_{\mathrm{discharged}}^{\mathrm{B}} \leq M^{\mathrm{pH}}\ y_{\mathrm{B}}^{\mathrm{Neu}} \tag{124}$$

$$\mathrm{Base} \leq M^{\mathrm{Base}}\ y_{\mathrm{B}}^{\mathrm{Neu}} \tag{125}$$

$$\mathrm{Cost}^{\mathrm{Neu}^{\mathrm{B}}} \leq M^{\mathrm{Cost}^{\mathrm{Neu}}}\ y_{\mathrm{B}}^{\mathrm{Neu}} \tag{126}$$

$$\mathrm{pH}_{\mathrm{mean}}^{\mathrm{A}} \leq M^{\mathrm{pH}}\ y_{\mathrm{A}}^{\mathrm{Neu}} \tag{127}$$

$$\mathrm{Total}^{\mathrm{H3O}^{\mathrm{A}}} \leq M^{\mathrm{Total}^{\mathrm{H3O}}}\ y_{\mathrm{A}}^{\mathrm{Neu}} \tag{128}$$

$$\mathrm{Total}^{\mathrm{OH}^{\mathrm{A}}} \leq M^{\mathrm{Total}^{\mathrm{OH}}}\ y_{\mathrm{A}}^{\mathrm{Neu}} \tag{129}$$

$$\mathrm{Waste4}^{\mathrm{A}} \leq M^{\mathrm{Waste4}}\ y_{\mathrm{A}}^{\mathrm{Neu}} \tag{130}$$

$$\mathrm{pH}_{\mathrm{discharged}}^{\mathrm{A}} \leq M^{\mathrm{pH}}\ y_{\mathrm{A}}^{\mathrm{Neu}} \tag{131}$$

$$\mathrm{Acid} \leq M^{\mathrm{Acid}}\ y_{\mathrm{A}}^{\mathrm{Neu}} \tag{132}$$

$$\mathrm{Cost}^{\mathrm{Neu}^{\mathrm{A}}} \leq M^{\mathrm{Cost}^{\mathrm{Neu}}}\ y_{\mathrm{A}}^{\mathrm{Neu}} \tag{133}$$

$$\mathrm{pH}_{\mathrm{mean}}^{\mathrm{C}} \leq M^{\mathrm{pH}}\ y_{\mathrm{C}}^{\mathrm{Neu}} \tag{134}$$

$$\mathrm{Total}^{\mathrm{H3O}^{\mathrm{C}}} \leq M^{\mathrm{Total}^{\mathrm{H3O}}}\ y_{\mathrm{C}}^{\mathrm{Neu}} \tag{135}$$

$$\mathrm{Total}^{\mathrm{OH}^{\mathrm{C}}} \leq M^{\mathrm{Total}^{\mathrm{OH}}}\ y_{\mathrm{C}}^{\mathrm{Neu}} \tag{136}$$

$$\mathrm{Waste4}^{\mathrm{C}} \leq M^{\mathrm{Waste4}}\ y_{\mathrm{C}}^{\mathrm{Neu}} \tag{137}$$

$$\mathrm{pH}_{\mathrm{discharged}}^{\mathrm{C}} \leq M^{\mathrm{pH}}\ y_{\mathrm{C}}^{\mathrm{Neu}} \tag{138}$$

The total flowrate after the neutralization process is given by,

$$\mathrm{W4} = \mathrm{W3} + \mathrm{Base}\ \rho_{\mathrm{Base}} + \mathrm{Acid}\ \rho_{\mathrm{Acid}} \tag{139}$$

$$\mathrm{Waste4} = \frac{\mathrm{W3}}{\rho_{\mathrm{waste}}} + \mathrm{Base} + \mathrm{Acid} \tag{140}$$

Color

Frequently, the industrial waste discharges (e.g., forestry products, textile, food, tannery) produce effluents that present a strong level of coloration. The level of color in industrial waste is regulated by legislations. The color may be quantified in terms of the absorbance of the stream. We can know the absorbance of the individual stream *i* before the optimization process, then we can calculate the index for the color (or absorbance) through a linear combination of the streams discharged, as follows,

$$\mathrm{Color}_{\mathrm{mean}} = \sum_{i \in \mathrm{NSOURCES}} (\mathrm{Ratio}_i\ \mathrm{Color}_i) \tag{141}$$

To get a linear disjunction, we define the following variables,

$$\mathrm{W4}^{\mathrm{Color}} = W4\ \mathrm{Color}_{\mathrm{mean}} \tag{142}$$

$$\mathrm{W4}^{\mathrm{ColorReg}} = W4\ \mathrm{Color}_{\mathrm{Reg}} \tag{143}$$

The color treatment process is applied when the color index in the waste steam is higher than the value stated by the environmental regulation. Then, we can formulate the following disjunction,

$$\begin{bmatrix} Y^{\mathrm{Color}} \\ \mathrm{W4}^{\mathrm{Color}} \geq \mathrm{W4}^{\mathrm{ColorReg}} \\ \mathrm{Cost}^{\mathrm{Color}} = (\mathrm{W4}^{\mathrm{Color}} - \mathrm{W4}^{\mathrm{ColorReg}})\mathrm{Costu}^{\mathrm{Color}}\ H_{\mathrm{Y}} \end{bmatrix} \vee \begin{bmatrix} \neg Y^{\mathrm{Color}} \\ \mathrm{W4}^{\mathrm{Color}} \leq \mathrm{W4}^{\mathrm{ColorReg}} \\ \mathrm{Cost}^{\mathrm{Color}} = 0 \end{bmatrix}$$

where Y^{Color} is a logical variable that is true when the index of color for the waste stream is higher than the one given by the environmental regulation. This disjunction can be modeled as follows,

$$\mathrm{W4}^{\mathrm{Color}} = \mathrm{W4}^{\mathrm{Color}^{1}} + \mathrm{W4}^{\mathrm{Color}^{2}} \tag{144}$$

$$\mathrm{W4}^{\mathrm{ColorReg}} = \mathrm{W4}^{\mathrm{ColorReg}^{1}} + \mathrm{W4}^{\mathrm{ColorReg}^{2}} \tag{145}$$

$$\mathrm{W4}^{\mathrm{Color}^{t}} \geq \mathrm{W4}^{\mathrm{ColorReg}^{1}} \tag{146}$$

$$\mathrm{Cost}^{\mathrm{Color}} = \left(\mathrm{W4}^{\mathrm{Color}} - \mathrm{W4}^{\mathrm{ColoReg}^{1}}\right)\mathrm{Costu}^{\mathrm{Color}}\ H_{\mathrm{Y}} \tag{147}$$

$$\mathrm{W4}^{\mathrm{Color}^{2}} \leq \mathrm{W4}^{\mathrm{ColorReg}^{2}} \tag{148}$$

$$\mathrm{W4}^{\mathrm{Color}^{1}} \leq M^{\mathrm{W4}^{\mathrm{Color}}}\ y^{\mathrm{Color}} \tag{149}$$

$$\mathrm{W4}^{\mathrm{ColorReg}^{1}} \leq M^{\mathrm{W4}^{\mathrm{Color}}}\ y^{\mathrm{Color}} \tag{150}$$

$$\mathrm{W4}^{\mathrm{Color}^{2}} \leq M^{\mathrm{W4}^{\mathrm{Color}}}\left(1 - y^{\mathrm{Color}}\right) \tag{151}$$

$$\mathrm{W4}^{\mathrm{ColorReg}^2} \le M^{\mathrm{W4}^{\mathrm{Color}}}\left(1 - y^{\mathrm{Color}}\right) \tag{152}$$

Odor

Odor nuisance from different industrial sources have become a serious environmental concern. One reason for the increasing number of odor complaints is that industrial plants have been located nearer to urbanized and residential areas.[38] The odor compounds often do not induce serious human health problems; however, they are the cause of nose, eye, and throat irritation, headaches, nauseas, diarrhea, vomiting, cough, sleep disturbances, and loss of appetite.[39] In most cases, odor substances are sulfides, nitrogen compounds, organic acids, aldehydes, and ketones, but measurement of odor emissions is difficult because of the large number of compounds present in the waste streams that cause odor. The European Norm EN 13725[40] and the ASTM Standard of Practice E679-91[41] measure the total odor impact in terms of odor units (ou/m^3 or ou/ft^3) and does not quantify the specific chemicals responsible for the odor. The instrument used to quantify the odor is called olfactometer. Therefore, the odor of the individual waste stream is known before the optimization process, and we can calculate the total odor of the waste stream using the property integration technique as follows,

$$\mathrm{Odor}_{\mathrm{mean}} = \sum_{i \in \mathrm{NSOURCES}} \left(\mathrm{Ratio}_i \ \mathrm{Odor}_i\right) \tag{153}$$

$$\mathrm{W5}^{\mathrm{Odor}} = \frac{\mathrm{W4\ Odor}_{\mathrm{mean}}}{\rho_{\mathrm{waste}}} \tag{154}$$

$$\mathrm{W5}^{\mathrm{OdorReg}} = \frac{\mathrm{W\ 4Odor}_{\mathrm{Reg}}}{\rho_{\mathrm{waste}}} \tag{155}$$

The odor treatment process is applied to the waste stream only when the odor index is higher than the one given by the environmental regulation. Otherwise, when the waste stream satisfies the environmental regulation for the odor index, the associated cost for the odor process is set as zero. Therefore, the following disjunction is formulated,

$$\begin{bmatrix} Y^{\mathrm{Odor}} \\ \mathrm{W5}^{\mathrm{Odor}} \ge \mathrm{W5}^{\mathrm{OdorReg}} \\ \mathrm{Cost}^{\mathrm{Odor}} = \left(\mathrm{W5}^{\mathrm{Odor}} - \mathrm{W5}^{\mathrm{OdorReg}}\right)\mathrm{Costu}^{\mathrm{Odor}}\ H_{\mathrm{y}} \end{bmatrix} \vee \begin{bmatrix} \neg Y^{\mathrm{Odor}} \\ \mathrm{W5}^{\mathrm{Odor}} \le \mathrm{W5}^{\mathrm{OdorReg}} \\ \mathrm{Cost}^{\mathrm{Odor}} = 0 \end{bmatrix}$$

The disjunction is modeled as follows,

$$\mathrm{W5}^{\mathrm{Odor}} = \mathrm{W5}^{\mathrm{Odor}^1} + \mathrm{W5}^{\mathrm{Odor}^2} \tag{156}$$

$$\mathrm{W5}^{\mathrm{OdorReg}} = \mathrm{W5}^{\mathrm{OdorReg}^1} + \mathrm{W5}^{\mathrm{OdorReg}^2} \tag{157}$$

$$\mathrm{W5}^{\mathrm{Odor}^1} \ge \mathrm{W5}^{\mathrm{OdorReg}^1} \tag{158}$$

$$\mathrm{Cost}^{\mathrm{Odor}} = \left(\mathrm{W5}^{\mathrm{Odor}^1} - \mathrm{W5}^{\mathrm{OdorReg}^1}\right)\mathrm{Costu}^{\mathrm{Odor}}\ H_{\mathrm{y}} \tag{159}$$

$$\mathrm{W5}^{\mathrm{Odor}^2} \le \mathrm{W5}^{\mathrm{OdorReg}^2} \tag{160}$$

$$\mathrm{W5}^{\mathrm{Odor}^1} \le M^{\mathrm{W5}^{\mathrm{Odor}}}\ y^{\mathrm{Odor}} \tag{161}$$

$$\mathrm{W5}^{\mathrm{OdorReg}^1} \le M^{\mathrm{W5}^{\mathrm{Odor}}}\ y^{\mathrm{Odor}} \tag{162}$$

$$\mathrm{W5}^{\mathrm{Odor}^2} \le M^{\mathrm{W5}^{\mathrm{Odor}}}\left(1 - y^{\mathrm{Odor}}\right) \tag{163}$$

$$\mathrm{W5}^{\mathrm{OdorReg}^2} \le M^{\mathrm{W5}^{\mathrm{Odor}}}\left(1 - y^{\mathrm{Odor}}\right) \tag{164}$$

Any property

Finally, we can state that any other specific property that may cause pollution to the environment can be modeled in the same way. Therefore, for any property, the property integration principle yields,

$$f_{\mathrm{Property}}\left(\mathrm{Property}_{\mathrm{mean}}\right) = \sum_{i \in \mathrm{NSOURCES}} f_{\mathrm{Property}}\left(\mathrm{Ratio}_i\ \mathrm{Property}_i\right) \tag{165}$$

$$Wn^{\mathrm{Property}} = Wn\ \mathrm{Property}_{\mathrm{mean}} \tag{166}$$

$$Wn^{\mathrm{PropertyReg}} = Wn\ \mathrm{Property}_{\mathrm{Reg}} \tag{167}$$

Accordingly, the following disjunction can be formulated,

$$\begin{bmatrix} Y^{\mathrm{Property}} \\ \mathrm{W}n^{\mathrm{Property}} \ge \mathrm{W}n^{\mathrm{PropertyReg}} \\ \mathrm{Cost}^{\mathrm{Property}} = \left(\mathrm{W}n^{\mathrm{Property}} - \mathrm{W}n^{\mathrm{PropertyReg}}\right)\mathrm{Costu}^{\mathrm{Property}}\ H_{\mathrm{y}} \end{bmatrix} \vee \begin{bmatrix} \neg Y^{\mathrm{Property}} \\ \mathrm{W}n^{\mathrm{Property}} \le \mathrm{W}n^{\mathrm{PropertyReg}} \\ \mathrm{Cost}^{\mathrm{Property}} = 0 \end{bmatrix}$$

which can be modeled as follows,

$$Wn^{\mathrm{Property}} = Wn^{\mathrm{Property}} + \mathrm{Wn}^{\mathrm{Property}^2} \tag{168}$$

$$Wn^{\mathrm{PropertyReg}} = Wn^{\mathrm{PropertyReg}^1} + Wn^{\mathrm{PropertyReg}^2} \tag{169}$$

$$Wn^{\mathrm{Property}^1} \ge Wn^{\mathrm{PropertyReg}^1} \tag{170}$$

Table 1. Sources Data for the Example

Source, i	W_i [kg/h]	$z_{i,\text{phenol}}$	$z_{i,\text{acetone}}$	ThOD [gO_2/l]	pH	ρ [kg/l]
1	3666.46	0.016	0.000	0.187	5.4	1.00017
2	1769.18	0.024	0.010	48.850	5.1	1.00017
3	1487.77	0.22	0.028	92.100	4.8	1.00017

$$\text{Cost}^{\text{Property}} = \left(Wn^{\text{Property}^1} - Wn^{\text{PropertyReg}^1}\right)\text{Costu}^{\text{Property}} H_{\text{y}} \tag{171}$$

$$Wn^{\text{Property}^2} \leq Wn^{\text{PropertyReg}^2} \tag{172}$$

$$Wn^{\text{Property}^1} \leq M^{Wn^{\text{Property}}}\, y^{\text{Property}} \tag{173}$$

$$Wn^{\text{PropertyReg}^1} \leq M^{Wn^{\text{Property}}}\, y^{\text{Property}} \tag{174}$$

$$Wn^{\text{Property}^2} \leq M^{Wn^{\text{Property}}}\left(1 - y^{\text{Property}}\right) \tag{175}$$

$$Wn^{\text{PropertyReg}^2} \leq M^{Wn^{\text{Property}}}\left(1 - y^{\text{Property}}\right) \tag{176}$$

Objective function

The objective function consists of the minimization of the total annual cost associated with both the mass integration and the waste treatment processes. The costs of the mass integration process include the cost due to the fresh sources and the piping costs to build the mass integration network. Piping costs are important to be accounted for, and they are a function of the layout (which is known before the mass integration) and the flowrate of the streams. To meet the environmental regulations, it may be necessary to treat the waste streams. The costs associated with the waste treatment process include the cost for the recovery of specific compounds in the waste streams, the cost to remove the toxic compounds, the cost of aeration to satisfy the theoretical oxygen demand regulation, the cost for the neutralization process, the cost to decrease color, odor, and any other property that may cause contamination. The objective function can be formulated as follows,

$$\begin{aligned}\text{TAC} = {} & \sum_{r\in\text{FRESH}} \text{Cost}_r^{\text{Fresh}} F_r\, H_{\text{Y}} \\ & + \sum_{\substack{i\in\text{SOURCES}\\ j\in\text{SINKS}}} \text{pip}_{\text{i,j}}\, w_{i,j} + \sum_{\substack{r\in\text{FRESH}\\ j\in\text{SINKS}}} \text{pip}_{\text{r,j}}\, f_{r,j} \\ & + \sum_{u\in\text{RECOV}} \text{Cost}_u^{\text{Recoveryu}} + \sum_{t\in\text{TOX}} \text{Cost}_{\text{t}}^{\text{Toxicity}} \\ & + \text{Cost}^{\text{ThoD}} + \text{Cost}^{\text{Neu}} + \text{Cost}^{\text{Color}} \\ & + \text{Cost}^{\text{Odor}} + \cdots + \text{Cost}^{\text{Property}}\end{aligned} \tag{177}$$

Even when the model presented here is nonconvex, a good initialization strategy for the optimization variables can yield excellent solutions using local optimization methods such as the outer approximation algorithm.[42] If a global optimal solution is of primary importance, then specialized solvers such as BARON[43] should be used, although the computing time may become an issue in these cases.

Case Study and Results

This section presents the application of the proposed method. The stream data for the example problem were taken from Hortua.[44] The process consists of the production of phenol from cumene, yielding acetone as a subproduct. This process was selected because phenol is particularly considered as a hazardous and toxic material.

For the mass integration process, two fresh sources are available with a phenol impurity of 0 and 0.012 mass fraction (kg-phenol/kg-total), and with unit costs of \$0.0013/kg and \$0.00088/kg, respectively. In addition there are three process sources; the stream data for these sources are given in Table 1. The data for the sinks are given in Table 2.

The environmental regulations applied to this specific process are as follows. The maximum concentration allowed to be discharged to the environment for acetone and phenol is 0.005 kg-phenol/kg-total. The toxicity must be zero, and the maximum concentration and discharge load of phenol, the toxic material, are 0.0000011 kg-phenol/kg-total and 0.00245393 kg/h, respectively.[45] The theoretical oxygen demand of the waste stream must be lower than 75 mg O_2/l, and finally the pH must be between 5.5 and 9.0.[46]

The unit costs for the recovery processes are 0.143 \$/kg and \$0.072 \$/kg for phenol and acetone, respectively. The unit cost for aeration is 0.013 \$/kg air diffused, and the unit costs for the H_2SO_4 and NaOH used for the neutralization process are \$46/l and \$31/l, respectively.

Table 3 gives the unit piping cost for the mass integration process.

Figure 4 shows the results for the case when only process constraints are considered, without including the waste treatment process. This scenario is included here because it represents a common solution approach to these types of problems. We refer to this structure as Solution A. Notice that the waste stream does not satisfy the environmental constraints; therefore, it will be necessary to include a waste treatment process to the solution obtained here.

Table 2. Sinks Data for the Example

Sink, j	G_j [kg/h]	$z_j^{\max}$
1	2721.55	0.015
2	1129.44	0.1
3	1995.80	0.015

Table 3. Piping Costs for the Example*

	Sources				
	Process, *i*			Fresh, *r*	
Sink, *j*	1	2	3	1	2
1	11.0231	4.4092	6.6138	9.9208	5.5115
2	7.7161	2.2046	11.0231	6.6138	2.2046
3	4.4092	8.8184	4.4092	7.7161	3.3069

*Units in [($ h)/(kg year)].

Figure 5 shows the solution of the example problem including all the environmental constraints (Solution B). Notice that the total waste is reduced in the solution that incorporates the waste treatment process by 11.1% with respect to the solution that considered only the process constraints. In addition, in the optimal solution shown in Figure 5, the total consumption of fresh source 1 (with an impurity concentration of phenol of 0) is increased by 76.1% with respect to Solution A of Figure 4; this yields a decrease in the concentration of phenol and acetone in the waste stream by 22.2 and 30%, respectively. The theoretical oxygen demand in the waste stream for the optimal solution that considers the waste treatment process is reduced by 27.4% with respect to the alternative solution of Figure 4. The pH in the optimal Solution B is increased by 0.93% with respect to Solution A.

Table 4 shows a summary of the costs associated with both solutions. To have a common comparison basis, the costs of the waste treatment processes that would be needed for Solution A were calculated after the optimization procedure. Notice in Table 4 that the sum of the costs associated with the process (fresh sources and piping costs) in Solution B is 8% higher than those required for Solution A. In addition, the total costs for the waste treatment process in the optimal Solution B is 41.3% lower than those required by the simplified Solution A. Therefore, the solution that simultaneously optimize the process and the waste treatment process yields a total annual cost with savings of 25.4% with respect to the solution that only optimizes the process. This result confirms the advantage to simultaneously consider mass and property integration and to trade off direct recycle, usage of fresh resource, and treatment of waste streams while satisfying process constraints and environmental regulations. It is also worth noting that the use of properties at the interface between the process and the environment provides an effective framework for incorporating environmental regulations into the process-design procedure. Unlike composition-based methods that cannot directly address environmental constraints (e.g., pH, color, toxicity, etc.), the developed property-based approach is indeed capable of simultaneously addressing the process and the environment.

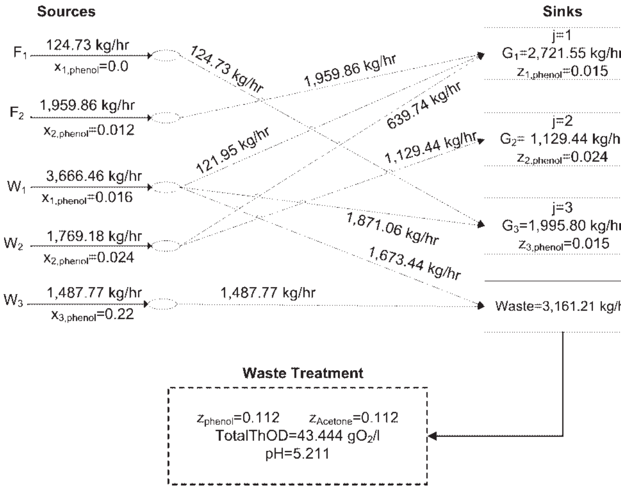


Figure 4. Mass integration without environmental constraints (Solution A).

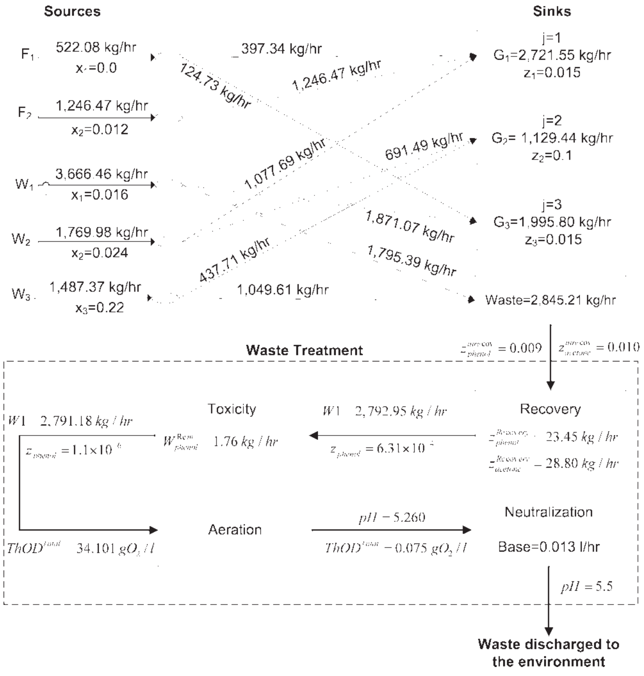


Figure 5. Mass integration including waste treatment process (Solution B).

This example has shown that if one does not consider the waste treatment cost to satisfy the environmental regulations as part of the mass integration problem, the model can lead to sub-optimum solutions. We have shown in this article how a simultaneous model can be formulated, which provides a better basis for the optimization of these types of systems.

Table 4. Comparison of Results

Concept	With Process Constraints (Solution A)	With Process and Environmental Constraints (Solution B)
Waste [kg/h]	3161.21	2845.21
Fresh sources cost [$/year]	15,146	14,318
Piping cost [$/year]	26,669	31,128
Recovery cost [$/year]	61,859	43,661
Toxicity cost [$/year]	7226	5098
Aeration cost [$/year]	161,083	43,363
Neutralization cost [$/year]	4567	3237
Total process costs [$/year]	41,816	45,446
Total waste treatment costs [$/year]	134,734	95,360
TAC [$/year]	176,550	140,807

Conclusions

A new framework has been introduced to (1) integrate the design of in-plant recycle/reuse networks with the end-of-pipe waste treatment facilities, (2) consider composition- and property-based constraints and process models. An optimization formulation has been developed to implement the devised framework. The model is based on disjunctive programming, and considers the technologies that are commonly used to treat wastewater streams so that they meet environmental regulations. The model is formulated with linear relationships within each one of the disjunctions, which aids its numerical solution. In addition to standard mass balance and composition constraints, the model incorporates property-based models, property mixing rules, and environmental constraints based on properties such as toxicity, theoretical oxygen demand, pH, color, and odor, and it is generalized to any other property that may cause pollution. The methodology has also shown how property integration can be used for cases in which a given property is difficult to estimate when there are many compounds in a waste stream. The formulation results in an MINLP model, which has been used to minimize the total annual cost of the system. The solution of the proposed model shows that the simultaneous consideration of mass and property integration and the tradeoff between in-plant recycle/reuse with wastewater treatment sections can yield important economic savings. The model did not show any numerical problems, and the CPU times required for the solutions of the example problem were relatively small.

Notation

Acid = acid added to a waste stream to meet environmental regulation for *pH*
Base = base added to a waste stream to meet environmental regulation for pH
c_{t} = concentration of toxic compound t
Color_i = index for the color of source *i*
$\mathrm{Color}_{\mathrm{Reg}}$ = maximum index for color allowed by environmental regulation
$\mathrm{Color}_{\mathrm{mean}}$ = index for the color of waste stream
$\mathrm{Cost}^{\mathrm{Aeration}}$ = unit cost for the aeration process
$\mathrm{Cost}^{\mathrm{Acid}}$ = unit cost for the acid
$\mathrm{Cost}^{\mathrm{Base}}$ = unit cost for the base
$\mathrm{Cost}^{\mathrm{Color}}$ = total cost for the color treatment
$\mathrm{Cost}_r^{\mathrm{Fresh}}$ = unit cost for the fresh source *r*
$\mathrm{Cost}^{\mathrm{Neu}}$ = total cost for the neutralization process
$\mathrm{CCost}^{\mathrm{Neu}^{\mathrm{B}}}$, $\mathrm{Cost}^{\mathrm{Neu}^{\mathrm{c}}}$ = disaggregated variables for $\mathrm{Cost}^{\mathrm{Neu}}$
$\mathrm{Cost}^{\mathrm{Odor}}$ = total cost for the odor treatment process
$\mathrm{Cost}^{\mathrm{Property}}$ = total cost for the property treatment process
$\mathrm{Cost}_u^{\mathrm{Recoveryu}}$ = total cost for recovery component *u*
$\mathrm{Cost}_u^{\mathrm{Recu}}$ = unit cost for recovery component *u*
$\mathrm{Cost}^{\mathrm{ThOD}}$ = total cost for the theoretical oxygen demand treatment process
$\mathrm{Cost}_t^{\mathrm{Taxicity}}$ = total cost for the toxicity treatment process for toxic *t*
$\mathrm{Cost}_t^{\mathrm{Toxic}}$ = unit cost for the toxicity treatment process for toxic *t*
$\mathrm{Costu}^{\mathrm{Color}}$ = unit cost for the color treatment process
$\mathrm{Costu}^{\mathrm{Odor}}$ = unit cost for the odor treatment process
$\mathrm{Costu}^{\mathrm{Property}}$ = unit cost for the property treatment process
$D_{\mathrm{Tox}_t}^{\mathrm{Max}}$ = maximum mass flowrate allowed to be discharged for toxic compound *t*
EFF_u = efficiency for the recovery process for component *u*
F_r = total flowrate consumed from fresh source *r*
$f_{r,j}$ = segregated flowrate from fresh source *r* to sink *j*
G_j = total flowrate inlet to sink *j*
H_{Y} = operating hours per year
$k_{1_{\mathrm{t}}}$ = constant for the toxicity relationship of t
$k_{2_{\mathrm{t}}}$ = constant for the toxicity relationship of t
M^{var} = upper limit for variable var
NFRESH = set for the fresh sources
NPROP = set for the number of properties considered
NSINKS = set for the number of sinks
NSOURCES = set for the number of sources
Odor_i = index for the odor for process source *i*
$\mathrm{Odor}_{\mathrm{mean}}$ = index for the odor of waste stream
$\mathrm{Odor}_{\mathrm{Reg}}$ = maximum index for the odor allowed by environmental regulation
pH = power of hydrogen
$\mathrm{pH}_{\mathrm{discharged}}$ = pH discharged to the environment for the waste stream
$\mathrm{pH}_{\mathrm{discharged}}^{\mathrm{B}}$, $\mathrm{pH}_{\mathrm{discharged}}^{\mathrm{A}}$, $\mathrm{pH}_{\mathrm{discharged}}^{\mathrm{C}}$ = disaggregated variables for $\mathrm{pH}_{\mathrm{discharged}}$
$\mathrm{pH}_{\mathrm{mean}}$ = pH mean for the waste stream
$\mathrm{pH}_{\mathrm{mean}}^{\mathrm{B}}$, $\mathrm{pH}_{\mathrm{mean}}^{\mathrm{A}}$, $\mathrm{pH}_{\mathrm{mean}}^{\mathrm{C}}$ = disaggregated variables for $\mathrm{pH}_{\mathrm{mean}}$
pip = unit piping costs from any source to any sink
$\mathrm{pOH}_{\mathrm{mean}}$ = mean value of pOH for the waste stream
$\mathrm{Property}_i$ = property for process source *i*
$\mathrm{Property}_{\mathrm{mean}}$ = mean property for a waste stream
Ratio_i = fractional contribution for each process source *i* to the waste stream
TAC = total yearly cost
$\mathrm{ThOD}^{\mathrm{Total}}$ = total theoretical oxygen demand for a waste stream
ThOD_i = theoretical oxygen demand for stream *i*
$\mathrm{Total}^{\mathrm{H3O}}$ = total moles of $\mathrm{H_3O^+}$ in a waste stream
$\mathrm{Total}^{\mathrm{H3O^B}}$, $\mathrm{Total}^{\mathrm{H3O^A}}$, $\mathrm{Total}^{\mathrm{H3O^C}}$ = disaggregated variables for $\mathrm{Total}^{\mathrm{H3O}}$
$\mathrm{Total}^{\mathrm{OH}}$ = total moles of $\mathrm{OH^-}$ in a waste stream
$\mathrm{Total}^{\mathrm{OH^B}}$, $\mathrm{Total}^{\mathrm{OH^A}}$, $\mathrm{Total}^{\mathrm{OH^C}}$ = disaggregated variables for $\mathrm{Total}^{\mathrm{OH}}$
TOX = set for toxic compounds
W_i = total mass flowrate from process source *i*
$w_{i,j}$ = segregated mass flowrate from process source *i* to sink *j*
waste_i = segregated mass flowrate from process source *i* to the waste stream
WASTE = total flowrate for a waste stream
Waste4 = volumetric flowrate for the stream after neutralization process
$\mathrm{Waste4^B}$, $\mathrm{Waste4^A}$, $\mathrm{Waste4^C}$ = disaggregated variables for Waste4

WINREC = inlet mass flowrate to the recovery process

WINREC_u = inlet mass flowrate for component u to the recovery process

$\mathrm{WINRECU}_u^1$, $\mathrm{WINRECU}_u^2$ = disaggregated variables for WINREC_u

$W_{\mathrm{t}}^{\mathrm{BT}}$ = mass flowrate for the toxic compound t before the toxicity treatment

$W_{\mathrm{t}}^{\mathrm{BT1}}$, $W_{\mathrm{t}}^{\mathrm{BT2}}$, $W_{\mathrm{t}}^{\mathrm{BT3}}$, $W_{\mathrm{t}}^{\mathrm{BT4}}$ = disaggregated variables for $W_{\mathrm{t}}^{\mathrm{BT}}$

W_u^{Recovery} = mass flowrate recovered for component u

$W_{\mathrm{t}}^{\mathrm{Rem}}$ = mass flowrate removed of toxic t

$W_{\mathrm{t}}^{\mathrm{Rem1}}$, $W_{\mathrm{t}}^{\mathrm{Rem2}}$, $W_{\mathrm{t}}^{\mathrm{Rem3}}$, $W_{\mathrm{t}}^{\mathrm{Rem4}}$ = disaggregated variables for $W_{\mathrm{t}}^{\mathrm{Rem}}$

$W_{\mathrm{t}}^{\mathrm{Rem3a}}$, $W_{\mathrm{t}}^{\mathrm{Rem3b}}$ = disaggregated variables for $W_{\mathrm{t}}^{\mathrm{Rem3}}$

$W_{\mathrm{t}}^{\mathrm{Rema3a}}$, $W_{\mathrm{t}}^{\mathrm{Rema3b}}$ = disaggregated variables for $W_{\mathrm{t}}^{\mathrm{Rema3}}$

$W_{\mathrm{t}}^{\mathrm{Remb3a}}$, $W_{\mathrm{t}}^{\mathrm{Remb3b}}$ = disaggregated variables for $W_{\mathrm{t}}^{\mathrm{Remb3}}$

W^{ThOD} = product of theoretical oxygen demand times flowrate

W^{ThOD^1}, W^{ThOD^2} = disaggregated variables for W^{ThOD}

$W^{\mathrm{ThOD}^{\mathrm{Reg}}}$ = product of theoretical oxygen demand regulation times flowrate

$W^{\mathrm{ThOD}^{\mathrm{Reg}\,1}}$, $W^{\mathrm{ThOD}^{\mathrm{Reg}\,2}}$ = disaggregated variables for $W^{\mathrm{ThOD}^{\mathrm{Reg}}}$

W1 = mass flowrate for the waste stream after the recovery process

$\mathrm{W1}^1$, $\mathrm{W1}^2$, $\mathrm{W1}^3$, $\mathrm{W1}^4$ = disaggregated variables for W1

W2 = mass flowrate for the waste stream after toxicity treatment process

W3 = mass flowrate inlet to the aeration process

W4 = mass flowrate for the waste stream after the neutralization process

$\mathrm{W4}^{\mathrm{Color}}$ = mass flowrate times the color index for the waste stream

$\mathrm{W4}^{\mathrm{Color}^1}$, $\mathrm{W4}^{\mathrm{Color}^2}$ = disaggregated variables for $\mathrm{W4}^{\mathrm{Color}}$

$\mathrm{W4}^{\mathrm{ColorReg}}$ = mass flow rate times the color index given by the environmental regulation

$\mathrm{W4}^{\mathrm{ColorReg}^1}$, $\mathrm{W4}^{\mathrm{ColorReg}^2}$ = disaggregated variables for $\mathrm{W4}^{\mathrm{ColorReg}}$

$\mathrm{W5}^{\mathrm{Odor}}$ = flowrate times odor index for the waste stream

$\mathrm{W5}^{\mathrm{Odor}^1}$, $\mathrm{W5}^{\mathrm{Odor}^2}$ = disaggregated variables for $\mathrm{W5}^{\mathrm{Odor}}$

$\mathrm{W5}^{\mathrm{OdorReg}}$ = flowrate times odor index given by the environmental regulation

$\mathrm{W5}^{\mathrm{OdorReg}^1}$, $\mathrm{W5}^{\mathrm{OdorReg}^2}$ = disaggregated variable for $\mathrm{W5}^{\mathrm{OdorReg}}$

W_{H3O} = concentration of ions $\mathrm{H_3O^+}$ in the waste stream

Wn^{Property} = flowrate times property for the waste stream

Wn^{Property^1}, Wn^{Property^2} = disaggregated variables for Wn^{Property}

$Wn^{\mathrm{PropertyReg}}$ = flowrate times property given by the environmental regulation

$Wn^{\mathrm{PropertyReg}^1}$, $Wn^{\mathrm{PropertyReg}^2}$ = disaggregated variables for $Wn^{\mathrm{PropertyReg}}$

W_{OH} = concentration of $\mathrm{OH^-}$ ions in a waste stream

Y_u^{Recov} = logic variable for the recovery process of component u

Y_{t} = percentage of mortality for toxic compound t

Y^{Color} = logic variable for the color treatment process

Y^{Odor} = logic variable for the odor treatment process

$Y_{\mathrm{A}}^{\mathrm{Neu}}$ = logic variable for the neutralization process with acid addition

$Y_{\mathrm{B}}^{\mathrm{Neu}}$ = logic variable for the neutralization process with base addition

$Y_{\mathrm{C}}^{\mathrm{Neu}}$ = logic variable for the neutralization process with no acid or base addition

Y^{Property} = logic variable for property

Y^{ThOD} = logic variable for the theoretical oxygen demand

$Y_{\mathrm{A_t}}^{\mathrm{Tox}}$ = logic variable for toxic treatment process for toxic t

$Y_{\mathrm{B_t}}^{\mathrm{Tox}}$ = logic variable to denote that toxic treatment process is not needed for toxic t

$Y_{1_{\mathrm{t}}}^{\mathrm{Tox}}$ = logic variable for case 1 for toxic treatment process for t

$Y_{2_{\mathrm{t}}}^{\mathrm{Tox}}$ = logic variable for case 2 for toxic treatment process for t

$Y_{3_{\mathrm{t}}}^{\mathrm{Tox}}$ = logic variable for case 3 for toxic treatment process for t

$Y_{3\mathrm{a_t}}^{\mathrm{Tox}}$ = logic variable for case 3a for toxic treatment process for t

$Y_{3\mathrm{b_t}}^{\mathrm{Tox}}$ = logic variable for case 3b for toxic treatment process for t

$z_{i,c}$ = given composition for process source i for component c

$z_{j,c}^{\mathrm{in}}$ = inlet composition for component c inlet to sink j

$z_{r,c}$ = given composition for fresh source r for component c

$z_{j,c}^{\max}$ = maximum concentration allowed in sink j for component c

$z_{j,c}^{\min}$ = minimum concentration allowed in sink j for component c

$z_{i,u}^{\mathrm{inrecov}}$ = inlet composition to the recovery process for component u from source i

z_u^{inrecov1}, $z_{i,u}^{\mathrm{inrecov2}}$ = disaggregated variables for $z_{i,u}^{\mathrm{inrecov}}$

z_u^{MaxEnv} = maximum discharge allowed by environmental regulation for component u

$Z_{\mathrm{Tox_t}}^{\mathrm{Max}}$ = maximum composition allowed to be discharged for toxic compound t

$z1_u$ = component composition after the recovery process

$z1_{\mathrm{t}}^1$, $z1_{\mathrm{t}}^2$, $z1_{\mathrm{t}}^3$, $z1_{\mathrm{t}}^4$ = disaggregated variables for $z1_{\mathrm{t}}$

$\mathrm{z2_t}$ = composition of waste stream after toxicity treatment process for toxic compound t

Greek letters

ρ_{Acid} = density of the acid used in the neutralization process

ρ_{Base} = density of the base used in the neutralization process

ρ_{waste} = density of the waste stream

$\psi_p\ (p_{j,p}^{\mathrm{in}})$ = property operator for property p at the inlet condition to sink j

$\psi_p\ (p_{i,p})$ = property operator for property p for process source i

$\psi_p\ (p_{r,p})$ = property operator for property p for fresh source r

$\psi_p^{\max}\ (p_{p,j})$ = maximum relation for property p in sink j

$\psi_p^{\min}\ (p_{p,j})$ = minimum relation for property p in sink j

Indices

i = process sources
in = inlet conditions
j = sinks
max = maximum value
min = minimum value
p = properties
r = fresh sources

t = toxic compound
u = hazardous component to be recovery
waste = waste stream

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Manuscript received Sept. 3, 2008, and revision received Jan. 2, 2009.