Impact of Multiple Storage in Wastewater Minimization for Multicontaminant Batch Plants: Toward Zero Effluent

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The mathematical technique presented in this paper deals with wastewater minimization within a multiple contaminant environment, where there are multiple storage vessels available for the storage of wastewater. In the multiple storage vessel situation, it is possible to dedicate certain storage vessels to the storage of wastewater with specific contaminants. The mathematical technique is extended to include operations where wastewater produced in one batch is reusable as feed for subsequent batches of the same product. This type of operation enables a plant to operate in an almost zero-effluent fashion. Product integrity is ensured by not allowing different types of wastewater to mix and storing each type of wastewater in a dedicated storage vessel. In both cases, the mathematical model determines the minimum wastewater target and the corresponding production schedule.

1. Introduction

Minimization of wastewater within the batch processing industry has gained much interest in the past few years. This is mainly due to the tightening of environmental legislation on plant effluent and the decreasing supply of freshwater. In the past, much focus has been on reducing wastewater within continuous processes, as these processes generally produce much larger volumes of water. Furthermore, methodologies for such processes do not need to take time into consideration.[1−4] Minimization of wastewater within batch processes is also important, because of the nature and levels of contaminants within the water. Batch processing is suited to the production of high-value products in small quantities and is, thus, ideally suited to agrochemical and pharmaceutical production. Generally, wastewater produced from such industries is contaminated with toxic substances in high concentrations. It would, thus, be preferable to reduce the production of this type of wastewater.

Wastewater-minimization methodologies in batch processes can be broadly divided into two groups, namely, graphical techniques and mathematical techniques. Wang and Smith[5] were one of the first to develop and apply a graphical wastewater-minimization technique to batch processes. They extended their WaterPinch technique to batch processes. The main drawback of the methodology was that it was more suited to semicontinuous processes as it was implicitly assumed that water is continuously used/available during a unit operation. Majozi et al.[6] extended the technique by Wang and Smith[5] to include strictly batch processes. This methodology also introduced a novel idea of using processing units as inherent storage for wastewater. Foo et al.[7] also proposed a graphical technique for wastewater minimization in batch processes. Their methodology was based on previous work done on mass exchange network design. The main drawbacks of graphical techniques are that they determine the wastewater target within a predefined schedule and they are unable to efficiently deal with multiple contaminants. In essence, graphical techniques are limited to single contaminants, as they are inherently limited to two dimensions. They are, thus, unable to deal with the multidimensionality of multiple contaminant problems.

Mathematical techniques, however, can easily deal with the multidimensionality of multicontaminant wastewater minimization. Grau et al.[8] extended their scheduling technique to include wastewater minimization with the emphasis on wastewater generated from unit cleaning. Almató et al.[9] also proposed a mathematically based wastewater-minimization technique. The objective of the technique was to find the optimal storage tank-to-unit connection. The technique is, however, based on the schedule being determined a priori. Similarly, Kim and Smith[10] derived a mathematical technique with the schedule being determined a priori. The technique is extended to include multiple contaminants. Majozi[11] developed a wastewater-minimization technique that determines the wastewater target together with the schedule to achieve the target. The technique is, however, restricted to single contaminants. It must be noted that the true minimum amount of wastewater can only be realized by allowing the production schedule to change. Hence, wastewater targets identified within a fixed schedule cannot be regarded as the absolute minimum, but rather the minimum for that specific schedule. This condition applies to both graphical and mathematical techniques.

Multiple contaminant wastewater minimization in batch processes with multiple storage possibilities has not been dealt with in past techniques. Most published techniques implicitly assume that wastewater streams are allowed to mix. In certain instances, this might not necessarily be the case. Consequently, to fully exploit any reuse opportunities, one should use multiple storage vessels with each storage vessel dedicated to storing certain types of wastewater.

The use of multiple storage vessels is specifically suited to situations where the possibility exists to reuse wastewater as product constituent. Such operations occur where the wastewater is generated from a separate operation to product production and contains product residue. In such operations, multiple storage vessels are used, since wastewater streams are not permitted to mix to maintain product integrity. Operations of this nature are amenable to zero-effluent operation. A typical example of such an operation is encountered in the pharmaceuticals industry during the production of some liquid products. In such instances, product is mixed in a vessel. Once the product

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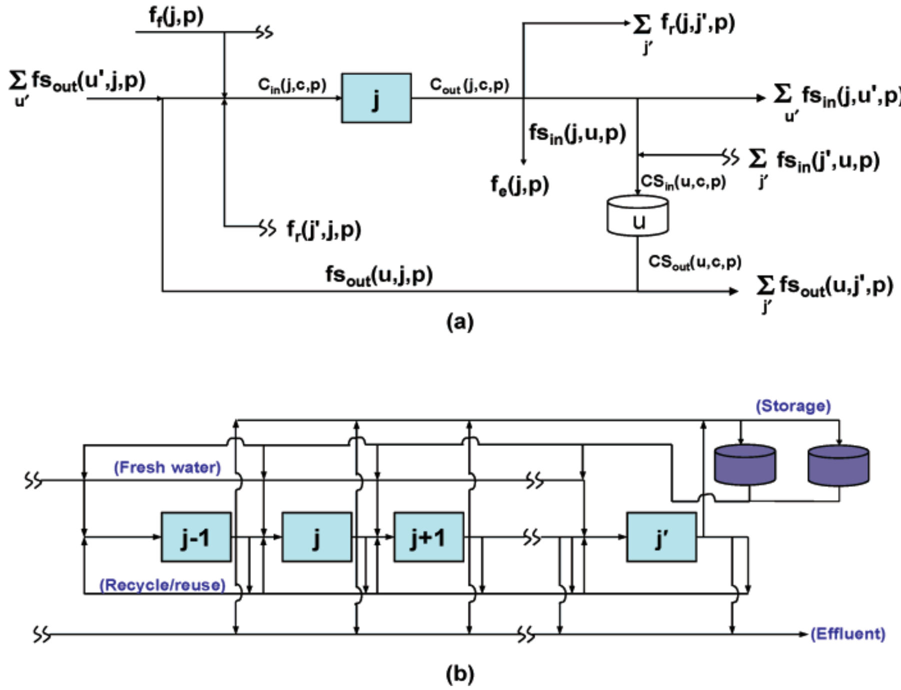

Figure 1. Superstructure for multiple storage vessel mathematical model.

has been removed, the vessel is washed. The water stemming from the washout thus contains any product residue and can, under the correct conditions, be reused as product constituents.

Presented in this paper is a mathematical technique for the minimization of multiple-contaminant wastewater where there are multiple storage vessels. The wastewater is minimized by considering all possible recycle/reuse opportunities, both indirectly and directly within the process prior to end-of-pipe treatment. The technique is able to maximize the wastewater-reuse opportunities in situations where mixing of streams is undesirable or limiting. The technique is extended to take into consideration operations where wastewater is reused as part of the product, thereby allowing the zero-effluent operational mode.

2. Mathematical Formulation

The mathematical formulation is described in two sections. The first section deals with the multiple storage vessel formulation, and the second section deals with the constraints necessary for the zero-effluent formulation.

2.1. Multiple Contaminants with Multiple Storage Vessels. The sets, variables, and parameters used in the formulation are listed in the Nomenclature section. The multiple storage vessel mathematical model is based on the superstructure given in Figure 1. Figure 1a represents any water-using unit. Figure 1b represents the overall plant superstructure. Figure 1a is a magnification of Figure 1b.

2.1.1. Mass Balance Constraints. 2.1.1.1. Unit Mass Balances. The first of the mass balances considered are water balances around the inlet and outlet of a unit. Constraint 1 is an inlet water balance. It states that the water entering a unit constitutes the water that is directly reused from other units, water reused from various storage vessels, and freshwater. This is similar for the outlet, where the water leaving the unit j is either directly reused in other units j', sent to storage, or discarded as effluent, as given in constraint 2. It is assumed that the operation taking place in the unit does not generate water; hence, the amount of water leaving a unit at a given time point is equal to the amount of water that entered the unit at the previous time point.

$$f_u(j, p) = \sum_{j'} f_r(j', j, p) + f_f(j, p) + \sum_u fs_{out}(u, j, p) \quad \forall\, j\, j' \in J, p \in P, u \in U \quad (1)$$

$$f_p(j, p) = \sum_{j'} f_r(j, j', p) + f_e(j, p) + \sum_u fs_{in}(j, u, p) \quad \forall\, j, j' \in J, p \in P, u \in U \quad (2)$$

Following this, a contaminant mass balance is done over the entrance to a unit. The contaminant mass entering a unit constitutes the contaminant mass from water directly reused from other units and the contaminant mass in water from various storage vessels. This is given in constraint 3. An overall contaminant mass balance over the unit must also be included. This is given in constraint 4.

$$c_{in}(j, c, p)\, f_u(j, p) = \sum_{j'} f_r(j', j, p) c_{out}(j', c, p) + \sum_u fs_{out}(u, j, p) cs_{out}(u, c, p) \quad \forall\, j, j' \in J, p \in P, c \in C, u \in U \quad (3)$$

$$f_p(j, p) c_{out}(j, c, p) = f_u(j, p-1) c_{in}(j, c, p-1) + M_{lost}(c, j) y(s_{in,j}, p-1) \quad \forall\, j \in J, p \in P, p > p_1, c \in C, s_{in,j} \in S_{in,j} \quad (4)$$

For each processing unit, there is a maximum amount of water that can be used by the operation. The maximum is determined through concentration considerations, provided this is within the physical capacity of a unit. A limiting component determines the maximum amount of water that can be used by a unit. The limiting component is the component that will have both the inlet and outlet concentrations at a maximum when water is reused. Constraint 5 defines the maximum water into a unit.

$$\bar{F}_w(j) = \max_{c \in C}\left\{\frac{M_{lost}(j, c)}{\bar{C}_{out}(j, c) - \bar{C}_{in}(j, c)}\right\} \quad \forall\, j \in J \tag{5}$$

Constraints 6−8 ensure that water entering a unit from various sources does not exceed the maximum defined in constraint 5.

$$f_u(j, p) \le \bar{F}_w(j)\left(\sum_{s_{in}} y(s_{in,j}, p)\right) \quad \forall\, s_{in,j} \in S_{in,j}, j \in J, p \in P \tag{6}$$

$$f_r(j', j, p) \le \bar{F}_w(j) y_r(j', j, p) \quad \forall\, j', j \in J, p \in P \tag{7}$$

$$fs_{out}(u, j, p) \le \bar{F}_w(j)\mathrm{ys}_{out}(u, j, p) \quad \forall\, j \in J, p \in P, u \in U \tag{8}$$

The inlet concentration into a unit is controlled using constraint 9. Similarly, the outlet concentration is constrained to a maximum for each component using constraint 10.

$$c_{in}(j, c, p) \le \bar{C}_{in}(j, c)\left(\sum_{s_{in}} y(s_{in,j}, p)\right) \quad \forall\, s_{in,j} \in S_{in,j}, j \in J, p \in P, c \in C \tag{9}$$

$$c_{out}(j, c, p) \le \bar{C}_{out}(j, c)\left(\sum_{s_{in}} y(s_{in,j}, p-1)\right) \quad \forall\, s_{in,j} \in S_{in,j}, j \in J, p \in P, p > p_1, c \in C \tag{10}$$

Apart from water balances around a unit, one also has to consider product mass balances. Constraint 11 is a product mass balance around a unit. This constraint states that the amount of raw material used constitutes the mass of product produced and the mass load given to the water.

$$m_u(s_{in,j}, p-1) = m_p(s_{out,j}, p) + \left(\sum_c M_{lost}(j, c)\right) y(s_{in,j}, p-1) \quad \forall\, s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, j \in J, p \in P, p > p_1, c \in C \tag{11}$$

2.1.1.2. Storage Mass Balances. Following the mass balances around a unit are mass balances around each storage vessel. These begin with a water balance around a storage vessel, given in constraint 12. This constraint states that the amount of water stored in a storage vessel at a time point is the amount of water stored at the previous time point and the difference between the inlet and outlet water at the same time point. This balance for the first time point is given in constraint 13.

$$\mathrm{qs}(u, p) = \mathrm{qs}(u, p-1) + \sum_j \mathrm{fs}_{in}(j, u, p) - \sum_j \mathrm{fs}_{out}(u, j, p) \quad \forall\, j \in J, p \in P, p > p_1, u \in U \tag{12}$$

$$\mathrm{qs}(u, p) = Q_0 - \sum_j \mathrm{fs}_{out}(u, j, p), \quad \forall\, j \in J, p \in P, p = p_1, u \in U \tag{13}$$

The inlet concentration into a storage vessel is defined in constraint 14. To control the type of water entering a storage vessel, constraint 15 is added. Constraint 15 ensures that the inlet concentration into a storage vessel does not exceed a predefined maximum. By setting the maximum to an appropriate level, one can control the type of water entering a storage vessel.

$$\mathrm{cs}_{in}(u, c, p) = \frac{\sum_j (\mathrm{fs}_{in}(j, u, p) c_{out}(j, c, p))}{\sum_j \mathrm{fs}_{in}(j, u, p)} \quad \forall\, j \in J, p \in P, c \in C, u \in U \tag{14}$$

$$\mathrm{cs}_{in}(u, c, p) \le \bar{C}\bar{S}_{in}(u, c) \quad \forall\, p \in P, c \in C, u \in U \tag{15}$$

A contaminant mass balance over a storage vessel is also done. This is given in constraint 16. The contaminant mass in a storage vessel at a time point is the contaminant mass in the storage vessel at the previous time point and the difference between the inlet and outlet contaminant mass. It is assumed that each storage vessel is ideally mixed; hence, the outlet concentration is the same as the concentration within the storage vessel. Constraint 17 defines the concentration within a storage vessel at the first time point.

$$\mathrm{cs}_{out}(u, c, p)\mathrm{qs}(u, p) = \mathrm{cs}_{out}(u, c, p-1)\mathrm{qs}(u, p-1) + \sum_j \mathrm{fs}_{in}(j, u, p)\mathrm{cs}_{in}(u, c, p) - \sum_j \mathrm{fs}_{out}(u, j, p)\mathrm{cs}_{out}(u, c, p) \quad \forall\, j \in J, p \in P, p > p_1, c \in C, u \in U \tag{16}$$

$$\mathrm{cs}_{out}(u, c, p) = \mathrm{Cs}^{O}_{out}(u, c) \quad \forall\, u \in U, c \in C, p \in P, p = p_1 \tag{17}$$

Constraint 18 ensures that the amount of water stored in a storage vessel at a time point does not exceed the capacity of the storage vessel. Similarly constraint 19 ensures that water entering a storage vessel is not more than the vessel capacity.

$$\mathrm{qs}(u, p) \le Q^{max}(u) \quad \forall\, p \in P, u \in U \tag{18}$$

$$\mathrm{fs}_{in}(j, u, p) \le Q^{max}(u)\mathrm{ys}_{in}(j, u, p) \quad \forall\, j \in J, p \in P, u \in U \tag{19}$$

At the end of the time horizon, the amount of water stored in each storage vessel should be zero. This is ensured through constraint 20. Storage of water at the end of a time horizon leads to a false impression of the amount of water saved. Water in a storage vessel at the end of the time horizon, in essence, is not saved and cannot be viewed as water reused because there is not a distinct reuse opportunity for the stored water.

$$\mathrm{qs}(u, p) = 0 \quad \forall\, p \in |P|, u \in U \tag{20}$$

The contaminant mass balances in the above constraints are bilinear, hence, nonconvex. Quesada and Grossman[12] proposed a relaxation linearization technique for such bilinear terms. During the application of the model to various examples, it was found that only one constraint needed linearization. The linearization of further terms led to excessive solutions times, which could not be justified since the relation technique is not exact. The full linearization is given in Appendix A.

Substituting the linearized form of the bilinear term yields constraint 21, which is the relaxed linearized form of constraint 4.

$$\Gamma_1(j, c, p) = c_{in}(j, c, p-1) f_u(j, p-1) + M(j, c) y(s_{in,j}, p-1) \quad \forall\, j \in J, c \in C, p \in P, p > p_1, s_{in,j} \in S_{in,j} \tag{21}$$

The model would not be complete without the consideration of time, which is mandatory in batch processes. This is dealt with in the following sections.

2.1.2. Scheduling Constraints. 2.1.2.1. Task Scheduling. The first scheduling constraint involves task duration. The time at which a task is finished in a unit is the time at which that task began, in the previous time point, and the duration of the task. This is given in constraint 22.

$$t_p(s_{out,j}, p) = t_u(s_{in,j}, p-1) + \tau(s_{in,j})y(s_{in,j}, p-1) \quad \forall\ s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (22)$$

Constraint 23 ensures that a unit can only start operating once it has finished processing the previous batch.

$$t_u(s_{in,j}, p) \geq t_p(s_{out,j}, p) - H(2 - y(s_{in,j}, p) - y(s_{in,j}{}', p-1)) \quad \forall\ s_{in,j}, s_{in,j}{}' \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (23)$$

To ensure that only one operation occurs in a unit at a time point, constraint 24 is added to the formulation.

$$\sum_{s_{in}} y(s_{in,j}, p) \leq 1, \quad \forall\ s_{in,j} \in S_{in,j}, p \in P \quad (24)$$

2.1.2.2. Feasibility Constraints. Constraints 25−29 are feasibility constraints. The constraints ensure that, if the ordinality of the time point corresponding to an event is larger than the previous time point, the time at which the event takes places occurs at a later absolute time. Constraints 25 and 26 hold for a processing unit, and constraints 27−29 hold for a storage vessel.

$$t_u(s_{in,j}, p) \geq t_u(s_{in,j}{}', p') - H(2 - y(s_{in,j}, p) - y(s_{in,j}{}', p')) \quad \forall\ s_{in,j}, s_{in,j}{}' \in S_{in,j}, p, p' \in P, p > p' \quad (25)$$

$$t_p(s_{out,j}, p) \geq t_p(s_{out,j}{}', p') - H(2 - y(s_{in,j}, p-1) - y(s_{in,j}{}', p'-1)) \quad \forall\ s_{in,j}, s_{in,j}{}' \in S_{in,j}, s_{out,j}, s_{out,j}{}' \in S_{out,j}, p, p' \in P, p > p' \quad (26)$$

$$ts_{in}(j, u, p) > ts_{in}(j', u, p') - H(2 - ys_{in}(j, u, p) - ys_{in}(j', u, p')) \quad \forall\ j, j' \in J, u \in U, p, p' \in P, p > p' \quad (27)$$

$$ts_{out}(u, j, p) > ts_{out}(u, j', p') - H(2 - ys_{out}(u, j, p) - ys_{out}(u, j', p')) \quad \forall\ j, j' \in J, u \in U, p, p' \in P, p > p' \quad (28)$$

$$ts_{out}(u, j, p) > ts_{in}(j', u, p') - H(2 - ys_{out}(u, j, p) - ys_{in}(j', u, p')) \quad \forall\ j, j' \in J, u \in U, p, p' \in P, p > p' \quad (29)$$

2.1.2.3. Storage Sequencing. The timing of the streams entering and leaving a storage vessel also needs to be scheduled. Constraints 30 and 31 ensure that the time at which water enters a storage vessel occurs at the same time as when the water is produced. Furthermore, water can only be sent to a storage vessel at a given time point if the unit producing the water operated at the previous time point. However, a unit can operate without sending water to a storage vessel. This is given in constraint 32.

$$ts_{in}(j, u, p) \geq t_p(s_{out,j}, p) - H(2 - ys_{in}(j, u, p) - y(s_{in,j}, p-1)) \quad \forall\ j \in J, s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1, u \in U \quad (30)$$

$$ts_{in}(j, u, p) \leq t_p(s_{out,j}, p) + H(2 - ys_{in}(j, u, p) - y(s_{in,j}, p-1)) \quad \forall\ j \in J, s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1, u \in U \quad (31)$$

$$ys_{in}(j, u, p) \leq \sum_{s_{in}} y(s_{in,j}p-1) \quad \forall\ s_{in,j} \in S_{in,j}, j \in J, p \in P, p > p_1, u \in U \quad (32)$$

The time at which water leaves a storage vessel must coincide with the starting time of the unit receiving the water. This is given in constraints 33 and 34. Constraint 35 ensures that, if water is sent from a storage vessel to a unit, the unit receiving the water is operating. However, a unit is allowed to operate and not receive water from a storage vessel.

$$ts_{out}(u, j, p) \geq t_u(s_{in,j}, p) - H(2 - ys_{out}(j, p) - y(s_{in,j}, p)) \quad \forall\ j \in J, s_{in,j} \in S_{in,j}, u \in U, p \in P \quad (33)$$

$$ts_{out}(u, j, p) \leq t_u(s_{in,j}, p) + H(2 - ys_{out}(u, j, p) - y(s_{in,j}, p)) \quad \forall\ j \in J, s_{in,j} \in S_{in,j}, u \in U, p \in P \quad (34)$$

$$ys_{out}(u, j, p) \leq \sum_{s_{in}} y(s_{in,j}, p), \quad \forall\ s_{in,j} \in S_{in,j}, j \in J, p \in P \quad (35)$$

Apart from the above constraints, constraints also have to be formulated to ensure the correct timing of the streams entering and leaving a unit relative to each other. Constraints 36 and 37 ensure that water streams entering a storage vessel from various units at a time point do so at the same time.

$$ts_{in}(j, u, p) \geq ts_{in}(j', u, p) - H(2 - ys_{in}(j, u, p) - ys_{in}(j', u, p)) \quad \forall\ j, j' \in J, u \in U, p \in P \quad (36)$$

$$ts_{in}(j, u, p) \leq ts_{in}(j', u, p) + H(2 - ys_{in}(j, u, p) - ys_{in}(j', u, p)) \quad \forall\ j, j' \in J, u \in U, p \in P \quad (37)$$

Similar constraints also hold for water leaving a storage vessel. Constraints 38 and 39 ensure that water streams leaving a storage vessel to various units at a time point do so at the same time.

$$ts_{out}(u, j, p) \geq ts_{out}(u, j', p) - H(2 - ys_{out}(u, j, p) - ys_{out}(u, j', p)) \quad \forall\ j, j' \in J, u \in U, p \in P \quad (38)$$

$$ts_{out}(u, j, p) \leq ts_{out}(u, j', p) + H(2 - ys_{out}(u, j, p) - ys_{out}(u, j', p)) \quad \forall\ j, j' \in J, u \in U, p \in P \quad (39)$$

Constraints 40 and 41 ensure that water streams entering and leaving a storage vessel at the same point do so at the same time.

$$ts_{out}(u, j, p) \geq ts_{in}(j', u, p) - H(2 - ys_{out}(u, j, p) - ys_{in}(j', u, p)) \quad \forall\ j, j' \in J, u \in U, p \in P \quad (40)$$

$$\mathrm{ts}_{\mathrm{out}}(u, j, p) \leq \mathrm{ts}_{\mathrm{in}}(j', u, p) + H(2 - \mathrm{ys}_{\mathrm{out}}(u, j, p) - \mathrm{ys}_{\mathrm{in}}(j', u, p)) \quad \forall\, j, j' \in J, u \in U, p \in P \quad (41)$$

The above constraints hold for each storage vessel within the operation.

2.1.2.4. Recycle Scheduling. In addition to scheduling of indirect reuse of water, i.e., involving intermediate storage, scheduling of direct reuse has to be considered. Constraints 42 and 43 ensure that the time at which water is recycled/reused coincides with the time at which that water is produced.

$$t_{\mathrm{r}}(j, j', p) \leq t_{\mathrm{p}}(s_{\mathrm{out},j}, p) + H(2 - y_{\mathrm{r}}(j, j', p) - y(s_{\mathrm{in},j}, p-1)) \quad \forall\, j, j' \in J, s_{\mathrm{in},j} \in S_{\mathrm{in},j}, s_{\mathrm{out},j} \in S_{\mathrm{out},j}, p \in P, p > p_1 \quad (42)$$

$$t_{\mathrm{r}}(j, j', p) \geq t_{\mathrm{p}}(s_{\mathrm{out},j}, p) - H(2 - y_{\mathrm{r}}(j, j', p) - y(s_{\mathrm{in},j}, p-1)) \quad \forall\, j, j' \in J, s_{\mathrm{in},j} \in S_{\mathrm{in},j}, s_{\mathrm{out},j} \in S_{\mathrm{out},j}, p \in P, p > p_1 \quad (43)$$

The time at which water is recycled/reused must also coincide with the time at which the water is used, i.e., the time at which the unit using the water begins to operate. This is ensured through constraints 44 and 45

$$t_{\mathrm{r}}(j, j', p) \leq t_{\mathrm{u}}(s_{\mathrm{in},j'}, p) + H(2 - y_{\mathrm{r}}(j, j', p) - y(s_{\mathrm{in},j'}, p)) \quad \forall\, j, j' \in J, s_{\mathrm{in},j'} \in S_{\mathrm{in},j}, p \in P \quad (44)$$

$$t_{\mathrm{r}}(j, j', p) \geq t_{\mathrm{u}}(s_{\mathrm{in},j'}, p) - H(2 - y_{\mathrm{r}}(j, j', p) - y(s_{\mathrm{in},j'}, p)) \quad \forall\, j, j' \in J, s_{\mathrm{in},j'} \in S_{\mathrm{in},j}, p \in P \quad (45)$$

Constraint 46 ensures that, if water is recycled/reused to a unit, the unit is operating at that time point. However, it is not a prerequisite for a unit to receive recycled/reused water to operate.

$$y_{\mathrm{r}}(j, j', p) \leq \sum_{s_{\mathrm{in}}} y(s_{\mathrm{in},j'}, p), \quad \forall\, s_{\mathrm{in},j'} \in S_{\mathrm{in},j}, p \in P, j, j' \in J \quad (46)$$

2.1.2.5. Time Horizon Constraints. Every event that occurs has to happen within the given time horizon. Constraints 47−51 ensure that the time describing each event is within the time horizon of interest.

$$\mathrm{ts}_{\mathrm{in}}(j, u, p) \leq H, \quad \forall\, j \in J, u \in U, p \in P \quad (47)$$

$$\mathrm{ts}_{\mathrm{out}}(u, j, p) \leq H, \quad \forall\, j \in J, u \in U, p \in P \quad (48)$$

$$t_{\mathrm{u}}(s_{\mathrm{in},j}, p) \leq H, \quad \forall\, s_{\mathrm{in},j} \in S_{\mathrm{in},j}, p \in P \quad (49)$$

$$t_{\mathrm{p}}(s_{\mathrm{out},j}, p) \leq H, \quad \forall\, s_{\mathrm{out},j} \in S_{\mathrm{out},j}, p \in P \quad (50)$$

$$t_{\mathrm{r}}(j, j', p) \leq H, \quad \forall\, j, j' \in J, p \in P \quad (51)$$

2.1.3. Objective Function. The objective function is the maximization of profit, where profit is the difference between the revenue of the product and the combined cost of the raw materials and treatment cost of the effluent, as given in constraint 52.

$$\max R = \sum_{p} \left(\sum_{s_{\mathrm{in}}, s_{\mathrm{out},j}} \mathrm{SP}(s_{\mathrm{out}}) m_{\mathrm{p}}(s_{\mathrm{out},j}, p) - \sum_{j} \mathrm{CR}(s_{\mathrm{in}}) m_{\mathrm{u}}(s_{\mathrm{in},j}, p) - \mathrm{CE} \sum_{j} f_{\mathrm{e}}(j, p) \right) \quad \forall\, j \in J, s_{\mathrm{in}}, s_{\mathrm{in},j} \in S_{\mathrm{in}}, s_{\mathrm{out}}, s_{\mathrm{out},j} \in S_{\mathrm{out}}, p \in P \quad (52)$$

Constraints 1−3, 5−52, and 75−78 describe the mathematical model for multiple storage vessels. The model takes on the form of a mixed-integer nonlinear program (MINLP), because of the concentration constraints and the fact that not all the nonlinear terms are linearized. In the next section, the multiple storage vessel model is extended to include a special type of operation where wastewater is reused as a product constituent, thereby allowing the operation to operate in a near-zero-effluent manner.

2.2. Zero-Effluent Mathematical Model. In certain processes, the main source of wastewater is from unit washouts and not a byproduct of a process. In such operations, the wastewater produced often contains valuable product residue that, under normal circumstances, is lost. Under correct conditions, it is possible to reuse the washout water as a constituent of a batch of the same product at a later stage. This type of operation is favorable as wastewater is almost zero and valuable product residue is recovered, sometimes with significant financial benefits. This type of operation can only occur when the intended product contains water as a constituent. The production of wastewater and product occur from separate operations, and the reuse of wastewater in product does not compromise product integrity.

The zero-effluent mathematical model is derived for two scenarios. The first is where the contaminant mass present in the wastewater is negligible, and the second is where the contaminant mass is not negligible. It is important to first define the type of unit operation that is considered in the derivation of the mathematical model. The unit operation can either be a mixing (processing) vessel or dedicated storage.

2.2.1. Unit Operation in Zero-Effluent Mode. The zero-effluent mathematical formulation is based on the following operation of a unit. The unit uses raw materials, and after a certain time, product is removed from the unit. At this time, the unit is washed out. This type of operation has certain implications on the number of time points used to describe it. Usually two time points are used to describe an operation, one for the beginning of the operation and one for the ending of an operation. In this case, however, three time points are used to describe the operation, one for the point at which the unit starts processing the raw materials, one for the point where the product is removed from the unit and the washout begins, and the last one where the washout ends. It is assumed that, whenever a unit operates, a washout will follow. This means that water from a washout will be removed from the unit after two time points, i.e., at the third time point.

Furthermore, the following is assumed during the derivation of the mathematical formulation:

(i) There is a fixed amount of water used in a washout;

(ii) The product is produced in batches of fixed size;

(iii) The ratio between raw material and water used in a product is fixed for each product; and

(iv) The required production over the given time horizon is known.

2.2.2. Storage in the Zero-Effluent Model. Wastewater streams containing different product residues are not permitted to mix. This ensures that, when water is reused, it will not compromise product integrity. Multiple storage vessels

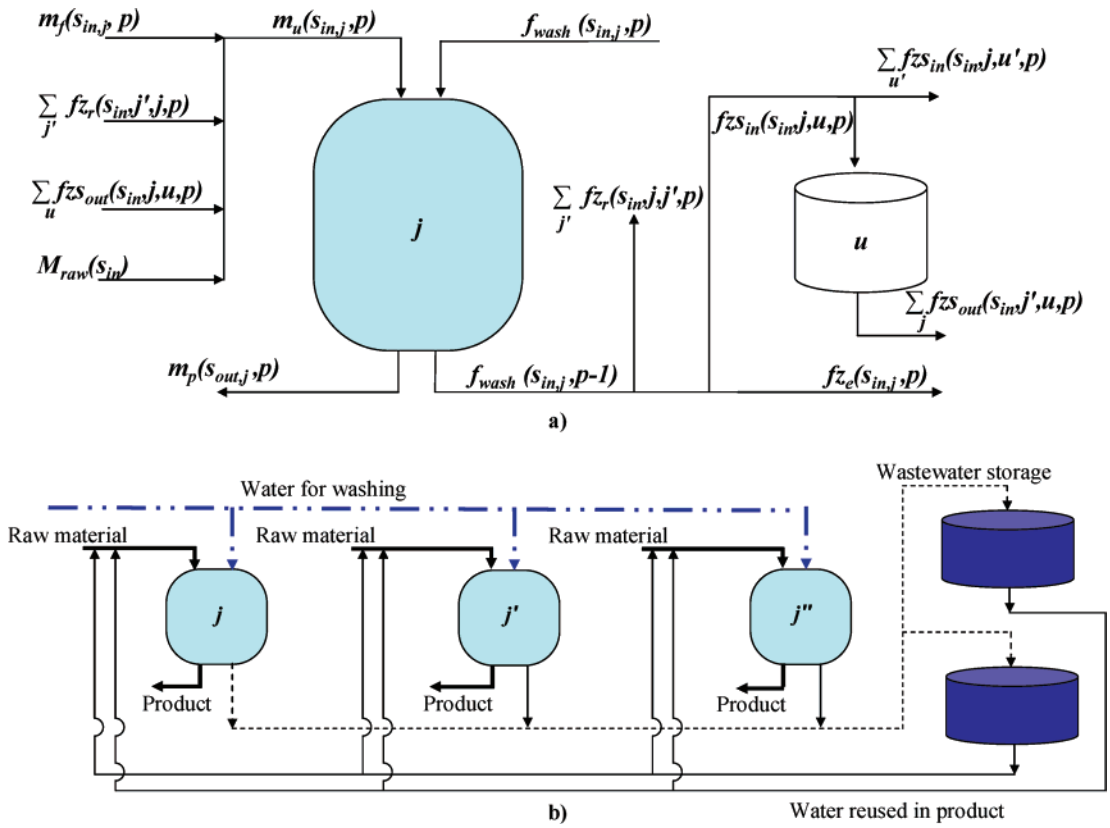

Figure 2. Superstructure for zero-effluent model.

are used to store wastewater, with each type of wastewater stored in a dedicated storage vessel. In essence, for N different wastewater streams, one would require N storage vessels.

The superstructure used in the zero-effluent mathematical model is given in Figure 2. Figure 2a represents a unit operating in the method described above, and Figure 2b represents the overall process. In Figure 2a, it can be seen that the mass of raw material used for product is the sum of the water directly reused, water from storage, freshwater, and raw materials other than water. Furthermore, the water leaving a unit after a washout is the sum of the water directly reused in product, water sent to a storage vessel for reuse at a later stage, and water discarded as effluent.

As mentioned previously, the zero-effluent model is an extension of the multiple storage vessel model. In the case of the mass balance constraints for a unit, the zero-effluent model shares no similarities with the multiple storage vessel model. However, this is not the case for mass balance constraints over a storage vessel and most of the scheduling constraints, as these constraints are similar.

2.2.3. Mass Balance Constraints for Negligible Contaminant Mass in Wastewater. 2.2.3.1. Product Mass Balances over a Unit. The first constraint considered is a raw material mass balance into a unit, as shown in constraint 53. The overall mass used as raw material is the sum of wastewater directly reused to the unit, water from storage, freshwater, and then any other raw materials needed. It is important to note that wastewater reused in product contains a compatible product. This equation is based on a fixed batch size; hence, the total amount of raw materials will be fixed. The amount of freshwater used for raw material is free to vary, but the ratio between water and other raw materials is constant. The fixed amount of raw material is ensured through constraint 54.

$$m_u(s_{in,j}, p) = \sum_{j'} \mathrm{fz}_r(s_{in}, j', j, p) + m_f(s_{in,j}, p) + \sum_{u} \mathrm{fzs}_{out}(s_{in}, u, j, p) + M_{raw}(s_{in})y(s_{in,j}, p) \quad \forall\ s_{in} \in S_{in}, j, j' \in J, p \in P, u \in U, s_{in,j} \in S_{in,j} \quad (53)$$

$$m_u(s_{in,j}, p) = M_u(s_{in})y(s_{in,j}, p), \quad \forall\ s_{in,j} \in S_{in,j}, p \in P, s_{in} \in S_{in} \quad (54)$$

The amount of water that is directly reused must not exceed the amount of water required in the product. This is given in constraint 55.

$$\mathrm{fz}_r(s_{in}, j', j, p) \le M_{water}(s_{in})y_r(j', j, p), \quad \forall\ s_{in} \in S_{in}, p \in P, j, j' \in J \quad (55)$$

Constraint 56 is a mass balance over a unit. In this case, the mass produced is equal to the mass of raw materials used.

$$m_p(s_{out,j}, p) = m_u(s_{in,j}, p-1), \quad \forall\ s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (56)$$

2.2.3.2. Washout Mass Balances over a Unit. It is assumed that, directly after product is pumped out of a unit, the unit is washed. The amount of water used for this is fixed and determined beforehand. The amount of water used for washing a unit is, thus, defined in constraint 57. Water leaving a unit from a washout can either be reused as part of a product directly, stored to be used later, or discarded, as given in constraint 58.

$$f_{wash}(s_{in,j}, p) = F_{water}(j)y(s_{in,j}, p - 1), \quad \forall\ s_{in,j} \in S_{in,j}, p \in P, p > p_1, j \in J \quad (57)$$

$$f_{wash}(s_{in,j}, p - 1) = \sum_{j'} fz_r(s_{in}, j, j', p) + fz_e(s_{in,j}, p) + \sum_u fzs_{in}(s_{in}, j, u, p) \quad \forall\ s_{in} \in S_{in}, j, j' \in J, p \in P, p > p_1, u \in U, s_{in,j} \in S_{in,j} \quad (58)$$

2.2.3.3. Mass Balance Constraints around a Storage Vessel. The mass balance constraints around a storage vessel are similar to constraints 12, 13, 18, and 19. The only difference is that the variables describing the storage are state specific in the zero-effluent model. In this scenario, the type of water stored in a storage vessel cannot be controlled through concentration constraints. However, binary variables describing the inlet of wastewater to a storage vessel not only contain information on the source and sink of water but also the state contained in the water. The water into a specific storage vessel is controlled by setting the inlet binary variables corresponding to incompatible states to zero.

Constraint 59 ensures that the amount of water reused by a process from storage does not exceed the amount of water required in the product.

$$fzs_{out}(s_{in}, u, j, p) \le M_{water}(s_{in})xs_{out}(s_{in}, u, j, p), \quad \forall\ s_{in} \in S_{in}, p \in P, j \in J, u \in U \quad (59)$$

2.2.4. Additional Mass Balance Constraints for Significant Contaminant Mass. In this case, the raw material, other than water, is not from a single source. The raw material mass is composed of the mass from bulk storage, the mass from the directly reused water, and the mass from the storage vessel, as given in constraint 60. Constraint 60 is nonlinear because the concentration inside each storage vessel is a variable.

$$m_{raw}(s_{in,j}, p) = m_{rb}(s_{in,j}, p) + \sum_{j'} fz_r(s_{in}, j', j, p)Cz_{out}(s_{in,j'}) + \sum_u fzs_{out}(s_{in}, u, j, p)cs(s_{in}, u, p) \quad \forall\ s_{in} \in S_{in}, j, j' \in J, u \in U, p \in P, s_{in,j'} \in S_{in,j} \quad (60)$$

In this scenario, constraints 16 and 17 also hold since contaminant balances have to be performed over each storage vessel.

2.2.5. Scheduling Constraints. 2.2.5.1. Unit Scheduling. Unit scheduling in this model is similar to the multiple storage vessel model with constraints 22 and 24−26 still holding. Constraint 61 is added and states that a unit can only start processing once it has been cleaned.

$$t_u(s_{in,j}, p) \ge t_{pw}(s_{in,j}', p') - H(2 - y(s_{in,j}, p) - y(s_{in,j}', p')) \quad \forall\ s_{in,j}, s_{in,j}' \in S_{in,j}, p \in P, p > p' \quad (61)$$

The washout of a unit also has to be scheduled. Constraint 62 is a duration constraint for the washout of a unit. It states that the ending time of a washout is the beginning time and the duration of the washout.

$$t_{pw}(s_{in,j}, p) = t_{uw}(s_{in,j}, p - 1) + \tau_{wash}(j)y(s_{in,j}, p - 2) \quad \forall\ s_{in,j} \in S_{in,j}, j \in J, p \in P, p > p_2 \quad (62)$$

Constraints 63 and 64 ensure that the time at which a washout begins coincides with the finishing time of a unit operation.

$$t_{uw}(s_{in,j}, p) \ge t_p(s_{out,j}, p) - H(1 - y(s_{in,j}, p - 1)) \quad \forall\ s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (63)$$

$$t_{uw}(s_{in,j}, p) \le t_p(s_{out,j}, p) - H(1 - y(s_{in,j}, p - 1)) \quad \forall\ s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p \ge p_1 \quad (64)$$

2.2.5.2. Scheduling for Direct Recycle/Reuse. The scheduling constraints that deal with the direct recycle/reuse of water for the zero-effluent model are very similar to constraints 42−46 in the multiple storage vessel model. However, the time at which the water is recycled/reused does not coincide with the time product is produced, but rather with the time that a washout ends.

2.2.5.3. Storage Vessel Scheduling. The first scheduling constraints considered for the storage vessel ensure that the time at which water is sent to a storage vessel coincides with the time at which this water is produced. In the zero-effluent case, the inlet time must coincide with the time at which the washout ends. This is given in constraints 65 and 66. Similar constraints hold for the outlet time; however, these constraints are similar to constraints 33 and 34 in the multiple storage vessel model as water is reused at the beginning of a unit operation.

$$ts_{in}(s_{in}, j, u, p) \ge t_{pw}(s_{in,j}, p) - H(1 - xs_{in}(s_{in}, j, u, p)) \quad \forall\ s_{in,j} \in S_{in,j}, j \in J, p \in P, s_{in} \in S_{in} \quad (65)$$

$$ts_{in}(s_{in}, j, u, p) \le t_{pw}(s_{in,j}, p) + H(1 - xs_{in}(s_{in}, j, u, p)) \quad \forall\ s_{in,j} \in S_{in,j}, j \in J, p \in P, s_{in} \in S_{in} \quad (66)$$

It is important to note that the storage scheduling constraints 27−29 and 36−41 also hold for the zero-effluent model.

Constraints 67 and 68 are modified versions of constraints 32 and 35. In the zero-effluent case, the binary variables describing water going to and from a storage vessel are state dependent.

$$xs_{in}(s_{in}, j, u, p) \le y(s_{in,j}, p - 2), \quad \forall\ s_{in} \in S_{in,j} \in J, p \in P, p > p_2, s_{in,j} \in S_{in,j} \quad (67)$$

$$xs_{out}(s_{in}, u, j, p) \le y(s_{in}, j, p), \quad \forall\ s_{in} \in S_{in}, j \in J, p \in P, s_{in,j} \in S_{in,j} \quad (68)$$

2.2.5.4. Time Horizon Constraints. The time horizon constraints given in constraints 47−51 also hold with the addition of constraints 69 and 70 for the times describing the beginning and ending of a washout.

$$t_{uw}(s_{in,j}, p) \le H, \quad \forall\ s_{in,j} \in S_{in,j}, p \in P \quad (69)$$

$$t_{pw}(s_{in,j}, p) \le H, \quad \forall\ s_{in,j} \in S_{in,j}, p \in P \quad (70)$$

2.2.5.5. Maximum Storage Time. Constraint 71 ensures that the length of time that water is stored in a storage vessel does not exceed a predetermined maximum length. In some processing industries, it is imperative to minimize the risk of microbial contamination. Thus, a maximum residence time of stored water is defined to ensure that the chances of microbial growth in the water are minimized. Constraint 72 is added to ensure that water leaves the storage vessel at the time point directly after the time point it entered. In this model, it is assumed that, at a time point, only one unit will send water to a storage vessel and, at the following time point, only one unit will receive water from a storage vessel.

$$\mathrm{ts_{out}}(s_{\mathrm{in}}, u, j, p) - \mathrm{ts_{in}}(s_{\mathrm{in}}, j', u, p-1) \leq \bar{T}_{\mathrm{stor}} + H(2 - \mathrm{xs_{out}}(s_{\mathrm{in}}, u, j, p) - \mathrm{xs_{in}}(s_{\mathrm{in}}, j', u, p-1)) \quad \forall\, s_{\mathrm{in}} \in S_{\mathrm{in}}, j, j' \in J, u \in U, p \in P, p > p_1 \quad (71)$$

$$\sum_{j,\, p'} \mathrm{xs_{out}}(s_{\mathrm{in}}, u, j, p') = \sum_{j,\, p'-1} \mathrm{xs_{in}}(s_{\mathrm{in}}, j, u, p'-1) \quad \forall\, s_{\mathrm{in}} \in S_{\mathrm{in}}, j \in J, u \in U, p \in P, p \geq p' \quad (72)$$

Constraint 73 ensures that a unit will not operate at consecutive time points. In essence, this ensures that a washout takes place.

$$y(s_{\mathrm{in},j}, p) + y(s_{\mathrm{in},j}', p-1) \leq 1 \quad \forall\, s_{\mathrm{in},j}, s_{\mathrm{in},j}' \in S_{\mathrm{in},j}, p \in P, p \geq p_1 \quad (73)$$

2.2.6. Objective Function. The objective function for the zero-effluent model is the minimization of effluent water, given in constraint 74. This objective function can be used since the required production for the given time horizon is known.

$$\min \sum_{p} \sum_{j} \sum_{s_{\mathrm{in}}} \mathrm{fz_e}(s_{\mathrm{in},j}, p), \quad \forall\, s_{\mathrm{in},j} \in S_{\mathrm{in},j}, p \in P \quad (74)$$

The zero-effluent model where the contaminant mass is negligible comprises constraints 12, 13, 18−20, 22, 24−29, 33, 34, 36−51, 53−59, and 61−74. For the case where the contaminant mass is not negligible, constraints 12−14, 16−20, 22, 24−29, 33, 34, 36−51, and 53−74 hold.

3. Illustrative Examples

Two illustrative examples are presented with the first illustrative example being solved using the multiple storage vessel model and the second illustrative example being solved using the zero-effluent model.

3.1. First Illustrative Example. The first illustrative example involves scheduling three processing units. Each unit produces a specific product. The wastewater generated from the first unit contains a single contaminant, i.e., contaminant 1. This is similar for the second processing unit, where the wastewater generated only contains a single contaminant, but, in this instance, it is contaminant 2. The third unit produces wastewater that contains three contaminants, namely, contaminants 1, 2, and 3. It is furthermore given that storage of any water containing contaminant 3 is not allowed. For this instance, two storage vessels are considered for the storage of wastewater: one for wastewater containing only contaminant 1 and one for wastewater containing only contaminant 2.

The concentration data used for the first example is given in Table 1. It is important to note that wastewater from process 3 can only be directly reused by unit three.

The required cost data is given in Table 2, as are the durations of each operation in each unit and the maximum water for each unit.

It is further stated that, in process 1, for every 1 kg of water used, 3 kg of raw material is used. In process 2, for every 1 kg of water used, 2 kg of raw material is used, and for process 3, for every 1 kg of water used, 1.5 kg of raw material is used. The size of each storage vessel used is 200 tons. The maximum inlet concentration into the first storage vessel for contaminant 1 is 50 000 ppm and for contaminant 2 is 0 ppm; for the second storage vessel, the maximum inlet concentration for contaminant 1 is 0 ppm and for contaminant 2 is 50 000 ppm. In both storage vessels, the inlet concentration of contaminant 3 is 0 ppm. The time horizon of interest for this example is 8 h. For this example, the objective function is the maximization of profit, as given in constraint 52.

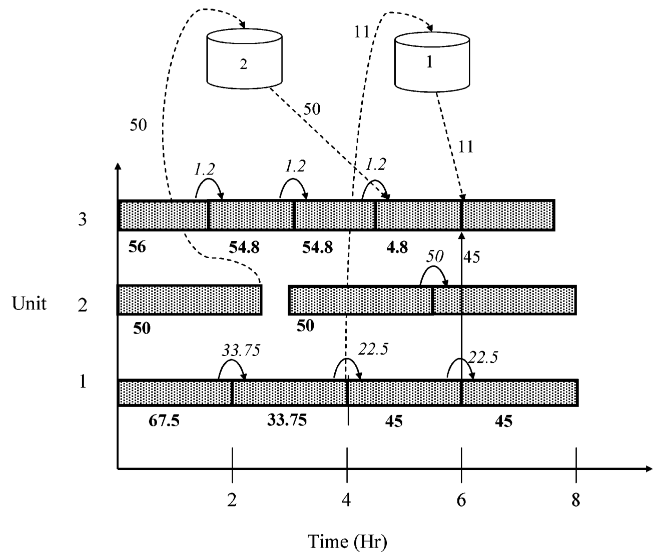

Figure 3. Schedule for first example.

Table 1. Concentration Data for Example One

process	contaminant	$\bar{C}_{\mathrm{in}}(j)$ (ppm)	$\bar{C}_{\mathrm{out}}(j)$ (ppm)	mass load (g)
1	1	5	15	675
	2	0	0	0
	3	0	0	0
2	1	0	0	0
	2	50	100	25 000
	3	0	0	0
3	1	120	220	5 600
	2	200	450	14 000
	3	200	9 500	520 800

Table 2. Cost Data for the Examples

	cost of product (c.u.)	cost of raw material (c.u.)	duration (h)	maximum water (ton)
process 1	2 300	108	2	67.5
process 2	2 000	82	2.5	50
process 3	1 050	95	1.5	56

The first example was solved in GAMS using DICOPT, with CPLEX as the MIP solver and CONOPT as the NLP solver. The resulting model had 192 binary variables with 8 time points being the optimal number of time points. The solution took 16.8 CPU s using a Pentium 4, 3.2 GHz processor. Four major iterations were required to find the solution. The resulting schedule is shown in Figure 3. The bold numbers represent freshwater fed into a unit, the italic numbers represent directly reused water, and the regular numbers represent water reused through the storage vessel. The water amounts given Figure 3 are in tons.

The schedule given in Figure 3 generates 461.7 tons of effluent. This is a savings of 34% when compared to the operation without recycle/reuse of wastewater. The value of the objective function is 2.65×10^6 c.u. It is important to note that the value of the objective function is not necessarily globally optimal, since the formulation is a MINLP.

3.2. Second Illustrative Example. The second example deals with the scheduling of three mixing vessels in zero-effluent mode. Each mixer can mix any one of three products. After mixing, the product is removed and the mixer is washed out. The washout water thus contains any product residue in the mixer. The washout water is of such a nature that it can be reused as a constituent in a subsequent batch of the same

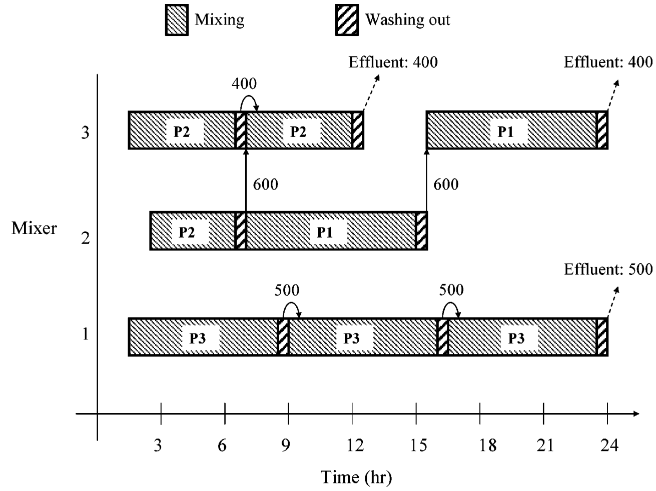

Figure 4. Schedule for zero-effluent example.

Table 3. Mixing Times and Raw Material Requirements

	mixing times (h)			water for raw material (kg)	raw material other than water (kg)
	mixer 1	mixer 2	mixer 3		
product 1	8	8	8	1600	400
product 2	5	4	5	1650	350
product 3	7	6	7	1800	200

product. The mixing times and raw material requirements are given in Table 3. Mixer 1 requires 500 kg of water for a washout, mixer 2 requires 600 kg of water for a washout, and mixer 3 requires 400 kg of water for a washout. The washing out of a mixer takes 30 min. There are three storage vessels available, with each storage vessel dedicated to the storage of wastewater containing a specific product residue. To avoid any product integrity issues, the different types of wastewater are not permitted to mix. In this example, it is assumed that the contaminant mass present in the washout water is not negligible, since 100 kg of product residue remains in each mixer after the product has been removed. The maximum residence time of the wastewater in any of the storage vessels is 6 h.

The resulting model was solved in GAMS using DICOPT. The NLP solver was CONOPT, and the MIP solver was CLPEX. The model had 288 binary variables. The solution time was 5 CPU s using a Pentium 4, 3.2 GHz processor. The optimal number of time points was 8. Three major iterations were required to find a solution. The resulting schedule is shown in Figure 4. The numbers in Figure 4 depict water reused as part of the product and generated as effluent. All the water amounts are in kilograms. The product mixed by each mixer is depicted by the letter "P" and the corresponding product number. It is important to note that the storage vessels were not needed in this schedule. As can be seen in the figure, the effluent generated is 1300 kg. This corresponds to a 66.7% savings in wastewater compared to the operation without reuse. Furthermore, 500 kg of product residue was recovered.

It is important to note that effluent is only produced when the required production of a product is met, and hence, there is no further opportunity for water reuse. Furthermore, washout water from the last batch of a product is not stored because it is not known when this water will be reused. This is ensured by constraint 20. It is further important to note that there was no storage of wastewater for the duration of the time horizon; hence, constraint 71 is, in essence, redundant. However, constraint 71 is present in the formulation and cannot be discarded, even in examples such as the one presented.

The methodology for both the multiple contaminant, multiple storage vessel case and the zero-effluent case serve as a means to determine the production schedule that will produce the least amount of effluent. In practice, the methodology would be applied to an existing plant with the required data captured before the solution of the methodology.

4. Concluding Remarks

A mathematical formulation for minimization of multiple-contaminant wastewater has been developed. The formulation takes multiple storage vessels into consideration and is, thus, able to deal with specific storage regimes. The model takes the form of an MINLP.

The multiple storage vessel formulation was extended to include a special type of operation where wastewater is reused as a constituent of a product. This type of water reuse enables an operation to operate in a near-zero-effluent manner. The formulation for the zero-effluent type of operation deals with scenarios where the contaminant mass is negligible and significant. The formulation uses multiple storage vessels for the storage of different types of wastewater, as different types of wastewater are not permitted to mix. This ensures product integrity is not compromised.

The multiple storage vessel formulation was applied to an illustrative example. The example involved the scheduling of an operation where there were three processing units. Units 1 and 2 produced wastewater with single, but different, contaminants, and unit 3 produced wastewater with multiple contaminants present. Two storage vessels were available for the storage of wastewater from units 1 and 2, respectively. The solution found a wastewater target of 461.7 tons of water, which is a 34% savings in wastewater.

The second illustrative example dealt with the scheduling of three mixing vessels. In this operation, water was reused as part of the product. The resulting schedule only produced 1300 kg of wastewater, which corresponds to 66.7% savings in wastewater.

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Appendix A

The linearization of the bilinear terms as discussed previously is as follows.

Let

$$C_{\text{out}}(j, c, p) f_{\text{p}}(j, p) = \Gamma_1(j, c, p)$$

with the following bounds on each variable,

$$0 \le c_{\text{out}}(j, c, p) \le \bar{C}_{\text{out}}(j, c)$$

$$0 \le f_{\text{p}}(j, p) \le \bar{F}_{\text{w}}(j)$$

then the following constraints hold.

$$\Gamma_1(j, c, p) \ge 0, \quad \forall\, j \in J, p \in P, c \in C \tag{75}$$

$$\Gamma_1(j, c, p) \ge \bar{F}_{\text{w}}(j) c_{\text{out}}(j, c, p) + \bar{C}_{\text{out}}(j, c) f_{\text{p}}(j, p) - \bar{F}_{\text{w}}(j) \bar{C}_{\text{out}}(j, c), \quad \forall\, j \in J, p \in P, c \in C \tag{76}$$

$$\Gamma_1(j, c, p) \le \bar{F}_{\text{w}}(j) c_{\text{out}}(j, c, p), \quad \forall\, j \in J, p \in P, c \in C \tag{77}$$

$$\Gamma_1(j, c, p) \le f_p(j, p)\bar{C}_{out}(j, c), \quad \forall\, j \in J, p \in P, c \in C \qquad (78)$$

Nomenclature

Sets

$P = \{p \mid p = \text{time point}\}$
$J = \{j \mid j = \text{unit}\}$
$C = \{c \mid c = \text{contaminant}\}$
$U = \{u \mid u = \text{reusable water storage vessel}\}$
$S_{in} = \{s_{in} \mid s_{in} = \text{input state into any unit}\}$
$S_{out} = \{s_{out} \mid s_{out} = \text{output state from any unit}\}$
$S = \{s \mid s = \text{any state}\} = S_{in} \cup S_{out}$
$S_{in,j} = \{s_{in,j} \mid s_{in,j} = \text{input state into unit } j\} \subset S_{in}$
$S_{out,j} = \{s_{out,j} \mid s_{out,j} = \text{output state from unit } j\} \subset S_{out}$

Continuous Variables

$f_u(j, p)$ = mass of water into unit j at time point p
$f_p(j, p)$ = mass water produced at time point p from unit j
$f_e(j, p)$ = mass of effluent water from unit j at time point p
$f_f(j, p)$ = mass of freshwater into unit j at time point p
$f_r(j', j, p)$ = mass of water recycled to unit j from j' at time point p
$fs_{in}(j, u, p)$ = mass of water to storage vessel u from unit j at time point p
$fs_{out}(u, j, p)$ = mass of water from storage vessel u to unit j at time point p
$q_s(u, p)$ = amount of water stored in storage vessel u at time point p
$c_{in}(j, c, p)$ = inlet concentration of contaminant c in unit j at time point p
$c_{out}(j, c, p)$ = outlet concentration of contaminant c in unit j at time point p
$cs_{in}(u, c, p)$ = inlet concentration of contaminant c in storage vessel u at time point p
$cs_{out}(u, c, p)$ = outlet concentration of contaminant c in storage vessel u at time point p
$m_u(s_{in,j}, p)$ = mass of raw material used in unit j at time point p
$m_p(s_{out,j}, p)$ = mass of product produced from unit j at time point p
$t_u(s_{in,j}, p)$ = time at which water or raw material is used at time point p in unit j
$t_p(s_{out,j}, p)$ = time at which water or product is produced at time point p from unit j
$t_r(j', j, p)$ = time at which water is recycled from unit j' to unit j at time point p
$ts_{in}(j, u, p)$ = time at which water goes to storage vessel u from unit j at time point p
$ts_{out}(u, j, p)$ = time at which water leaves storage vessel u to unit j at time point p
$fz_r(s_{in}, j', j, p)$ = mass of water containing s_{in}, reused between unit j and j' at time point p
$m_f(s_{in,j}, p)$ = mass of freshwater used in unit j for inlet state s_{in} at time point p
$m_{raw}(s_{in,j}, p)$ = mass of raw material other than water used in unit j for inlet state s_{in} at time point p
$m_{rb}(s_{in,j}, p)$ = mass of raw materials, other than water, used from bulk storage in unit j at time point p
$cs(s_{in}, u, p)$ = concentration of state s_{in} in storage vessel u at time point p
$fzs_{out}(s_{in}, u, j, p)$ = mass of water containing state s_{in} reused from storage vessel u to unit j at time point p
$fzs_{in}(s_{in}, j, u, p)$ = mass of water containing state s_{in} sent to storage vessel u from unit j at time point p
$f_{wash}(s_{in,j}, p)$ = mass of water used for a washout of unit j at time point p
$fz_e(s_{in,j}, p)$ = mass of water containing state s_{in} discarded as effluent from unit j at time point p
$t_{uw}(s_{in,j}, p)$ = time at which a washout begins in unit j at time point p
$t_{pw}(s_{in,j}, p)$ = time at which a washout ends in unit j at time point p

Binary Variables

$y(s_{in,j}, p)$ = binary variable for usage of state s_{in} in unit j at time point p
$y_r(j', j, p)$ = binary variable for recycle from unit j' to unit j at time point p
$ys_{in}(j, u, p)$ = binary variable for water into storage vessel u from unit j at time point p
$ys_{out}(u, j, p)$ = binary variable for usage of water from storage vessel u to unit j at time point p
$xs_{in}(s_{in,j}, u, p)$ = binary variable for water containing state s_{in} sent to storage vessel u from unit j at time point p
$xs_{out}(s_{in}, u, j, p)$ = binary variable for water containing state s_{in} sent to unit j at time point p from storage vessel u

Parameters

$SP(s_{out})$ = selling price of product s_{out} (c.u./(kg of product))
$CR(s_{in})$ = cost of raw material s_{in}(c.u./(kg of raw material))
CE = cost of effluent treatment (c.u./(kg of water))
$M_{lost}(c, j)$ = mass load of contaminant c added from unit j to the water stream during the washout
$\bar{F}_w(j)$ = maximum amount of water to unit j
$\bar{C}_{in}(c, j)$ = maximum inlet concentration of contaminant c in unit j
$\bar{C}_{out}(c, j)$ = maximum outlet concentration of contaminant c from unit j
$\tau(s_{in,j})$ = mean processing time of state s_{in} in unit j
$Q_s^0(u)$ = initial amount of water stored in storage vessel u
$\bar{Q}_s(u)$ = maximum storage capacity of a storage vessel u
$CS_{out}^{O}(c, u)$ = initial concentration of contaminant c in the storage vessel u
$\overline{CS}_{in}(c, u)$ = maximum inlet concentration of contaminant c into storage vessel u
$M_{raw}(s_{in})$ = fixed mass of raw material, other than water, used for state s_{in}
$M_u(s_{in})$ = fixed mass of total raw materials used for state s_{in}
$M_{water}(s_{in})$ = mass of water used as raw materials for state s_{in}
$F_{water}(j)$ = amount of water used to washout unit j
$\tau_{wash}(j)$ = duration of washout of unit j
$\bar{T}_{stor}$ = maximum storage time of water in a storage vessel
$Cz_{out}(s_{in,j})$ = outlet concentration of washout water from unit j

Literature Cited

(1) Wang, Y. P.; Smith, R. Wastewater Minimization. *Chem. Eng. Sci.* **1994**, *49*, 981.
(2) Doyle, S. J.; Smith, R. Targeting Water Reuse with Multiple Contaminants. *Trans. Inst. Chem. Eng.* **1997**, *75b*, 181.
(3) Alva-Argáez, A.; Kokossis, A. C.; Smith, R. Wastewater Minimization of Industrial Systems Using an Integrated Approach. *Comput. Chem. Eng.* **1998**, *22* (Suppl.), s741.
(4) Hallale, N. A New Graphical Targeting Method for Water Minimization. *Adv. Environ. Res.* **2002**, *6*, 377.
(5) Wang, Y. P.; Smith, R. Time Pinch Analysis. *Chem. Eng. Res. Des.* **1995**, *73*, 905.
(6) Majozi, T.; Brouckaert, C. J.; Buckley, C. A. A Graphical Technique for Wastewater Minimization in Batch Processes. *J. Environ. Manage.* **2006**, *78*, 317.

(7) Foo, D. C. Y.; Manan, Z. A.; Tan, Y. L. Synthesis of Maximum Water Recovery Network for Batch Process Systems. *J. Clean. Prod.* **2005**, *13*, 1381.

(8) Grau, R.; Graells, M.; Corominas, J.; Espuña, A.; Puigjaner, L. Global Strategy for Energy and Waste Analysis in Scheduling and Planning of Multiproduct Batch Chemical Processes. *Comput. Chem. Eng.* **1996**, *20*, 853.

(9) Almató, M.; Sanmartí, E.; Espuña, A.; Puigjaner, L. Rationalizing Water Use in the Batch Process Industry. *Comput. Chem. Eng.* **1997**, *21*, s971.

(10) Kim, J. K.; Smith, R. Automated Design of Discontinuous Water Systems. *Process Saf. Environ. Prot.* **2004**, *82*, 238.

(11) Majozi, T. Wastewater Minimization Using Central Reusable Storage in Batch Plants. *Comput. Chem. Eng.* **2005**, *29*, 1631.

(12) Quesada, I.; Grossmann I. E. Global Optimization of Bilinear Process Networks with Multicomponent Flows. *Comput. Chem. Eng.* **1995**, *19*, 1219.

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