# Storage Design for Maximum Wastewater Reuse in Multipurpose Batch Plants

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This paper presents an algorithm for the minimization of reusable water storage in multipurpose batch plants. The algorithm is based on a two-stage approach, with each stage focusing on a dedicated objective function. In the first stage, the objective is the minimization of freshwater, given the maximum reusable water storage capacity. After the minimum freshwater target has been set, it is then fixed and used as an input parameter in the second stage. In the second stage, central reusable water storage capacity is a variable that must be optimized, subject to the minimum freshwater target set in the first stage. The overall formulation is based on a continuous-time approach developed by Majozi and Zhu [*Ind. Chem. Eng. Res*. **2001**, *40* (25), 5935−5949], using a so-called state sequence network, and is an extension of recently published work on wastewater minimization using central reusable water storage in batch plants [Majozi, *Comput. Chem. Eng*. **2005**, *29* (7), 1631−1646]. The algorithm has been applied to a case study in which a >45% savings in freshwater demand was observed, compared to the case without the exploitation of water recycle and reuse. Moreover, a >60% reduction in reusable water storage capacity was observed, in comparison to the situation in which the central reusable water storage capacity is fixed a priori. It is worthy of mention that the presented methodology is only applicable to batch processes that are characterized by single contaminants. Furthermore, the mathematical formulation on which it is based is nonlinear (mixed-integer nonlinear programming, MINLP) and nonconvex, which implies that global optimality cannot be guaranteed, except in special cases.

## 1. Introduction

Most of the recent work in process integration of batch processes has focused on wastewater minimization, with limited or no consideration for storage optimization.[1−9] Earlier work has described a continuous-time approach that used a so-called state sequence network,[1] and later work described wastewater minimization using central reusable water storage in batch plants.[2] Wang and Smith[3] developed a graphical technique for wastewater minimization in single contaminant processes. In their method, the plant production schedule was assumed to be given, which implies that the start and finish times of water-using operations were known before optimization. The advantage of this method is its transparency at each step of the optimization procedure, thereby allowing the user to apply practical judgment. Grau et al.[4] developed a mathematical technique for waste minimization with an emphasis on the waste that was generated during changeover. However, this method is readily applicable to multiproduct batch processes, rather than multipurpose batch processes. It is also based on the assumption that there exists an optimal production plan within which the sequencing of various campaigns is optimized to minimize changeover costs. Heuristics were then applied to obtain a feasible solution. A similar technique was developed by Almató et al.[5] This technique utilizes storage tanks to override the time constraint in the exploration of reuse and recycle opportunities. The capacity of storage tanks was not optimized, because these were implicitly assumed to exist. Because of the size of the resultant model, the solution procedure also involves heuristics in the determination of the feasible solution.

Yao and Yuan[6] developed a discrete time mathematical model for waste minimization in batch processes by optimizing production campaigns. The resultant mixed-integer nonlinear programming (MINLP) problem was solved using stochastic optimization. The major drawback of discrete time methodologies is their explosive binary dimension, which renders them inadequate for practical purposes. Puigjaner et al.[7] used the work of Almató et al.[5] to develop a software tool to assist engineers in the decision-making about water management in batch process industries. Recently, Majozi et al.[9] developed a graphical targeting and design technique for batch processes in which the schedule or sequencing of water-using operations is predefined.

In all of the aforementioned methods, the main concern is freshwater or wastewater minimization without any focus on the capacity of central reusable water storage. Central reusable water storage has a critical role in wastewater minimization, because it allows the time dimension to be bypassed, thereby allowing the recycling and reuse of water. In batch processes, however, this can become a critical issue, because the available space is usually limited. As a result, the reusable water storage capacity might have to be justified before inclusion in the production train. Nonetheless, this justification need not compromise the minimum amount of freshwater and wastewater.

This paper presents a methodology that intends to minimize the reusable water storage capacity while minimizing the amount of freshwater requirement and wastewater generation. These objectives are conflicting in nature, because an increase in the reusable water storage capacity allows a reduction in freshwater use, because of increased water reuse. On the other hand, a reduction in the reusable water storage capacity results in increased freshwater use, as a result of reduced water reuse. This paper addresses this conflict in objectives through the use of a two-stage solution procedure. The mathematical formulation upon which this procedure is based is a continuous-time MINLP that has been presented earlier by Majozi.[2]

## 2. The Nature of the Problem

This section gives detailed information on the nature of the problem at hand. First, the problem that the proposed algorithm intends to address is presented, followed by a concise problem statement.

**2.1. Problem Description.** Storage is well-known to have a significant role in bypassing the time dimension that is inherent in batch facilities. This allows for the reuse and recycling of water across different time intervals within a given time horizon,

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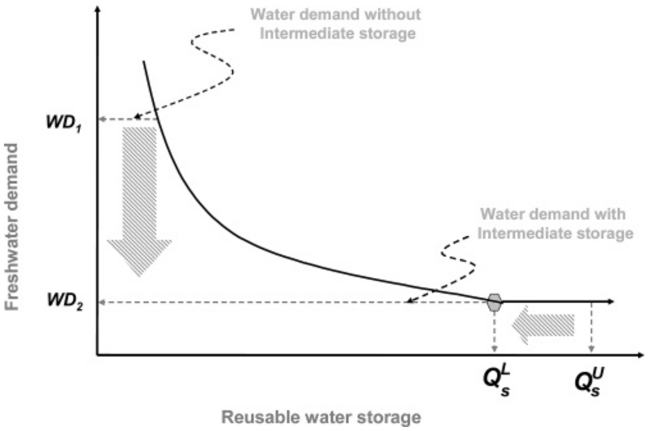


**Figure 1.** Impact of reusable water storage on freshwater demand.

thereby reducing the overall freshwater demand and wastewater generation. This is depicted in Figure 1, where $WD_1$ is the freshwater demand in the absence of intermediate water storage and $WD_2$ is the freshwater demand in the presence of storage. It is worthy of mention, however, that the absence of intermediate storage does not necessarily forbid the exploitation of direct recycle and reuse opportunities if time and concentration constraints allow. For example, a process that is finishing at time $t$ can always directly supply reusable water to another process starting at time $t$, as long as concentration constraints are not violated. The presence of intermediate storage further improves opportunities for water recycling and reuse, because water that cannot be directly reused or recycled can be stored for later use.

In situations characterized by significant physical constraints, which is a common encounter in batch production facilities, the size of reusable water storage might surface as one of the significant causes for concern. In these situations, the minimum storage capacity, which might involve total elimination, is mandatory. Figure 1 shows that there exists a minimum amount of storage, $Q_s^L$, beyond which the overall water demand for the operations involved is not affected. In most wastewater minimization formulations, the upper bound in water storage, i.e., $Q_s^U$, which is usually known a priori, is used during the optimization of freshwater use and wastewater generation. However, this might be much larger than the minimum water storage that corresponds to the minimum freshwater use and wastewater generation. This particular observation has always been overlooked in the literature. In Figure 1, note that the objectives which are being addressed are of a conflicting nature, because the minimization of freshwater use requires an increase in reusable water storage.

**2.2. Problem Statement.** More succinctly, the problem addressed in this paper can be stated as follows. Each water-using operation—which includes (i) the contaminant mass load, (ii) the water requirement, (iii) the duration or start and finish times to achieve the desired effect (e.g., mass transfer, degree of cleanliness of the vessel, etc.), (iv) maximum *potential* reusable water storage, (v) maximum inlet and outlet water concentrations, and (vi) time horizon of interest—determines the minimum reusable water storage, which is concomitant with the *minimum* freshwater requirement or wastewater generation. In this instance, the minimum reusable water storage could correspond to the complete elimination of reusable water storage, provided that the minimum freshwater requirement is not compromised. Mainly for this reason, reusable water storage is considered to be potential rather than existing in condition (iv). In condition (iii), if the duration instead of the start and finish times is given, then the minimization of storage should be considered within an overall scheduling framework in which the start and finish times become optimization variables.

## 3. Mathematical Model

The mathematical model presented in this section is based on the superstructure given in Figure 2 for wastewater minimization, which uses central reusable water storage of fixed capacity;[2] the sets, variables, and parameters used in the mathematical model are listed in Table 1. The superstructure represents a situation where there is potential for reusable water storage. In this situation, water used in each water-using

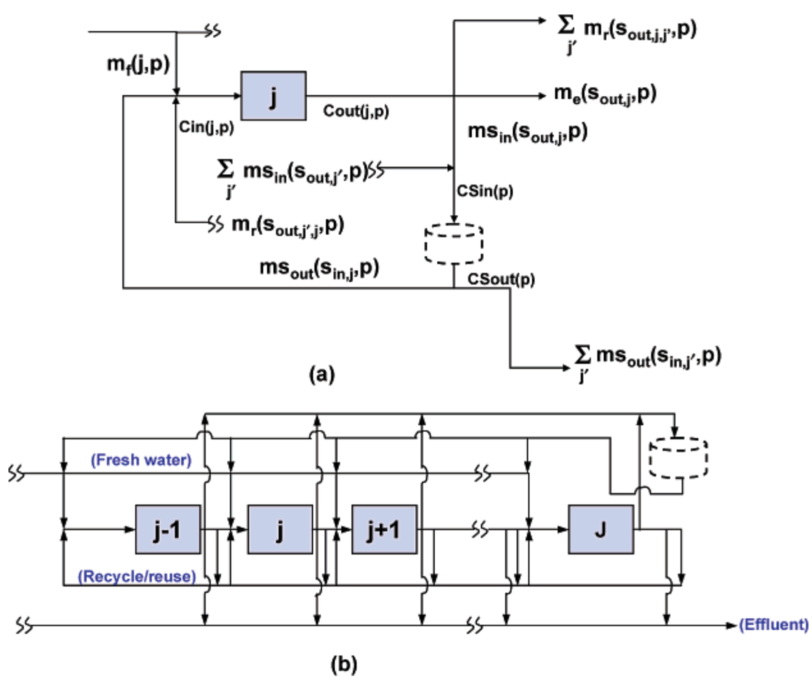


**Figure 2.** Superstructure for the mathematical formulation with *potential* reusable water storage: (a) magnified schematic diagram and (b) condensed schematic diagram.

**Table 1. Sets, Variables, and Parameters in the Mathematical Model**

| term | definition/comment |
|---|---|
| | Sets |
| $J$ | $\{j \mid j$ is a unit$\}P = \{p \mid p$ is a time point$\}$ |
| $S_{in,j}$ | $\{s_{in,j} \mid s_{in,j}$ is an input state to unit $j\}$ |
| $S_{out,j}$ | $\{s_{out,j} \mid s_{out,j}$ is an output state from unit $j\}$ |
| $S_{out,j,j'}$ | $\{s_{out,j,j'} \mid s_{out,j,j'}$ is a recycled state from unit $j$ to unit $j'\}$ |
| $S$ | $\{s \mid s$ is a state$\} = S_{in,j}\ \bar{C}_{out,j}\ \bar{C}_{out,j,j'}$ |
| | Variables |
| $C_{out}(j,p)$ | outlet concentration from unit $j$ at time point $p$ |
| $C_{in}(j,p)$ | inlet concentration to unit $j$ at time point $p$ |
| $CS_{out}(p)$ | outlet concentration from storage at time point $p$ |
| $CS_{in}(p)$ | inlet concentration to storage at time point $p$ |
| $m_e(s,p)$ | amount of state $s$ removed as effluent at time point $p$, $s \in S_{out,j}$ |
| $m_f(s,p)$ | amount of freshwater used in unit $j$ at time point $p$, $s \in S_{in,j}$ |
| $m_p(s,p)$ | amount of state $s$ produced at time point $p$, $s \in S_{out,j}$ |
| $m_u(s,p)$ | amount of state $s$ used at time point $p$, $s \in S_{in,j}$ |
| $m_r(s,p)$ | amount of state $s$ recycled or reused between two units $j$ and $j$' at time point p, $s \in S_{out,j,j'}$ |
| $ms_{in}(s,p)$ | amount of state $s$ that is transferred to storage at time point $p$, $s \in S_{out,j}$ |
| $ms_{out}(s,p)$ | amount of state $s$ that is transferred from storage to a particular unit $j$ at time point $p$, $s \in S_{in,j}$ |
| $qs(p)$ | amount of water stored at time point $p$ |
| $t_p(s,p)$ | time at which state $s$ is produced at time point $p$, $s \in S_{out,j}$ |
| $t_r(s,p)$ | time at which state $s$ is recycled or reused between two units $j$ and $j$' at time point $p$, $s \in S_{out,j,j'}$, |
| $t_u(s,p)$ | time at which state $s$ is used at time point $p$, $s \in S_{in,j}$ |
| $ts_{in}(s,p)$ | time at which state $s$ is transferred to storage from operation $j$ at time point $p$, $s \in S_{out,j}$ |
| $ts_{out}(s,p)$ | time at which state $s$ is transferred to operation $j$ from storage at time point $p$, $s \in S_{in,j}$ |
| $y(s,p)$ | binary variable associated with usage of state $s$ at time point $p$, $s \in S_{in,j}$ |
| $y_r(s,p)$ | binary variable associated with recycle or reuse between two units $j$ and $j$' at time point $p$, $s \in S_{out,j,j'}$ |
| $ys_{in}(s,p)$ | binary variable associated with the transfer of state $s$ from operation $j$ to storage at time point $p$, $s \in S_{out,j}$ |
| $ys_{out}(s,p)$ | binary variable associated with the transfer of state $s$ from storage to operation $j$ at time point $p$, $s \in S_{in,j}$ |
| | Parameters |
| $\bar{C}_{out}(j)$ | maximum outlet contaminant concentration from unit $j$ |
| $\bar{C}_{in}(j)$ | maximum inlet contaminant concentration to unit $j$ |
| $H$ | time horizon of interest |
| $M(j)$ | mass-load of contaminant in unit $j$ |
| $\bar{M}_u(j)$ | limiting/maximum water requirement in unit $j$ |
| $\underline{M}_u(j)$ | minimum water requirement in unit $j$ |
| $Q_s^0(s)$ | initial amount of state $s$ stored |
| $Q_s^U$ | maximum capacity of reusable water storage |
| $Q_s^L$ | minimum capacity of reusable water storage |
| $Q_s^L(p)$ | minimum capacity of reusable water storage at time point $p$ |
| $\tau(s_{in,j},p)$ | mean processing time for a state |
| $V_j$ | capacity of a particular unit $j$ |

operation $j$ can be supplied from the freshwater header, the recycle/reuse water header, the reusable water storage header, or a combination of the three headers. Water from each operation $j$ can be recycled to the same operation, reused in downstream processes, transferred to reusable water storage, and/or removed as effluent. If minimum freshwater requirement can be attained without reusable water storage, the option of receiving water from or transferring water to storage is nullified. For the sake of clarity, only water streams are shown in Figure 2. The index $p$ that appears in all the variables shown in the superstructure depicted in Figure 2 captures the essence of time. Figures 2a and 2b show a magnified and condensed view of the superstructure, respectively. Each of the water-using operations shown in the superstructure could either exist as an isolated entity or form part of a complete batch chemical process. Different water-using operations in the superstructure could belong to the same or distinct processes. The other process units in a complete batch plant are deliberately omitted from the diagram, because the focus of the mathematical formulation is only on water operations.

This mathematical model is composed of two sets of constraints that are built within the same framework. One set of constraints focuses on the exploration of water reuse/recycle opportunities, and the other focuses on proper sequencing to capture the time dimension. Although this model has been presented in detail elsewhere,[2] it is presented here in sufficient detail to facilitate understanding.

**3.1. Water Reuse/Recycle Constraints.** In regard to exploring the recycle and reuse opportunities within a complete batch process, two mass-transfer scenarios are mathematically formulated in the following sections. The first scenario is based on a fixed outlet concentration and fixed contaminant mass load from each water-using operation. In this scenario, the outlet concentration is always the maximum possible in a given water-using operation. This situation allows for the quantity of water used in the operation to vary from the limiting water requirement. The limiting water requirement is the amount of water required if the initial contaminant concentration in a water-using operation corresponds to the maximum permissible concentration. The second scenario is based on a fixed contaminant mass load and fixed water requirement for each water-using operation. In this situation, the inlet and outlet water concentrations are allowed to vary within predefined bounds. More succinctly, in the first scenario outlet concentration is a parameter and the flow rate is a variable, whereas in the second scenario, the opposite is true. However, in both scenarios, the mass load is fixed. The practical relevance of these scenarios can be justified by noting the following two examples.

The first scenario is typical of a washing operation, wherein the contaminant amount is fixed, e.g., washing a process vessel that is used in a fixed recipe. In this case, using a lesser amount of water will result in a higher concentration of contaminant in the wastewater stream for a fixed contaminant mass load. However, there is a limit to this outlet concentration, which is set by process conditions (such as saturation point, corrosion issues, etc.). This limit determines the minimum amount of freshwater that can be used. The second scenario, on the other hand, is typical of a liquid−liquid extraction operation, wherein for a given amount of organic phase, a certain amount of aqueous phase is required to remove a fixed amount of contaminant. This scenario is a common encounter in agrochemical operations where organic solvents are used as reaction media and water is used to remove inorganic salts that form as byproducts during the reactions. In this situation, the amounts of the aqueous (water) and organic phases are determined by the capacity of the equipment used. It is evident that, in this scenario, the outlet concentration does not need to be fixed at any level, but it should not exceed the maximum allowed.

**3.1.1. Scenario 1: Formulation for a Fixed Outlet Concentration and Fixed Contaminant Mass Load.** This formulation is based on the superstructure described in Figure 2.

$$m_u(s_{in,j},p) = \sum_{s_{out,j',j}} m_r(s_{out,j',j},p) + m_f(s_{in,j},p) + ms_{out}(s_{in,j},p) \quad (\forall\, j,j' \in J,\, p \in P,\, s_{in,j} \in S_{in,j},\, s_{out,j',j} \in S_{out,j',j}) \tag{1}$$

$$m_p(s_{out,j},p) = m_e(s_{out,j},p) + \sum_{s_{out,j,j'}} m_r(s_{out,j,j'},p) + ms_{in}(s_{out,j},p) \quad (\forall\, j,j' \in J,\, p \in P,\, s_{out,j} \in S_{out,j},\, s_{out,j,j',p} \in S_{out,j,j'}) \tag{2}$$

$$m_p(s_{out,j},p)C_{out}(j,p) = m_u(s_{in,j},p-1)C_{in}(j,p-1) + M(j)y(s_{in,j},p-1) \quad (\forall\, j \in J,\, s_{in,j} \in S_{in,j},\, s_{out,j} \in S_{out,j},\, p \in P,\, p > p_1) \tag{3}$$

$$C_{in}(j,p) = \sum_{s_{out,j',j}} m_r(s_{out,j',j},p)C_{out}(j',p) + ms_{out}(s_{in,j},p)CS_{out}(p) / \left[\sum_{s_{out,j',j}} m_r(s_{out,j',j},p) + m_f(s_{in,j},p) + ms_{out}(s_{in,j},p)\right] \quad (\forall\, j,j' \in J,\, p \in P,\, s_{out,j',j} \in S_{out,j',j},\, s_{in,j} \in S_{in,j}) \tag{4}$$

$$C_{out}(j,p) = \bar{C}_{out}(j)y(s_{in,j},p-1) \quad (\forall\, j \in J,\, p \in P,\, p > p_1,\, s_{in,j} \in S_{in,j}) \tag{5}$$

$$\underline{M}_u(j)y(s_{in,j},p) \le m_u(s_{in,j},p) \le \bar{M}_u(j)y(s_{in,j},p) \quad (\forall\, s_{in,j} \in S_{in,j},\, p \in P) \tag{6}$$

Constraint (1) states that the inlet stream into any operation $j$ is composed of a recycle/reuse stream, a freshwater stream, and a stream from reusable water storage. On the other hand, the outlet stream from operation $j$ can be removed as effluent, reused in other processes, recycled to the same operation, and/or sent to reusable water storage, as shown in constraint (2). Constraint (3) describes the mass balance around unit $j$. It states that the contaminant mass-load difference between the outlet and inlet streams for the same unit $j$ is the contaminant mass load picked up in unit $j$. The inlet concentration into operation $j$ is the ratio of the contaminant amount in the inlet stream and the quantity of the inlet stream, as stated in constraint (4). The amount of contaminant in the inlet stream to operation $j$ consists of the contaminant in the recycle/reuse stream and the contaminant in the reusable water storage stream. Constraint (5) states that the outlet concentration from any unit $j$ is fixed at a maximum predefined concentration corresponding to the same unit. Note that the streams are expressed in quantities instead of flow rates, which is indicative of any batch operation. The total quantity of water used at any point in time must be within the bounds of the equipment unit involved, as stated in constraint (6). The storage-specific constraints are described as follows.

$$qs(p) = qs(p-1) + \sum_{s_{out,j}} ms_{in}(s_{out,j},p) - \sum_{s_{in,j}} ms_{out}(s_{in,j},p) \quad (\forall\, j \in J,\, p \in P,\, p > p_1,\, s_{out,j} \in S_{out,j},\, s_{in,j} \in S_{in,j}) \tag{7}$$

$$qs(p_1) = Q_s^0 - \sum_{s_{in,j}} ms_{out}(s_{in,j},p_1) \quad (\forall\, j \in J,\, s_{in,j} \in S_{in,j}) \tag{8}$$

$$qs(p) \le Q_s^U \quad (\forall\, p \in P) \tag{9}$$

$$CS_{in}(p) = \frac{\sum_{s_{out,j}} ms_{in}(s_{out,j})C_{out}(j,p)}{\sum_{s_{out,j}} ms_{in}(s_{out,j},p)} \quad (\forall\, j,j' \in J,\, p \in P,\, s_{out,j',j} \in S_{out,j',j}) \tag{10}$$

$$CS_{out}(p) = qs(p-1)CS_{out}(p-1) + \sum_{s_{out,j}} ms_{in}(s_{out,j})C_{out}(j,p) / \left[qs(p-1) + \sum_{s_{out,j}} ms_{in}(s_{out,j},p)\right] \quad (\forall\, j,j' \in J,\, p \in P,\, p > p_1,\, s_{out,j',j} \in S_{out,j',j}) \tag{11}$$

$$CS_{out}(p_1) = CS_{out}^0 \tag{12}$$

Constraint (7) describes the mass balance around the reusable water storage tank. It states that the amount stored at any time point $p$ is determined by the amount stored at the previous time point $p - 1$ plus the difference between the quantity transferred from and the quantity transferred to the water-using operations at time point $p$. However, at the beginning of the time horizon of interest, none of the water-using operations are complete and ready to be transferred to storage. Also, the amount stored at the previous time point corresponds to the initial amount of reusable water available in storage ($Q_s^0$). Therefore, at the beginning of the time horizon, constraint (8) replaces constraint (7). Constraint (9) ensures that the amount of water stored at any point in time does not exceed the reusable water storage capacity.

Constraints (10) and (11) respectively give the inlet and outlet concentrations for the reusable water storage tank. At any given time point $p$, the inlet concentration is the ratio of the contaminant mass load in all streams transferred from water-using operations to the overall quantity of the stream transferred to the reusable water storage tank. The outlet concentration at any time point $p$ is defined as the contaminant load at the previous time point $p - 1$ plus the contaminant load in the incoming stream from water-using operations divided by the total quantity of reusable water in the storage tank. This is also the definition of the contaminant concentration inside the reusable water storage tank. Hence, it is assumed that the outlet concentration from the storage tank is the same as the concentration inside the tank. This is, indeed, a valid assumption if perfect mixing is achieved within the tank. It is evident that constraint (11) is not applicable at the beginning of the time horizon of interest, for reasons similar to those for constraint (7). Therefore, constraint (12) replaces constraint (11) at the beginning of the time horizon. These constraints constitute a complete water reuse/recycle mathematical model, which is a nonconvex MINLP, because of the bilinear terms encountered in constraints (3), (4), (10), and (11).

**3.1.2. Scenario 2: Formulation for a Fixed Water Quantity and Fixed Contaminant Mass Load.** In a situation where the quantity of water required in any given operation is fixed, constraints (5) and (6) must be modified as follows.

$$C_{out}(j,p) \le \bar{C}_{out}(j) y(s_{in,j}, p-1) \qquad (\forall\ j \in J, p \in P, p > p_1, s_{in,j} \in S_{in,j}) \quad (13)$$

$$m_u(s_{in,j},p) = \bar{M}_u(j) y(s_{in,j},p) \qquad (\forall\ s_{in,j} \in S_{in,j}, p \in P) \quad (14)$$

The foregoing constraints only consider material balances. However, batch operations are characterized by time-dependent activities, which require dedicated constraints. These are given in the following section.

**3.2. Sequencing/Scheduling Constraints.** The sequencing set of constraints focuses on capturing the time dimension, which is intrinsic in batch operations. The following constraints, which are applicable irrespective of the chosen scenario (scenario 1 or scenario 2), constitute the scheduling set of constraints for the proposed mathematical model.

$$y_r(s_{out,j,j'},p) \le y(s_{in,j'},p) \qquad (\forall\ s_{out,j,j'} \in S_{out,j,j'}, s_{in,j'} \in S_{in,j'}, p \in P, j,j' \in J) \quad (15)$$

$$t_r(s_{out,j,j'},p) \le t_p(s_{out,j},p) + H(1 - y_r(s_{out,j,j'},p)) \qquad (\forall\ j,j' \in J, s_{out,j,j'} \in S_{out,j,j'}, s_{out,j} \in S_{out,j}, p \in P) \quad (16)$$

$$t_r(s_{out,j,j'},p) \ge t_p(s_{out,j},p) - H(1 - y_r(s_{out,j,j'},p)) \qquad (\forall\ j,j' \in J, s_{out,j,j'} \in S_{out,j,j'}, s_{out,j} \in S_{out,j}, p \in P) \quad (17)$$

$$t_r(s_{out,j,j'},p) \le t_u(s_{in,j'},p) + H(1 - y_r(s_{out,j,j'},p)) \qquad (\forall\ j,j' \in J, s_{out,j,j'} \in S_{out,j,j'}, s_{in,j'} \in S_{in,j'}) \quad (18)$$

$$t_r(s_{out,j,j'},p) \ge t_u(s_{in,j'},p) - H(1 - y_r(s_{out,j,j'},p)) \qquad (\forall\ j,j' \in J, s_{out,j,j'} \in S_{out,j,j'}, s_{in,j'} \in S_{in,j'}, p \in P) \quad (19)$$

$$t_u(s_{in,j},p) \ge t_p(s_{out,j},p) - H(2 - y(s_{in,j},p) - y(s_{in,j},p-1)) \qquad (\forall\ j \in J, s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1) \quad (20)$$

$$t_u(s_{in,j},p) \ge t_p(s_{in,j},p') - H(2 - y(s_{in,j},p) - y(s_{in,j},p')) \qquad (\forall\ j \in J, s_{in,j} \in S_{in,j}, p,p' \in P, p \ge p') \quad (21)$$

$$t_u(s_{out,j},p) \ge t_p(s_{out,j},p') - H(2 - y(s_{out,j},p) - y(s_{out,j},p')) \qquad (\forall\ j \in J, s_{out,j} \in S_{out,j}, p,p' \in P, p \ge p') \quad (22)$$

Constraint (15) states that, if water is reused from operation $j$ to operation $j'$ at a given time point $p$, then operation $j'$ should commence at time point $p$. However, the fact that operation $j'$ commences at time point $p$ does not necessarily mean that there is a corresponding recycle/reuse stream at time point $p$. This is due to the fact that operation $j'$ could be using freshwater or water from storage, instead of recycle/reuse stream from another process $j$. Constraints (16) and (17) together ensure that water recycle/reuse from operation $j$ to operation $j'$ coincides with the completion of operation $j$ at time point $p$. Similarly, constraints (18) and (19) ensure that water recycle/reuse from operation $j$ to operation $j'$ coincides with the start of operation $j'$ at time point $p$. Constraint (20) states that any operation $j$ will start after the previous task in the same operation $j$ is complete at time point $p$. Constraints (21) and (22) respectively state that, if an operation $j$ starts or ends at two distinct time points, then the later time point must correspond to a later time. These constraints have been proven to improve computer processing unit (CPU) time and ensure robustness and feasibility in the model. The following sequence constraints are specific to the existence of reusable water storage.

$$ts_{in}(s_{out,j},p) \ge t_p(s_{out,j},p) - H(1 - ys_{in}(s_{out,j},p)) \qquad (\forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P) \quad (23)$$

$$ts_{in}(s_{out,j},p) \le t_p(s_{out,j},p) + H(1 - ys_{in}(s_{out,j},p)) \qquad (\forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P) \quad (24)$$

$$ys_{in}(s_{out,j},p) \le y(s_{in,j},p-1) \qquad (\forall\ j \in J, s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1) \quad (25)$$

Constraints (23) and (24) stipulate that, when the water stream is transferred from operation $j$ to reusable water storage, then the time of transfer should coincide with the completion of operation $j$. However, operation $j$ will only be completed and be able to transfer water to storage at time point $p$ if it started at time point $p - 1$. Also, the fact that operation $j$ commenced at time point $p - 1$ does not necessarily mean that it will transfer water to storage at time point $p$, because this water could be immediately reused/recycled and/or removed as effluent. This is captured by constraint (25). The following constraints (constraints (26)−(28)) are similar to constraints (23)−(25) but apply to the outlet stream of reusable water storage.

$$ts_{out}(s_{in,j},p) \ge t_u(s_{in,j},p) - H(1 - ys_{out}(s_{in,j},p)) \qquad (\forall\ j \in J, s_{in,j} \in S_{in,j}, p \in P) \quad (26)$$

$$ts_{out}(s_{in,j},p) \le t_u(s_{in,j},p) + H(1 - ys_{out}(s_{in,j},p)) \qquad (\forall\ j \in J, s_{in,j} \in S_{in,j}, p \in P) \quad (27)$$

$$ys_{out}(s_{in,j},p) \le y(s_{in,j},p) \qquad (\forall\ j \in J, s_{in,j} \in S_{in,j}, p \in P) \quad (28)$$

Constraints (26) and (27) state that, when water stream is transferred from storage to any operation $j$ for reuse, then the time of transfer must coincide with the start of operation $j$. Constraint (28) ensures that, whenever a water stream is transferred from storage to operation $j$ at time point $p$, operation $j$ then must commence at time point $p$. However, operation $j$ can start at time point $p$, even if there is no reusable water stream transferred from storage, because water could be received from recycle/reuse and freshwater streams.

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

$$ts_{out}(s_{in,j},p) \ge ts_{out}(s_{in,j'},p) - H(2 - ys_{out}(s_{in,j},p) - ys_{out}(s_{in,j'},p)) \qquad (\forall\ j,j' \in J, s_{in,j},s_{in,j'} \in S_{in,j}, p \in P) \quad (30)$$

$$ts_{out}(s_{in,j},p) \le ts_{out}(s_{in,j'},p) + H(2 - ys_{out}(s_{in,j},p) - ys_{out}(s_{in,j'},p)) \qquad (\forall\ j,j' \in J, s_{in,j},s_{in,j'} \in S_{in,j}, p \in P) \quad (31)$$

Constraint (29) ensures that, if reusable water is transferred from reusable water storage to operation $j'$ at time point $p'$ and later transferred to the same or another operation $j$ at time point $p$, the later time point then must correspond to a later time. If the transfer of water from reusable water storage to different operations $j$ and $j'$ occurs at the same time point $p$, this time point then must correspond to exactly the same time as that enforced by both constraints (30) and (31).

$$ts_{in}(s_{out,j},p) > ts_{in}(s_{out,j'},p') - H(2 - ys_{in}(s_{out,j},p) - ys_{in}(s_{out,j'},p')) \qquad (\forall\ j,j' \in J, s_{out,j},s_{out,j'} \in S_{out,j}, p,p' \in P, p > p') \quad (32)$$

$$ts_{\text{in}}(s_{\text{out},j},p) \geq ts_{\text{in}}(s_{\text{out},j'},p) - H(2 - ys_{\text{in}}(s_{\text{out},j},p) - ys_{\text{in}}(s_{\text{out},j'},p)) \quad (\forall\, j,j' \in J,\, s_{\text{out},j},s_{\text{out},j'} \in S_{\text{out},j},\, p \in P) \tag{33}$$

$$ts_{\text{in}}(s_{\text{out},j},p) \leq ts_{\text{in}}(s_{\text{out},j'},p) + H(2 - ys_{\text{in}}(s_{\text{out},j},p) - ys_{\text{in}}(s_{\text{out},j'},p)) \quad (\forall\, j,j' \in J,\, s_{\text{out},j},s_{\text{out},j'} \in S_{\text{out},j},\, p \in P) \tag{34}$$

Constraints (32)−(34) are similar to constraints (29)−(31) but apply to the inlet stream of reusable water storage.

$$ts_{\text{in}}(s_{\text{out},j},p) > ts_{\text{in}}(s_{\text{in},j'},p') - H(2 - ys_{\text{out}}(s_{\text{out},j},p) - ys_{\text{in}}(s_{\text{out},j'},p')) \quad (\forall\, j,j' \in J,\, s_{\text{in},j} \in S_{\text{in},j},\, s_{\text{out},j},s_{\text{out},j'} \in S_{\text{out},j},\, p,p' \in P,\, p > p') \tag{35}$$

$$ts_{\text{out}}(s_{\text{in},j},p) \geq ts_{\text{in}}(s_{\text{out},j'},p) - H(2 - ys_{\text{out}}(s_{\text{out},j},p) - ys_{\text{in}}(s_{\text{out},j'},p)) \quad (\forall\, j,j' \in J,\, s_{\text{in},j} \in S_{\text{in},j},\, s_{\text{out},j},s_{\text{out},j'} \in S_{\text{out},j},\, p \in P) \tag{36}$$

$$ts_{\text{out}}(s_{\text{in},j},p) \leq ts_{\text{in}}(s_{\text{out},j'},p) + H(2 - ys_{\text{out}}(s_{\text{out},j},p) - ys_{\text{in}}(s_{\text{out},j'},p)) \quad (\forall\, j,j' \in J,\, s_{\text{in},j} \in S_{\text{in},j},\, s_{\text{out},j},s_{\text{out},j'} \in S_{\text{out},j},\, p \in P) \tag{37}$$

Constraint (35) states that, if reusable water is transferred from operation *j*' to storage at time point *p*' and later transferred from reusable water storage to the same or another operation *j* at time point *p*, the latter transfer then must correspond to a later time. On the other hand, if the transfer of reusable water into and out of reusable water storage occurs at the same time point *p*, then this should correspond to the same time; i.e., the time of transfer from operation *j*' to reusable water storage must be equal to the time of transfer from reusable water storage to operation *j*. This is captured by constraints (36) and (37).

**3.3. Additional Constraints.** To ensure that all the reusable water from storage is completely reused within the chosen time horizon, a constraint for zero storage at the end of the time horizon is formulated, as shown in eq 38:

$$qs(p) = 0, \qquad p = |P| \tag{38}$$

Alternatively, constraint (39) might be used. This constraint ensures that the overall amount of freshwater used equals the overall amount of effluent produced over the time horizon of interest. This condition ascertains that no water remains in reusable water storage at the end of the time horizon.

$$\sum_{s_{\text{out},j}}\sum_{p} m_{\text{e}}(s_{\text{out},j},p) = \sum_{s_{\text{in},j}}\sum_{p} m_{\text{f}}(s_{\text{in},j},p) \quad (p \in P,\, s_{\text{out},j} \in S_{\text{out},j},\, s_{\text{in},j} \in S_{\text{in},j}) \tag{39}$$

The two sets of constraints presented in sections 3.1 and 3.2 constitute an overall mathematical model, which is used in the proposed two-stage solution algorithm.

**3.4. Objective Function.** The objective function for the mathematical model is dependent on the stage of the two-stage solution approach. In the first stage, the objective is simply to minimize the amount of freshwater, given a fixed capacity of central reusable water storage. However, in the second stage, the objective is to minimize the capacity of reusable water storage, while obeying the minimum amount of freshwater obtained in the first stage. Therefore, in the second stage, the central reusable water storage capacity is no longer fixed, but rather is treated as a variable with a known upper bound. The following section gives the detailed solution procedure.

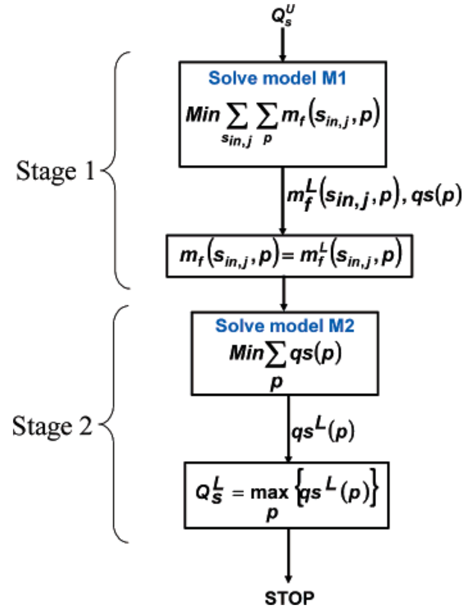


**Figure 3.** Algorithm for reusable water storage minimization.

## 4. Solution Procedure

The solution procedure for the problem previously stated involves two optimization stages in which freshwater and reusable water storage capacity are minimized sequentially, as explained in section 4.1 below.

**4.1. Two-Stage Optimization Algorithm for Freshwater and Reusable Water Storage Minimization.** The optimization procedure presented in this paper entails two stages, as summarized in Figure 3. In the first stage, a mathematical model for minimization of the freshwater requirement is solved based on the maximum potential reusable water storage, $Q_{\text{s}}^{U}$. For clarity, this model will be referred to as model M1 in this paper. In the second stage, the minimum freshwater requirement obtained from model M1 is used as an input parameter in another mathematical model for which the objective function is the minimization of reusable water storage; this model will be referred to as model M2 in this paper. Because different amounts of reusable water will be stored at various intervals within the time horizon of interest, the minimum reusable water storage capacity will correspond to the maximum amount of reusable water stored at any point within the time horizon of interest, as obtained from model M2 (see eq 40).

$$Q_{\text{s}}^{L} = \max_{p} \{q_{\text{s}}^{L}(p)\} \tag{40}$$

All the solutions presented in the following case study were obtained using a 1.5 GHz Pentium M processor and GAMS 2.5/DICOPT. The nonlinear programming (NLP) and mixed-integer linear programming (MILP) combination of solvers selected for DICOPT were CONOPT and CPLEX 7.0, respectively.

## 5. Case Study

To illustrate the application of the proposed algorithm, a completely batch operation that involves liquid−liquid extraction

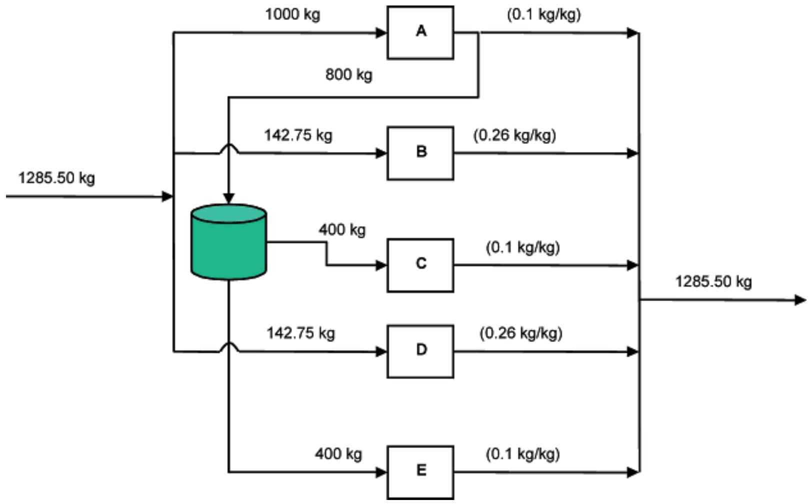


**Figure 4.** Water reuse/recycle network for minimum water use (for model M1).

**Table 2. Data for the Case Study**

| operation, $j$ | water (kg) | $\bar{C}_{out}(j)$ (kg salt/ kg water) | $\bar{C}_{in}(j)$ (kg salt/ kg water) | $t_u(s,p)$ (h) | $t_p(s,p)$ (h) | $M(j)$ (kg) |
|---|---|---|---|---|---|---|
| A | 1000 | 0.1 | 0 | 0 | 3 | 100 |
| B | 280 | 0.51 | 0.25 | 0 | 4 | 72.8 |
| C | [300, 400] | 0.1 | 0.1 | 4 | 5.5 | 0 |
| D | 280 | 0.51 | 0.25 | 2 | 6 | 72.8 |
| E | [300, 400] | 0.1 | 0.1 | 6 | 7.5 | 0 |
| **total** | **2360** | | | | | **245.6** |

(product washing) with water as the aqueous phase in the production of three agrochemical products A, B, and D, is considered.[9] The data for the production of these products are shown in Table 2. These agrochemical products are produced in batch reactors. All three reactions form sodium chloride (NaCl) as a byproduct, which is later removed from the final product. The removal of this byproduct is affected by the use of freshwater. It is worth mentioning that, although the objective of the washes is to remove NaCl, there are always traces of organics in water. In formulating the problem, however, it was assumed that the concentration of these organics is virtually negligible.

In the case of product A, the reaction occurs in an organic solvent that is highly immiscible with water, so that water is required solely for washing the salt. In the case of products B and D, however, water is used as the reaction solvent, and a further quantity is used to wash the product. While investigating this secondary washing of products B and D, it was observed that the salt load removed from the product was essentially zero, because of the fact that most of it had been removed with the reaction solvent water. However, it was considered that the washing step should not be discarded, because it constituted a quality control precaution in the case of unforeseen process problems. The secondary washing stages for products B and D are shown as operations C and E in Table 2. The foregoing explanation justifies the zero-contaminant mass loads corresponding to these operations. The minimum amount of water required in the secondary washing operation is 300 kg per batch, whereas the maximum amount is 400 kg.

The timing of the reaction and washing sequences is considered to be fixed byproduct requirements, which implies that there is no freedom to change the sequence to optimize the use of water.

**5.1. Computational Results.** The corresponding mathematical formulation entails 5534 constraints, as well as 1217 continuous and 280 binary variables. In solving model M1, on average, 4000 nodes were explored in the branch and bound search tree. The solution required three major iterations and required 309.41 CPU seconds to obtain the optimal solution of 1285.50 kg. This corresponds to a 45.53% reduction in freshwater demand, compared to the amount of water required in a situation in which there is no reuse (i.e., 2360 kg). A water reuse/recycle network that corresponds to this solution is shown in Figure 4, and the Gantt chart is shown in Figure 5. As evident from the Gantt chart, storage is necessitated by the time gaps between operations A and C, as well as between operations A and E. However, it is worth mentioning that global optimality of this optimal value cannot be proven, because of nonconvexity of the mathematical model at hand. A better optimum might exist.

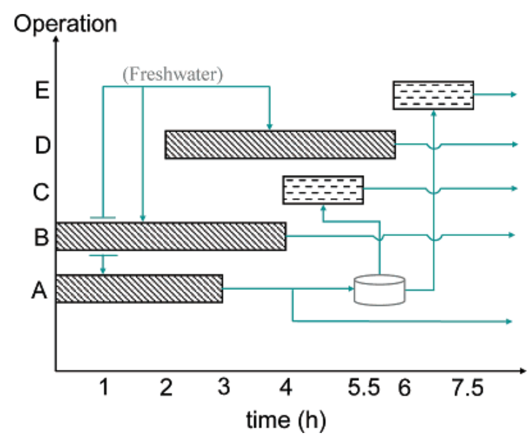


**Figure 5.** Gantt chart corresponding to minimum water use (for model M1).

After the minimum water requirement has been obtained, it is then used as an input parameter in the determination of minimum reusable water storage, i.e., stage 2 of the algorithm. Figure 6 shows the water reuse network with minimum reusable water storage, without compromising the minimum freshwater requirement. The corresponding Gantt chart is shown in Figure 7. This shows a reduction of 500 kg from the initial 800 kg used in stage 1 of the algorithm, i.e., 62.5% reduction in capacity. The major reduction in storage capacity is due to the recycle water stream from operation C back to storage. This water stream is later reused in operation E, which its concentration allows. Model M2 involved two major iterations and was

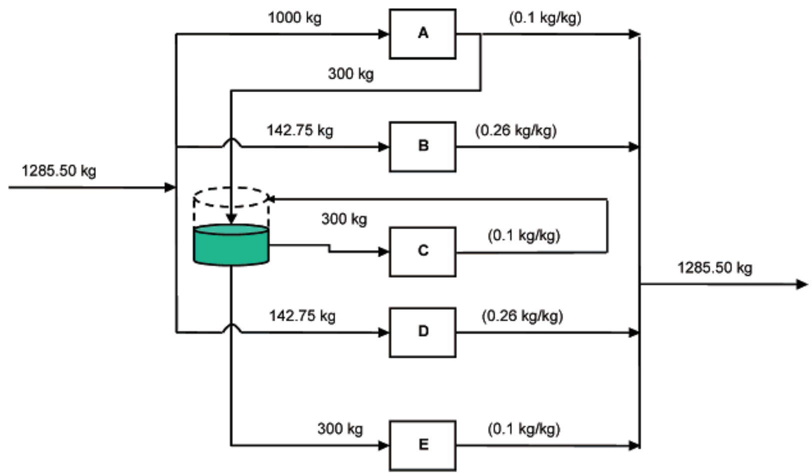


**Figure 6.** Water reuse/recycle network for minimum reusable water storage (for model M2).

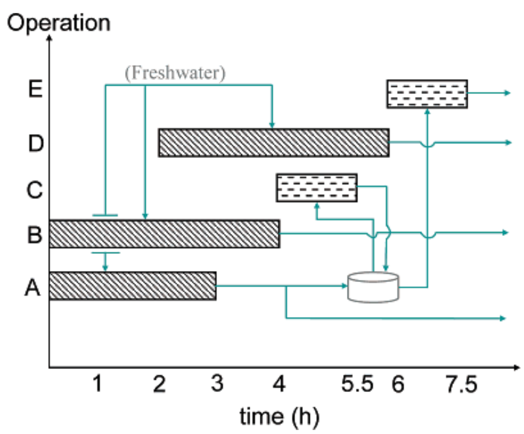


**Figure 7.** Gantt chart corresponding to minimum reusable water storage (for model M2).

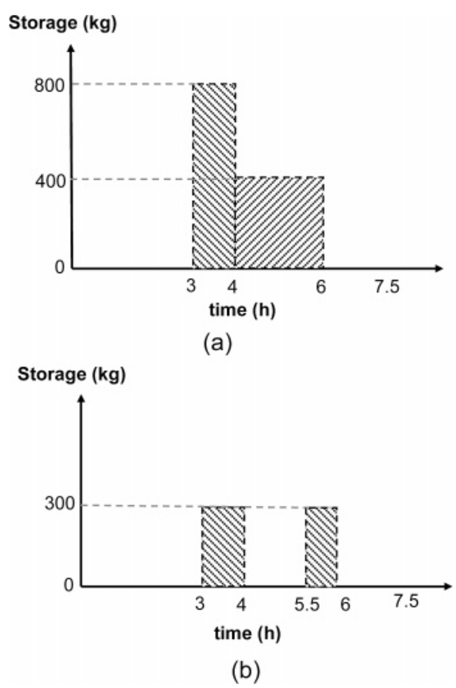


**Figure 8.** Storage profiles for (a) model M1 and (b) model M2.

solved in only 1.51 CPU seconds, because of the reduction in the number of variables. The reusable water storage profiles for models M1 and M2 are shown Figures 8a and 8b, respectively.

## 6. Concluding Remarks

An algorithm for the minimization of reusable water storage in batch facilities has been developed. The algorithm involves a two-stage approach. In the first stage, the objective is to minimize the freshwater requirement, given an upper bound on reusable water storage. After the minimum water has been determined, it is then fixed and used as an input parameter in the second stage, of which the objective is the minimization of storage. This procedure ensures that storage is minimized without compromising the freshwater demand. Application of this procedure to a simple case study has shown more than a 45% reduction in freshwater demand and a 62.5% reduction in reusable water storage requirement. Because the mathematical formulation is based on a continuous-time framework, the problem was solved within a reasonable compuer processing unit (CPU) time, i.e., 309.41 CPU seconds for the first stage and 1.51 CPU seconds for the second stage.

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