# Optimal Synthesis of Water Networks for Addressing High-concentration Wastewater in Coal-based Chemical Plants

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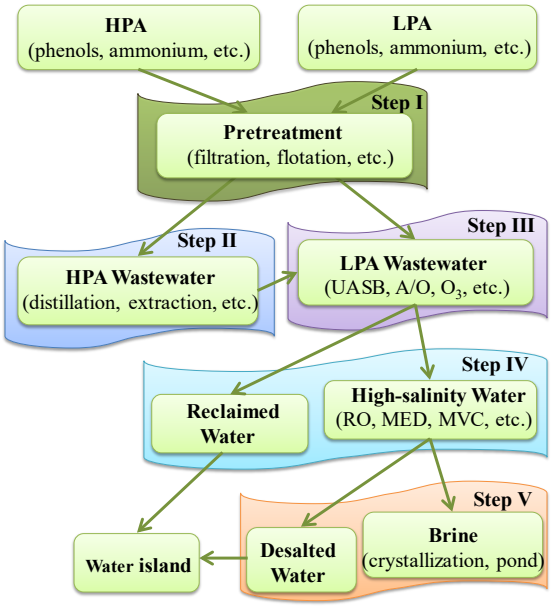
**Abstract** : This paper outlines the development of an optimization-based method for synthesizing a water network which incorporates various treatment technologies to address the high-concentration wastewater in coal-based chemical plants. One important feature of the proposed approach is that it associates a multi-step wastewater treatment design within a source-regeneration-distribution-sink superstructure. This design can enforce certain design and structural specifications to tighten the model formulation and enhance solution convergence. A mixed integer non-linear programming problem is formulated based on the proposed superstructure, which involves unit-specific shortcut models instead of the fixed impurities removal model to describe it accurately. The proposed method for water network synthesis is demonstrated using two case studies which determine the effect of streams composition and wastewater treatment technologies on the total network cost, freshwater consumption, and the water network design. The results highlight the ability of the proposed model for the developed water network synthesis, by computing quickly and realizing the goals of cost-saving and discharge-reduction.

**Keywords:**

High-concentration wastewater; water network synthesis; multi-step wastewater treatment, shortcut models

**Abstract Graphic:**




## Synopsis

High-concentration wastewater is effectively addressed by considered a systematic optimization-based method integrated with a multi-step wastewater treatment design.

## 1. INTRODUCTION

The large-scale coal development activity in developing countries has long been criticized for its harmful environmental impacts, which can be largely attributed to wastewater-related problems. Specifically, coal-based chemical plants generate wastewater streams that usually contain a great amount of toxic pollutants and have complex impurities, resulting in an ever-growing public concern for sustainability.[1] For example, more than 244 categories of toxic compounds have been detected in the effluent of a coal gasification process.[2] Among them, phenols and ammonia have been listed as priority pollutants because of their high hazardous effects; ammonia in wastewater discharging into natural waters would cause water eutrophication and even serious ecological disaster. Aside from the phenols-ammonia issues, dissolved inorganic salt is easy to accumulate during wastewater treatment but extremely difficult to dispose of; while suspended solids in the effluent would make the water extraordinarily turbid with low visibility.

To address these refractory impurities, several state-of-the-art treatment technologies, including a series of physical and chemical methods have been devised for the stringent goals of pollutant reduction. Previous studies indicated that the featured impurities can be handled by either a specified technology or a combination of technologies as follows: (1) solids elimination (i.e., sedimentation3, filtration4, etc.); (2) ammonia removal (i.e., adsorption5, air stripping6, etc.); (3) phenols removal (i.e., electrocoagulation7, extraction8, distillation,9 etc.), and (4) Inorganic salt desalination (i.e. reverse osmosis-RO10, multiple-effect distillation-MED11, crystallization,12etc.). More details has been summarized in the references.13 However, these emerging technologies employed in the wastewater treatment system of coal-based chemical plants have faced an important barrier that has prevented their effective application. This barrier stems from the fact that the wastewaters are traditionally treated in a common centralized facility where all the effluents from the various processes are mixed before treatment, leading to processing of large volumes of wastewater with low concentrations of impurities. Thus, it will become necessary to develop systematic strategies to

determine the best available technologies and enable system integration to be performed effectively.

In order to remove this barrier, distributed effluent treatment strategies proposed by Wang and Smith14 can segregate effluents for treatment where appropriate and mix them where appropriate. For effluent treatment system design and targeting, it is well known that insight-based water pinch15 and mathematical optimization16 techniques are the two fundamental approaches. The former can graphically determine the maximum reuse/recycle, minimum freshwater requirement, and minimum wastewater discharge. Bai et al.17 developed three sequential mathematical models with process decomposition to optimize single contaminant regeneration reuse water systems. Deng et al.18 presented the generalized improved problem table to target the concentration- and property-based total water network with multiple partitioning interception units. Soo et al.19 proposed a new waste treatment composite curve to locate the minimum treatmentflow rate for multiple treatment units. The water pinch approach offers a low computational expense in generating the solutions for water networks, but it is often inherently limited to the scope of practical problems, especially for the water network in coal-based chemical plants. Alternatively, the mathematical optimization-based technique requires construction of a superstructure network representation of design alternatives for the network problems at hand considering their full complexities of cost functions, multiple impurities, diverse treatment methods, and various constraints.20−23 Tovar- Facio et al.7 presented an optimization approach to incorporate electrocoagulation into water network for oil refineries to minimize the cost of the waste-management system. Sotelo-Pichardo et al.24 developed a MINLP model for the optimal synthesis and retrofitting of water networks considering growing demand projections. Abass et al.25 proposed a superstructure-based optimization approach for synthesis of a multiregenerator network for simultaneous water and energy minimization. These works mainly combine multiple unit-specific shortcut models in a single step for the purpose of modeling accuracy, increasing the computational burden. In order to address the computational problem, recent works have involved the development of specified rules and simplified strategies. Liu et al.26 introduced a

new concept termed total treatmentflow rate to design wastewater treatment networks with multiple contaminants. Khor et al.27 proposed a superstructure withfixed topology for a water network through logical constraints. Carrero-Parreno et al.28 introduced a new approach which can identify the optimal pretreatment sequence of flowback water from shale gas production. However, most of these models greatly simplified the treatment units by usingfixed recoveries, creating a gap for their applicability. Yang et al.13 developed a unifying approach combining various technologies capable of removing all the major types of impurities through the use of short-cut models. Lu et al.29 recently extended this approach by accounting for the dynamic influent under different discharge standards and penalty rates. This unifying approach, nevertheless, involves large-scale nonconvex terms and requires specified decomposition algorithms. Moreover, when the removals of some priority pollutants (phenols and ammonia) are considered, the superstructure should be modified to accommodate the realistic structure of the water network of coal-based chemical plants.

To gain a more realistic and manageable model, this work takes advantage of the previous knowledge to develop a systematic optimization-based method with multiple wastewater regeneration technologies for addressing the high-concentration wastewater in coal-based chemical plants. The main contributions of this work are three fold. First, a collection of the major treatment technologies is introduced to particularly address the phenolsammonia issues. Second, the removal efficiencies of the selected technologies are obtained by means of unit-specific shortcut models instead of thefixed values. Last but not least, we propose a tailored multistep wastewater treatment (MWT) design embedded in the three-stage superstructure. The original model is updated in the light of the proposed water network to tighten the formulation and enhance the solution convergence to the optimization. Thefinal mathematical model for the synthesis of the water network is a disjunctive programming formulation that is reformulated as a MINLP problem, which minimizes the total annual cost of the system.

## 2. PROBLEM STATEMENT

The problem addressed in this study can be stated as follows.

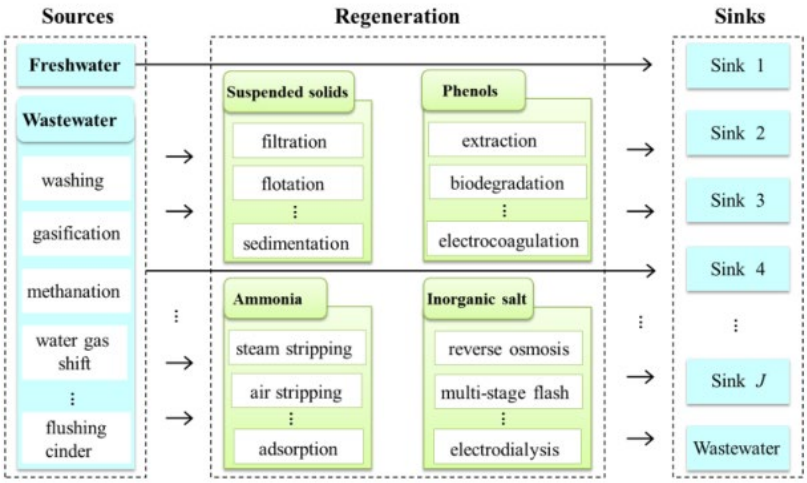



**Figure 1.** Source−regeneration−distribution-sink water network superstructure.

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In order to achieve the targets of water use reduction and cost saving in the coal-based chemical plants, a comprehensive multistage water network superstructure featured by source-regeneration-sink is proposed. As illustrated in Figure 1, this superstructure, which represents the water network problem related to all potential process units and flow connections for system integration, is detailed in the following sections.

The coal-based chemical plants consume water and generate wastewater which normally contains multiple impurity substances and each substance has a different concentration. In this study, the multiple substances of focus include suspended solids, ammonia, phenols, and inorganic salt, which are present in the vast majority of coal-based chemical wastewaters in a separate or joint form. Depending on the total concentration of impurities and technological processes, the water sources can be categorized into three distinct levels that include high-concentration wastewater $I_1$ (generated from washing, flushing, and syngas clean up units, etc.), low-concentration wastewater $I_2$ (generated from gasification, methanation, and water gas shift units, etc.), and contaminant-free freshwater $I_3$. In general, the high concentration wastewaters indicate that the phenols concentration is more than 50

mg/L or the ammonia concentration is greater than 500 mg/L. Otherwise, it is the low-concentration one.

A treatment system, as the core of the present water network, is mainly designed to dispose of the various unwanted impurities in the wastewater of coal-based chemical plants. In this work, a specialized MWT design nested in the superstructure is proposed aiming to achieve these goals: (1) avoid the complex configuration of a water network, (2) effectively reduce the capacity of the new mathematical model based on this proposed water network, (3) enhance the solution convergence to the optimization, and (4) rule out the phenomenon that violated the reality in advance. The schematic framework of the proposed MWT design is shown in Figure 2. According to the properties of coal-based chemical wastewater, the proposed MWT design prioritizes the removal sequence of the different types of impurities present in the wastewater. In particular, the prioritization can refer to not only the properties of toxicity and pH value but also the detrimental effects on the removal efficiency of other impurities. The MWT design is described in detail by the following steps:

**Step I:** This is a pretreatment step that deeply removes the suspended solid by the sedimentation or flotation in the wastewater streams. $T_1$ represents the treatment units used in this step. The suspended solid is ranked the first to be removed by reason that it is relatively easy to handle and free from other impurity interference. On the contrary, they would do harm to the postprocessing for the other impurities, e.g. equipment obstruction.

**Step II:** The high-concentration phenols-ammonia (HPA) wastewater can significantly inhibit the effects of some key reactions such as biodegradation and nitrification due to their toxicities to micro-organisms. Hence, the hazards of phenols-ammonia must be thoroughly addressed making the quality of the effluent meet the requirement for the subsequent processing. However, note that the dissolved acid gases such as $H_2S$ and $CO_2$ in wastewater have been removed effectively in advance due to their corrosive effects on the downstream equipment, resulting in

an alkaline environment with a pH value up to 9. This high pH value increases the degree of difficulty in phenols removal. In order to facilitate the phenols removal, the pH value of the wastewater is decreased to below 7 through disposing of the dissolved ammonia. In this step, the HPA wastewater is disposed of in series by a variety of alternative treatment units ($T_2$), such as air stripping, adsorption, solvent extraction, and distillation, etc.

**Step III:** The source water together with the treated effluents from the former step undergoes a deep purification as their impurities are dissatisfied with the specification. These waters can

be collectively referred to as low-concentration phenolsammonia (LPA). The available purification units (T3) include aerobic biological treatments (moving the bed biofilm reactor,

powdered activated carbon sludge,fluidized-bed bioreactor, etc.), anaerobic biological treatments (up-flow anaerobic sludgebed (UASB), expended granular sludge bed, two-stage anaerobic

filter bed, etc.), combined biological treatments (anoxic−oxic(A/O), anerobic−anoxic−oxic, etc.), and advanced treatment processes (ozone oxidation (O3), Fenton oxidation, etc.).

**Step IV:** In the process of treating wastewater, several necessary operations such as evaporation, distillation, mixing, and chemical addition, potentially concentrate some of the impurities, especially for the inorganic salt, which necessitate an extra desalination process to hedge against the resulting brine-related issue. The treated effluent from previous steps can be categorized into two, namely, reclaimed water and high-salinity water. The former can be introduced to the sinks directly, while the latter must be desalinated through either membrane-based separation (RO, electrodialysis (ED), etc.) or thermal desalination (MED, multistageflash (MSF), etc.). A set of treatment units in this step is denoted by the symbol T4. Regardless of which method is selected, note that the inlet phenols−ammonia contaminant must be removed essentially in the previous step.

**Step V:** The brine rejected by the separators or the evaporators in the former step is sent to either the crystallization system or the evaporation pond for salt precipitation, while the desalted water enters the sinks for bein Sinks are water-using units that are capable of receiving any water resources from freshwater and treated wastewater as long as they are satisfied with the particular sink demands on both the flow rate and concentrations. The water resources can be (1) directly reused in other process units, (2) mixed with each other and sent to some particular sinks, or (3) discharged to the environment as wastewaters if their concentration conforms to the local regulations. It should be noted that the freshwater is not directly sent to a wastewater sinkg reused directly. T5 represents the treatment units used in this step.

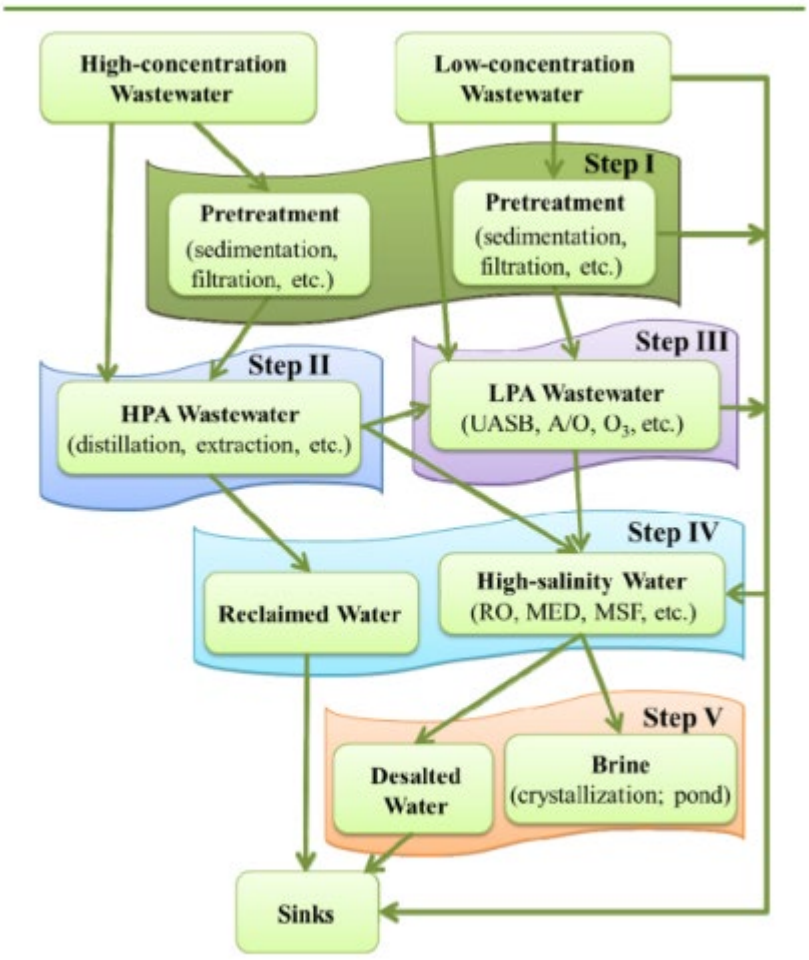


**Figure 2.** Schematic framework of the proposed MWT design.

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# 3. MODEL FORMULATION

A mathematical model containing the shortcut models is formulated based on the proposed multistep water network superstructure. Before developing the model formulation, the following sets are described: sources $I$={$I_1$, $I_2$, $I_3$}, treatment units $T$={$T_1$, $T_2$, $T_3$, $T_4$, $T_5$ }, sinks $J$={1, 2, …, $n$}.

## 3.1. Mass Balance for Sources

As mentioned previously, the proposed water network considers three levels of water supply, which includes a set of high-concentration wastewater sources I1={1, 2, …, HW}, a set of low-concentration wastewater sources I2={1, 2, …, LW}, and a set of freshwater sources I3={1, 2, …, FW}. The mass balances for these three levels of sources are modelled as follows.

### 3.1.1 High-Concentration Wastewater

Prior to entering the sinks for reuse, each high-concentration wastewater source has the potential to be split into multiple substreams for undergoing a preliminary process or a deep purification in the treatment units, as described by:

$$m_{ih}^{out} = \sum_{t} m_{ih,t}, \quad \forall ih \in I_1, \ \forall t \in \{T_1, T_2\} \tag{1}$$

where $m_{ih}^{out}$ is the flow rate of high-concentration wastewater leaving the source ih; mih,t is the flow rate from source ih to the treatment unit t.

### 3.1.2 Low-Concentration Wastewater

Compared with the high-concentration wastewater sources, the low-concentration ones have more options. They can be fed to a pretreatment unit (T1); biological degradation treatment unit (T3); high-salinity water treatment unit (T4), or sinks (J), depending on the impurity concentrations of these source waters. The formulation is given by:

$$m_{il}^{out} = \sum_{t} m_{il,t} + \sum_{w} m_{il,w}, \quad \forall il \in I_2,\ \forall t \in \{T_1, T_3, T_4\},\ \forall j \in J \tag{2}$$

where $m_{il}^{out}$ is the flow rate of low-concentration wastewater going away from the source il; mil,t is the flow rate from source il to the treatment unit t; mil,j is the flow rate from source il to the sink j.

### 3.1.3 Freshwater Source

Freshwater is part of the sources with a flexible flow rate, which can be sent to the sinks for usage. Note that freshwater should be prevented from being sent directly to a treatment unit and the environment as wastewater to prevent an environmentally unsustainable utilization. The total outlet stream of the freshwater is equal to the sum of freshwater sent to the sinks,

$$m_{r}^{out} = \sum_{w} m_{r,j}, \quad \forall r \in I_3,\ \forall j \in J \tag{3}$$

where $m_{r}^{out}$ is the total flow rate of freshwater leaving the source r; mr,j is the flow rate from source r to the sink j.

## 3.2. Mass and Concentration Balances for the Treatment System

Flow rate and concentration balances are conducted for all streams entering the treatment system. The high-concentration wastewaters are not reused directly until the impurities of focus are removed, while the low-concentration ones are open to reuse/recycle relying on the component concentration limits of the treatment units and the sinks.

There are various technology candidates for the removal of each type of impurity in each step shown in Figure 2. The superstructure based on the proposed MWT design allows for the selection of a subset of the best available treatment technologies through the use of the generalized disjunctive programming (GDP) formulation. The selection and operating variables of alternative treatment technologies within each step are optimized.

$$\begin{bmatrix} Y_t \in \text{True} \\ c_{t,p}^{in} \geq c_{p,\min}^{in} \\ c_{t,p}^{in} \leq c_{p,\max}^{in} \\ C_t^{cc} = f_1(m_t^{in}) \\ C_t^{oc} = f_2(m_{t\ t}^{in}, c_t^{in}) \end{bmatrix} \vee \begin{bmatrix} Y_t \in \text{False} \\ c_{t,p}^{in} \leq c_{p,\min}^{in} \\ C_t^{cc} = 0 \\ C_t^{oc} = 0 \end{bmatrix} \vee \begin{bmatrix} Y_t \in \text{False} \\ c_{t,p}^{in} \geq c_{p,\max}^{in} \\ C_t^{cc} = 0 \\ C_t^{oc} = 0 \end{bmatrix} \tag{4}$$

$$Y_t \in \{\text{True,False}\}, \forall t \in \text{treatments}$$

In the disjunctive formulation, Yt is a Boolean variable and takes the value < True > (when the treatment t is chosen for the system). Then, the impurity concentration of streams split into the treatment t must be varied between the allowable minimum and maximum values, and the costs of capital and operating are calculated. Otherwise, the value of the Boolean variable Yt is False. The concentration of the inlet stream of treatment t is either lower than the allowable minimum concentration or greater than the allowable maximum value. Meanwhile, the value of the capital cost and the operating cost is zero. $C_t^{cc}$ and $C_t^{oc}$ represent the capital cost and operating cost of the treatment t. $m_t^{in}$ is the total inlet flow rate of the treatment t. $c_{t,p}^{in}$ is the concentration of the inlet stream of the treatment t.

Besides, it should be emphasized that the wastewater treatment efficiencies of the critical technology are modelled by a set of shortcut functions based on the previous literature. These shortcut models are employed in the GDP formulation.

### 3.2.1 Pre-treatment Unit

As shown in Figure 2, the pre-treatment unit in the Step I only can receive wastewater from the sources, either the high- or low-concentration wastewater. The total inlet streams ($m_{prh}^{in}$ and $m_{prl}^{in}$) of the pretreatment unit and the corresponding concentration of impurity p ($c_{prh,p}^{in}$ and $c_{prl,p}^{in}$) are given by:

$$m_{prh}^{in} = \sum_{i} m_{i,prh}, \qquad \forall prh \in T_1,\ \forall i \in \{I_1\} \tag{5}$$

$$m_{prh}^{in} c_{prh,p}^{in} = \sum_{i} m_{i,prh} c_{i,p}, \quad \forall prh \in T_1,\ \forall i \in \{I_1\},\ \forall p \in P \tag{6}$$

$$m_{prl}^{in} = \sum_{i} m_{i,prl}, \qquad \forall prl \in T_1,\ \forall i \in \{I_2\} \tag{7}$$

$$m_{prl}^{in} c_{prl,p}^{in} = \sum_{i} m_{i,prl} c_{i,p}, \quad \forall prl \in T_1,\ \forall i \in \{I_2\},\ \forall p \in P \tag{8}$$

where ci,p is the concentration of impurity p of source i, mi,prh and mi,prl are the flow rates from source i to the high-and low-concentration pre-treatment unit.

After being pre-treated, the HPA wastewater is further introduced to the extraction column, rectifying column, etc., included in the HPA wastewater treatment unit for rejecting the dissolved phenols-ammonia. The flow rate from the pre-treatment unit to the HPA wastewater treatment unit (mprh,t) and the corresponding concentration balance of impurity p ($c_{prh,p}^{out}$) are characterized by:

$$m_{prh}^{out} = \sum_{t} m_{prh,t}, \qquad \forall prh \in T_1,\ t=T_2 \tag{9}$$

$$c_{prh,p}^{out} = (1-\beta_{prh,p}) c_{prh,p}^{in}, \quad \forall prh \in T_1,\ \forall p \in P \tag{10}$$

where $m_{prh}^{out}$ is the total outlet flow rate of the pretreatment unit, βprh,p is the removal ratio of impurities by the pre-treatment unit.

The LPA wastewater from the pretreatment unit is not allowed to enter into the HPA wastewater treatment unit but can be sent either to the biological treatment unit, the high-salinity water treatment unit, or directly to the sinks. The flow rate ($m_{prl}^{out}$) and concentration ($c_{prl,p}^{out}$) balances of the outlet stream are given by:

$$m_{prl}^{out} = \sum_{t} m_{prl,t} + \sum_{w} m_{prl,w}, \qquad \forall prl \in T_1,\ \forall t \in \{T_3, T_4\},\ \forall j \in J \tag{11}$$

$$c_{prl,p}^{out} = (1-\beta_{prl,p}) c_{prl,p}^{in}, \quad \forall prl \in T_1,\ \forall p \in P \tag{12}$$

where mprl,t and mprl,w are the flow rates from the pretreatment to the LPA wastewater treatment and the sink; βprl,p is the removal ratio of impurities by the pretreatment unit.

In Step I shown in Figure 2, the sedimentation process emerges as a preferable method due to its lower capital and operational costs in comparison with other available pre-treatment technologies. In particular, the standard rectangular tank of choice shown in Figure S1 (available in the Supporting Information) can remove the suspended solid. Classic removal efficiency (βsd,tss) of sedimentation by a rectangular tank can be calculated by the detention time (dtsd,tss) and the suspended solid (TTS), which is modelled by a hyperbolic function expressed in Eq. (13).11,30

$$\beta_{sd,tss}=1-\frac{dt_{sd,tss}}{a_{sd,tss}+b_{sd,tss}dt_{sd,tss}} \tag{13}$$

where asd,tss and bsd,tss are the empirical constants obtained from the literature and the corresponding values are 0.0075 and 0.014.11

### 3.2.2 HPA Wastewater Treatment Unit

In Eq. (14) the left side represents the total flow rate ($m_{aph}^{in}$) of streams entering the HPA wastewater treatment unit, while the right side is the flow rates of the incoming stream from high-concentration wastewater sources and pre-treatment unit shown in Figure 2. The concentration ($c_{aph,p}^{in}$) of impurity p of the inlet stream ($m_{aph}^{in}$) can be calculated by Eq. (15).

$$m_{aph}^{in}=\sum_{i}m_{i,aph}+\sum_{t}m_{t,aph},\quad \forall aph\in T_2\ \ \forall i\in\{I_1\},\ t=T_1 \tag{14}$$

$$m_{aph}^{in}c_{aph,p}^{in}=\sum_{i}m_{i,aph}c_{i,p}+\sum_{t}m_{t,aph}c_{t,p}^{out},\quad \forall aph\in T_2,\ \forall i\in\{I_1\},\ t=T_1,\ \forall p\in P \tag{15}$$

where mi,aph and mt,aph are the flow rates from source i and pre-treatment unit to the HPA wastewater treatment unit aph, respectively.

The stream ($m_{aph}^{out}$) leaving the HPA wastewater treatment unit can be sent to the LPA ones, the

high-salinity water treatment unit, and the sinks. The balance of total flow rate and concentration ($c^{out}_{aph,p}$) can be obtained by:

$$m^{out}_{aph} = \sum_{t} m_{aph,t} + \sum_{w} m_{aph,w}, \quad \forall aph \in T_2, \ \forall t \in \{T_3, T_4\}, \ \forall j \in J \tag{16}$$

$$c^{out}_{aph,p} = (1-\beta_{aph,p}) c^{in}_{aph,p}, \quad \forall aph \in T_2, \quad \forall p \in P \tag{17}$$

where βaph,p is the removal ratio of ammonia or phenols by the HPA wastewater treatment unit (aph).

Removal performances of ammonia by air stripping and adsorption are described as follows. Based on previous experimental research,5, 6 the relationship between the removal efficiency and the initial ammonia concentration can be quantitatively obtained as given by Eqs. (18-19). Figure 3 illustrates the corresponding characteristic curves which have a multiple function relationship.

$$\beta_{air,am} = 3\times10^{-13} \times (c^{in}_{air,am})^3 - 2\times10^{-8} \times (c^{in}_{air,am})^2 + 0.0003\times(c^{in}_{air,am}) + 98.574 \tag{18}$$

$$\beta_{abs,am} = -0.0013\times(c^{in}_{abs,am})^2 + 0.1373\times(c^{in}_{abs,am}) + 58.16 \tag{19}$$

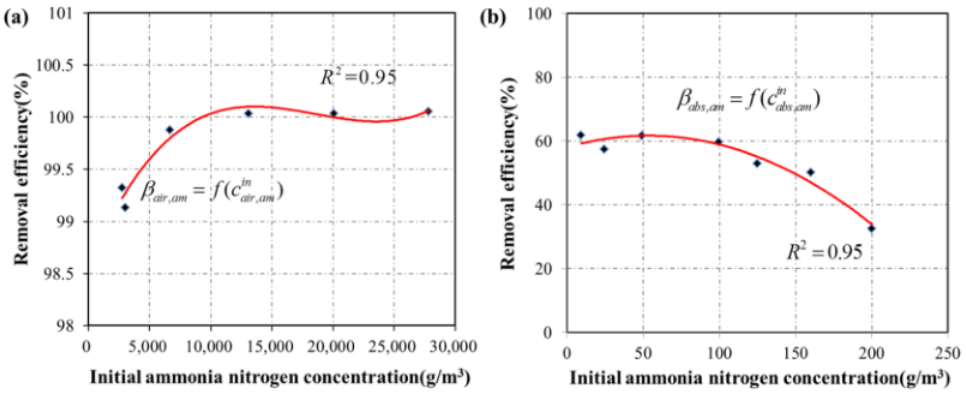


**Figure 3.** Removal efficiency of ammonia treatment unit: (a) air stripping and (b) adsorption.

< Figure 3. Removal efficiency of ammonia treatment unit: (a) air stripping and (b) adsorption. >

Extraction is a common approach to treating the HPA wastewater and its schematic diagram is shown in Figure S2 (available in the Supporting Information). The removal efficiency of phenols by

extraction can be modelled by Eq. (20) according to previous research13, which reveals a quadratic function relationship between the inlet phenol content and removal efficiency, as shown in Figure 4.

$$\beta_{ext,phe}=8\times10^{-6}\times(c^{in}_{ext,phe})^2-0.0463\times c^{in}_{ext,phe}+100.67 \qquad 12\le c^{in}_{ext,phe}\le 3000 \tag{20}$$

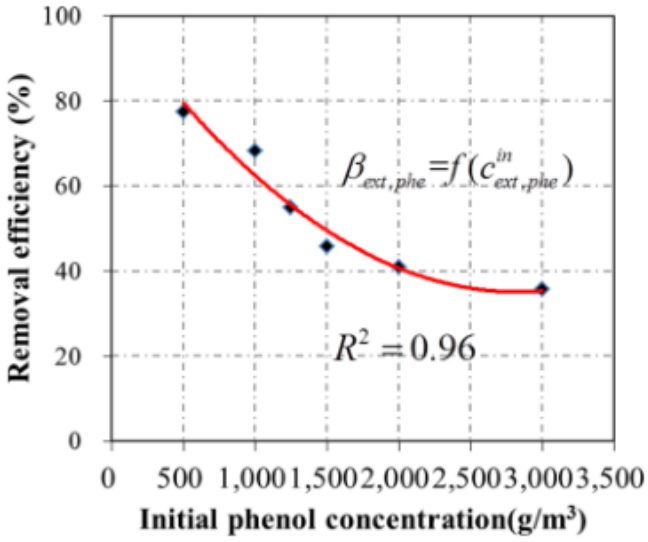


**Figure 4.** Removal efficiencies of extraction unit.

<Place **Figure 4** here>

### 3.2.3 LPA Wastewater Treatment Unit

The inlet stream ( $m^{in}_{apl}$ ) of the LPA wastewater treatment unit is constituted by the lowconcentration wastewater source (mi,apl) and the treated water (mt,apl) from the steps I and II shown in Figure 2. The balances of the flow rate and corresponding concentration ( $c^{in}_{apl,p}$ ) of impurity p are given by:

$$m^{in}_{apl}=\sum_i m_{i,apl}+\sum_t m_{t,apl}, \quad \forall apl\in T_3,\ \forall i\in\{I_2\},\ \forall t\in\{T_1,T_2\} \tag{21}$$

$$m^{in}_{apl}c^{in}_{apl,p}=\sum_i m_{i,apl}c_{i,p}+\sum_t m_{t,apl}c^{out}_{t,p}, \quad \forall apl\in T_3,\ \forall i\in\{I_2\},\ \forall t\in\{T_1,T_2\},\ \forall p\in P \tag{22}$$

In Eq. (23) the amount of the outlet stream ( $m^{out}_{apl}$ ) from this treatment unit is composed of the flow rates of streams to the high-salinity water treatment unit and the sinks. The corresponding

concentration ($c_{apl,p}^{out}$) of impurity p of the outlet stream is given in Eq. (24), which is calculated by the removal efficiency of ammonia and phenols (βapl,p) and the initial inlet concentration.

$$m_{apl}^{out} = \sum_{t} m_{apl,t} + \sum_{w} m_{apl,w}, \quad \forall apl \in T_3, \ \forall t = T_4 \ \ \forall j \in J \tag{23}$$

$$c_{apl,p}^{out} = (1-\beta_{apl,p}) c_{apl,p}^{in}, \quad \forall apl \in T_3, \ \ \forall p \in P \tag{24}$$

Previous studies20, 21 have proved experimentally that the electrocoagulation and biodegradation are capable of processing wastewater streams containing phenolic compounds. The schematic diagrams of these two treatment technologies are shown in Figure S3 (available in the Supporting Information). In particular, the removal efficiency of phenol can be determined using the functions given by Eqs. (25-27). These are modelled by analyzing the experimental data of El-Ashtoukhy et al.32 and Jiang et al.33, and employing the correlation shown in Figure 5. The fitted curve in Figure 5(a) is a linear function relation, while the one in Figure 5(b) is a piecewise function curve in which the upper part is a linear function curve and the lower part is a quadratic function curve.

$$\beta_{ele,phe} = \text{-}0.3005 \times c_{ele,phe}^{in} + 108.74 \qquad 12 \le c_{ele,phe}^{in} \le 250 \tag{25}$$

$$\beta_{bio\_1,phe} = \text{-}0.0113 \times c_{bio,phe}^{in} + 101.58 \qquad 12 \le c_{bio,phe}^{in} \le 400 \tag{26}$$

$$\beta_{bio\_2,phe} = 0.0006 \times (c_{bio,phe}^{in})^2 - 0.8766 \times c_{bio,phe}^{in} + 356.9 \qquad 400 < c_{bio,phe}^{in} \le 800 \tag{27}$$

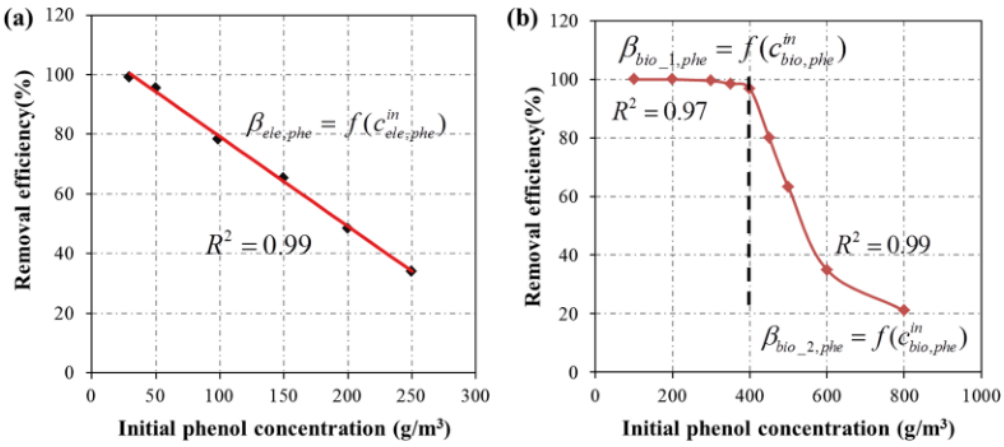


**Figure 5.** Removal efficiency of the phenol treatment units: (a) electrocoagulation and (b) biodegradation.

<Place **Figure 5** here>

### 3.2.4 High-salinity Water Treatment Unit.

The inlet streams ($m_{hs}^{in}$) of the high-salinity water treatment unit in step IV of the MWT design include, 1) the low-concentration source water (mi,hs), 2) the treated water (mt,hs) from the pre-treatment, HPA- and LPA-wastewater treatment units. The balances of the total flow rate and concentration ($c_{hs,p}^{in}$) of impurity p are shown in Eqs. (28-29).

$$m_{hs}^{in} = \sum_{i} m_{i,hs} + \sum_{t} m_{t,hs}, \quad \forall hs \in T_4, \ \forall i \in \{I_2\}, \ \forall t \in \{T_1, T_2, T_3\} \tag{28}$$

$$m_{hs}^{in} c_{hs,p}^{in} = \sum_{i} m_{i,hs} c_{i,p} + \sum_{t} m_{t,hs} c_{t,p}^{out}, \quad \forall hs \in T_4, \ i \in \{I_2\}, \ \forall t \in \{T_1, T_2, T_3\}, \quad \forall p \in P \tag{29}$$

The effluent from this treatment unit goes either to the further treatment unit or to the sinks entirely depending on its concentrations. The total flow rate ($m_{hs}^{out}$) leaving the treatment unit is equal to the flow rate of the stream requiring deep treatment plus the stream to the sinks, which is given in Eq. (30). The concentration ($c_{hs,p}^{out}$) of impurity p of the outlet stream is relevant to the treatment technology employed in this step and the concentration of the inlet stream. This relationship is shown in Eq. (31):

$$m_{hs}^{out} = \sum_{t} m_{t,hs} + \sum_{w} m_{hs,w}, \quad \forall hs \in T_4, \ \forall t = T_5, \quad \forall w \in W \tag{30}$$

$$c_{hs,p}^{out} = (1 - \beta_{hs,p}) c_{hs,p}^{in}, \quad \forall hs \in T_4, \quad \forall p \in P \tag{31}$$

where $\beta_{hs,p}$ is the removal ratio of inorganic salt by the high-salinity water treatment unit (*hs*).

RO is the most important unit used to treat the high-salinity water. However, it is strict with the feed composition due to the membrane fouling or damage by contaminants. In order to avoid membrane fouling or damage, various treatment processes mentioned above are required before the stream is fed to the RO, especially for the HPA-wastewater. Figure S4 (available in the Supporting Information) is the schematic of an RO desalination process

The permeate flux is related to the membrane water permeability (Pw), the membrane thickness (Lm), the pressure drop across the membrane ($\Delta p$), the osmosis pressure ($\Delta \pi$). The values of these parameters is given in Table S1.

$$N_w = A_w(\Delta p - \Delta \pi) \tag{32}$$

$$A_w = \frac{P_w}{L_m} \tag{33}$$

where Aw is the water permeability coefficient.

The pressure drop across the membrane can be calculated from the pressure of the feed side and permeate side of the membrane, while the osmosis pressure can be approximated by the Van't Holl equation.

$$\Delta p = \frac{p_{ro}^{in} + p_{ro}^{bl}}{2} - p_{ro}^{out} \tag{34}$$

$$\Delta \pi = \frac{\gamma RT}{M}(c_{ro,TDS}^{in} - c_{ro,TDS}^{out}) \tag{35}$$

where $p_{ro}^{in}$, $p_{ro}^{bl}$, and $p_{ro}^{out}$ are the pressures of the feed stream, retentate pressure, and permeate stream, respectively. $c_{ro,TDS}^{in}$ and $c_{ro,TDS}^{out}$ are the solute concentrations of the feed stream and permeate stream, respectively.

Due to the solute diffusion through the membrane, the solute flux (Ns) can be approximated by the expression:

$$N_s = A_s(c_{ro,TDS}^{in} - c_{ro,TDS}^{out}) \tag{36}$$

$$A_s = \frac{D_s K_s}{L_m} \tag{37}$$

where As is the solute permeability coefficient, Ds is the solute diffusion coefficient, Ks is the distribution coefficient.

The solute balance can be calculated by:

$$N_s = \frac{N_w c_{ro,TDS}^{in}}{c_{w2}} \tag{38}$$

where cw2 is the solvent concentration of the permeate stream. cw2 can be nearly solvent density as it is dilute solution in general.

The rejection ratio (βro) is equal to the ratio of concentration difference on both sides of the membrane to the solute concentration of the feed stream, which can be given by:

$$\beta_{ro} = \frac{c_{ro,TDS}^{in} - c_{ro,TDS}^{out}}{c_{ro,TDS}^{in}} \tag{39}$$

Combining Eqs. (32-39) can eliminate the terms Nw and Ns, and in this way the βro is finalized as follows:

$$\beta_{ro} = \frac{B(\Delta p - \Delta \pi)}{1 + B(\Delta p - \Delta \pi)} \tag{40}$$

$$B = \frac{A_w}{A_s c_{w2}} \tag{41}$$

### 3.2.5 Brine Treatment Unit

The brine rejected from step IV shown in Figure 2 is collected in a waste tank. Prior to being fed to a crystallizer or evaporation pond, this brine is processed in a brine treatment unit to successively remove the dissolved calcium sulfate and adjust its pH value with caustic soda. Note that the solvent water in the brine is not reusable and thus not taken into account in the mass balance.

## 3.3. Mass and Concentration Balances for Sinks

The sinks receive water from two types of streams. These streams are the water source (mi,j) from the low-concentration wastewater stream and freshwater, and the regenerated water (mt,j) from various treatment units, respectively. In eq 42, the totalflow rate (mjin) of streams entering a specific

sink j can be expressed as follows:

$$m_{wi}^{in} = \sum_{i} m_{i,wi} + \sum_{t} m_{t,w}, \quad \forall j \in J,\ j \neq waste\ \forall i \in \{I_2, I_3\},\ \forall t \in \{T_1, T_2, T_3, T_4\} \tag{42}$$

Furthermore, a set of impurity balances are required before any process sink to calculate the resulting concentration inlet to any one sink. These balances need to take into account the impurity of all inlet streams. The concentration balance of impurity p for sink j (cj,pin ) can be calculated by eq 43.

$$m_{w}^{in} c_{w,p}^{in} = \sum_{i} m_{i,w} c_{i,p} + \sum_{t} m_{t,w} c_{t,p}^{out}, \quad \forall i \in \{I_2, I_3\},\ \forall t \in \{T_1, T_2, T_3, T_4\},\ \ \forall p \in P \tag{43}$$

Note that the wastewater stream can be expressed as a sink with a variable flow rate as well. Equations 44 and 45 are used to model the total inlet flow rate and concentration of impurity p for wastewater. Similar to the other sinks, the wastewater stream is constituted by any one stream from the water resource except for the freshwater.

$$m_j = \sum_{i} m_{i,j} + \sum_{t} m_{t,j},\ j = waste,$$
$$\forall i \in I_2,\ \forall t \in \{T_1,\ T_2,\ T_3,\ T_4\} \tag{44}$$

$$m_j c_{j,p} = \sum_{i} m_{i,j} c_{i,p} + \sum_{t} m_{t,j} c_{t,p}^{out},\ j = waste,$$
$$\forall i \in I_2,\ \forall t \in \{T_1,\ T_2,\ T_3,\ T_4\},\ \forall p \in P \tag{45}$$

## 3.5. Model Constraints

### 3.5.1 Constrains for Treatment System

The impurity concentration ($c_{t,p}^{in}$) of the inlet stream for a particular treatment unit is subject to the upper ($c_{t,p}^{UB}$) and lower ($c_{t,p}^{LB}$) bounds due to the limitations of treatment capacity, non-negative concentration, and other requirements. In general, the lower bound is not equal to zero for a

treatment unit.

$$c_{t,p}^{LB} \le c_{t,p}^{in} \le c_{t,p}^{UB}, \quad \forall t \in T, \forall p \in P \tag{46}$$

### 3.5.2 Constrains for Sinks

The concentrations of impurity *p* for the sink *j* and wastewater sink should satisfy the following constraints, which are expressed as inequality implying that the concentration of a given impurity in a particular sink must be specified a certain range. In most cases, the lower bound is zero. The inequality equations are given by:

$$c_{j,p}^{LB} \le c_{j,p}^{in} \le c_{j,p}^{UB}, \quad \forall j \in J, \forall p \in P \tag{47}$$

$$c_{waste,p}^{LB} \le c_{waste,p} \le c_{waste,p}^{UB}, \quad \forall p \in P \tag{48}$$

where $c_{j,p}^{LB} / c_{j,p}^{UB}$, $c_{waste,p}^{LB} / c_{waste,p}^{UB}$ are the lower/upper bounds of the impurity p for the sink j and wastewater, respectively.

## 3.6. Objective Function

The main objective is to minimize the total annual cost (TAC) of the water network in the coal-based chemical plant. The objective function is constituted by the total operating cost (Coc) and the capital cost (Ccc):

$$TAC = C_{oc} + C_{cc} \tag{49}$$

The total operating cost consists of the freshwater cost ($C_r^{oc}$), operating cost for piping ($C_{pip}^{oc}$) (e.g. piping maintenance), operating costs ($C_t^{oc}$) for the multiple treatment technologies, which is expressed by:

$$C_{oc} = C_r^{oc} + C_{pip}^{oc} + \sum_t C_t^{oc}, \ \forall t \in T, \tag{50}$$

The corresponding formulations of each item on the right side of Eq. (50) are given by Eqs. (51-53).

$$C_r^{oc} = H_Y \sum_r UC_r m_r^{out}, \ \forall r \in I_3 \tag{51}$$

$$\begin{aligned} C_{pip}^{oc} =& H_Y \sum_{\substack{r\in I_3 \\ w\in W}} UC_{pip} m_{r,w} + H_Y \sum_{\substack{ih\in I_1 \\ t\in\{T_1,T_2\}}} UC_{pip} m_{ih,t} + H_Y \sum_{\substack{il\in I_2 \\ t\in\{T_1,T_3,T_4\}}} UC_{pip} m_{il,t} + H_Y \sum_{\substack{il\in I_2 \\ w\in W}} UC_{pip} m_{il,w} \\ &+ H_Y \sum_{\substack{prh\in T_1 \\ aph\in T_2}} UC_{pip} m_{prh,aph} + H_Y \sum_{\substack{prl\in T_1 \\ t\in\{T_3,T_4,T_6\}}} UC_{pip} m_{prl,t} + H_Y \sum_{\substack{prl\in T_1 \\ w\in W}} UC_{pip} m_{prl,w} + H_Y \sum_{\substack{prh\in T_2 \\ t\in\{T_3,T_4\}}} UC_{pip} m_{prh,t} \\ &+ H_Y \sum_{\substack{prh\in T_2 \\ w\in W}} UC_{pip} m_{prh,w} + H_Y \sum_{\substack{apl\in T_3 \\ t\in\{T_4,T_6\}}} UC_{pip} m_{apl,t} + H_Y \sum_{\substack{apl\in T_3 \\ w\in W}} UC_{pip} m_{apl,w} + H_Y \sum_{\substack{w\in W_6 \\ j\in J}} UC_{pip} m_{w,j} \end{aligned} \tag{52}$$

$$C_t^{oc} = H_Y \sum_t f(m_t^{in}, c_t^{in}, \xi), \quad \forall t \in T \tag{53}$$

where HY is the annual operating time, UCr and UCpip, are the unit costs of freshwater and pipe line maintenance, respectively. The values of these parameters are listed in Table S2 in the Supporting Information. The operating costs of all treatment units are fully detailed in the Supporting Information.

The total capital cost is constituted by the piping capital cost ($C_{pip}^{cc}$) and capital costs ($C_t^{cc}$) of various treatment technologies, which is described by:

$$C_{cc} = \sum_{pip} C_{pip}^{cc} + \sum_t C_t^{cc}, \ \forall t \in T \tag{54}$$

In the above equation, it is necessary to calculate each term in detail. The cost mainly includes fixed and variable costs, which are determined as follows:

$$G_{r,t} = D_{r,t} \left( \frac{vc^{pip} m_{r,t}}{3600\upsilon} \right) + x_{r,t} fc^{pip} \tag{55}$$

$$C_{pip}^{oc}=K_F\left(\begin{array}{l}\sum\limits_{\substack{r\in I_3\\ t\in T}}G_{r,t}+\sum\limits_{\substack{ih\in I_1\\ t\in\{T_1,T_2\}}}G_{ih,t}+\sum\limits_{\substack{il\in I_2\\ t\in\{T_1,T_3,T_4\}}}G_{il,t}\sum\limits_{\substack{il\in I_2\\ w\in W}}G_{il,w}+\sum\limits_{\substack{prh\in T_1\\ aph\in T_2}}G_{prh,aph}\\ +\sum\limits_{\substack{prl\in T_1\\ t\in\{T_3,T_4\}}}G_{prl,t}+\sum\limits_{\substack{prl\in T_1\\ w\in W}}G_{prl,w}+\sum\limits_{\substack{prh\in T_2\\ t\in\{T_3,T_4\}}}G_{prh,t}+\sum\limits_{\substack{prh\in T_2\\ w\in W}}G_{prh,w}\\ +\sum\limits_{\substack{apl\in T_3\\ t\in\{T_4\}}}G_{apl,t}+\sum\limits_{\substack{apl\in T_3\\ w\in W}}G_{apl,w}+\sum\limits_{\substack{w\in W\\ j\in J}}G_{w,j}\end{array}\right) \tag{56}$$

$$C_t^{cc}=K_F\left(\sum_t x_t^{cc}fc_t^{cc}+\sum_t vc_t\left(m_t^{in}\right)^{\alpha_t}\right),\qquad \forall t\in T \tag{57}$$

where v is the velocity and all the pipes are assumed to operate at the same fluid velocity, D is a 1-norm Manhattan distance between any two units for piping interconnections and the values are listed in Table S3 in the Supporting Information; Table S2 in the Supporting Information shows the variable cost (vc) and fixed investment (fc) of all treatment units, x is a binary variable used to model the existence of units, $\alpha$ is an exponent for the capital costs function used to consider the economies of scale and the value is listed in Table S4 in the Supporting Information; and KF represents the factor used to annualize the inversion. All pipes are assumed to be of the same material properties and the KF can be determined by the fractional interest rate (m) and the plant lifespan (n). The values of the parameters related to the piping are shown in Table 1.

$$K_F=\frac{m(1+m)^n}{(1+m)^n-1} \tag{58}$$

**Table 1. Model Parameters Related to Computation Costs**

| Parameter | Symbol | Value[a] |
|---|---|---|
| interest rate | $m$ | 5% |
| plant lifespan | $n$ | 5 year |
| variable cost for carbon steel piping | $vc^{pip}$ | 7200 |
| fixed investment for carbon steel piping | $fc^{pip}$ | 250 |
| velocity | $v$ | 1 m/s |

[a]Date extracted from ref 34.

<Place **Table 1** here>

# 4. CASE STUDIES

The proposed optimization formulation is implemented on two industrial-scale case studies (namely Case A and Case B) of the water network of coal-based chemical plants in Northwest China. The MINLP problem associated with the case studies was implemented using GAMS 24.7.1 and solved on a computer with an Intel Core i7 at 3.60 GHz with 8 GB memory. Global solver ANTIGONE35 in GAMS 24.7.1 modelling environment was used for solving the MINLP problem. The solver BARON was also tested for all case studies investigated, but no numerical solution can be obtained because of the difficulty associated with finding a feasible solution for the variables involved in the larger number of nonconvex bilinear terms. The optimality gap of the MINLP problem was 10-9 at each iteration in order to ensure the validity of the solution.

To demonstrate the applicability and advantages, for each case study, we compare the results of freshwater consumption, treatment cost, (including operating cost and capital cost), piping cost and TAC among two reference optimization schemes and the proposed one as follows.

Scheme 1 (without integration): This employs a traditional centralized treatment approach[27] to address the wastewater streams without consideration of system integration. In particular, all the wastewater streams are not directly reused or recycled in any of the sinks in the existing chemical plant under study. Instead, an offsite end-of-pipe effluent treatment facility is utilized to collect and treat the wastewater streams from various processes.

Scheme 2 (direct integration without MWT design): The case study is solved by considering a direct water network integration within the source-regeneration-distribution-sink superstructure shown in Figure 1. In other words, the superstructure allows interconnections of its elements in all the potential alternative configurations for implementing direct water reuse, recycle, and regeneration. In this scheme, the proposed MWT design shown in Figure 2 is uninvolved in this

superstructure. Then, the removal sequence of different types of impurities present in the wastewater is flexible in this scheme. Therefore, all the binary variables associated with the selection of treatment technologies or pipe connections are determined by the model optimization.

Scheme 3 (integrated with MWT design): This case study is solved by considering the proposed MWT design in the superstructure. In this scheme, the removal sequence of different types of impurities is fixed. and the prioritization has been described previously. As a consequence, the binary variables and the continuous variables in relation to the MWT design are specified in advance for reducing the model size. For example, the binary variable xih,hs used to determine the existence of pipe connections between high-concentration sources and high-salinity water treatment unit is equal to zero. Accordingly, the continuous variable mih,hs denoting theflow rate of the connecting stream is not considered.

**Case A**. This case study considers six sources, six sinks, as well as a simplified set of impurity including phenols and inorganic salt. Sources 1 and 2 are high-concentration wastewaters, and sources 3−5 are low-concentration ones. Furthermore, it has been assumed that the treatment technologies considered in this case study include extraction, distillation, biodegradation, electrocoagulation, and reverse osmosis. The detailed values offlow rates, impurities concentrations, and the specifications of process sources and sinks are given in Table 2.

## Table 2. Basic Date of Sources and Sinks for Case A

| Sources | Flow rate ($m^3/h$) | Phenols (mg/L) | Inorganic salt ($kg/m^3$) |
|---|---|---|---|
| 1 | 363 | 1300 | 2.5 |
| 2 | 183 | 1400 | 2.5 |
| 3 | 534 | 0.5 | 2.6 |
| 4 | 425 | 0.3 | 2.7 |
| 5 | 650 | 0.1 | 2.8 |
| 6 (freshwater) | variable | 0 | 0 |

| Sinks | Flow rate ($m^3/h$) | Maximum allowable inlet concentration | |
|---|---|---|---|
| 1 | 465 | 10 | 2.5 |
| 2 | 195 | 10 | 2.6 |
| 3 | 578 | 0.3 | 2.6 |
| 4 | 450 | 0.2 | 2.7 |
| 5 | 950 | 0.1 | 2.8 |
| 6 (wastewater) | variable | 1 | 2.0 |

**Table 3. Results of Water Network for Case A**

| Case A | Freshwater ($m^3/y$) | Treatment cost ($/y) | | Piping cost ($/y) | TAC ($/y) |
|---|---|---|---|---|---|
| | | Operating cost | Capital cost | | |
| Scheme 1 | 8,232,000 | 28,918,147 | 5,712,567 | 165,898 | 43,028,612 |
| Scheme 2 | 4,220,905 | 22,036,616 | 9,406,917 | 397,915 | 36,062,353 |
| Scheme 3 | 4,599,611 | 15,545,520 | 10,828,212 | 298,973 | 31,272,316 |

<Place **Table 3** here>

## Table 4. Model Size and Computational Statistics for Schemes 2 and 3

| Computational side and statistics | Scheme 2 | Scheme 3 |
|---|---|---|
| No. of binary variables | 111 | 69 |
| No. of nonconvex nonlinear terms | 46 | 46 |
| No. of bilinear/quadratic terms | 110 | 66 |

<Place **Table 4** here>

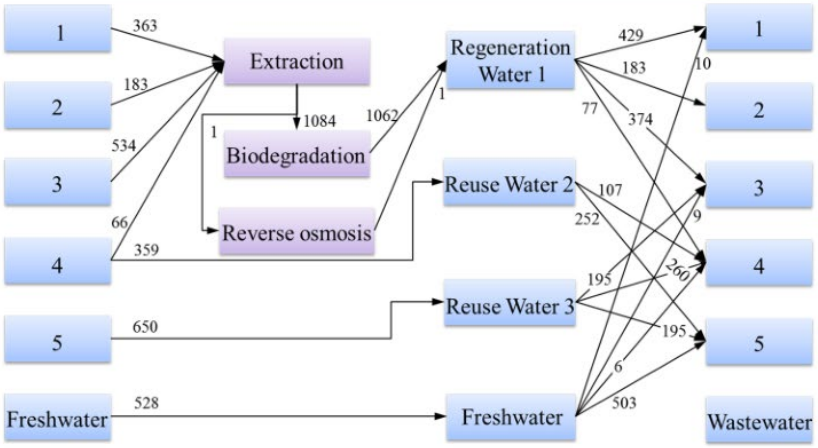


**Figure 6.** Water network for Scheme 2 (unit: $m^3/h$).

<Place **Figure 6** here>

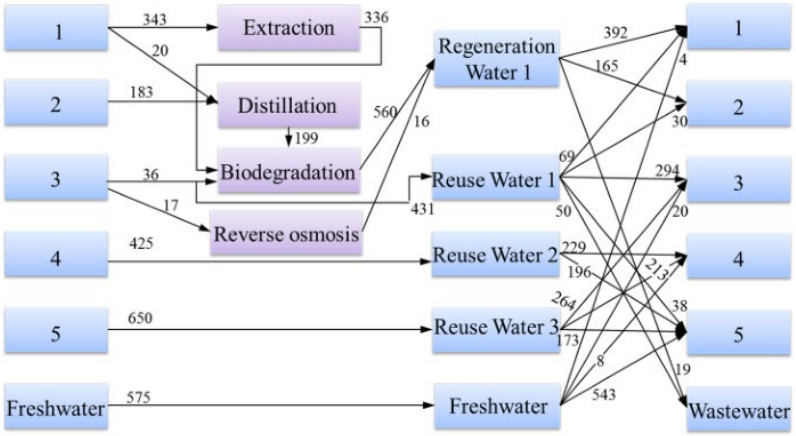


**Figure 7.** Optimal water network for Scheme 3 (unit: $m^3/h$).

<Place **Figure 7** here>

In this work, Scheme 1 based on the traditional centralized treatment approach is mainly used as a benchmark among these three schemes. Undoubtedly, it gives rise to the highest amounts of freshwater consumption, treatment cost, and TAC in the absence of system integration, as listed in Table 3. For example, the freshwater consumption for Scheme 1 is approximately 45% higher than that of Scheme 3, amounting to an annual increase of  3692,389m3. Therefore, this traditional centralized treatment approach severely increases the project economics and the water footprint for the coal-based chemical plants particularly in the water-deficient areas.

For Scheme 2, the original model formulation cannot be solved to optimality in more than 86,400 s of CPU time due to the large numbers of binary variables and nonconvex bilinear terms as listed in

Table 4. A series of simplification strategies, as follows, is taken to enable Scheme 2 to be solvable, (1) utilize appropriate bounds and initial values for the variables, (2) employ 10-3 optimality gap instead of 10-9, (3) solve the problem by segmentation model. In this way, an integer solution is obtained and the corresponding water network is shown in Figure 6. As a comparison, the inclusion of the proposed MWT design in Scheme 3 remarkably decreases the numbers of binary variables and the bilinear terms by 38% and 40%, respectively. This enables an optimal solution to be achieved in approximately 30 s. The optimal water network of this scheme, given in Figure 7, is coincidence with that of Scheme 2 in the network configuration, connection model, and volume flow rate. The main difference comes from the treatment unit selection for the phenols removal. In particular, for Scheme 2 the treatment units of choice are the extraction and the biodegradation, and reverse osmosis, while Scheme 3 requires an additional distillation unit. However, Scheme 2 increases the TAC by $44,790,037 as compared to Scheme 3. The increment can be attributed to the costly operating cost caused by the wastewater amounting up to 1000 m3/y needing to be processed by the extraction unit and the biodegradation unit in series for Scheme 2. As a contrast, Scheme 2 yields an optimal solution that only processes 343 m3/y wastewater in the extraction unit and approximately 500 m3/y and 200 m3/y wastewater in the biodegradation and distillation units, respectively. The more detailed information associated with the treatment cost, including the operating cost and capital cost, of the selected treatment technologies for the case study is listed in Table S5 (available in the Supporting Information). Moreover, the current solution of Scheme 2 is an integer solution, which results in a gap deviating from its optimal solution.

**Case B**. This involves a much more complex and realistic case study which is solved by considering the impurities of the suspended solids, ammonia, phenols, and inorganic salt. In addition, eight kinds of treatment technologies including sedimentation, air stripping, adsorption, extraction, distillation, biodegradation, electrocoagulation, and reverse osmosis, are taken into account in the water network superstructure. Flow rates, impurity concentrations, specifications of the process

sources and sinks are detailed in Table 5. Note that the high-concentration wastewaters are sources 1 and 2, and low-concentration ones are sources 3−5.

**Table 5. Basic Date of Sources and Sinks for Case B**

| Sources | Flow rate ($m^3/h$) | Suspended solids (mg/L) | Ammonia (mg/L) | Phenols (mg/L) | Inorganic salt ($kg/m^3$) |
|---|---|---|---|---|---|
| 1 | 363 | 1300 | 3500 | 1300 | 2.5 |
| 2 | 183 | 1900 | 3000 | 1400 | 2.5 |
| 3 | 534 | 15 | 15 | 0.5 | 2.6 |
| 4 | 425 | 12 | 10 | 0.3 | 2.7 |
| 5 | 650 | 20 | 5 | 0.1 | 2.8 |
| 6 (freshwater) | variable | 0 | 0 | 0 | 0 |
| Sinks | Flow rate ($m^3/h$) | Maximum allowable inlet concentration | | | |
| 1 | 465 | 45 | 50 | 10 | 2.5 |
| 2 | 195 | 50 | 55 | 10 | 2.6 |
| 3 | 578 | 10 | 10 | 0.3 | 2.6 |
| 4 | 450 | 10 | 5 | 0.2 | 2.7 |
| 5 | 950 | 10 | 5 | 0.1 | 2.8 |
| 6 (wastewater) | variable | 70 | 50 | 1 | 2.0 |

<Place **Table 5** here>

**Table 6. Results of Water Network for Case B**

| Case B | Freshwater ($m^3/y$) | Treatment cost ($/y) | | Piping cost ($/y) | TAC ($/y) |
|---|---|---|---|---|---|
| | | Operating cost | Capital cost | | |
| Scheme 1 | 8,232,000 | 42,829,833 | 19,051,289 | 264,368 | 70,377,490 |
| Scheme 2 | – | – | – | – | – |
| Scheme 3 | 6,997,673 | 26,950,304 | 28,230,360 | 469,949 | 62,648,286 |

<Place **Table 6** here>

**Table 7. Model Size and Computational Statistics for Schemes 2 and 3**

| Computational size and statistics | Scheme 2 | Scheme 3 |
|---|---|---|
| No. of binary variables | 202 | 130 |
| No. of nonconvex nonlinear terms | 113 | 112 |
| No. of bilinear/quadratic terms | 518 | 348 |

<Place **Table 7** here>

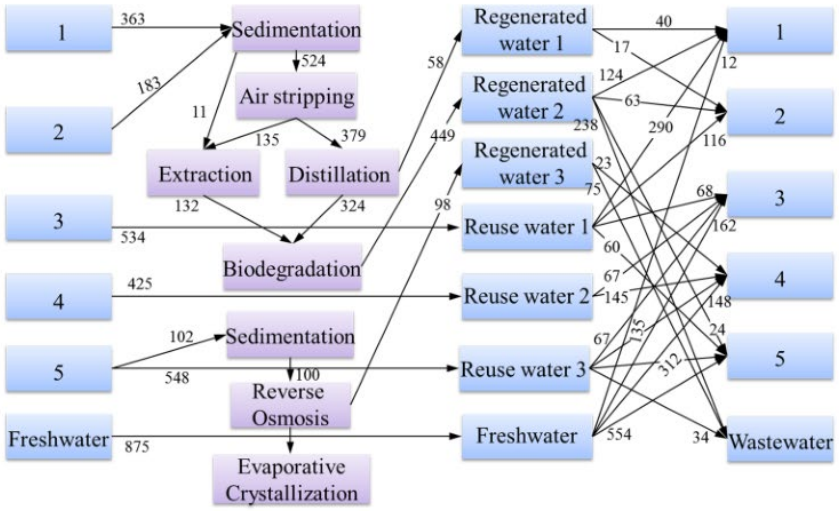


**Figure 8.** Optimal water network for Scheme 3 (unit: $m^3/h$).

<Place **Figure 8** here>

The results for Case B are summarized in Table 6. Like Case A, Scheme 1 ignores the system integration leading to the highest amounts of freshwater consumption, treatment cost, and TAC. When it comes to Scheme 2, it is unable to guarantee optimality under the current computing resource even though the simplification strategies mentioned in Case A are used to solve the problem. This phenomenon is attributed to the large-scale numbers of 0-1 variables and the bilinear terms, as listed in Table 7. For Scheme 3, by means of the MWT design, the numbers of these parameters are significantly reduced to 130 and 348, respectively. Thus, an optimal solution can be obtained in approximately 1,314 s.

Figure 8 depicts the optimal water network configuration for Scheme 3. As shown, multiple treatment units including sedimentation, air stripping, extraction, distillation, biodegradation, and RO are selected to dispose of the impurities to their allowable concentrations. In comparison with Case A, the optimal solution of Case B involves a more complex configuration of water network and requires a greater number of wastewater treatment units. For example, the RO unit is an integrant part of the water network in Scheme 3 as the water (source 5) untreated by the RO unit cannot meet the sink's requirement. The permeate from this unit is sent to the sinks directly, while the rejected brine needs an enrichment treatment until the dissolved salts are essentially precipitated in an

evaporation−crystallization unit. Thereupon, in this case study Scheme 3 inevitably results in double growths in both the treatment cost and TAC as compared to the same scheme used in Case A. It can also be seen that this optimal water network features a distributed wastewater treatment network which segregates and mixes effluent streams for appropriate treatment. For example, a part of the distillation unit effluent (324 m3/h) passes through the biodegradation unit for a further reduction of phenols, while the others directly bypass it for reuse. This distributed wastewater treatment network has significant advantages over the centralized effluent treatment network. As listed in Table 6, compared to Scheme 1, the freshwater consumption and operating cost in Scheme 3 are reduced from8,232,000 to 6,997,673 m3 and 42,829,833 to 26,950,304 $/y, respectively. These reductions further transformed into a remarkable saving in the TAC of the optimal water network which declines from $70,377,490 for Scheme 1 to $62,648,286 for Scheme 3. The more detailed information associated with the treatment cost of the selected treatment technologies for the case study is given by Table S6 (available in the Supporting Information). From the above discussion, we can draw the conclusion that the MWT design agrees with industrial practice in facilitating the water network optimization process and achieving a faster computation.

# 5. CONCLUSION

This study developed a superstructure-based water network synthesis method, which integrated multiple treatment technologies to reuse, recycle, and regenerate wastewater streams in a coal-based chemical plant. Importantly, a MWT design embedded with the water network was proposed to enforce a certain design and to tighten the model formulation. The mathematical model of the proposed water network presented a MINLP model, which has been incorporated with multiple unit-specific shortcut models. Two case studies were presented to demonstrate the effectiveness and feasibility of the proposed method. The results of these case studies revealed that the proposed water network synthesis model incorporating the MWT design can significantly achieve freshwater consumption reduction and be cost saving. Moreover, the model based on the proposed water

network enhanced the convergence to an optimal solution that is practically reliable and manageable.

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# NOMENCLATURE

**Set**

| | |
|---|---|
| *I* | sources |
| *T* | technologies/methods |
| *J* | sinks |
| *P* | impurities |

**Subscript**

| | |
|---|---|
| *i* | source *i* |
| *ih* | high-concentration wastewater source *ih* |
| *il* | low-concentration wastewater source *il* |
| *r* | freshwater source *r* |
| *t* | technology/method *t* |
| *prh* | treatment technology used to treat HPA wastewater in step I |
| *prl* | treatment technology used to treat LPA wastewater in step I |
| *aph* | treatment technology in HPA wastewater treatment unit of step II |
| *apl* | treatment technology in LPA wastewater treatment unit of step III |
| *hs* | treatment technology in high-salinity water treatment unit of step IV |
| *br* | treatment technology in brine treatment unit of step V |
| *wi* | water island |
| *j* | sink |
| *p* | impurity of water |
| waste | wastewater |

**Various**

| | |
|---|---|
| *m* | flow rate |
| *c* | concentration of impurity |

$\beta$ removal ratio

$C$ cost

**Parameters**

$H_Y$ annual operating time

$K_F$ factor used to annualize the inversion

$UC$ unit cost

$D$ distance between any two units

$fc$ fixed investment

$vc$ variable investment

$x$ binary variable

$v$ velocity

$\alpha$ exponent for the capital costs function

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