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Optimal Synthesis of Property-Based Wastewater Network with Multiple Regenerators in Coal-Based Chemical Plants

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Coal-based chemical industries usually generate wastewater containing various compositions and high concentration of pollutants. This causes more intensely environmental and social concerns compared with other process industries like oil refineries. This work addresses the synthesis and optimization of superstructure-based multi-contaminant wastewater network with the consideration of reuse, recycle, and regeneration of wastewater streams in coal-based chemical plants. This wastewater network is formulated as multiple unit-specific shortcut models of wastewater regenerators including electrocoagulation, biodegradation, and reverse osmosis in place of conventional regeneration models with fixed outlet concentration (or contaminant removal ratio) to describe the mass transfer and cost functions. The physical and chemical properties (such as pH, temperature, and the concentrations of phenols and sodium chloride in the wastewater) are taken into account in the proposed wastewater network. A disjunctive programming formulation is developed to address the influences of wastewater compositions and treatment technologies on the costs for wastewater management system, freshwater consumption, and wastewater network design. The effectiveness and feasibility of the proposed model is demonstrated in two case studies of practical coal-based chemical industry.

1. Introduction

Many developing countries such as China still heavily rely on coal as a major feedstock for producing synthetic fuels and bulk chemicals due to the low-cost and huge reserve of coal in China (Elliott et al., 1981). In a typical coal-based chemical plant, significant quantities of water are needed for washing, cooling, and reacting. Compared with petro-chemical industries, coal-based chemical industries usually generate the wastewater with more complex compositions. It contains a large number of toxic compounds (phenols, ammonium, heavy metal-ions.) and dissolved salts (sodium chloride, magnesium chloride.), which should be removed prior to its discharge to the environment (Li et al., 2011). Phenols are highly toxic compounds even at low concentration, so the discharge of wastewater containing phenols is severely restricted. Several methods have been used to treat the phenolic wastewater, such as electrocoagulation (Tovar-Facio et al., 2015), Fenton (Ji et al. 2016), and biodegradation (Jiang et al., 2015). In these methods, the electrocoagulation treatment with a relatively low treatment cost is more effective for the low-concentration phenols degradation. While the biodegradation treatment possesses high removal efficiency but leads to high treatment cost. Other properties, like salt concentrations are also the vital factors, since they may accumulate unless an effective desalination process is proposed for the water recycle/reuse. An effective desalination technology has been proven by using reverse osmosis (RO) membrane separation to obtain clean and even drinkable water (Lee et al., 2011).
With the increasing pressure of water scarcity and environmental concern, efficient strategies for minimizing freshwater consumption have become significantly important. It is a crucial task to develop a superstructure-based multi-contaminant water network for coal-based chemical plant. Multiple technologies in the unit-specific shortcut models have been integrated to reuse, recycle, and regenerate wastewater streams in the coal-based chemical plant.

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Mathematical optimization technique is one of the methods widely-used to achieve the optimal water networks. This technique can deal with the problems considering the computational complexity caused by various costs, multiple properties, and constraints. To improve the mathematical optimization technique for water network, Tovar-Facio et al. (2015) proposed a property-based integration technique to optimize the allocation and manipulation of streams in specified units. Fan et al. (2016) designed a water networks with multiple contaminant. Wang et al. (2016) proposed a framework for the synthesis of total water network in batch plants when varieties of treatment units are available.

To the best of our knowledge, the existing publications rarely consider the water network optimization in coal-based chemical plants. In this paper, a systematic technique based on properties with wastewater regeneration is proposed. The wastewater regenerators include electrocoagulation, biodegradation, and reverse osmosis. The model for the water network synthesis is formulated as a mixed integer nonlinear programming (MINLP) problem with the objective of minimizing the total annual cost of the system which is described as the sum of the total operating costs and the annual capital costs.

2. Methods and Materials

The problem statement in this work can be stated as follows.

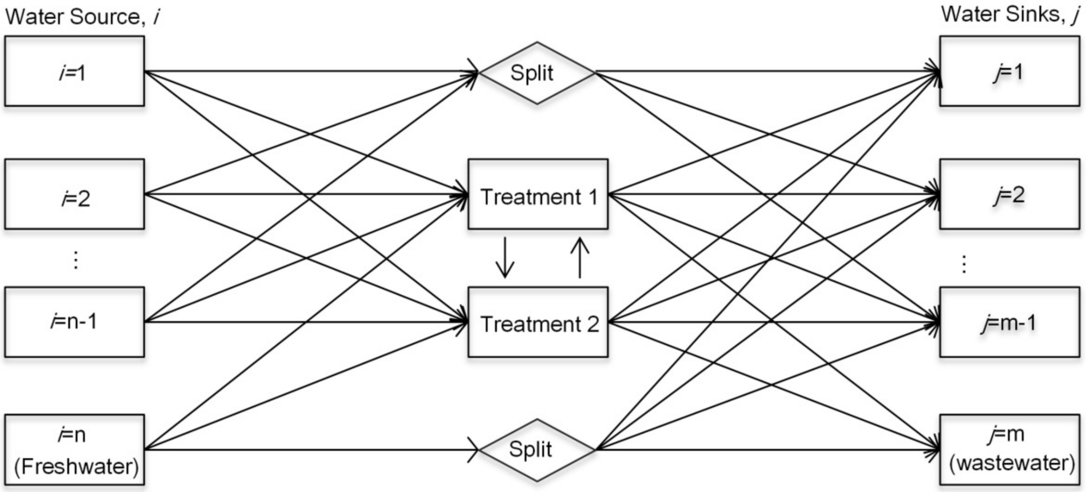

Figure 1: The proposed water network superstructure in coal-based chemical plants.

Following information is assumed to be given before the water network modelling: (1) a set of water sources and their flow rates and properties, (2) a freshwater source and its properties, but with variable and unlimited flow rate, (3) multiple regenerators including electrocoagulation and biodegradation, (4) a set of water sinks with flow rates and the maximum/minimum allowable properties, (5) a wastewater sink with maximum allowable properties and unlimited flow rate. The goal of the model is to find the optimal water network configuration to determine the minimum freshwater consumption, wastewater generation, and the total annual cost for process system.

In this paper, an integrated multiple properties with a given set of sources (including freshwater), a set of treatment units, and a set of sinks (including wastewater discharge) are considered. The mathematical formulations proposed in this work include the mass balances and property constrains for the splitters and mixers in the superstructure as shown in Figure 1. The mathematical model based on the superstructure is presented in the following equations, which is a generalized disjunctive programming (GDP) formulation.

$$F_n = \sum_i F_i \qquad \forall i, n \in m_{out}, m \in \text{sources} \qquad (1)$$

$$F_n C_n = \sum_i F_i C_i \qquad \forall i, n \in m_{out}, m \in \text{sources} \qquad (2)$$

$$F_n = \sum_j F_j \qquad \forall j, n \in m_{in}, m \in \text{sinks} \qquad (3)$$

$$F_n C_n = \sum_j F_j C_j \qquad \forall j, n \in m_{in}, m \in \text{sinks} \qquad (4)$$

$$C_j^{\min} \le C_j \le C_j^{\max} \qquad \forall j \qquad (5)$$

$$F_n = \sum_t F_t \qquad \forall t, n \in m_{in}, m \in \text{treatments} \qquad (6)$$

$$F_n C_n = \sum_t F_t C_t \qquad \forall t, n \in m_{in}, m \in \text{treatments} \qquad (7)$$

$$F_n = \sum_t F_t \qquad \forall t, n \in m_{out}, m \in \text{treatments} \qquad (8)$$

$$F_n C_n = \sum_t F_t C_t \qquad \forall t, n \in m_{out}, m \in \text{treatments} \qquad (9)$$

$$\begin{bmatrix} Y_t \\ C_n \geq C_{\min} \\ C_n \leq C_{\max} \\ IC_t = f_1(F_n) \\ OC_t = f_2(F_n, C_n) \end{bmatrix} \qquad Y_t \in \{\text{Ture}, \text{False}\}, \forall t, n \in m_{in}, m \in \text{treatments} \qquad (10)$$

In the above equations, F_i, F_j and F_t are the flow rates (m^3/h) of any stream of source i, sink j and treatment t in the superstructure. C_i, C_j, and C_t are the properties of any stream of source i, sink j, and treatment t in the superstructure. In the disjunctive formulation, Y_t indicates if treatment t is chosen for the system, the concentration of phenols inlet the treatment t must be greater than the minimum value and less than the maximum value. IC_t and OC_t represent the capital cost and operating cost of treatment t.

The potential influences on the removal performance of key properties are illuminated by consisting the pH, sodium chloride concentration, and temperature of the treated wastewater. These important properties are adjusted to the desired conditions using a pre-treatment unit. Since the desired operating conditions for the electrocoagulation and biodegradation are considered before the wastewater goes into the regenerators, only initial phenols concentration is optimized. As shown in Figure 2, the correlations between initial phenols concentration and removal efficiency are obtained based on the experimental data. In Eqs (11)-(13), γ is the removal efficiency for the electrocoagulation or the biodegradation.

$$\gamma_a = -0.3005 C_n + 108.74 \qquad 12 \leq C_n \leq 250 \qquad (11)$$

$$\gamma_{b1} = -0.0113 C_n + 101.58 \qquad 100 \leq C_n \leq 400 \qquad (12)$$

$$\gamma_{b2} = 0.0006 C_n^2 - 0.8766 C_n + 356.9 \qquad 400 \leq C_n \leq 800 \qquad (13)$$

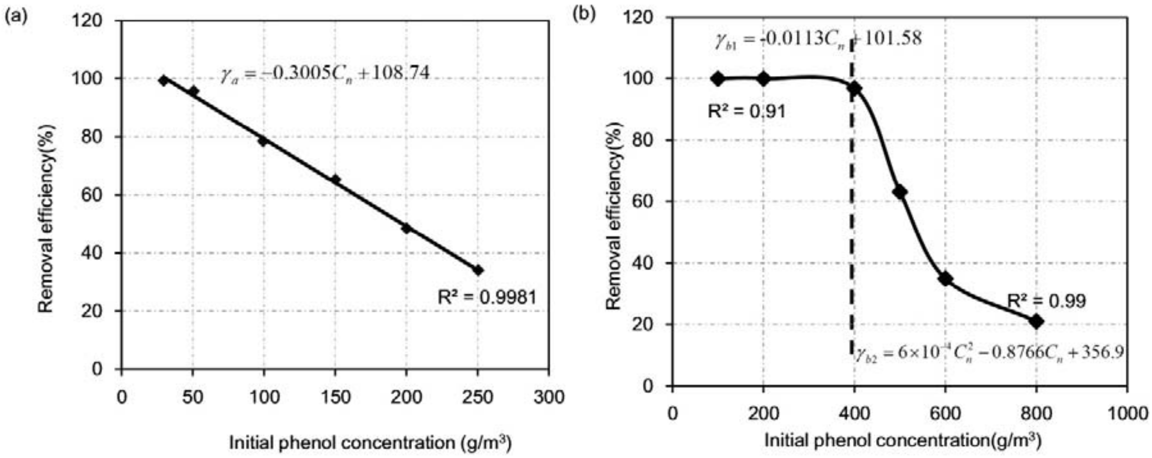

Figure 2: Removal efficiency of the treatments. (a): Electrocoagulation; (b): Biodegradation

3. Results and discussion

Two illustrative case studies (Case 1 and Case 2) under three scenarios are carried out to demonstrate the applicability of the proposed technique. For each case study, scenarios 1 and 2 are solved considering either electrocoagulation or biodegradation, while in scenario 3 both conditions are considered. The basic data for the two case studies are collected from a large-scale coal-based chemical plant in China. The MINLP problem associated with the two case studies are implemented using GAMS 24.7.1 and solved on a computer with an Intel Core i7 at 3.60 GHz with 8 GB memory. The BARON solver in GAMS 24.7.1 modelling environment is employed to solve the problem. The optimality gap of the MINLP problem at each iteration is 10^{-9} in order to ensure the validity of the solution. The total CPU time takes approximately 0.9-31 s for the Case 1 and 30-104 s for the Case 2.

Case 1. In the Case 1, six water sources and four sinks are considered. The flow rates and contaminant concentrations of these sources and sinks are detailed in Table 1.

In the first two scenarios, large amounts of wastewater are generated during the reuse/recycle process. Figure 3 shows that, in the scenarios 3, all the process sources are reused and no wastewater is observed. This is because in this scenario, the effluent leaving the biodegradation is sent to the electrocoagulation for undergoing a deeper clean-up, instead of being directly reused in the water sinks. Thus, scenario 3 results in significant reductions in freshwater consumption, treatment cost, and total annual cost as listed in Table 2. The unit cost ratio of treated wastewater to freshwater falls by nearly half from 4.79 for the scenario 1 to 2.45 for the scenario 3, which demonstrates the advantage of using both electrocoagulation and biodegradation in water networks.

Table 1: Flow Rates and Properties of Process Sources for the Case 1

Sources	Flow rate (m^3/h)	Phenol (mg/L)	NaCl (kg/m^3)	pH	Temperature (K)
1	550	20	1.8	7.1	302
2	363	460	2.5	7.5	303
3	220	325	1.7	6.8	297
4	425	150	2.5	7.0	300
5	45	15	3.5	8.5	315
6(freshwater)	variable	0	0	7.0	298
Sinks	Maximum inlet concentration			Allowed inlet range	
1	765	15	2.5	6.3 - 7.7	293 - 312
2	276	36	2.6	6.7 - 8.0	296 - 315
3	578	45	2.7	6.6 - 7.4	294 - 308
4(wastewater)	variable	1	2.0	6.8 - 8.0	293 - 308

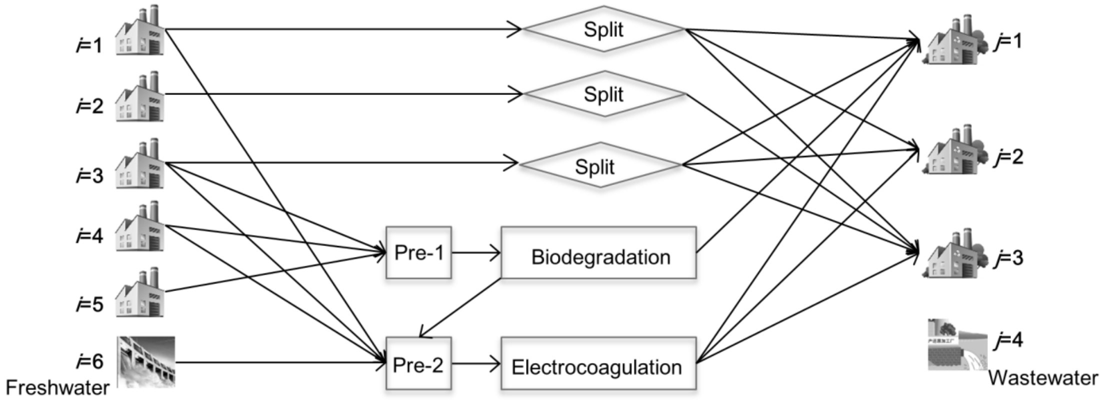

Figure 3: Optimal water network for scenario 3 of the Case 1.

Table 2: Optimal Results of Water Network for the Case 1

Case 1	Freshwater (m^3/y)	Freshwater cost (\$/y)	Treatment cost (\$/y)	Total annual cost(\$/y)	Ratio*
Scenario 1	4.46×10^7	4.46×10^7	2.71×10^8	3.16×10^8	4.79
Scenario 2	4.95×10^5	4.95×10^5	3.26×10^7	3.31×10^7	2.85
Scenario 3	2.99×10^5	2.99×10^5	2.10×10^7	2.13×10^7	2.45

Case 2. The problem in the Case 2 includes eight water sources and seven sinks and the flow rates and properties of these sources and sinks are given in Table 3.

For the Case 2, likewise, the first two scenarios generate large amounts of wastewater in the regeneration process. The optimal water network of the scenario 3 is shown in Figure 4. Here, zero wastewater discharge is achieved and all the process sources are reused, which is consistent with those of the Case 1. Unlike the

Case 1, the wastewater is treated by the electrocoagulation and the RO in the scenario 3. It is noted that the Case 2 is in line with the Case 1 in the tendencies of their costs and freshwater consumption, as shown in Table 4. It shows a significant decrease in the unit cost ratio of treated wastewater to freshwater from 3.49 (scenario 1) to 2.39 (scenario 3). This proves the superiority of the proposed method for water network design.

Table 3: Flow Rates and Properties of Process Sources for the Case 2

Sources	Flow rate (m^3/h)	Phenol (mg/L)	NaCl (kg/m^3)	pH	Temperature (K)
1(freshwater)	variable	0	0	7.0	298
2	600	450	2.5	7.0	295
3	163	230	3.5	6.5	293
4	825	35	2.0	7.0	310
5	32	320	3.0	7.4	298
6	36	400	3.5	6.5	325
7	97	82	2.0	6.5	298
8	547	149	3.0	6.8	293
Sinks	Maximum inlet concentration			Allowed inlet range	
1	825	50	3.0	5.3 - 7.5	290 - 310
2	163	40	2.6	6.5 - 8.0	300 - 315
3	67	30	2.5	5.6 - 7.8	300 - 315
4	382	20	2.0	5.8 - 8.1	294 - 311
5	80	15	2.9	5.9 - 7.9	294 - 312
6	897	18	2.0	6.0 - 8.0	297 - 313
7(wastewater)	variable	1	2.0	6.8 - 8.0	293 -308

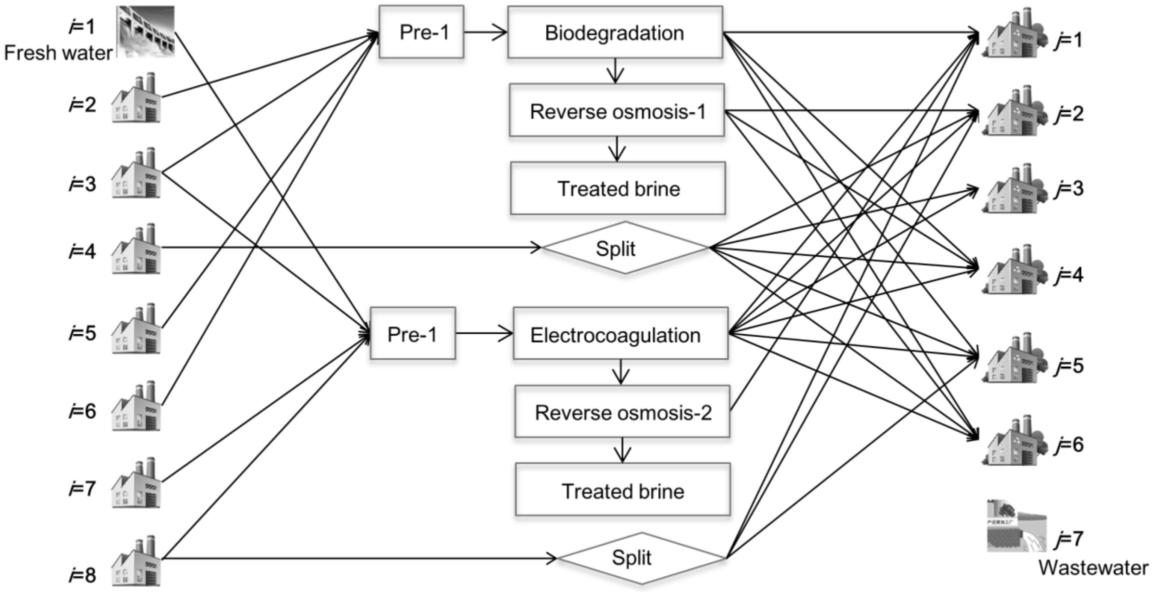

Figure 4: Optimal water network for scenario 3 of the Case 2.

Table 4: Optimal Results of Water Network for the Case 2

Case 1	Freshwater (m^3/y)	Freshwater cost (\$/y)	Treatment cost (\$/y)	Total annual cost(\$/y)	Ratio*
Scenario 1	6.27×10^7	6.27×10^7	3.11×10^8	3.74×10^8	3.90
Scenario 2	1.78×10^6	1.78×10^6	5.16×10^7	5.34×10^7	3.19
Scenario 3	1.22×10^6	1.22×10^6	2.73×10^7	2.85×10^7	2.39

4. Conclusion

In this work, a novel method for optimizing water network superstructure was developed in the coal-based chemical plants. Due to the variable characteristics of the wastewater streams, several treatment systems were included in the superstructure which allows the adjustment of wastewater properties. The mathematical model of the proposed water network addressed wastewater properties, pH, temperature, and the concentration of phenols and sodium chloride. By the use of two wastewater treatment techniques, electrocoagulation and biodegradation, we were able to obtain an optimal water network to minimize the total cost and freshwater consumption. Two case studies were presented to demonstrate the effectiveness and implementation of the proposed scheme. The results in this work showed that integrating the models of two treatment units in a water network superstructure can lead to a decrease in the unit cost ratio of treated wastewater to freshwater from 4.79 to 2.45 for the Case 1 and 3.90 to 2.39 for the Case 2.

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