AIChE

Process Development of Treatment Plants for Dyeing Wastewater

Ka Y. Fung, Chin M. Lee, and Ka M. Ng
Dept. of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong

Christianto Wibowo
ClearWaterBay Technology Inc., 4000 W. Valley Blvd., Suite 100, Pomona, CA 91789

Zhiyi Deng
Dept. of Chemical Engineering, Xiangtan University, Hunan 411105, China

Chaohai Wei
Dept. of Environmental Science and Technology, South China University of Technology, Guangdong 510006, China

DOI 10.1002/aic.12798

A three-step methodology that integrates experiments, modeling and synthesis has been developed for the systematic development of a plant for treating dyeing wastewater for discharge and/or reuse. First, wastewater characteristics, discharge water standards, and reuse water quality specifications, etc. are collected as input information. Heuristics developed in our industrial practice and gleaned from the literature are used to guide the designer to come up with preliminary flow sheet alternatives. Then, bench-scale experiments and pilot plant tests for the relevant unit operations are performed. A computer code accepts the bench-scale and pilot plant experimental data for regression of model parameters and determines the superior process configuration and equipment operating conditions through sensitivity analysis. The workflow among various stakeholders to reach the final design is presented. Possible extension of the methodology to other industrial wastewater treatment plants is discussed. © 2011 American Institute of Chemical Engineers *AIChE J*, 58: 2726–2742, 2012
Keywords: integrated process design, wastewater treatment and reuse, process simulation, dyeing plant, workflow diagram

Introduction

A dyeing plant consumes an enormous amount of water, ranging from several thousand to over 10,000 m^3 per day. A typical dyeing plant for polyester and cotton, the two most common fabrics, consists of a number of pretreatment steps as well as the dyeing step (Figure 1). Water is consumed in almost all these steps as indicated by the shaded boxes. In addition to the dyes, a wide variety of inorganics, wetting agents, surfactants and sequestering agents are used in different parts of the process. These chemicals have to be removed from the wastewater so that the treated water can be either discharged to the environment or better yet reused in the dyeing plant. Various techniques such as biotreatment, coagulation, advanced oxidation, adsorption, ion exchange, multimedia filtration, and membrane filtration are used for this purpose. For a given dyeing plant, the challenge is to develop the best flow sheet configuration along with the operating conditions that produces the discharge water and reuse water with the required qualities.

Rodriguez-Roda et al.[1] and Vidal et al.[2] proposed a conceptual design method with which the process units in a wastewater treatment plant were selected based on a hierarchical decision process, design history and process simulation. The hierarchical decision process was implemented with a decision support tool which decomposes complex decisions into a number of simpler sub-decisions. Freitas et al.[3] also proposed a conceptual design method in which an expert system coupled to an external program for computational calculations and a database of physical and chemical properties about pollutants and their treatability data to come up with a wastewater treatment flow sheet. Yang and Kao[4] also developed an expert system to come up with a suitable process configuration for a given waste stream. Process simulators with focus on biotreatment processes such as GPS-X and EnviroPro have been used for wastewater treatment plant simulation.[5,6] Various optimization techniques such as Monte Carlo simulation[7] and model-based optimization[8] have also been applied in the area of wastewater treatment.

Additional Supporting Information may be found in the online version of this article.

Correspondence concerning this article should be addressed to K. M. Ng at kekmng@ust.hk.

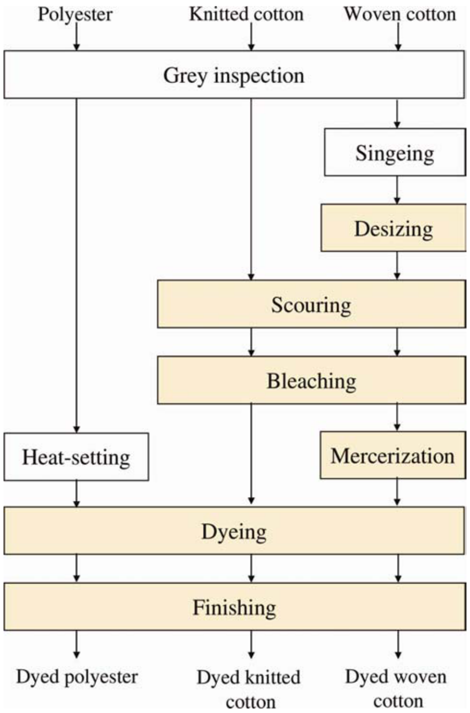


Figure 1. Polyester and cotton dyeing processes (shaded boxes represent steps that require water as a carrier for chemicals).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In addition, a large number of studies[9,10] have investigated the minimization of fresh water consumption by considering the manufacturing plant and its wastewater treatment plant as a whole using different mathematical programming techniques. While these studies have provided useful insights, little has been done on the use of experimental data to develop an industrial wastewater treatment plant for a given industrial wastewater effluent stream.

This is a serious omission because a manufacturing plant such as a dyeing plant can contain many different dyes and additives. At present, most of these industrial wastewater treatment plants with distinct characteristics have been developed primarily based on the experience of the engineer. The aforementioned simulation and optimization tools could not be used because of the absence of suitable data. A wastewater treatment plant can be over-designed, adopts an inappropriate technology or uses an excessive amount of water treatment chemicals, thus incurring needless capital cost and/or operating cost. Day-to-day plant operational problems might also arise in the absence of a well thought out design.

To fill this gap, a design methodology which integrates experiments, modeling and synthesis has been formulated. First, input information for plant design such as wastewater characteristics, flow rate, and discharge and reuse water quality requirements is collected. Flow sheet alternatives are then generated. Model parameters regressed from suitable bench-scale and pilot plant experiments along with other design parameters are used in a computer code for flow sheet evaluation. The example in this article captures the issues, water characteristics and experimental data we encountered in applying this methodology for the design of several wastewater treatment plants. Although this study focuses on a dyeing plant because of the experience obtained in our industrial collaborations, the methodology can be readily adapted for other manufacturing plants.

Input Information

The input information required for synthesizing a wastewater treatment process for a dyeing plant is summarized in Table 1. First, the wastewater needs to be characterized. In addition to wastewater flow rate and lumped parameters such as chemical oxygen demand (COD) and total suspended solids (TSS), concentrations of some ions and heavy metals are also needed. For example, the concentration of PO_4^{3-}, which comes from Na_3PO_4 used in cotton dyeing, has to be measured to ensure that it is below the limit of discharge to surface water of 0.5 ppm. Components that can affect the performance of the wastewater treatment plant such as surfactants that can foul the ultrafiltration (UF) and reverse osmosis (RO) membranes need to be identified. Second, discharge and reuse water specifications need to be identified. Table 2 gives a list of discharge effluent specifications from the Department of Environmental Protection of Guangdong Province, China.[11] As can be seen, specifications for discharge to surface water are tighter than those to a local sewage plant. Table 3 provides an example of the reuse water specifications in the United States.[12] In practice, instead of relying on such general rules, a pilot test is often conducted to ensure that the reuse water is sufficiently good for the manufacturing plant. Relevant plant information such as the type of fabric being dyed and the various sources of wastewater in the dyeing plant (Figure 1), among others, has to be identified. It may be cheaper to treat a stream with high COD and one with low COD separately than treating the combined stream. The potential fluctuations in the characteristics of the influent wastewater need to be estimated as the

Table 1. Input Information Required for Wastewater Treatment Plant Process Design

- Wastewater characteristics
    - ○ Wastewater flow rate
    - ○ Oxygen demand: chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD_5)
    - ○ Total suspended solids (TSS), total dissolved solids (TDS), total solids (TS = TDS + TSS)
    - ○ Total nitrogen (TN), total phosphorus (TP)
    - ○ Others: pH, conductivity, color, temperature, oil content
    - ○ Concentration of specific elements, ions and chemicals
        - ■ Ions or chemicals that are added in the dyeing plant or wastewater treatment plant, if they are included in the reuse water or discharge effluent specifications
        - ■ Same for specific elements, especially heavy metals
        - ■ Components that affect the performance of the wastewater treatment plant (e.g., chemicals that lead to scaling in membrane filters)
        - ■ Components that are added in high concentration in the dyeing process
- Discharge or reuse water specifications
    - ○ Percentage of water reuse from the wastewater
    - ○ TDS, TSS
    - ○ Metals content (e.g., Fe, Mn, Cu)
    - ○ Hardness
- Dyeing plant information
    - ○ Type of fabric
    - ○ Chemicals used in the process
    - ○ Variation of wastewater flow rate and concentration within a production cycle

Table 2. Discharge Limit to Surface Water and Local Sewage Plant in Guangdong Province of China

	Surface Water	Local Sewage Plant
pH	6–9	6–9
Color	40	–
TSS (ppm)	60	400
BOD_5 (ppm)	20	300
COD (ppm)	100	500
PO_4^{3-} (ppm)	0.5	–
NH_4^+ (ppm)	10	–
Total copper (ppm)	0.5	2

treatment plant has to be designed to cope with such disturbances.

Synthesis of Flow Sheet for Wastewater Treatment

The generic flow sheet of the wastewater treatment plant is depicted in Figure 2. Physicochemical treatment and biotreatment are the major sub-processes for removing pollutants in wastewater. Treated water is then further purified by water purification and water disinfection before being reused in the upstream manufacturing process. Depending on the wastewater characteristics, one or more sub-processes can be bypassed and the heuristics for making such decisions are summarized in Table 4.

Biotreatment lowers COD in the wastewater by degrading organics to simpler compounds. Before biodegradation, physicochemical treatment is needed if the wastewater characteristics adversely affect the performance of biotreatment. Biodegradability as represented by the BOD_5 to COD ratio, COD, and component concentrations are some of the parameters used for deciding whether physicochemical treatment is required. The proportion of COD, total nitrogen (TN), and total phosphorus (TP) is important because a proper amount of nutrients in the wastewater is essential for the growth of the microorganisms. Polyvinyl alcohol (PVA) is known to biodegrade slowly under conventional biotreatment conditions.[16] A pretreatment step such as the Fenton reaction could be used for PVA removal. Toxic substances such as heavy metals may have inhibitory effects on the biotreatment bacteria. Toxicity tests have to be carried out to determine whether effluents from the manufacturing plant are toxic to bacteria.

After physicochemical treatment, biotreatment is used to degrade organic compounds in the wastewater. Note that for wastewater with low organic loadings, biotreatment is ineffective and physicochemical treatment alone may be sufficient to remove the pollutants in it. Biotreatment is normally followed by water purification to remove residual organics as complete mineralization is hard to realize in biotreatment. Inorganic salts are also removed in water purification such that water can be reused for the dyeing processes. However, even if no reuse is desired, water purification is still required if the effluents from biotreatment do not meet the discharge specifications. Finally, water disinfection is applied.

Table 3. Quality of Reuse Water in Textile Industry According to the US EPA

	Limit
Hardness (ppm)	25
TDS (ppm)	100
TSS (ppm)	5
Color	5
Fe (ppm)	0.1
Mn (ppm)	0.01
Cu (ppm)	0.01

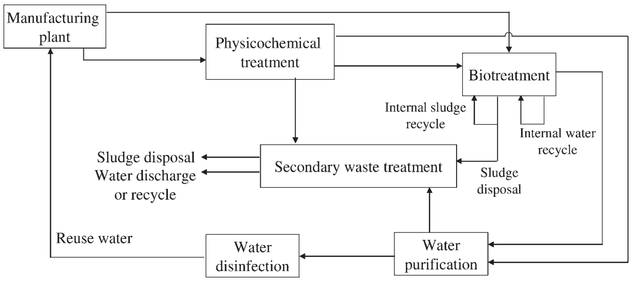


Figure 2. Generic flow sheet of wastewater treatment plant.

After deciding whether a sub-process is needed in wastewater treatment, the sub-process flow sheets as depicted in Figure 3 have to be designed. Heuristics for selecting the unit operations for these sub-processes are summarized in Table 5. Chemicals used in and the secondary wastes generated from these treatment units are summarized in Table 6.

Physicochemical treatment

In this sub-process (Figure 3a), the dyeing effluent first passes through a screening unit to remove any debris and large particles before reaching an equalization tank, the size of which is sufficiently large that it dampens the fluctuations in the flow rate and composition of the wastewater from the manufacturing plant. The wastewater treatment facilities are

Table 4. Heuristics for Selecting Sub-processes in Wastewater Treatment Plant

- Physicochemical treatment is needed if wastewater characteristics adversely affect the performance of biotreatment. These include
    - Wastewater with low biodegradability ($BOD_5/COD < 0.2$).[13]
    - The ratio of COD:TN:TP does not meet the nutrient requirement for anaerobic process (200:5:1) and aerobic process (100:5:1).
    - Wastewater contains persistent organic pollutants such as polyvinyl alcohol.[14]
    - Wastewater contains organics such as alcohols, long chain fatty acids and chlorinated compounds that cannot be hydrolyzed into intermediate compounds by anaerobic biotreatment.
    - Wastewater contains chemicals present at a concentration inhibitory or toxic to biotreatment.[15] For example,
        - TDS > 16,000 ppm
        - TSS > 100 ppm
        - Salt concentration > 5000 ppm
        - Alkali and alkaline earth metals (e.g., [Na] > 3500 ppm, [Mg] > 1000 ppm, [K] > 2500 ppm, [Ca] > 2500 ppm)
        - Heavy metals (e.g., soluble [Cu] > 0.5 ppm, total [Cu] > 50 ppm, soluble [Cr(VI)] > 3 ppm, total [Cr(VI)] > 200 ppm, soluble [Ni] > 2 ppm, soluble [Fe] > 1000 ppm)
        - Other chemicals (e.g., $[NH_3] > 1500$ ppm, Soluble $[S^{2-}] > 200$ ppm)
- Biotreatment is not needed for wastewater with low organics loading. Physicochemical treatment alone may be sufficient.
- Water purification is needed if residual organics or inorganic salts are present in the biotreatment effluents at a concentration higher than the reuse water limit or discharge limit.

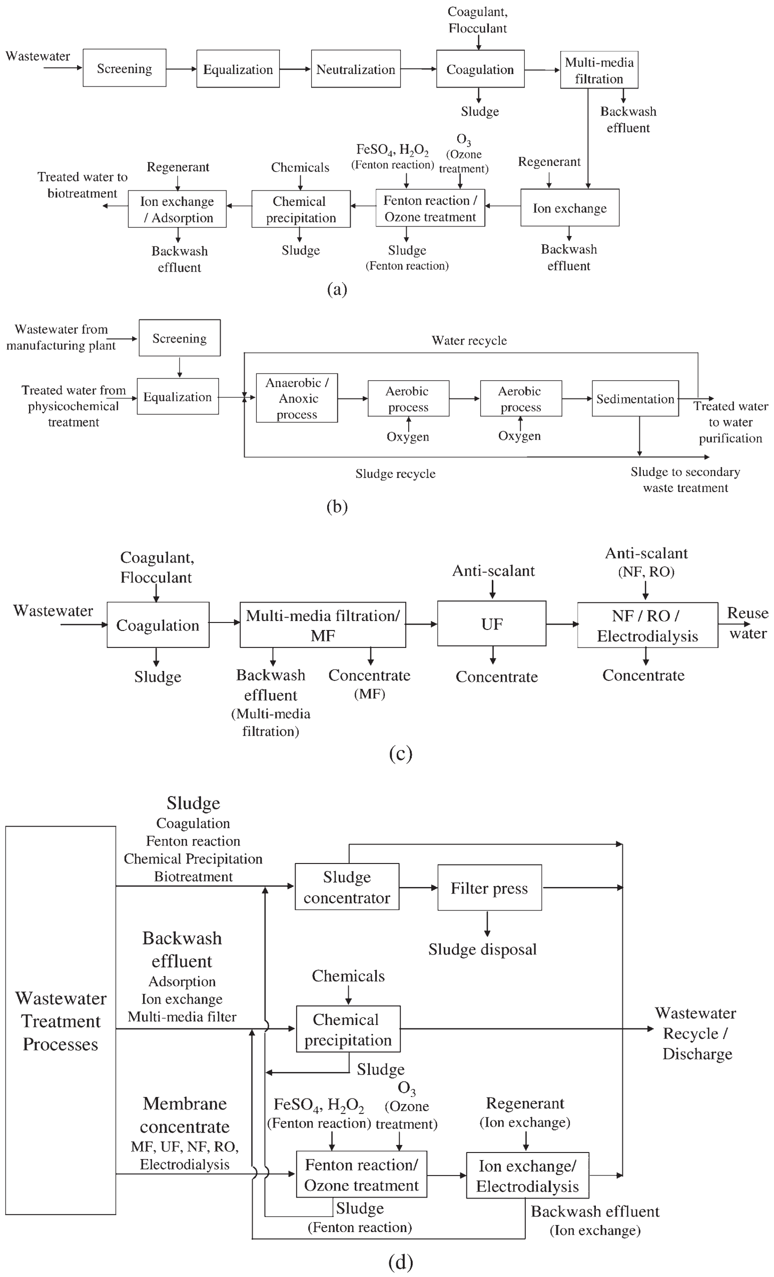


Figure 3. Process flow sheet for sub-processes (a) physicochemical treatment; (b) biotreatment; (c) water purification; (d) secondary waste treatment.

designed based on the expected average, rather than extreme, flow conditions. The effluent then enters a neutralization tank if pH adjustment is needed.

Insoluble particles are then removed if TSS is larger than 100 ppm. Coagulants are often added to aid the removal of such suspended solids and colloids. After removing the sludge, the resulting stream, with TSS less than 100 ppm and without a high concentration of free oil and grease, can now be sent to a multimedia filtration column. Without coagulation and sedimentation, the filtration column may require frequent backwash.

While ion exchange, chemical precipitation or adsorption can be used to remove salts to enhance biodegradability, Fenton reaction and ozone treatment are more common for treatment of dyeing wastewater. Fenton reaction can be applied to a wide spectrum of pollutants. Ozone treatment is effective only for pollutants containing conjugated double bonds or aromatic groups. Also, it is not suitable for high COD removal as ozone does not completely break down the pollutants.

Inorganic ions may need to be removed by ion exchange as they adversely affect advanced oxidation processes. For ozone treatment, Cl^- reacts through series reactions to form Cl_2 which in turn reacts with ozone in acidic pH, while Cl^- and SO_4^{2-} react with hydroxyl radicals directly in alkaline pH, hence reducing the amount of ozone and hydroxyl radicals available for reacting with the pollutants.[19] Other anions commonly used in textile processing such as HCO_3^-, CO_3^{2-}, NO_3^-, $H_2PO_4^-$ also have various scavenging effects on hydroxyl radicals.[20] Anions such as $H_2PO_4^-$, Cl^-, and SO_4^{2-} also form complexes with Fe^{2+} and Fe^{3+} in Fenton reaction, slowing or even inhibiting the reaction.[21–23]

Table 5. Heuristics for Selecting Techniques for Individual Sub-processes

Physicochemical treatment

- Neutralization is needed if pH adjustment is necessary.
- Remove insoluble particles then soluble substances, if TSS > 100 ppm.
- Insoluble particles removal
  - Use coagulation to remove colloids and suspended solids.
  - Use multimedia filtration after coagulation if a lower concentration of suspended solids is desired.
  - Do not use multimedia filtration if wastewater contains > 100 ppm of suspended solids or high concentration of free oil, grease, abrasive and fibrous solids as they lower the effectiveness of the column and require frequent backwash. Instead, adjust the conditions of an upstream coagulation unit to lower their concentration.[17]
- Soluble substances removal and biodegradability enhancement
  - Use ozone treatment to improve biodegradability only if major pollutants contain conjugated double bonds (—N=N—, —C=C—) or aromatic groups.[18]
  - Do not use ozone treatment if a high COD removal is desired.
  - Use adsorption to improve biodegradability only if the major pollutants degrade slowly and do not oxidize well.
  - Consider using ion exchange to precede ozone treatment and Fenton reaction, if inorganic salts are present at a concentration detrimental to the subsequent processes.[19–23]
  - Consider removing heavy metals after Fenton reaction as some heavy metals (e.g., Ni, Co) may have catalytic effect, if they are present at a concentration detrimental to biotreatment.[24]

Biotreatment

- Aerobic biotreatment alone is sufficient for treating wastewater with high biodegradability ($BOD_5/COD > 0.4$) and low COD (<1000 ppm).[13]
- Anaerobic process preceding aerobic process is needed for wastewater with lower biodegradability ($BOD_5/COD = 0.2–0.4$).
- A second stage aerobic process is needed for wastewater with hard to degrade pollutants.

Water purification

- Insoluble particles removal
  - Use multimedia filtration or microfiltration as a protective unit to membrane filtration. Coagulant can be added at the inlet of multimedia filter to increase floc size.
  - Consider using ultrafiltration for wastewater containing predominantly submicron solids (1–20 nm).
- Dissolved organics and salts removal
  - Consider electrodialysis if high water recovery (>90%) is required.
  - If the removal efficiencies of the major pollutants are very different for the same adsorbent or ion exchange resin, prefer membrane filtration over adsorption and ion exchange.
  - Use ultrafiltration to remove dissolved organics and macromolecules with molecular weight between 300 and 300,000 g/mol.[17]
  - Use nanofiltration or reverse osmosis to remove dissolved salts smaller than 300 g/mol.[17]
  - Add anti-scalant to nanofiltration or reverse osmosis if membrane fouling or scaling is likely to occur.
  - Use ultrafiltration as a protective unit before reverse osmosis.
  - Do not use adsorption if wastewater contains >25 ppm of suspended solids.

Secondary waste treatment

- Sludge from coagulation and biotreatment
  - Send the sludge to sludge concentrator and then filter press. Wastewater removed from sludge concentrator is recycled to equalization tank while sludge from filter press is disposed.
- Backwash effluents and wastewater from adsorbent and resin regeneration
  - Send backwash effluents to a local sewage treatment plant.
  - If the regenerated effluent comes from heavy metal adsorption, apply chemical precipitation to meet the discharge criteria for heavy metals.
- Concentrate treatment
  - Recycle concentrate to upstream processes whenever it is cost effective. If direct recycle is not possible due to salt accumulation in the plant, treat it with a salt removal system such as ion exchange before recycling.
  - The destination of the recycle stream must allow for the major pollutants to be degraded or removed in subsequent processes.
  - Discharge concentrate to surface water or local sewage plant if recycling is too expensive. Use Fenton reaction and ion exchange to lower COD and remove salts in the concentrate, respectively, if the discharge effluents do not meet the discharge specifications. Place Fenton reaction before ion exchange as the inorganic salts used in Fenton reaction have to be removed before discharge.
  - Consider discharging NF and RO concentrate to an evaporation pond if the plant is located in a region with high evaporation rates, level terrain and low land costs.[25]

Biotreatment

Physicochemically treated wastewater is mixed with effluents from those units of the manufacturing plant that are readily biodegradable in an equalization tank before entering biotreatment (Figure 3b). For influents to the biotreatment step that are easily biodegradable, aerobic biotreatment alone is sufficient. However, for influents with low biodegradability, an anaerobic process is used before the aerobic process to partially break down the pollutants for easier degradation in the aerobic process. For influents with even lower biodegradability, a two-stage aerobic process can be used. For influents with high TN and TP, it is beneficial to recycle part of the supernatant to the anaerobic unit. This is because nitrates produced in the aerobic process can be reduced to nitrogen by denitrification in the anaerobic process while polyphosphates generated by phosphorus organisms can be used to sustain cell growth in the anaerobic process.

Water purification

The effluent from the biotreatment section contains a variety of compounds which include acetates, formates, benzoates, carboxylic acids, alcohols, etc.[26,27] Various techniques such as coagulation, multimedia filtration, adsorption, ion exchange, and membrane filtration are commonly applied in water purification to remove these degraded organics and dissolved inorganic salts (Figure 3c). General guidelines for the process synthesis of the water purification sub-process are summarized in Table 5. Membrane filtration is preferred over adsorption and ion exchange because it is not specific to a chemical species. The former depends on molecular size

Table 6. Available Techniques for Wastewater Treatment

Treatment Techniques	Major Substances Removed: Suspended Solids	Colloids	Dissolved Organics	Dissolved Salts	Input Chemicals	Secondary Wastes
Coagulation	✓	✓			Coagulant, flocculant	Sludge
Multimedia filtration	✓	✓			–	Backwash effluent
Ozone treatment			✓		Ozone	–
Fenton reaction			✓		$FeSO_4$, H_2O_2	Sludge
Ion exchange				✓	Regenerant	Backwash effluent
Adsorption			✓	✓	Regenerant	Backwash effluent
Chemical precipitation			✓	✓	Chemicals	Sludge
Anaerobic process			✓		–	Sludge
Aerobic process			✓		Oxygen	Sludge
Sedimentation (for sludge recycling in biotreatment)	✓				–	Sludge
Microfiltration (MF)	✓				–	Concentrate
Ultrafiltration (UF)		✓	✓		Anti-scalant	Concentrate
Nanofiltration (NF)			✓	✓	Anti-scalant	Concentrate
Reverse osmosis (RO)			✓	✓	Anti-scalant	Concentrate
Electrodialysis				✓	–	Concentrate

while the latter on chemical interactions. Also, electrodialysis is preferred over membranes if larger than 90% water recovery is required.

Secondary waste treatment

Secondary wastes are produced from the sub-processes and can be classified into three main categories: sludge, backwash effluents, and membrane concentrates (Figure 3d). Sludge concentrator and filter press are used to recover the sludge for disposal. Backwash effluents can be sent to a local sewage treatment plant if the discharge criteria are met. Otherwise, chemical precipitation may be required to remove heavy metals and suspended solids.

Membrane concentrates constitute a significant portion of secondary wastes. The concentrate to feed volume ratio ranges from 1–10% for microfiltration (MF) and UF, 15–30% for nanofiltration (NF), and 15–60% for RO.[28] Concentrates from MF and UF contain suspended solids and colloidal particles while NF and RO concentrates contain ions and small organic compounds. Various options are possible for handling membrane concentrates which include recycling to the upstream manufacturing process, discharge to surface water or sewers, and evaporation ponds.[29] Recycling to an upstream unit of the wastewater treatment plant is obviously preferred as it increases the amount of reuse water. This is possible for MF and UF concentrates because the relatively small volume of the concentrates does not necessitate a large increase in the capacity of the wastewater treatment plant. Any suspended solids and colloidal particles rejected by these membranes should be removed by coagulation and filtration so that there is no accumulation of these substances in the wastewater treatment plant. For NF and RO concentrates, direct recycling to upstream processes is more challenging as this would lead to salt accumulation in the plant. Ion exchange or electrodialysis can be used to remove these salts before recycling to upstream units but this might lead to a massive increase in the plant equipment size due to the large concentrate to feed volume ratio for NF and RO. Nonetheless, recycling all concentrates is a must if zero emission of wastewater is to be realized.

Evaluation of Flow Sheet Alternatives

Selection of base case design and operating parameters

After synthesizing the flow sheet for the wastewater treatment plant, material balance calculations are carried out to determine the flows in each stream. In case a specific chemical is part of the specifications for the wastewater, its concentration has to be tracked as well. For example, if $FeCl_3$ is used as a coagulant and since Fe concentration is part of the reuse water specifications in Table 3, Fe concentration has to be monitored. Design equations for the wastewater processing units are summarized in Table 7, together with typical values for some of the model parameters. Model parameters that are case specific and cannot be accurately predicted are obtained by experiments. Such experiments for the primary unit operations are summarized in Table 8; those for secondary units such as screening, sludge concentrator and filter press are not included. Some of the key issues for the primary units are discussed below.

Coagulation. A coagulation tank typically involves three compartments: a mixing tank, a flocculating chamber, and a sedimentation tank. Component removal efficiency which depends on coagulant dosage and solution pH is an important parameter. An empirical relationship can be used for regression of data obtained from a jar test (Eq. 1). A quadratic relationship with respect to dosage is common if coagulation is dominated by charge neutralization. Another important aspect is the settling characteristics of coagulated flocs, represented by the so-called batch flux G (Eq. 2), which is a product of batch settling velocity u_s and solids concentration C_s. A batch settling test is carried out to obtain a correlation[30] between u_s and C_s

$$\ln u_s = m_s C_s + b_s \qquad (24)$$

where m_s and b_s are empirical constants.

In a continuously-operated sedimentation tank with a given feed flow rate and solids concentration, the sedimentation tank area A and the underflow withdrawal rate Q_u have to be selected such that the feed flux would not exceed the overall downward flux at any point in the tank. The operating line (Eq. 3) represents the settling performance for given

Table 7. Design or Empirical Equations for Each Treatment Unit in the Wastewater Treatment Plant

Design/Empirical Equations	Design Parameters (Typical Values)
Coagulation	
Component removal efficiency, f_i	C_{Coag} (300–800 ppm) pH
$f_i = f_i\left(C_{\mathrm{Coag}}, \mathrm{pH}\right)$ (1)	
Settling performance	
$G = C_{\mathrm{s}} \exp(m_{\mathrm{s}} C_{\mathrm{s}} + b_{\mathrm{s}})$ (2)	Q_{u} A
$G = \frac{Q_{\mathrm{f}} C_{\mathrm{s,f}}}{A} - \frac{Q_{\mathrm{u}}}{A} C_{\mathrm{s}}$ (3)	
Fenton reaction	
Fraction of COD removal, f_{COD}	
$f_{\mathrm{COD}} = \frac{at}{1+bt}$ (4)	$C_{\mathrm{FeSO_4}}$ (80–800 ppm) $\frac{C_{\mathrm{FeSO_4}}}{C_{\mathrm{H_2O_2}}}$ (0.1–1) t
$a = a_1 \ln \frac{C_{\mathrm{FeSO_4}}}{C_{\mathrm{H_2O_2}}} + a_2 \ln C_{\mathrm{FeSO_4}}$ (5)	
$b = b_1 \ln \frac{C_{\mathrm{FeSO_4}}}{C_{\mathrm{H_2O_2}}} + b_2 \ln C_{\mathrm{FeSO_4}}$ (6)	
Ozone treatment	
Ozone absorption rate, $G_{\mathrm{O_3}}$ (fast reaction regime)	
$G_{\mathrm{O_3}} = -a_i C^*_{\mathrm{O_3}} \sqrt{\varepsilon_{\mathrm{O_3}} D_{\mathrm{O_3}} \mathrm{COD}}$ (7)	v_{g} $C_{\mathrm{O_3,in}}$ L D
Bubble column reactor design equation	
$v_{\mathrm{g}} \frac{dC_{\mathrm{O_3}}}{dz} - G_{\mathrm{O_3}} \frac{\pi D^2 \beta}{4} = 0; \quad \begin{array}{l} z = 0, C_{\mathrm{O_3}} = C_{\mathrm{O_3,in}} \\ z = L, C_{\mathrm{O_3}} = C_{\mathrm{O_3,out}} \end{array}$ (8)	
Chemical precipitation	
Component removal efficiency, f_i	
$f_i = f_i(C_{\mathrm{chemical}})$ (9)	C_{chemical}
Anaerobic and aerobic biotreatment	
Fraction of COD removal, f_{COD}	t (anaerobic process: 8–24 h, aerobic process: 4–12 h)
$f_{\mathrm{COD}} = \frac{\mathrm{at}}{1+bt}$ (10)	
Adsorption and ion exchange	
Adsorption zone length, L_{AZ}	
$L_{\mathrm{AZ}} = \frac{4Q}{\pi K N_0 D^2}\left[\ln\left(\frac{C_0}{C_{\mathrm{b}}} - 1\right) - \ln\left(\frac{C_0}{C_{\mathrm{e}}} - 1\right)\right]$ (11)	C_{b}/C_0 (0.1) C_{e}/C_0 (0.9) D (<4 m) v (3–25 m/h) L (<18 m)
Bed service time, t_{b}	
$t_{\mathrm{b}} = \frac{N_0}{C_0 v} L - \frac{1}{K C_0} \ln\left(\frac{C_0}{C_{\mathrm{b}}} - 1\right)$ (12)	
Multimedia filtration	
$\ln \frac{C}{C_0} = \sum_i k'_i L_i$ (13)	L_i
$k'_i = k'_{i,0} + m_i t$ (14)	D (<4 m)
Microfiltration and ultrafiltration	
Permeate flow rate for element j, $Q_{\mathrm{p},j}$	$Q_{\mathrm{p},j}$ (1.4–4.2 m^3/h) S_{E} (35–75 m^2) Y_{des} (0.8) S SR N_{A} N_{E}
$Q_{\mathrm{p},j} = \kappa_j \Delta P_j S_{\mathrm{E}}$ (15)	
Permeate concentration of component i for element j, $C_{\mathrm{p},i}$	
$C_{\mathrm{p},i} = (1 - \sigma_i) C_{\mathrm{f},i}$ (16)	
Membrane system configuration	
$\frac{Q_{\mathrm{f}} Y_{\mathrm{des}}}{Q_{\mathrm{p},j}} = n = \sum_{\mathrm{s}} N_{\mathrm{A,s}} N_{\mathrm{E,s}}$ (17)	

(*Continued*)

Table 7. (Continued)

Design/Empirical Equations	Design Parameters (Typical Values)
Nanofiltration and reverse osmosis	
Permeate flow rate for element j, $Q_{\mathrm{p},j}$ $Q_{\mathrm{p},j} = \kappa_j \bar{\pi}_j S_{\mathrm{E}} (TCF)(FF) \left(P_{\mathrm{f},j} - \frac{\Delta P_{\mathrm{fc},j}}{2} - P_{\mathrm{p},j} - \bar{\pi} + \pi_{\mathrm{p},j} \right) \quad (18)$ Permeate concentration of component i for element j, $C_{\mathrm{p},i}$ $C_{\mathrm{p},i} = B_i \mathrm{Pf}(\mathrm{TCF}) \left(\frac{C_{\mathrm{f},i} + C_{\mathrm{c},i}}{2} \right) \left(\frac{N_{\mathrm{E}} S_{\mathrm{E}}}{Q_{\mathrm{f}}} \right) \quad (19)$ Membrane system configuration $\frac{Q_{\mathrm{f}} Y_{\mathrm{des}}}{Q_{\mathrm{p},j}} = n = \sum_{\mathrm{s}} N_{\mathrm{A,s}} N_{\mathrm{E,s}} \quad (20)$	T (298 K) FF (0.8) $Q_{\mathrm{p},j}$ (0.5–1.5 $\mathrm{m^3/h}$) Y_{des} (0.6–0.7) S_{E} (30–40 $\mathrm{m^2}$) S (2) SR (2:1) N_{A} N_{E} (6 or 8)
Electrodialysis	
Diluate $C_{\mathrm{d}}^{\mathrm{eq}}$ and concentrate $C_{\mathrm{c}}^{\mathrm{eq}}$ equivalent concentration for cell pair j $\ln \frac{C_{\mathrm{c}}^{\mathrm{eq}} C_{\mathrm{d,f}}^{\mathrm{eq}}}{C_{\mathrm{d}}^{\mathrm{eq}} C_{\mathrm{c,f}}^{\mathrm{eq}}} + \frac{\Lambda_{\mathrm{m}} (R_{\mathrm{c}} + R_{\mathrm{a}})(C_{\mathrm{d,f}}^{\mathrm{eq}} - C_{\mathrm{d}}^{\mathrm{eq}})}{t_{\mathrm{c}}} = \frac{\Lambda_{\mathrm{m}} \xi A U_{\mathrm{lim}}}{t_{\mathrm{c}} \mathrm{FQ} \sum_{\mathrm{c}} z_{\mathrm{c}} \upsilon_{\mathrm{c}}} \quad (21)$ $U_{\mathrm{lim}} = i_{\mathrm{lim}} \left(\frac{t_{\mathrm{c}}}{\Lambda_{\mathrm{m}} C_{\mathrm{d}}^{\mathrm{eq}}} + \frac{t_{\mathrm{c}}}{\Lambda_{\mathrm{m}} C_{\mathrm{c}}^{\mathrm{eq}}} + R_{\mathrm{c}} + R_{\mathrm{a}} \right) \quad (22)$ $i_{\mathrm{lim}} = a C_{\mathrm{d}}^{\mathrm{eq}} v^{\mathrm{b}} \quad (23)$	R_{a} R_{c} t_{c} ξ (0.9) A

values of A and Q_{u} (which is the difference between the feed flux and the flux induced by underflow withdrawal). The derivation of the design equations that can be used to properly size a sedimentation tank is given in the Appendix. The calculation should begin with the determination of the maximum feed flux (Eq. A10). As the volumetric flow rate and solids concentration of the feed are given, the minimum sedimentation tank area corresponding to the maximum feed flux can be easily calculated. Once the feed flux G_{f} has been fixed by selecting an area larger than the minimum tank area, $C_{\mathrm{s,crit}}$ can be calculated from Eq. A5 and the corresponding minimum underflow withdrawal rate $Q_{\mathrm{u,crit}}$ can be calculated from Eq. A7. The larger the selected tank area, the smaller the minimum underflow withdrawal rate; this also means that it is possible to achieve a higher solids concentration in the underflow. This tradeoff should be given proper consideration in designing a sedimentation tank.

Fenton Reaction. Chemical dosage and residence time are the primary design parameters for Fenton reaction. Samples are collected at different times during batch experiments to determine the kinetic parameters. Fraction of COD removal, f_{COD}, in Fenton reaction can be described by Eq. 4. Kinetic parameters a and b depend on the concentration of $\mathrm{FeSO_4}$ and hydrogen peroxide (Eqs. 5 and 6).

Ozone Treatment. As other gas–liquid reactions, various regimes have been proposed for ozone reaction. Fast kinetic regime has been reported for wastewater treatment of textile effluents[31] and the ozone absorption rate can be described by Eq. 7. If a bubble column reactor where gas is in plug flow and liquid well mixed is used, the ozone concentration profile at steady state can be represented by Eq. 8. If Henry's law is used to relate the ozone concentration at the interface, $C_{\mathrm{O_3}}^*$, to its concentration in the bulk, $C_{\mathrm{O_3}}$, Eq. 25 is obtained after integration

$$\ln \frac{C_{\mathrm{O_3,in}}}{C_{\mathrm{O_3,out}}} = \frac{a_i \pi D^2 RT \beta L \sqrt{\varepsilon_{\mathrm{O_3}} D_{\mathrm{O_3}}}}{4 v_{\mathrm{g}} \mathrm{He}} \sqrt{\mathrm{COD}} \tag{25}$$

where $C_{\mathrm{O_3,in}}$ and $C_{\mathrm{O_3,out}}$ are the ozone concentration at the reactor inlet and outlet, respectively. As ozone diffuses more slowly in water containing organics, the rate coefficient depends on the ratio of ozone diffusivity in water containing organics $D'_{\mathrm{O_3}}$ to that in organic-free water, $D_{\mathrm{O_3}}$

$$\varepsilon_{\mathrm{O_3}} = k \frac{D'_{\mathrm{O_3}}}{D_{\mathrm{O_3}}} \tag{26}$$

where k is the reaction rate constant. The rate coefficient can be obtained by regressing experimental data at different ozone concentrations in the feed. As the kinetic regime usually cannot be determined from the outset of the experiment, its validity has to be checked after obtaining the rate coefficient. Interested readers are referred to Beltran[32] for the design equations for other regimes and reactor configurations.

Chemical Precipitation. The type of precipitation chemicals and their dosage are the major design parameters for chemical precipitation. Chemicals that produce less sludge and have good settling characteristics and component removal efficiency are usually identified by experimental screening. Similar to coagulation, the removal efficiency is system specific and an empirical relationship can be developed by regressing experimental data obtained in experiments (Eq. 9).

Biotreatment. Batch kinetic experiments are carried out for biotreatment. Samples are collected during experiments to determine the kinetic parameters in Eq. 10 for COD removal in anaerobic and aerobic processes. A more robust model which includes the kinetic parameters of microbiological processes such as growth and endogenous respiration can be included if desirable.[33]

Table 8. Experiments and Analytical Tests Required for Treatment Units in the Wastewater Treatment Plant to Obtain Model Parameters for Computer Simulation

Experiments and Data Collection	Model Parameters for Simulation
Coagulation	
Jar tests—Vary coagulant dosage and solution pH and collect supernatant to measure TDS, COD, and concentration of chemicals that need to be monitored.	Empirical constants (Eq. 1)
Batch settling test—Coagulated flocs with different concentrations are placed in a measuring cylinder to track the settling velocity (height of settling interface) against time	m_s, b_s (Eq. 24)
Fenton reaction	
Batch kinetic experiments—Vary Fenton chemicals dosage and collect samples at different times to measure TDS, COD, and concentration of chemicals that need to be monitored.	a_1, a_2, b_1, b_2 (Eqs. 5 and 6)
Ozone treatment	
Batch kinetic experiments—Vary ozone concentration in the feed and collect samples at different times to measure COD and concentration of chemicals that react with O_3 or hydroxyl radicals.	ε_{O_3} (Eq. 25)
Chemical precipitation	
Jar tests—Vary chemical dosage and collect supernatant to measure TDS, COD, and concentration of chemicals that need to be monitored.	Empirical constants (Eq. 9)
Anaerobic and aerobic biotreatment	
Batch kinetics experiments—Collect samples at different times to measure TDS, TSS, and COD.	a, b (Eq. 10)
Adsorption, Ion exchange	
Column experiments—Pass wastewater through a column with adsorbent or resin and collect samples along the column at different times to measure TDS, COD, and concentration of chemicals that need to be monitored. Also recorded are the feed flow rate and column diameter of the laboratory column.	K, N_0 (Eq. 27)
Multimedia filtration	
Column experiments—Pass wastewater through a column and collect samples along the column at different times to measure TSS. Also, record feed flow rate and column diameter of the laboratory column.	$k'_{i,0}$, m_i (Eq. 14)
MF, UF, NF, RO	
Membrane experiments—Pass wastewater through a pilot-scale membrane unit and collect samples of permeate when the system reaches steady state. TDS, TSS, and concentration of chemicals that distribute between permeate and concentrate are monitored.	MF, UF: σ_i, κ (Eq. 16) NF, RO: B_i (Eq. 18)
Electrodialysis	
Limiting current density measurement—Measure the current as a function of the applied voltage across an ion-exchange membrane for different salt concentrations.	a, b (Eq. 23)

Adsorption and Ion Exchange. Column experiments are carried out for adsorption and ion exchange processes. The data of solute concentration as a function of column length and time can be used for scale-up using the bed depth service time (BDST) method. The BDST curve gives the relationship between dimensionless concentration C_0/C_t at a specific column length L and time t

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{KN_0L}{v}-KC_0t \tag{27}$$

where K is the adsorption rate constant, N_0 is the adsorption capacity, and v is linear velocity. N_0 and K can be obtained by data regression. The adsorption zone length L_{AZ} determines the length of the bed where adsorption of pollutants actually takes place. It can be estimated by the distance between the BDST curves at breakthrough time and exhaustion time, which could be obtained by setting the dimensionless concentration in Eq. 27 to be dimensionless breakthrough concentration C_0/C_b and dimensionless exhaustion concentration C_0/C_e (Eq. 11). The length, diameter and number of adsorption columns can then be determined. The regeneration frequency can be estimated using the breakthrough time of the adsorption column (Eq. 12).

Multimedia Filtration. Multimedia filters can be sized using semi-empirical equations proposed by Yao et al.[34] which rely heavily on experimental data. Similar to the adsorption study, column experiments are carried out and samples are collected along the column during the experiment. If the filter media and linear velocity are the same for the experimental column and the actual filter, a simplified equation can be used to relate bed length L to the dimensionless concentration (C/C_0).

$$\ln\frac{C}{C_0}=k'L \tag{28}$$

As multimedia filters usually contain more than one layer of packings in the filter bed, the design equation is generalized to Eq. 13 which includes the thickness of each layer of the filter bed L_i. As the performance of the filter may change over time due to particle deposition, the empirical constant k'_i is a function of time (Eq. 14). By specifying the percentage of removal across the multimedia filter and the service time between two backwashes, the height of the multimedia filter is determined.

Membrane Filtration. The transport mechanisms are different for different membrane filters. Convective transport is the dominant mechanism for MF and UF, while diffusion is the dominant mechanism for NF and RO. Hence, different models are applied to estimate the permeate flow rate and concentration across a membrane element (Eqs. 15, 16, 18, and 19). In addition to the generic equations, correlations that are specific to a particular brand or manufacturer have to be applied to solve the equations. Table 9 lists the correlations for a Dow RO membrane BW30-365-FR.[35] If such correlations are not available, membrane permeability can also be estimated from pilot-scale experiments. The solute transport properties (σ_i or B_i) can also be regressed from experimental data.

An industrial membrane system is often configured in a number of stages (S), with each stage consisting of a number of parallel arrays (N_A) and each array consisting of a number of individual membrane elements in series (N_E). The number of parallel arrays in one stage to the same in another stage is referred to as the stage ratio (SR). Such a multistage system typically has a higher water recovery by feeding the concentrate of one stage to the next stage. Usually, several such

Table 9. Correlations for DOW RO Membrane BW30-365-FR

Membrane permeability, κ

$$\kappa = \begin{cases} 0.125 & \text{for } \bar{\pi}<25 \\ 0.125 - 0.011\left(\frac{\bar{\pi}-25}{35}\right) & \text{for } 25 \leq \bar{\pi}<200 \\ 0.070 - 0.0001(\bar{\pi} - 200) & \text{for } 200 \leq \bar{\pi}<400 \end{cases} \tag{29}$$

Osmotic pressure, π

$$\pi = 1.199 \times 10^{-2}(\mathrm{TDS}) - 1.822 \times 10^{-7}(\mathrm{TDS})^2 + 1.807 \times 10^{-11}(\mathrm{TDS})^3 \tag{30}$$

Single stage concentrate side pressure drop, ΔP_{fc}

$$\Delta P_{\mathrm{fc}} = 1.08 \times 10^{-2}\left(Q_{\mathrm{f}} - \frac{Q_{\mathrm{f}}Y}{2}\right)^{1.52} \tag{31}$$

Temperature correction factor, TCF

$$\mathrm{TCF} = \exp\left[U\left(\frac{1}{298} - \frac{1}{T}\right)\right];\ U = \begin{cases} 2640 & \text{for } T \geq 298\mathrm{K} \\ 3020 & \text{for } T < 298\mathrm{K} \end{cases} \tag{32}$$

Concentration polarization factor, *Pf*

$$\mathrm{Pf} = \exp(0.7Y) \tag{33}$$

membrane systems are used in parallel for plants with a large feed flow rate. Knowing the desired recovery (Y_{des}) of the system, the total number of membrane elements (n) can be estimated by considering the typical permeate flow rate for one membrane element which is usually given in the product catalog. Note that the permeate flow rate (Q_{p}) and element surface area (S_{E}) in Table 7 are for reference only. The performance of the proposed membrane system can be determined by first simulating an individual element and the concentrate of that element is fed to the next element and so on.

Electrodialysis. Limiting current density, which depends on the solution properties and the cell configuration, determines the effectiveness of salt separation in an electrodialysis cell.[36] The limiting current density i_{lim} is commonly expressed as an empirical equation (Table 7) and its empirical constants can be determined by measuring the current density across the membrane as a function of applied voltage for different diluate concentrations. The diluate and concentrate concentration can then be calculated by Eqs. 21–23. The diluate is recycled to the manufacturing plant while the concentrate is sent to secondary waste treatment. Note that the ion concentrations in the design equations for electrodialysis are equivalent salt concentration (C^{eq}).

$$C^{\mathrm{eq}} = \sum_{\mathrm{c}} z_{\mathrm{c}}\upsilon_{\mathrm{c}}C^{\mathrm{s}} = \sum_{\mathrm{a}} |z_{\mathrm{a}}|\upsilon_{\mathrm{a}}C^{\mathrm{s}} \tag{34}$$

where C^{s} is the salt concentration; z_{c} and z_{a} are the valences, and υ_{c} and υ_{a} the stoichiometric coefficients of cations and anions, respectively.

Process simulation

A computer code based on Microsoft Excel has been developed for the simulation of the wastewater treatment plant using the design equations summarized in Table 7. Equalization tank is not considered in the simulation, and the feed to the wastewater treatment plant is assumed to be constant. Sludge concentrator and filter press are also not considered as they contribute only a small fraction of the total flow.

The computer code performs overall material balance, regression of model parameters, and prediction of plant performance in terms of the water characteristics in the different streams of the treatment plant. Important wastewater parameters such as COD and the concentrations of specific components that have been identified in wastewater characterization are included in the simulation. Since it is impossible to account for all the individual species in the wastewater, in addition to COD, two additional lumped parameters total dissolved solid (TDS) and TSS are used as pseudo-components to represent the dissolved and suspended pollutants in the wastewater, respectively. The measurement of the TDS and TSS of the samples is labor intensive. Instead, conductivity (Λ) and turbidity (τ) are measured and TDS and TSS are in turn determined using the following correlations

$$\mathrm{TDS} = m\Lambda + d \tag{35}$$

$$\mathrm{TSS} = c_1\tau_{\mathrm{adj}}^2 + c_2\tau_{\mathrm{adj}} + c_3 \tag{36}$$

$$\tau_{\mathrm{adj}} = \tau - c_4\mathrm{TDS} \tag{37}$$

where c_1, c_2, c_3, c_4, d, and m are constants to be determined for the calibration curve. Equation 37 shows that the contribution of TDS to turbidity is removed before using τ_{adj} in the TSS correlation (Eq. 36).

With this computer code, design parameters are varied to ensure that the wastewater treatment plant produces water that satisfies both the reuse water and discharge water quality specifications. Alternative flow sheet configurations can be compared. In addition, sensitivity analysis allows the determination of operating parameters and disturbances on the performance of the wastewater treatment plant. All these issues are illustrated in the example below.

Example

This example considers the design of a treatment plant for a dyeing plant producing 9000 tonnes of wastewater per day. The experimental data are actual data as measured but the design is not that of the actual plant. Chemicals that are used in this typical dyeing process include sodium hydroxide, sodium carbonate, sodium sulfate, hydrogen peroxide, acetic acid, and organic chemicals such as reactive dyes and surfactants which also contain Na^+, Ca^{2+}, and PO_4^{3-}. The treatment plant is designed to reuse about 60% of the wastewater from the dyeing plant. Discharge effluents and reuse water should meet the specifications listed in Tables 2 and 3, respectively. The characteristics of the wastewater from the dyeing plant are summarized in Table 10. Ca^{2+} and PO_4^{3-} were measured in wastewater characterization as they are part of the reuse water and discharge effluent specifications. Na^+ was measured because it is often added in large amounts in a dyeing process. As membrane filtration is commonly used in wastewater treatment, scaling chemicals such as Ca^{2+}, CO_3^{2-}, and SO_4^{2-} were also measured.

Base case process design

The base case wastewater treatment plant (Figure 4) is developed based on the heuristics summarized in Tables 4 and 5. As the wastewater has low biodegradability (BOD_5/COD = 0.2), physicochemical treatment is needed for this process. Fenton reaction is selected to enhance the biodegradability of the wastewater. As heavy metals and ions are not present at a concentration that is detrimental to Fenton reaction and biotreatment, ion exchange or adsorption is not necessary.

Table 10. Characteristics of Wastewater from a Cotton Dyeing Plant

Feed flow rate (m^3/day)	9000
Conductivity, Λ (μS/cm)	4700
Turbidity, τ (NTU)	91.3
COD (ppm)	567
BOD_5 (ppm)	121
pH	4.4
TSS (ppm)	82.8
TDS (ppm)	2855.1
Ca^{2+} (ppm)	12.1
SO_4^{2-} (ppm)	894
PO_4^{3-} (ppm)	8.7
CO_3^{2-} (ppm)	3.2
Na^+ (ppm)	1043.9
Total Fe (Fe^{2+} + Fe^{3+}) (ppm)	2.3

Due to the low biodegradability of wastewater, sequential anaerobic and aerobic processes are selected for biotreatment. Water purification is needed after biotreatment to remove degraded products and inorganic salts for water reuse. Insoluble particles and degraded products from biotreatment are first removed by coagulation. Then, UF and RO are used to remove the remaining dissolved organics and dissolved salts to a sufficiently low level. As a protective measure to the membrane elements, multimedia filtration is used before membrane filtration. The RO permeate is recycled back to the dyeing plant for reuse.

Secondary wastes generated from various processes have to be treated. Sludge generated from Fenton reaction, biotreatment and coagulation is first concentrated in the sludge concentrator. Concentrated sludge is then passed to the filter press where the sludge is compacted to remove water and disposed. Wastewater removed from the sludge concentrator and filter press is recycled back to the equalization tank. The backwash effluent from multimedia filtration and ion exchange are discharged to a local sewage plant. In the base case, the UF concentrate is recycled to the coagulation tank while the RO concentrate is discharged to surface water. As RO concentrate usually exceeds the discharge limit, Fenton reaction and ion exchange are used to remove organics and inorganic salts, respectively. The flow sheet of recycling the RO concentrate to the equalization tank will be kept as a process alternative.

Process simulation and base case results

Experimental data were collected and entered into the computer code. These experimental data are provided as Supporting Information. Model parameters obtained from data regression for all process units are summarized in Table 11 while the design parameters used for the base case are given in Table 12. COD removal for Fenton reaction and biotreatment were measured at different operating conditions such as chemicals dosage and retention time. $FeSO_4$ and H_2O_2 dosages are selected to be 400 ppm and 600 ppm, respectively, which are in the mid-range of the typical values suggested in Table 7. The ratio of $FeSO_4$ to H_2O_2 is slightly higher than the mid-range value as reactive dyes usually degrade slowly. Process simulation shows that 1.5 hr residence time of Fenton reaction with the dosage stated above provides 58.6% COD removal in this step, while 16 hr and 8 hr hydraulic retention time in the anaerobic process and aerobic process result in 17.3% and 32.4% COD removal in the respective units.

Jar tests for coagulation were carried out to measure TSS removal at various coagulant dosages. A coagulant dosage of 500 ppm is selected for the base case. Flocs settling characteristics at the optimum dosage was measured for the design of the sedimentation tank. Its area could be selected such that the feed solids flux is smaller than its maximum value of 1.2 kg/m^2 h while the underflow flow rate is larger than its minimum flow rate of 4 m^3/h to provide complete TSS removal. Instead, a sedimentation tank with a cross-sectional area of 30 m^2 and an underflow flow rate of 3.5 m^3/h are used for the base case to provide 88.9% TSS removal according to process simulation. The remaining TSS is removed in the multimedia filter.

Column experiments were performed for multimedia filtration and turbidity was measured at various column lengths at regular time intervals. The base-case column is designed such that its superficial velocity is similar to that of the experimental system. A diameter of 3.2 m is used for each of the four filtration columns in parallel. Simulation results of the base case show that to provide nearly complete removal of TSS and allow for bed regeneration every 12 hours, a bed depth of 1.2 m is required to provide at least 97% removal of TSS.

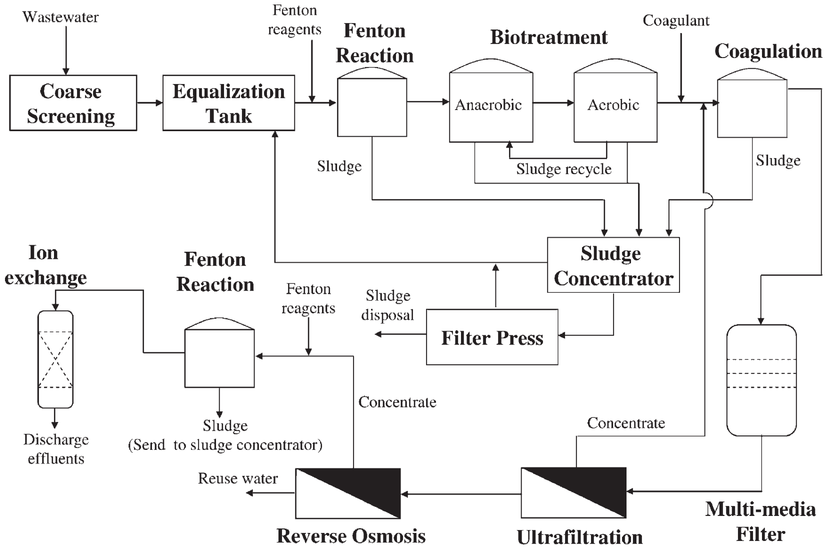


Figure 4. Process flow sheet for the base case.

Table 11. Model Parameters for the Base Case

Fenton reaction—Empirical constants in Eqs. 5–6	
a_1	0.44
a_2	0.66
b_1	−0.097
b_2	0.97
Biotreatment—Empirical constants in Eq. 10	
Anaerobic process	
a	0.025
b	0.093
Aerobic process	
a	0.071
b	0.095
Coagulation	
Empirical constants in Eq. 1	
a	−0.35
b	0.78
c	0.0019
Empirical constants in Eq. 24	
m_s	−0.56
b_s	0.19
Multimedia filtration—Empirical constants in Eq. 14	
k_0	0.17
m	−3.9
Ultrafiltration—Component removal efficiency in Eq. 16	
σ_{TSS}	1
σ_{TDS}	0
κ (m/h bar)	0.086
Reverse osmosis—Diffusion coefficients (m/h) in Eq. 19	
B_{TDS}	0.16
$B_{Ca^{2+}}$	0.028
$B_{SO_4^{2-}}$	0.014
$B_{PO_4^{3-}}$	0.014
$B_{CO_3^{2-}}$	0.014
B_{Na^+}	0.028
B_{Fe}	0.028
Fenton reaction—Empirical constants in Eqs. 5 and 6	
a_1	0.065
a_2	0.11
b_1	0.14
b_2	0.12
Ion exchange—Empirical constants in Eq. 27	
K_{Na^+} (m^3/kg h)	1.03
N_{0,Na^+} (kg/m^3)	374.9
$K_{SO_4^{2-}}$ (m^3/kg h)	1.14
$N_{0,SO_4^{2-}}$ (kg/m^3)	301.7

Table 12. Design Parameters for the Base Case

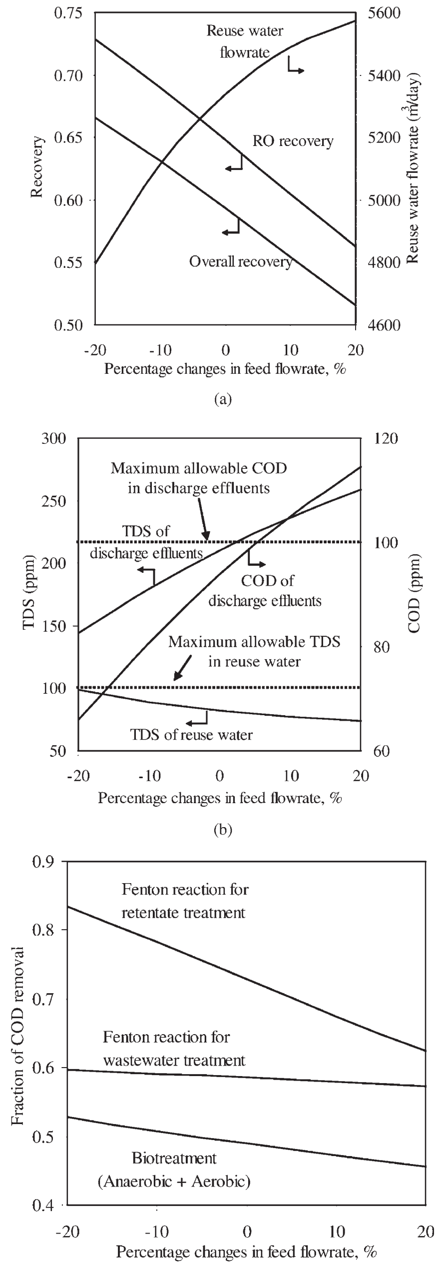
Fenton reaction	
$FeSO_4$ dosage, C_{FeSO_4} (ppm in Fe)	400
H_2O_2 dosage, $C_{H_2O_2}$ (ppm)	600
Residence time, t (h)	1.5
Biotreatment	
Anaerobic process: hydraulic retention time, t (h)	16
Aerobic process: hydraulic retention time, t (h)	8
Coagulation	
Coagulant dosage, C_{coag} (ppm)	500
Sedimentation tank area, A (m^2)	30
Underflow flow rate, Q_u (m^3/h)	3.5
Multimedia filtration	
Number of parallel columns	4
Column diameter, D (m)	3.2
Column length, L (m)	1.2
Service time, t_b (h)	12
Ultrafiltration	
Number of parallel membrane systems	4
Number of stages, S	1
Stage 1: number of parallel arrays, N_A	48
Stage 1: number of elements in series per array, N_E	1
Pressure difference across membrane, ΔP (bar)	0.61
Reverse osmosis	
Number of parallel membrane systems	4
Number of stages, S	2
Stage ratio, SR	2:1
Stage 1: number of parallel arrays, N_A	10
Stage 1: number of elements in series per array, N_E	6
Stage 2: number of parallel arrays, N_A	5
Stage 2: number of elements in series per array, N_E	6
Operating temperature, T (K)	298
Pressure difference across membrane, ΔP (bar)	13.75
Fenton reaction for concentrate treatment	
$FeSO_4$ dosage, C_{FeSO_4} (ppm in Fe)	200
H_2O_2 dosage, $C_{H_2O_2}$ (ppm)	600
Residence time, t (h)	4
Ion exchange	
Number of parallel columns	2
Column diameter, D (m)	2.6
Column length (cationic resin), L (m)	1.2
Column length (anionic resin), L (m)	1.9
Service time, t_b (h)	12

Pilot scale experiments were carried out for UF and RO membrane filtration to estimate the various membrane parameters. Since only TDS and TSS data were available from the pilot scale RO experiments, it is assumed that salt removal follows the typical rejection ratio obtained from the membrane manufacturer. The ratio is 0.003 for SO_4^{2-}, PO_4^{3-}, and CO_3^{2-}, and 0.006 for Ca^{2+}, Na^+, and total Fe (Fe^{2+} + Fe^{3+}). The permeate flow rate per element for UF and RO is 47 m^3/day and 15 m^3/day, respectively. Therefore, the base case requires 192 UF elements and 360 RO elements. Following a typical membrane system configuration (Table 7), UF membrane elements are arranged as one single stage while RO elements are arranged as a two-stage process with a SR of 2:1. There are 4 UF and RO membrane systems in parallel. UF has 48 parallel arrays in each membrane system. For each system in RO, the first stage has 10 parallel arrays, each with 6 elements in series; the second stage has 5 parallel arrays, again each with 6 elements in series.

Similar to Fenton reaction for pretreatment, batch kinetic experiments of Fenton reaction to treat the RO concentrate was performed. Fe and H_2O_2 dosages are selected to be 200 ppm and 600 ppm, respectively. A residence time of 4 hr is selected. For the ion exchange column used in concentrate treatment, only concentrations of Ca^{2+} and SO_4^{2-} were measured in the column experiments. The removal efficiencies of the other ions are assumed to be similar to Ca^{2+} for cations and SO_4^{2-} for anions in our simulation. Two ion exchange columns, each with a diameter of 2.6 m, are used and the superficial velocity is similar to that in the experimental study. To allow for column regeneration every 12 hours, the

Table 13. Simulation Results for the Base Case and the Alternative Flow Sheet

	Base Case		Alternative Flow Sheet
	Reuse Water	Discharge Effluents	Reuse Water
Flow rate (m^3/day)	5340	2583	7691
Overall recovery (%)	59.3	–	85.4
COD (ppm)	3.3	93.8	2.5
TSS (ppm)	0	0	0
TDS (ppm)	81.8	210.1	44.0
Ca^{2+} (ppm)	0.057	0.087	0.024
$SO_4{}^{2-}$ (ppm)	2.09	8.64	1.15
$PO_4{}^{3-}$ (ppm)	0.011	0.044	0.005
$CO_3{}^{2-}$ (ppm)	0.0077	0.023	0.0032
Na^+ (ppm)	5.6	8.80	2.3
Total Fe (ppm)	0	0	0



(a)

(b)

(c)

Figure 5. Effect of percentage changes in feed flow rate on (a) recovery, (b) reuse water and discharge effluent quality, (c) fraction of COD removal in Fenton reaction and biotreatment.

lengths of cation and anion column are selected to be 1.2 m and 1.9 m, respectively.

The base case provides a reuse water flow rate of 5340 m^3/day, equivalent to 59.3% overall recovery. The characteristics of the reuse water and discharge effluent are summarized in Table 13, and they meet the reuse water and discharge effluent specifications.

Sensitivity analysis

Sensitivity analysis is performed on the base case to study the effect of plant disturbances and variation of operating parameters on plant performance. This ensures that the wastewater treatment plant is designed with sufficient plant capacity to cope with the variations.

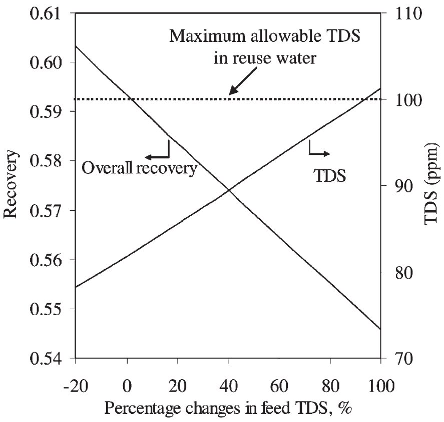
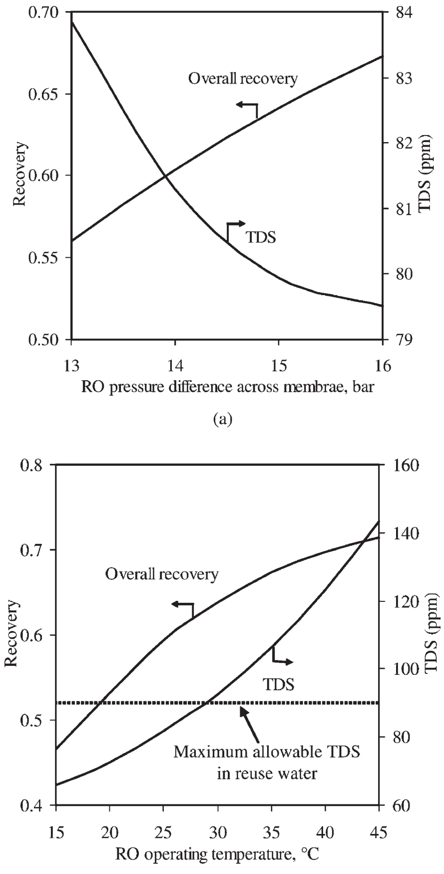


Figure 6. Effect of percentage changes in feed TDS on recovery and TDS for reuse water.

Effect of Feed Flow Rate Variation. Increasing feed flow rate is expected to produce more reuse water. Simulation results show that a 20% increase in feed flow rate only leads to 4.4% increase in reuse water flow rate, as increasing feed flow rate decreases RO recovery and overall recovery (Figure 5a). Increasing feed flow rate decreases the TDS of reuse water as the salt rejection ratio is higher at lower recovery (Figure 5b). For a discharge limit of 100 ppm for COD, increasing the feed flow rate even by 5% leads to a



(a)

(b)

Figure 7. Effect of (a) RO pressure difference across membrane and (b) RO operating temperature on recovery and TDS of reuse water.

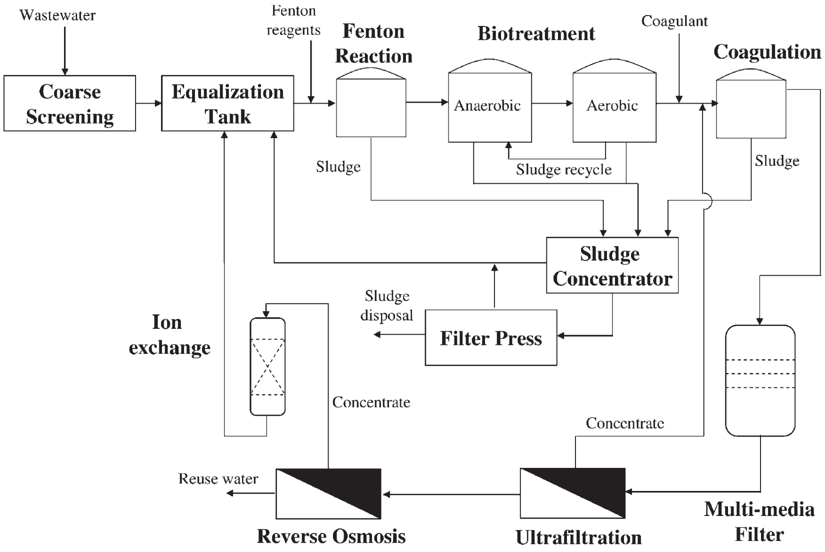


Figure 8. Alternative flow sheet for the base case.

discharge effluent that exceeds the limit. Similarly, the TDS of the reuse water exceeds the upper limit if the feed flow rate decreases by more than 20%. Figure 5c shows that an increase in feed flow rate leads to a decrease in the fraction of COD removal in the Fenton reaction units and the biotreatment pond, primarily due to a shorter residence time.

Effect of Variations in Feed TDS Concentration. Increasing the feed TDS concentration increases its concentration in the reuse water and it exceeds the reuse water TDS limit if the feed TDS concentration is doubled (Figure 6). Increasing TDS concentration also increases the osmotic pressure in RO system which leads to a smaller RO recovery and hence less reuse water is obtained.

Higher Recovery and Lower TDS Concentration. The RO pressure and temperature can be varied to obtain a higher overall recovery with a lower TDS concentration, say 65% and 90 ppm, respectively, in the reuse water. Increasing pressure forces more water through the membrane leading to a higher recovery and a lower TDS concentration in the reuse water. Indeed, increasing the RO pressure to 15.5 bar increases the overall recovery to 64.9% and produces a reuse water with 79.7 ppm TDS (Figure 7a). Increasing temperature increases the diffusion rate of both water and salts across the membrane leading to a higher overall recovery, but also a higher TDS concentration in the reuse water. For the desired reuse water specifications, increasing the RO temperature is not an option. Operating at 30°C only increases the recovery to 63.9%, but increases the TDS concentration to 92.6 ppm (Figure 7b).

Flow sheet alternative with recycled RO concentrate

Instead of discharging the RO concentrate, it is important to consider recycling it to the equalization tank if zero emission is to be realized (Figure 8). To avoid salt accumulation in the wastewater treatment plant, the concentrate is first passed to an ion exchange column. Simulation results show that a much higher overall recovery (85.4%) and a lower TDS concentration (44 ppm) are obtained (Table 13). However, an increase in the plant capacity is required to accommodate the recycle flow, as summarized in Table 14. Larger tanks have to be built for equalization, Fenton reaction and biotreatment. The number of multimedia filters, ion exchange columns and membrane units has to be increased. This is because the RO recovery for the alternative flow sheet (51.6%) is much lower than that for the base case recovery (64.8%), and the capital investment and operating cost of the wastewater treatment plant increase drastically.

Conclusions

An integrated design methodology has been developed for the design of a wastewater treatment plant such that the water can be reused for the upstream manufacturing process. This conceptual design method is particularly suited for wastewater effluents with pollutants that might vary widely from plant to plant. It has three elements: process synthesis, experiments, and simulation. The tasks for developing such a wastewater treatment and reuse plant are organized in a systematic workflow as presented in Figure 9. Input information such as wastewater characteristics, design of the manufacturing plant, and discharge or reuse water specifications is first obtained. Flow sheet alternatives are synthesized based on heuristics, which are based on our own industrial experience and information in the literature. Depending on the unit operations selected for the wastewater treatment plant, the relevant bench-scale or pilot plant experiments are performed. These experiments were selected based on whether they are useful in industrial practice and the related short-cut models were formulated to keep the simulation as easy to perform as possible. Then, these experimental results are entered into a computer code to regress model parameters for process simulation. Flow sheet alternatives developed using the heuristics are compared using the same computer code to determine the best process alternative and the corresponding operating conditions. Our experience shows that the simulations often provide insights for new alternatives and additional experiments may need to be performed. Sensitivity analysis is also carried out using the computer code to study the impact of plant disturbances on the performance of the wastewater treatment plant.

The list of wastewater treatment techniques summarized in this article can be extended to include any new wastewater treatment techniques, chemicals and materials. For example, salt removal by ion concentration polarization has

Table 14. Comparison of Design Parameters Between the Base Case and the Alternative Flow Sheet

	Base Case	Alternative Flow Sheet
Fenton reaction		
Inlet flow rate (m^3/day)	9,000	16,217
Biotreatment		
Inlet flow rate (m^3/day)	8,654	15,580
Multimedia filtration		
Number of parallel columns	4	7
Ultrafiltration		
Number of parallel membrane systems	4	4
Number of stages, S	1	1
Stage 1: number of parallel arrays, N_A	48	86
Stage 1: number of elements in series per array, N_E	1	1
Reverse osmosis		
Number of parallel membrane systems	4	4
Number of stages, S	2	2
Stage ratio, SR	2:1	2:1
Stage 1: number of parallel arrays, N_A	10	12
Stage 1: number of elements in series per array, N_E	6	6
Stage 2: number of parallel arrays, N_A	5	6
Stage 2: number of elements in series per array, N_E	6	6
Ion exchange		
Number of parallel columns	2	5

been developed recently to provide a one-step operation to remove 99% of the salts contained in sea water.[37] The various developments in water purification science such as antifouling technology for membranes and the development of new materials for water disinfection discussed by Shannon et al.[38] can be considered as well. The impact of such techniques and materials can be rapidly evaluated in the computer code. Of course, other commercial codes such as Aspen Plus and HYSYS can be used as well but our Excel based code is very flexible and easy to use for the present purpose.

The characteristics of wastewater treatment plants for different manufacturing processes are different. For example, while organics and inorganics are the major pollutants to be removed in dyeing and brewing effluents, heavy metals are the major ones in printed circuit board wastewater. Also, for some manufacturing plants, its waste streams should be treated separately. For example, for printed circuit board effluents, the suspended solids resulted from board drilling can be easily separated by filtration. There is no point to mix it with the rinsing water from the plating step and send the combined stream to the wastewater treatment plant. This design methodology is being extended to consider printed circuit board and other manufacturing plants.

Acknowledgments

Financial support from Fong's Water Technology Co., Ltd. is gratefully acknowledged.

Notation

a = empirical constant
a_1, a_2 = empirical constants
a_i = interfacial area, 1/m
A = area, m^2
b = empirical constant
b_1, b_2 = empirical constants
b_s = empirical constant for Eq. 24
B = diffusion coefficient across membrane, m/h
BOD_5 = 5-day biochemical oxygen demand, ppm
C_0/C_t = dimensionless concentration in Eq. 27 for adsorption, dimensionless
c_1, c_2, c_3, c_4 = empirical constants for calibration curve
C = concentration, mg/L
C_b = breakthrough concentration, kg/m^3
C_e = exhaustion concentration, kg/m^3
C^{eq} = equivalent salts concentration, keq/m^3
C_s = solids concentration, kg/m^3
C^s = salts concentration for electrodialysis, kg/m^3
C_{O_3} = ozone concentration in the bulk, mol/m^3
$C^*_{O_3}$ = ozone concentration at the gas–liquid interface, mol/m^3
COD = chemical oxygen demand, ppm or mol/m^3 (for ozone treatment calculation)
d = empirical constant for calibration curve
D = diameter, m
D_{O_3} = diffusivity of ozone in organic free water, m^2/s
D'_{O_3} = diffusivity of ozone in water containing organics, m^2/s
f_i = component removal efficiency, dimensionless
F = Faraday constant, A s/mol
FF = fouling factor, dimensionless
G = batch solids flux, kg/m^2 h
G_{O_3} = ozone absorption rate, mol/m^3 s
He = Henry's law constant, Pa m^3/mol
i_{lim} = limiting current density, A/m^2
k, k' = empirical constants
k'_i = empirical constant obtained for each layer i in multimedia filter
K = adsorption rate constant, m^3/kg h
L = length, m
L_{AZ} = adsorption zone length, m
L_i = length of each layer i in multimedia filter, m

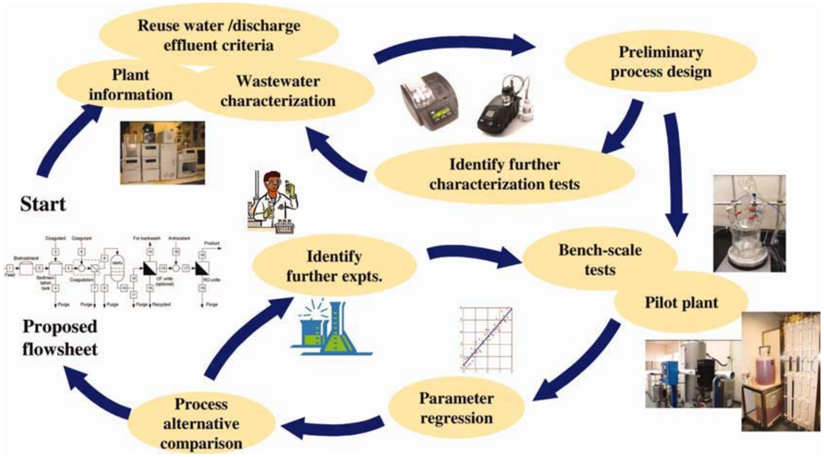


Figure 9. Workflow diagram for wastewater treatment plant design.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

m = empirical constant for calibration curve
m_i = empirical constant obtained for each layer i in multimedia filter
m_s = empirical constant for Eq. 24
MF = microfiltration
n = total number of membrane elements, dimensionless
N_0 = adsorption capacity, kg/m^3
N_A = number of parallel arrays in each stage, dimensionless
N_E = number of membrane elements in series per array, dimensionless
NF = nanofiltration
P = pressure, bar
ΔP = pressure difference across membrane, bar
ΔP_{fc} = single stage concentrate side pressure drop, bar
Pf = concentration polarization factor, dimensionless
Q = volumetric flow rate of liquid, m^3/h
R = universal gas constant, J/mol K
R_a, R_c = resistance of anionic and cationic membrane, respectively, Ω m^2
RO = reverse osmosis
S = number of stages, dimensionless
S_E = membrane surface area, m^2
SR = stage ratio, dimensionless
t = residence time, h
t_b = breakthrough (service) time, h
t_c = distance between cationic membrane and anionic membrane, m
T = temperature, K
TCF = temperature correction factor, dimensionless
TDS = total dissolved solids, ppm
TN = total nitrogen, ppm
TP = total phosphorus, ppm
TS = total solids, ppm
TSS = total suspended solids, ppm
u_s = settling velocity, m/h
U = temperature correcting coefficient, K
U_{lim} = limiting voltage drop, V
UF = ultrafiltration
v = linear velocity, m/h
v_g = volumetric flow rate of ozone, m^3/s
Y = permeate recovery, dimensionless
Y_{des} = desired permeate recovery, dimensionless
z = vertical distance of the column reactor, m
z_a, z_c = valences of anions and cations, respectively, dimensionless

Greek letters

β = liquid holdup, dimensionless
ε_{O_3} = rate coefficient of ozonation reaction, m^3/mol s
ξ = current utilization, dimensionless
κ = membrane permeability, m/h bar
Λ = conductivity, μS/cm
Λ_m = molar conductivity, S m^2/keq
π = osmotic pressure, bar
$\bar{\pi}$ = average concentrate side osmotic pressure, bar
σ = fraction of solute carried by convection with the solvent rejected by the pores of the membrane, dimensionless
τ = turbidity, NTU
τ_{adj} = adjusted turbidity, NTU
υ_a, υ_c = stoichiometric coefficients of anions and cations, respectively, dimensionless

Subscripts

0 = initial
c = concentrate in membrane filtration and electrodialysis
d = diluate in electrodialysis
Coag = coagulant
crit = critical
f = feed
$FeSO_4$ = ferrous sulfate
H_2O_2 = hydrogen peroxide
i = component index
in = inlet
j = element j in membrane filtration
max = maximum
out = outlet
p = permeate in membrane filtration
S = stage S in membrane filtration
u = underflow

Literature Cited

1. Rodriguez-Roda I, Poch M, Banares-Alcantara R. Conceptual design of wastewater treatment plants using a design support system. *J Chem Technol Biotechnol*. 2000;75:73–81.
2. Vidal N, Banares-Alcantara R, Rodriguez-Roda I, Poch M. Design of wastewater treatment plants using a conceptual design methodology. *Ind Eng Chem Res*. 2002;41:4993–5005.
3. Freitas ISF, Costa CAV, Boaventura RAR. Conceptual design of industrial wastewater treatment processes: primary treatment. *Comput Chem Eng*. 2000;24:1725–1730.
4. Yang CT, Kao JJ. An expert system for selecting and sequencing wastewater treatment processes. *Water Sci Technol*. 1996;34(3-4): 347–353.
5. Beck C, Prades G, Sadowski AG. Activated sludge wastewater treatment plants optimization to face pollution overloads during grape harvest periods. *Water Sci Technol*. 2005;51(1):81–88.
6. Petrides D, Cruz R, Calandranis J. Optimization of wastewater treatment facilities using process simulation. *Comput Chem Eng*. 1998;22:S339–S346.
7. Chen J, Beck MB. Towards designing sustainable urban wastewater infrastructures: a screening analysis. *Water Sci Technol*. 1997;35(9):99–112.
8. Rivas A, Irizar I, Ayesa E. Model-based optimization of wastewater treatment plants design. *Environ Model Software*. 2008;23:435–450.
9. Gunaratnam M, Alva-Argaez A, Kokossis A, Kim JK, Smith R. Automated design of total water systems. *Ind Eng Chem Res*. 2005;44:588–599.
10. Putra ZA, Amminudin KA. Two-step optimization approach for design of a total water system. *Ind Eng Chem Res*. 2008;47:6045–6057.
11. Department of Environmental Protection of Guangdong Province. DB4426 Guangdong Province Water Pollutants Discharge Limit. 2005.
12. U.S. Environmental Protection Agency. *Guidelines for Water Reuse*. Washington: US EPA, 2004:19.
13. Ahn DE, Chang WS, Yoon TI. Dyestuff wastewater treatment using chemical oxidation, physical adsorption and fixed bed biofilm process. *Process Biochem*. 1999;34:429–439.
14. Larking DM, Crawford RJ, Christie GBY, Lonergan GT. Enhanced degradation of polyvinyl alcohol by *Pycnoporus cinnabarinus* after pretreatment with Fenton's reagent. *Appl Environ Microbiol*. 1999;65:1798–1800.
15. Celenza GJ. *Industrial Waste Treatment Process Engineering*, Vol. 2. Pennsylvania: Technomic Publishing, 1999.
16. Fujita M, Ike M, Kawagoshi Y, Miyata N. Biotreatment of persistent substances using effective microorganisms. *Water Sci Technol*. 2000;42(12):93–106.
17. Celenza GJ. *Industrial Waste Treatment Process Engineering*, Vol. 3. Pennsylvania: Technomic Publishing. 1999.
18. Khadhraoui M, Trabelsi H, Ksibi M, Bouguerra S, Elleuch B. Discoloration and detoxification of a Congo red dye solution by means of ozone treatment for a possible water reuse. *J Hazard Mater*. 2009;161:974–981.
19. Muthukumar M, Selvakumar N. Studies on the effect of inorganic salts on decolouration of acid dye effluents by ozonation. *Dyes Pigments*. 2004;62:221–228.
20. Riga A, Soutsas K, Ntampegliotis K, Karayannis V, Papapolymerou G. Effect of system parameters and of inorganic salts on the decolorization and degradation of Procion H-exl dyes. Comparison of H_2O_2/UV, Fenton, UV/Fenton, TiO_2/UV and TiO_2/UV/H_2O_2 processes. *Desalination*. 2007;211:72–86.
21. Lu MC, Chen JN, Chang CP. Effect of inorganic ions on the oxidation of dichlorvos insecticide with Fenton's reagent. *Chemosphere*. 1997;35:2285–2293.
22. Lu MC, Chang YF, Chen IM, Huang YY. Effect of chloride ions on the oxidation of aniline by Fenton's reagent. *J Environ Manage*. 2005;75:177–182.
23. Siedlecka EM, Wieckowska A, Stepnowski P. Influence of inorganic ions on MTBE degradation by Fenton's reagent. *J Hazard Mater*. 2007;147:497–502.
24. Uygur A. An overview of oxidative and photooxidative decolorisation treatments of textile waste waters. *JSDC*. 1997;113:211–217.
25. Ahmed M, Shayya WH, Hoey D, Mahendran A, Morris R, Al-Handaly J. Use of evaporation ponds for brine disposal in desalination plants. *Desalination*. 2000;130:155–168.

26. Li Y, Xi DL. Decolorization and biodegradation of dye wastewaters by a facultative-aerobic process. *Environ Sci Pollut Res*. 2004;11:372–377.
27. Franciscon E, Zille A, Fantinatti-Garboggini F, Silva IS, Cavaco-Paulo A, Durrant LR. Microaerophilic-aerobic sequential decolourization/biodegradation of textile azo dyes by a facultative *Klebsiella* sp. strain VN-31. *Process Biochem*. 2009;44:446–452.
28. van der Bruggen B, Lejon L, Vandecasteele C. Reuse, treatment and discharge of the concentrate of pressure-driven membrane processes. *Environ Sci Technol*. 2003;37:3733–3738.
29. Chelme-Ayala P, Smith DW, El-Din MG. Membrane concentrate management options: a comprehensive critical review. *Can J Civ Eng*. 2009;36:1107–1119.
30. Christian JB. Improved clarifier and thickener design and operation. *Chem Eng Prog*. 1994;90(7):50–56.
31. Arslan-Alaton I, Balcioglu IA, Bahnemann DW. Advanced oxidation of a reactive dyebath effluent: comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A processes. *Water Res*. 2002;36:1143–1154.
32. Beltran FJ. *Ozone Reaction Kinetics for Water and Wastewater Systems*. Florida: Boca Raton, 2004.
33. Gujer W, Henze M, Mino T, van Loosdrecht M. Activated sludge model No. 3. *Water Sci Technol*. 1999;39:183–193.
34. Yao KM, Habibian MT, O'Melia CR. Water and waste water filtration: concepts and applications. *Environ Sci Technol*. 1971;5:1105–1112.
35. Dow Chemical Company. FILMTEC^{TM} Reverse Osmosis Membranes Technical Manual. Available at http://www.dowwaterandprocess.com/support_training/literature_manuals/prod_manuals.htm. Accessed October 11, 2010.
36. Strathmann H. *Operating Principle of Electrodialysis and Related Processes. Ion-exchange Membrane Separation Processes*. Amsterdam: Elsevier, 2004.
37. Kim SJ, Ko SH, Kang KH, Han J. Direct seawater desalination by ion concentration polarization. *Nat Nanotechnol*. 2010;5:297–301.
38. Shannon MA, Bohn PW, Elimelech M, Georgiadis JG, Marinas BJ, Mayes AM. Science and technology for water purification in the coming decades. *Nature*. 2008;452:301–310.

Appendix: Derivation of Design Equations for Sedimentation Tank

A sedimentation tank has to be operated in such a way that the feed flux is always smaller than the overall downward flux at any point in the tank to prevent solids from going to the overflow. For a given feed flux, there is a minimum underflow flow rate below which this condition is no longer satisfied. This critical loading condition occurs when the operating line is tangent to the batch flux curve (Figure A1). The critical solids content $C_{s,crit}$ can be found by equating the slope of the batch flux curve at the intersection point to the slope of the operating line

$$\left.\frac{dG}{dC_s}\right|_{C_s=C_{s,crit}} = -\frac{G_f}{C_{s,u}} \tag{A1}$$

Because of similar triangles

$$\frac{G_f}{C_{s,u}} = \frac{G_{crit}}{C_{s,u}-C_{s,crit}} \tag{A2}$$

where G_{crit} is the solids flux corresponding to the critical solids content. Substituting Eq. A2 into Eq. A1 and applying the expression for G in Eq. 2 (Table 7), we obtain

$$m_sC_{s,crit}+1 = -\frac{C_{s,crit}}{C_{s,u}-C_{s,crit}} \tag{A3}$$

which can be rearranged to give

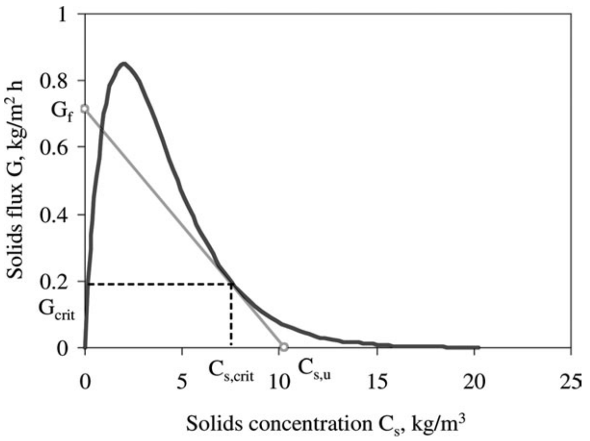


Figure A1. Batch flux curve and operating line at critical loading condition.

$$C_{s,u} = \frac{m_sC_{s,crit}^2}{m_sC_{s,crit}+1} \tag{A4}$$

Substitution back to Eq. A1 gives

$$m_sC_{s,crit}^2\exp\left(m_sC_{s,crit}+b_s\right) = -G_f \tag{A5}$$

which can be solved to obtain $C_{s,crit}$. Since at critical loading condition the overflow is free of suspended solids, material balance over the sedimentation tank gives

$$Q_uC_{s,u} = Q_fC_{s,f} \tag{A6}$$

Substituting Eq. A4 into Eq. A6 gives the underflow rate at critical loading condition

$$Q_{u,crit} = Q_fC_{s,f}\left(\frac{m_sC_{s,crit}^2}{m_sC_{s,crit}+1}\right)^{-1} \tag{A7}$$

which is the minimum underflow rate for the given feed flux.

If the feed flux is too large, the slope of the operating line equals to the gradient of the batch flux curve only at its inflexion point, which means that the condition for no solids in the overflow cannot be satisfied. The maximum feed flux $G_{f,max}$ can be found by examining Eq. A3, which is a quadratic equation in $C_{s,crit}$. For this equation to have real roots, the discriminant must be non-negative, leading to the condition

$$C_{s,u} \geq -\frac{4}{m_s} \tag{A8}$$

A critical condition occurs when the two sides of Eq. A8 are equal, implying that Eq. A3 has exactly one solution

$$C_{s,crit} = \frac{C_{s,u}}{2} = -\frac{2}{m_s} \tag{A9}$$

Substituting Eqs. A8 and A9 into Eq. A5 gives the maximum feed flux

$$G_{f,max} = -\frac{4}{m_s}\exp(b_s-2) \tag{A10}$$

Manuscript received Nov. 18, 2010, and revision received Sept. 8, 2011.