Optimizing Bleaching Operating Conditions Based on Mathematical Programming to Reduce AOX Emissions

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ABSTRACT: This study describes the optimization of a eucalyptus elemental chlorine-free (ECF) bleach plant to reduce adsorbable organic halogen (AOX). The correlations between operating conditions of each stage and pulp quality indices as well as the AOX content in wastewater are analyzed, taking an ECF bleaching technology (D_0EpPD_1) as an example. The calculation models of pulp quality indices and AOX content in wastewater are established. Then, an optimization model aiming at minimizing AOX emission is structured. The model shows a good simulation effect because the errors between the calculated and experimental values are within 6.3%. By analyzing the impact of various operating conditions on AOX emissions, it was found that chlorine dioxide reduced in the D_0 stage has the greatest impact on AOX. The optimization results show that AOX can be reduced from 90.84 to 79.58 kg/h, a decrease of 12.5%. The verification experiment results based on the optimized operating conditions showed that the experimental results are in good agreement with the calculated results of the optimization model, and the effect of reducing AOX based on the optimization model is obvious.
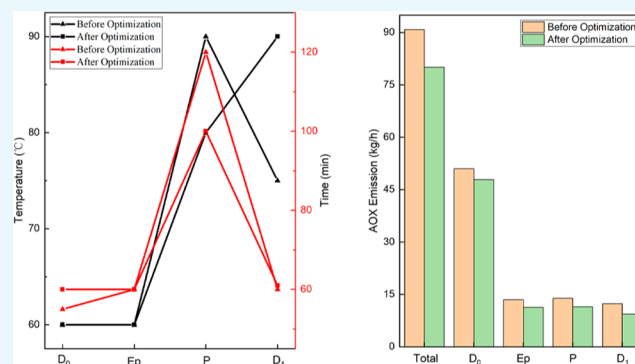
1. INTRODUCTION

With the strengthening of public awareness about environmental protection and the increasingly strict management of wastewater discharge by the government, as a traditional manufacturing industry, the paper industry is often associated with large consumption of freshwater and the production of wastewater containing toxic components in recent years.[1] Its effluent contains suspended matter (mostly fiber), fatty acids, tannin, resin acids, lignin, and its derivatives.[2,3] As the most typical bleaching process, elemental chlorine-free (ECF) bleaching produces adsorbable organic halogens (AOXs) that may contain more than 300 different chlorinated organic compounds, most of them being lipophilic, which can accumulate in organisms and are difficult to degrade.[4] Many studies have been carried out on reducing AOX emissions by adding pretreatment processes, for example, by increasing the pretreatment of hot chlorine dioxide delignification[5] or enzymes (polyxylanase[6,7] and laccase[6]) and installing an oxygen delignification stage before ECF bleaching,[8] which can reduce the emission of AOX significantly in the chlorine dioxide (D_0) bleaching segment. However, since the addition of pretreatment will increase the new equipment investment or operation cost, it is necessary to find operation conditions corresponding to the lowest AOX emission of the bleaching system based on the optimization method to reduce AOX emission.

Parthasarathy et al. conducted a laboratory delignification experiment using gaseous chlorine dioxide (ClO_2) rather than the liquid phase, which reduced ClO_2 consumption and AOX.[9] Shi et al. studied the kinetic model of vanillyl alcohol and veratryl alcohol reacting with ClO_2 to generate AOX and found that the pH value, chlorine dioxide dosage, lignin model compound concentration, and reaction temperature had effects on AOX.[10] Lei et al. investigated the kinetics and mechanisms for the delignification of ClO_2 in an aqueous solution by 5,5′-diallyl-2,2′-dihydroxy-3,3′-dimethoxybiphenyl.[11] Song et al. constructed the kinetics of laccase-aided chlorine dioxide bleaching and discussed the effects of laccase dosage, hydrogen peroxide dosage, and reaction temperature on the AOX content.[12] Other researchers developed kinetic models of the first or second chlorine dioxide bleaching stage to analyze the factors influencing the reaction rate of AOX.[13−15] These studies have shown that AOX emissions can be predicted by the kinetic model of AOX formation, and the AOX emission can be decreased by adjusting the operating conditions based on the
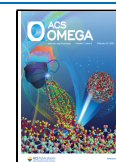
kinetic model. Barroca found that the amount of chlorine dioxide presented a nonlinear relationship with the decrease in the light absorption coefficient based on a kinetic model of AOX formation.[16] Hamzeh et al. designed and optimized a new ECF bleaching technology using low-charged ClO_2 in each chlorine dioxide bleaching (D) stage. This reduced the consumption of ClO_2 by 30−35% and AOX emissions by 50%.[17] As mentioned above, the emission of AOX can be reduced by adjusting the process conditions of chlorine dioxide bleaching to reduce the consumption of chlorine dioxide. Meanwhile, bleaching is carried out in a series of stages; most of the research works have focused on one segment or local of the bleaching system, and there is no relevant research on AOX emission reduction from the global perspective of the bleaching system.

To obtain the optimization model of reducing AOX emission, it is necessary to establish the mathematical models of AOX emission in each bleaching stage. Meanwhile, reducing the AOX emission should not affect the bleaching-quality indices. Thus, the correlation between the operating conditions (such as chemical dosage, bleaching temperature, bleaching time, pH value of the bleaching liquid) and AOX emission as well as pulp quality indices should be analyzed at first. The variables that affect AOX and pulp quality have been the subject of numerous studies. Pulp quality is typically measured by brightness, the Kappa number, and viscosity.[18,19] We also studied the effects of operating conditions on the three components (cellulose, hemicellulose, and lignin) in bleached pulp and steam consumption in our previous study.[20] The above research results will be the basis for the establishment of models between the operating conditions and AOX emission as well as pulp quality indices. Then, an optimization model for minimizing AOX emission can be constructed. The potential of AOX emission reduction can be forecast by utilizing the optimization model on the premise of meeting the bleaching-quality requirements.

2. RESULTS AND DISCUSSION

2.1. Verifying of Correlations in the Optimization Model. To verify the accuracy of the calculation model for pulp quality indices and the AOX content in the optimal model (please see Sections 2 and 3 of the Supporting Information for detailed deductions), verification experiments were carried out, and the calculated results were compared with the experimental values based on operating conditions. The operating conditions are as follows

D_0 stage: $F_{ClO2,D0}$ 2.5%, T_{D0} 65 °C, t_{D0} 65 min , pH = 3

Ep stage: $F_{H2O2,Ep}$ 0.6%, T_{Ep} 68 °C, t_{Ep} 63 min , $F_{NaOH,Ep}$ 1.3%

P stage: $F_{H2O2,P}$ 2.4%, T_P 80 °C, t_P 100 min , $F_{NaOH,P}$ 1.5%

D_1 stage: $F_{ClO2, D1}$ 1%, T_{D1} 70 °C, t_{D1} 61 min , pH = 4

The calculated values of pulp quality and AOX contents in wastewater are shown in Table 1. Also, the experimental values are listed.

As shown in Table 1, the maximum difference between calculated and experimental brightness is less than 2% (1.61%), and the error of final brightness (after D_1 stage) is about 1.09%; it can be considered that the calculated values based on the models conform to the experimental values. For the Kappa

Table 1. Calculated and Experimental Values of the Optimization Model

bleach stage		D_0	Ep	P	D_1
brightness	calculated value (% ISO)	54.33	73.85	84.75	88.26
	experimental value (% ISO)	54.05	72.68	84.40	87.31
	relative error (%)	0.52	1.61	0.41	1.09
viscosity	calculated value (mL/g)	873.6	818.3	746.5	648.2
	experimental value (mL/g)	833.2	806.5	734.1	644
	relative error (%)	5.2	1.46	1.69	0.65
Kappa number	calculated value (mL/g)	5.53	3.18	2.45	1.11
	experimental value (mL/g)	5.29	3.37	2.53	1.04
	relative error (%)	4.54	5.64	3.16	6.73
AOX content	calculated value (mg/L)	62.71	13.27	13.68	11.38
	experimental value (mg/L)	59.2	13.05	14.6	11.2
	relative error (%)	5.93	1.69	6.3	1.61

number, the difference between the predicted value and the experimental value shows greater errors than brightness because using the test method of the Kappa number it is difficult to determine the endpoint of titration. However, the final calculated values of viscosity and the Kappa number are very close to the experimental results. Moreover, the calculated values of these indicators are in line with those found by previous investigators.[21−24]

2.2. Effect Analysis of Operating Condition Changes on AOX Emission. To explore the influence of various parameters on the AOX content, the effect of a parameter on the AOX content was discussed by carrying out a large number of single-factor experiments with the other parameters remaining unchanged; the results of the experiments are shown in Figure 1.

Among the chemical dosages, the dosage of ClO_2 in the D_0 stage has the most significant effect on AOX. When ClO_2 increases from 0.5 to 3%, the content of AOX increases from 27 to 76 mg/L, as shown in Figure 1a. The temperature in the D_0 stage produced a significant increase in AOX from 32 to 44 mg/L for a temperature increase from 40 to 50 °C, while the temperature in the Ep stage has little influence on AOX emission, as seen from Figure 1b. As shown in Figure 1c, the content of AOX gradually increases with the extension of bleaching time. The bleaching time of the D_0 stage showed the greatest influence on AOX emission. When the time increases from 40 to 50 min, the AOX emission increases from 54 to 64 mg/L. The pulp quality is controlled by adding sodium hydroxide and hydrogen peroxide in Ep and P segments. As shown in Figure 1d, AOX decreases as the pH increases in both the D_0 and D_1 stages. However, the D_0 stage showed the greatest reduction in AOX with pH increase.

In conclusion, the analysis shows that the operating conditions of D_0 have the most significant effect on the AOX content, which showed consistent conclusions with other studies.[15] Therefore, as mentioned in the literature,[25−27] controlling the operating conditions of this stage is key to reducing AOX emission.

2.3. Comparison between before and after Optimization. The final purpose of this research is to optimize the
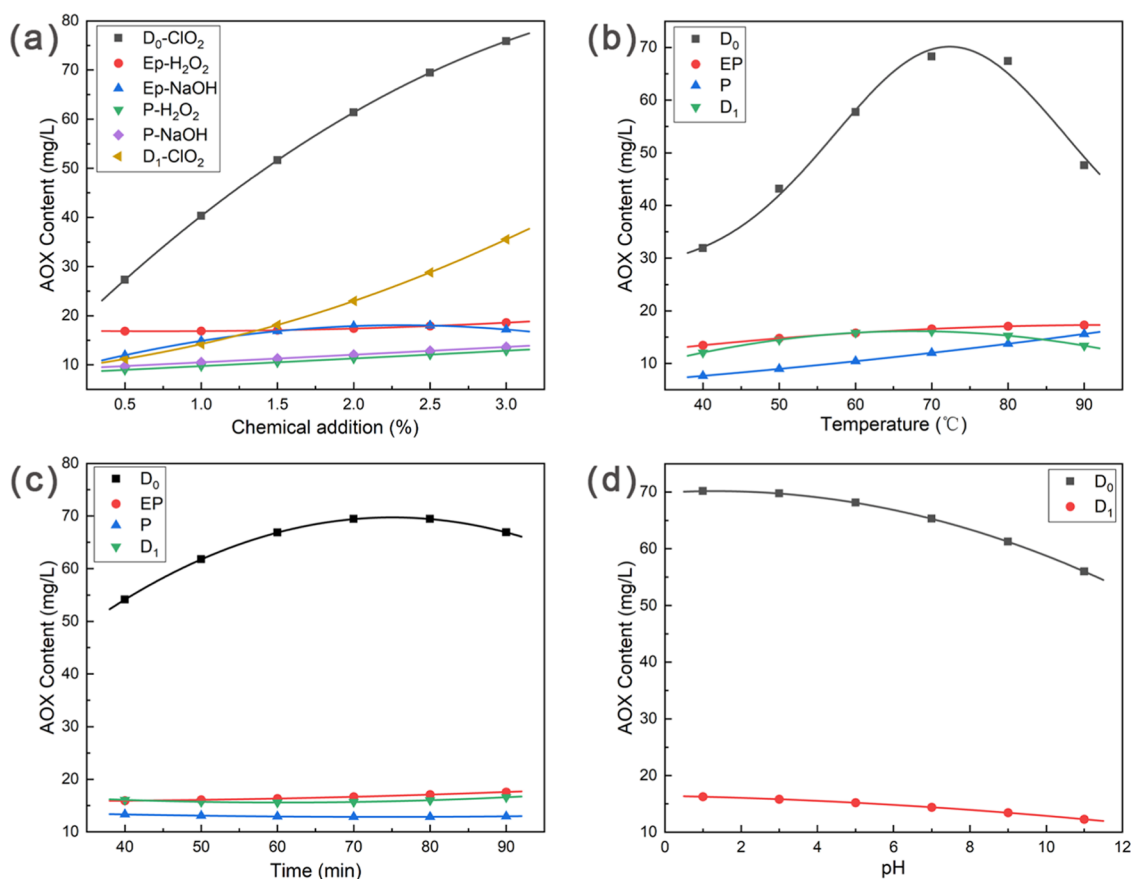
Figure 1. Effects of chemical dosage (a), bleaching temperature (b), bleaching time (c), and pH value (d) of each stage on the AOX content.

bleaching operating conditions to minimize AOX emission while maintaining the pulp quality. The optimization model is solved using the "fmincon" of MATLAB. AOX emissions before and after optimization with the corresponding operating conditions are shown in Table 2. To relate the results to industrial production, formation of AOX is prorated to 100 tons of bleached pulp (dryness: 90%) per day.

Table 2 shows that the quality indices of bleached pulp after optimization (brightness 87.4% ISO), viscosity (638 mL/g), and Kappa number (0.61 mL/g) meet the constraints. However, the AOX emission in each stage is reduced. It can be summarized as follows.

D_0 stage: The AOX emission is reduced from 51.05 to 47.92 kg/h when the dosage of ClO_2 is reduced from 2.7 to 2.5%, the bleaching time increased by 5 min, and the pH was adjusted to 3.5.

Ep stage: The emission is reduced from 13.53 to 11.28 kg/h by reducing the dosage of NaOH from 1.55 to 1.00%.

P stage: The emission is reduced from 13.91 to 11.51 kg/h when the dosage of H_2O_2 is reduced from 2.5 to 2.4%, the temperature decreased to 10 °C, and the time decreased to 20 min.

D_1 stage: The emission is reduced from 12.34 to 9.37 kg/h when the dosage of ClO_2 is decreased from 1.2 to 1.0% and the pH was adjusted to 4.

The optimization model shows that the brightness decreased primarily due to the decrease in chemical dosage in D_0 and Ep, and the brightness loss can be compensated for by greatly increasing the bleaching temperature of D_1. It can be seen from

Table 2 that the brightness of the optimized pulp is reduced by 0.27% and the viscosity is reduced by −1.27%.

After optimization, the total emission of AOX decreased from 90.84 to 79.58 kg/h, a decrease of 12.51%. Meanwhile, by comparing the optimized pulp quality indices with the actual values of the factory, it can be seen that the predicted values of the optimization model can meet the requirements of the factory. Therefore, the optimization strategy can be regarded as a way to reduce AOX emission.

2.4. Verification Experiments. Experiments were carried out according to the optimized conditions in Table 2. The calculated and experimental values of parameters in each stage after optimization are shown in Table 3.

By analyzing the pulp brightness of each segment, the errors between the calculated value and experimental value were found to be within 1.37%, which showed that the calculated results were in good agreement with the experimental results, also verifying the effectiveness of the model. Similarly, similar conclusions can be obtained by analyzing viscosities and Kappa numbers. The optimized results showed that the optimized pulp quality can meet the requirements of the bleached pulp. The measured total AOX emission is 79.58 kg/h, which is slightly less than the calculated value (80.09 kg/h), and the error is only 0.64%, which confirms that the high accuracy of the predicted results is consistent with the reality.

3. CONCLUSIONS

The principal conclusions of this study are as follows.

(1) The mathematical model of the whole bleaching process is established, and the error between the calculation

Table 2. Comparison of Indicators before and after Optimization

bleaching stage	parameter	before optimization	after optimization
D_0	$F_{ClO2,D0}$ (%)	2.7	2.5
	T_{D0} (°C)	60	60
	t_{D0} (min)	55	60
	pH_{D0}	3	3.5
	$y_{b,D0}$ (% ISO)	55	53.97
	viscosity (mL/g)	895	885
	Kappa number (mL/g)	5.75	5.81
	$y_{AOX,1}$ (kg/h)	51.05	47.92
Ep	$F_{H2O2,Ep}$ (%)	0.5	0.6
	T_{Ep} (°C)	60	60
	t_P (min)	60	60
	$F_{NaOH,Ep}$ (%)	1.55	1
	$y_{b,Ep}$ (% ISO)	74.67	72.49
	viscosity (mL/g)	815	834
	Kappa number (mL/g)	3.42	3.54
	$y_{AOX,2}$ (kg/h)	13.53	11.28
P	$F_{H2O2,P}$ (%)	2.5	2.4
	T_P (°C)	90	80
	t_P (min)	120	100
	$F_{NaOH,P}$ (%)	1.5	1.5
	$y_{b,P}$ (% ISO)	83.5	82.39
	viscosity (mL/g)	667	752
	Kappa number (mL/g)	2.45	2.31
	$y_{AOX,3}$ (kg/h)	13.91	11.51
D_1	$F_{ClO2,D1}$ (%)	1.2	1
	T_{D1} (°C)	75	90
	t_{D1} (min)	60	60.75
	pH_{D1}	3	4
	$y_{b,D1}$ (% ISO)	87.64	87.4
	viscosity (mL/g)	630	638
	Kappa number (mL/g)	0.85	0.61
	$y_{AOX,4}$ (kg/h)	12.34	9.37

Table 3. Comparison between Calculated and Experimental Values

bleaching stage	parameter	calculated value	experimental value	error (%)
D_0	pulp brightness (% ISO)	53.97	54.37	0.74
	viscosity (mL/g)	885	873	1.37
	Kappa number (mL/g)	5.81	5.53	5.06
	AOX (kg/h)	47.92	45.90	4.40
Ep	pulp brightness (% ISO)	72.49	71.51	1.37
	viscosity (mL/g)	834	818	1.96
	Kappa number (mL/g)	3.54	3.47	2.02
	AOX (kg/h)	11.28	12.16	7.24
P	pulp brightness (% ISO)	82.39	82.23	0.19
	viscosity (mL/g)	752	746	0.80
	Kappa number (mL/g)	2.31	2.45	5.71
	AOX (kg/h)	11.51	12.29	6.35
D_1	pulp brightness (% ISO)	87.64	87.22	0.48
	viscosity (mL/g)	638	644	0.93
	Kappa number (mL/g)	1.11	1.04	6.73
	AOX (kg/h)	9.37	9.23	1.52

results based on the optimization model and the results of the verification experiment is between 0.41 and 6.3%, indicating that the optimization model has good accuracy.

(2) Decreased chlorine dioxide in the D_0 stage has the greatest impact on AOX. The resulting brightness decrease could be offset by changing the operating conditions in the following stages.

(3) AOX emissions can be decreased by 12.51% while losing 0.27% brightness and −1.27% viscosity.

The mathematical model established in this study can better predict the pulp quality and AOX emission. If a large number of online data are collected for fitting, there is no doubt that the accuracy of the model will be further improved. The mathematical model and optimization method developed in this study show the prospect of further optimization, such as reducing the cost and realizing multiple objectives of bleaching.

4. METHODOLOGY

4.1. System Boundary. We take the bleaching system of a pulp mill in Guangxi Province of China as an example; in an ECF bleaching sequence (D_0EpPD_1), as shown in Figure 2, chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), and sodium

hydroxide (NaOH) are used as the main bleaching agents to degrade the chromogenic groups or improve the brightness in the bleaching process. At the same time, the reaction temperature and pH value of the bleaching solution were controlled to promote the reaction.[28−33]

During the chlorine dioxide bleaching process, the hypochlorous acid (HClO) generated increases as the dosage of ClO_2 increases and reacts rapidly with lignin to form AOX.[34,35] Under acidic conditions, ClO_2 is transformed into HClO and chlorine, which reacts with lignin to form AOX. In the Ep and P stages, lignin was further oxidized by H_2O_2, chlorinated lignin in the D_0 stage was dissolved, and the content of AOX increased.[36] The acidic fragment formed in the D_0 stage reacted with alkali to obtain lignin degradation products with a negative ion structure, which accelerated the dissolution process of lignin.[37] The extension of bleaching temperature and bleaching time in each stage was conducive to the formation of AOX. Thus, the formation of AOX can be controlled by adjusting the operating conditions of the bleaching process.

From the perspective of the whole bleaching system, the inputs including the initial quality indices of unbleached pulp ($y_{b,0}$, $y_{v,0}$, $y_{k,0}$), the operating conditions of each stage (chemical dosages, bleaching temperature, and bleaching time of each stage), and pulp quality indices (brightness $y_{b,D1}$, viscosity $y_{v,D1}$, Kappa number $y_{k,D1}$) should be considered as outputs besides AOX emissions (y_{AOX}). To obtain the mathematical relationship between operating conditions and pulp quality indices as well as the AOX content, a large number of single-factor experiments were designed and carried out in each bleaching stage. In addition, relevant test methods of industry standard were adopted to obtain the pulp quality and AOX content (please refer to Section 1 of the Supporting Information for details).

4.2. Optimization Model for the Bleaching Process. The nonlinearity of the bleaching process and the adaptability of nonlinear programming have been considered in previous studies.[38,39] The nonlinear programming optimization model is
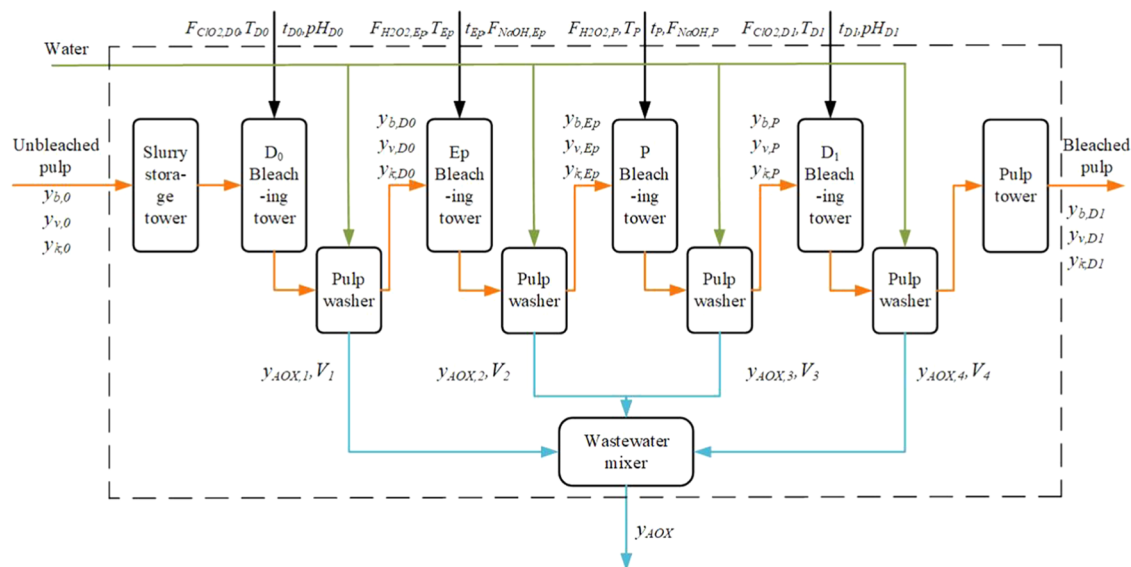
Figure 2. System boundary of a typical bleaching process.

adopted to solve the optimal operation condition to reduce AOX emission. In general, to establish the optimization model, we must determine the objective function and its calculation formula according to the research objective at first. Second, the constraints should be determined according to the actual production, including the equality constraint, the inequality constraint, and the range of independent variables. Then, model parameters or the initial values of the variables are selected based on practice. Eventually, relevant tools or software must be selected to obtain the solution of the optimization model.

4.2.1. Objective Function. From the previous analysis, the objective of our optimization is to reduce the emission of AOX in bleaching wastewater, so the objective function of the optimization model is the minimum emission of AOX (Min $F(x)$) for the whole bleaching process. Min $F(x)$ is determined by combining the AOX from the stages and optimizing this total, as expressed by eq 1.

$$\text{Min } F(x) = \text{Min } y_{\text{AOX}} = \text{Min } \sum_{i=1}^{N} V_i \times y_{\text{AOX},i} \tag{1}$$

Here, $F(x)$ is the objective function for AOX emissions from the whole bleaching process; N is the number of bleaching stages, $y_{\text{AOX},i}$ is the AOX content in the wastewater of stage i, mg/L; and V_i is the volume flow rate of the wastewater generated in stage i, L/h. Wastewater from each stage is pumped back to the preceding stage as washing water. Therefore, AOX will accumulate and ultimately be discharged to the wastewater treatment plant as shown in Figure 2. The total AOX emission (y_{AOX}, kg/h) can be calculated from eq 2.

$$y_{\text{AOX}} = \sum_{i=1}^{N} V_i \times y_{\text{AOX},i} = \sum_{i=1}^{N} V_i \times f_{\text{AOX},i} \tag{2}$$

The equation for calculating V_i is

$$V_i = \frac{m_p \times d_p}{c_i \times \prod_{i=i+1}^{N} (1 - l_i)} \tag{3}$$

Here, m_p is the bleached pulp production, t/h; d_p is the dryness fraction of the air-dried pulp, %; c_i is the pulp consistency of stage i; and l_i is the bleaching loss of the pulp in stage i, %.

Assuming the AOX formed in each stage enters the wastewater completely after washing and ignoring the impacts of unbleached pulp, the correlation between the experimental conditions and the AOX emission of each stage can be expressed by eqs 4−7. In these equations, $y_{\text{AOX},1}$, $y_{\text{AOX},2}$, $y_{\text{AOX},3}$, and $y_{\text{AOX},4}$ represent the AOX contents of wastewater after D_0, Ep, P, and D_1 bleaching stages, respectively, mg/L.

$$y_{\text{AOX},1} = f_{\text{AOX}} (F_{\text{ClO}_2,\text{D}_0}, \ T_{\text{D}_0}, \ t_{\text{D}_0}, \ \text{pH}_{\text{D}_0}) \tag{4}$$

$$y_{\text{AOX},2} = f_{\text{AOX}} (F_{\text{H}_2\text{O}_2,\text{Ep}}, \ T_{\text{Ep}}, \ t_{\text{Ep}}, \ F_{\text{NaOH,Ep}}) \tag{5}$$

$$y_{\text{AOX},3} = f_{\text{AOX}} (F_{\text{H}_2\text{O}_2,\text{P}}, \ T_{\text{P}}, \ t_{\text{P}}, \ F_{\text{NaOH,P}}) \tag{6}$$

$$y_{\text{AOX},4} = f_{\text{AOX}} (F_{\text{ClO}_2,\text{D}_1}, \ T_{\text{D}_1}, \ t_{\text{D}_1}, \ \text{pH}_{\text{D}_1}) \tag{7}$$

Equations 4−7 were obtained by fitting the experimental results; please see Section 2 of the Supporting Information for the detailed deductions. Combined with eqs 1−7, it can be obtained that the yield of the bleached pulp, the discharge of wastewater, and the operating conditions of each bleaching stage (chemical dosage, bleaching temperature, bleaching time, pH value) have impacts on AOX emissions. In the actual production, the yield of bleached pulp and the discharge of wastewater are basically stable, and the discharge of AOX can be controlled by changing the operating conditions of each stage.

4.2.2. Constraints. It is appropriate to reduce AOX emissions only when the pulp quality meets the requirements. Quality indices of the bleached pulp should meet the quality requirements of the market pulp or the enterprise's own goals, which can be expressed in eq 8.

$$\begin{cases} y_{\text{b},\text{D}_1} \geq y_{\text{b,set}} \\ y_{\text{v},\text{D}_1} \geq y_{\text{v,set}} \\ y_{\text{k},\text{D}_1} \geq y_{\text{k,set}} \end{cases} \tag{8}$$

Here, the variables are defined as follows.

$y_{\text{b,set}}$, $y_{\text{v,set}}$, and $y_{\text{k,set}}$ are the required values of brightness, viscosity, and Kappa number of the bleached pulp, respectively.

Pulp quality indices of the bleached pulp have been set as constraints for the optimization model. Therefore, the calculation models of pulp quality indices should be established. As shown in Figure 2, the initial values of the unbleached pulp are defined as brightness $y_{b,0}$, viscosity $y_{v,0}$, and Kappa number $y_{k,0}$. Quality index outputs of the previous stage are the inputs of the next stage. The pulp quality indices after the D_1 stage are the final quality of the whole system. Taking brightness as an example, the brightness of the bleached pulp is a multistage accumulation, and the correlations between inputs and outputs can be expressed by eqs 9−12.

$$\Delta y_{b,D_1} = y_{b,D_1} - y_{b,P} = f_b\left(F_{ClO_2,D_1}, T_{D_1}, t_{D_1}, pH_{D_1}\right) \qquad (9)$$

$$\Delta y_{b,P} = y_{b,P} - y_{b,Ep} = f_b\left(F_{H_2O_2,P}, T_P, t_P, F_{NaOH,P}\right) \qquad (10)$$

$$\Delta y_{b,Ep} = y_{b,Ep} - y_{b,D_0} = f_b\left(F_{H_2O_2,Ep}, T_{Ep}, t_{Ep}, F_{NaOH,Ep}\right) \qquad (11)$$

$$\Delta y_{b,D_0} = y_{b,D_0} - y_{b,0} = f_b\left(F_{ClO_2,D_0}, T_{D_0}, t_{D_0}, pH_{D_0}\right) \qquad (12)$$

Here, the variables are defined as follows.

$F_{ClO2,D0}$, $F_{H2O2,Ep}$, $F_{NaOH,Ep}$, $F_{H2O2,P}$, $F_{NaOH,P}$, and $F_{ClO2,D1}$ represent the dosage of various chemicals of each stage

T_{D0}, T_{Ep}, T_P, and T_{D1} are the bleaching temperatures of each stage.

t_{D0}, t_{Ep}, t_P, and t_{D1} are the bleaching times of each stage.

pH_{D0} and pH_{D1} are the pH values of D_0 and D_1 stages, respectively.

Equations 9−12 can be obtained by fitting the correlation between AOX emissions and operating conditions in each stage. The output brightness of whole bleaching system can be obtained by solving eqs 9−12 in sequence, where the output of previous stage being the input of the next stage, as shown in eq 13.

$$\begin{aligned} y_{b,D_1} = \; & y_{b,0} + f_b\left(F_{ClO_2,D_0}, T_{D_0}, t_{D_0}, pH_{D_0}\right) \\ & + f_b\left(F_{H_2O_2,Ep}, T_{Ep}, t_{Ep}, F_{NaOH,Ep}\right) \\ & + f_b\left(F_{H_2O_2,P}, T_P, t_P, F_{NaOH,P}\right) \\ & + f_b\left(F_{ClO_2,D_1}, T_{D_1}, t_{D_1}, pH_{D_1}\right) \end{aligned} \qquad (13)$$

This approach is also used to determine the changes in viscosity and the Kappa number in different stages. To ensure the quality of the pulp, the operating conditions should be changed within a reasonable range.[40] Therefore, it can be presented by eq 14 that the variation of the main parameters should obey the rules as follows.

$$\begin{cases} F_{min,ClO_2} \leq F_{ClO_2,D_0} + F_{ClO_2,D_1} \leq F_{max,ClO_2} \\ F_{min,NaOH} \leq F_{NaOH,Ep} + F_{NaOH,P} \leq F_{max,NaOH} \\ F_{min,H_2O_2} \leq F_{H_2O_2,Ep} + F_{H_2O_2,P} \leq F_{max,H_2O_2} \\ T_{min,i} \leq T_i \leq T_{max,i} \\ t_{min,i} \leq t_i \leq t_{max,i} \\ pH_{min,i} \leq pH_i \leq pH_{max,i} \end{cases} \qquad (14)$$

The definition of variables is as follows:

$F_{min,ClO2}$, $F_{max,ClO2}$, $F_{min,NaOH}$, $F_{max,NaOH}$, $F_{min,H2O2}$, and $F_{max,H2O2}$ are the minimum and maximum total doses of ClO_2, $NaOH$, and H_2O_2, respectively.

$T_{min,i}$, $T_{max,i}$, $t_{min,i}$, $t_{max,i}$, $pH_{min,i}$, and pH_{max} are the minimum and maximum bleaching temperatures, bleaching times, and pH values of stage i, respectively.

4.2.3. Model Parameters, Solving, and Verifying. Parameters or initial conditions of industrial bleaching plants are adopted according to the information of a bleaching workshop of pulp suppliers and relevant books. These are shown in Table 4.

Table 4. Values of Model Parameters and Initial Conditions

parameters or coefficients	value	parameters or coefficients	value
c_i	10%[a]	$F_{min,H2O2}$	1%[b]
l_i	2%[a]	$F_{max,H2O2}$	2.5%[b]
$y_{b,set}$	87% ISO[a]	$T_{min,i}$	50 °C[b]
$y_{v,set}$	600 mL/g[a]	$T_{max,i}$	95 °C[b]
$y_{k,set}$	1.5 mL/g[a]	$t_{min,i}$	30 min[b]
$F_{min,ClO2}$	0.5%[b]	$t_{max,i}$	180 min[b]
$F_{max,ClO2}$	5.5%[b]	$pH_{min,i}$	1[b]
$F_{min,NaOH}$	2%[b]	$pH_{max,i}$	7[b]
$F_{max,NaOH}$	5%[b]		

[a]Collected according to the practice of the pulp plant. [b]Selected according to the related content of ref 40.

The function "fmincon" of MATLAB 2018 software (Math-Works Corp., Natick) is adopted to solve the models. To verify the feasibility of the optimization model, a series of bleaching experiments were conducted according to the optimal solution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06691.

> Detailed experimental methods and conditions (Tables S1 and S2), mathematical calculation model of AOX content in each bleaching effluent (Table S3), and the mathematical calculation models of brightness, viscosity, and the Kappa number of each pulp segment (Tables S4 and S5) (PDF)

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Notes
The authors declare no competing financial interest.

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