Soft Sensor Model of Adsorbable Organic Halogen Based on Bleached Pulp Quality Indices

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Adsorbable organic halogen (AOX) produced during the bleaching process contains polychlorinated dibenzo-*p*-dioxins. To predict AOX in a timely and economical manner during pulp bleaching, a soft sensor model based on pulp quality indices was developed by analyzing the correlation between the AOX in the bleaching effluent and the whiteness, Kappa number, and intrinsic viscosity of the pulp. Variations of the main components during pulp bleaching were considered to determine their effects on wastewater AOX content. The results showed that the models can predict the AOX content of bleaching wastewater precisely and rapidly. The high relevant between pulp components and whiteness, Kappa number, and intrinsic viscosity allows the soft sensor model to predict AOX value without interference of components. The developed model has practical importance for monitoring AOX emissions and controlling pollution, which is essential for the global optimization of bleached pulp production cost, pulp quality, and environmental impact. Additionally, it adapts to the requirement of intelligent control of the bleaching process.

Keywords: Soft sensor; Modeling; Quality indices; Pulp components; Adsorbable organic halogen (AOX)

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INTRODUCTION

Adsorbable organic halogen (AOX) in bleach plant wastewater can contain more than 300 different chlorinated organic compounds, some of which are polychlorinated dibenzo-*p*-dioxins that are strongly carcinogenic (Sow *et al.* 2014). Most substances in AOX are lipophilic, they can accumulate in organisms, and they are difficult to degrade (Suntio *et al.* 1998). Some of these compounds are carcinogenic and harmful to the endocrine system of living organisms (Earl and Reeve 1990). The traditional elemental chlorine-based bleach sequences produce large amounts of AOX, which is the main organic pollutant in bleach plant wastewater. Since the early 1990s, elemental chlorine-free (ECF) and total chlorine-free (TCF) bleaching sequences have appeared and developed rapidly. Both ECF and TCF bleaching processes can greatly reduce the generation of AOX in bleaching wastewater (Bajpai 2012). Many studies have found that a certain amount of AOX is still produced in ECF and TCF bleaching wastewater (Stratton 2001; Nie *et al.* 2013; Yao *et al.* 2018a).

Due to the great harm that AOX compounds can cause to the environment, many researchers have conducted multiple studies on the mechanism of AOX formation. Shi *et al.* (2019) studied the effect of lignin structure on the generation of adsorbable organic halogens during chlorine dioxide bleaching and concluded that the combination of phenolic and non-phenolic structures can promote AOX formation. Lehtimaa *et al.* (2010a) studied the change of AOX under various prebleaching conditions of an oxygen-delignified hardwood pulp; the study indicated that AOX is rapidly formed at the beginning of the bleaching sequence. Kolar *et al*. (1983) studied the chemical reactions in the bleaching stage of chlorine dioxide pulp. Chlorine dioxide was initially reduced not only to chlorite by a single electron mechanism, but also to chlorine monoxide by a double electron mechanism, and then to hypochlorous acid by lignin or chlorine dioxide. Svenson *et al*. (2002) studied the inorganic reaction of chlorine dioxide bleaching cork kraft pulp, and concluded that the low pH reaction produced mainly epoxidation products and chlorinated organic substances, while hypochlorous acid content increased. Svenson *et al.* (2006) studied inorganic reactions in chlorine dioxide bleaching of softwood kraft pulp; the maximum bleaching efficiency for a D-1 stage was reported to occur when the end pH was between 3 and 4. Ni *et al*. (1993) studied the formation mechanism of chlorine organics in the process of chlorine dioxide prebleaching in sulfate pulp, and obtained the main chemical reaction process of forming chlorate.

Many researchers have studied how to reduce AOX generation. Sharma *et al.* (2014) studied the effect of xylanase treatment of sulfate pulp to reduce AOX in bleaching wastewater; the study showed that the content of AOX in the bleaching wastewater was reduced 34%. Isoaho *et al.* (2018) studied the degradation of AOX in wastewater from a cork sulfate pulp mill that used an ECF bleaching sequence; the study indicated that AOX removal rate is approximately 70% under certain Fenton reaction conditions. Qin *et al.* (2018) studied the adsorption and removal of organic halogens with activated carbon and the authors revealed that activated carbon efficiently removes AOX. Yao *et al.* (2017) reduced the amount of AOX formed during bleaching of bagasse with chlorine dioxide by removing the hemicelluloses in the pulp with hot water extraction. Nie *et al.* (2015) used xylanase to remove hexenuronic acids in the bagasse pulp, which reduced the AOX generated during chlorine dioxide bleaching. Zhang *et al.* (2018a) studied the removal of hexenuronic acids from bagasse to reduce the generation of AOX in chlorine dioxide bleaching. The above articles all describe the decreasing of AOX emissions by studying the chemical process of AOX generation, and there are few studies on AOX emission control through mathematical modeling. Soft measurement technology has been applied extensively in the pulp and paper industry because it is a fast and accurate way to measure certain parameters that are difficult to quantify using current sensors. Karlström and Hill (2017) built soft measurement models for the measurement of brightness, tensile strength, tensile index of hand-made paper of CTMP. Zhang *et al.* (2016) built some soft measurement models for the estimation of the freeness and viscosity of an alkaline peroxide mechanical pulp (APMP); the proposed soft sensor demonstrated a better performance than the back propagation (BP) method and is regarded as of a comparable quality to the support vector regression algorithms method. Galicia *et al.* (2001) studied the application of soft measurement methods to a continuous digester compared to the traditional dynamic partial least squares soft sensor, the proposed approach not only improved prediction but also provided multiple-step-ahead prediction.

Although many investigators have performed research on how to reduce the generation of AOX during bleaching, there still has been limited research work on the measurement of AOX. The existing measurement technology using an AOX analyzer for measurement has the disadvantages of long sample preparation time, strict requirements on the pH value, and the high price of activated carbon. A day or more of delay may be experienced if samples need to be sent to a centralized lab for analysis. For instance, a specialized testing institution can use a Mutil X 2500 AOX analyzer. Thus, it would be valuable to be able to predict the results of such tests by reference to current values of data that is routinely measured at the mill.

The main source of AOX is the reaction of lignin in the pulp with chlorine or hypochlorous acid (Nie *et al.* 2014); the whiteness of the pulp increases as the lignin content in the pulp decreases. Hence, there is a strong correlation between AOX content and pulp whiteness. Intrinsic viscosity represents the average degree of polymerization of the carbohydrates in the pulp fibers. A decrease in pulp viscosity during bleaching is accompanied by the degradation of lignin and hemicelluloses, which also affects AOX formation (Zhang *et al.* 2018b). Therefore, the pulp's intrinsic viscosity also has correlation with the AOX emission. The Kappa number represents the residual lignin content of the pulp (Choi and Kwon 2019). Hence, AOX content increases with the decrease of Kappa number value of the pulp during bleaching. Therefore, establishing an AOX soft sensor model that is based on some parameters of daily measurements during the bleaching process can make the AOX measurement more convenient and rapid. This study will focus on the correlation between the AOX content and different quality indices of pulp in the first portion of an ECF bleaching sequence that uses chlorine dioxide. Meanwhile, the correlation between wastewater AOX content and three major components of pulp (cellulose, hemicelluloses, and lignin) will be analyzed to support some of the results mentioned. This research will be helpful to the optimization of the whole bleaching process, in view of the environment, economic cost and quality indices of bleached pulp. AOX emission can be predicted in a timely manner after process adjustment if an AOX soft measurement model is established on occasions when the optimization of bleaching process should be implemented or the operating conditions of bleaching would be adjusted. Such a practice adapts to the requirements of today's industrial internet and intelligent manufacturing.

EXPERIMENTAL

Bleaching Experiments

The bleaching experiments were completed with an unbleached eucalyptus kraft pulp that came from Guangxi Hong Yuan Pulp Co., Ltd. (Guangxi, China). Chlorine dioxide was supplied by Guangxi Yongkai Sugar Paper Co., Ltd. (Guangxi, China). The unbleached pulp had the following initial conditions: whiteness of 35.38% ISO; intrinsic pulp viscosity of 951 mL/g; Kappa number of 19.59 mL/g; cellulose content of 59.23%; hemicellulose content of 33.93%; lignin content of 2.37%; and holocellulose content of 93.16%. The chlorine dioxide delignification stage of the ECF sequence was selected as the object of the study; a total of 24 grouped experiments were conducted with four factors (effective chlorine dosage, bleaching temperature, bleaching time, and bleaching pH value) with each at six different levels. The experimental results are shown in Table 1.

Table 1. Single Factor Experimental Results

Serial	pH	Temp. (°C)	Time (min)	Chlorine Dioxide Dosage (% on Pulp)	White-ness (% ISO)	Intrinsic Viscosity (mL/g)	Kappa Number (mL/g)	Cellulose (%)	Lignin (%)	Hemi-celluloses (%)	Holocell -ulose (%)	AOX (mg/L)
1	3	70	65	0.7	42.79	924	10.34	87.25	0.98	8.73	95.98	40.6
2	3	70	65	1.2	46.49	918	9.08	90.03	0.72	8.60	98.63.	43.4
3	3	70	65	1.7	47.82	907	8.77	90.10	0.7	8.27	98.37	43.6
4	3	70	65	2.2	49.84	897	7.45	90.23	0.68	3.34	93.57	45.2
5	3	70	65	2.7	59.85	869	4.74	91.50	0.56	2.50	94.00	50.4
6	3	70	65	3.2	61.72	801	3.80	92.36	0.42	1.92	94.28	52.7
7	3	40	65	2.2	57.18	890	5.40	90.94	0.64	3.11	94.05	45.2
8	3	50	65	2.2	61.10	831	4.71	92.24	0.45	2.07	94.31	46.1
9	3	60	65	2.2	61.19	815	4.17	92.24	0.44	2.07	94.31	46.7
10	3	70	65	2.2	61.78	784	3.80	92.44	0.36	1.73	94.17	50.2
11	3	80	65	2.2	65.29	759	3.40	92.79	0.28	1.14	93.93	52.3
12	3	90	65	2.2	65.62	733	2.60	92.95	0.24	0.94	93.89	55.5
13	3	70	35	2.2	56.67	890	5.48	90.65	0.66	3.11	93.76	44.2
14	3	70	45	2.2	58.21	876	5.09	91.19	0.60	2.7	93.89	48.3
15	3	70	55	2.2	60.31	866	4.70	91.70	0.55	2.34	94.04	50.7
16	3	70	65	2.2	60.78	854	4.30	91.85	0.54	2.26	94.11	52.3
17	3	70	75	2.2	60.94	839	4.20	92.12	0.51	2.25	94.37	55.1
18	3	70	85	2.2	65.17	767	3.40	92.52	0.34	1.16	93.68	56.2
19	1	70	65	2.2	49.39	846	3.10	90.48	0.48	2.23	92.71	52.4
20	3	70	65	2.2	58.21	907	3.20	90.26	0.53	2.52	92.78	48.3
21	5	70	65	2.2	56.36	912	3.50	90.21	0.54	2.70	92.91	47.2
22	7	70	65	2.2	51.88	931	3.50	90.03	0.59	2.88	92.91	43.2
23	9	70	65	2.2	51.54	937	4.10	88.75	0.68	3.78	92.53	42.1
24	11	70	65	2.2	46.54	945	4.30	86.42	0.75	4.02	90.44	36.7

Methods

The intrinsic viscosity, whiteness, Kappa number, and other indices of the bleaching pulp, as well as the relative content of cellulose, hemicelluloses, lignin, and the content of AOX in bleaching wastewater were measured for analysis correlation. The cellulose content was calculated by the holocellulose content minus the hemicellulose content (Yang 2001), where the holocellulose content was measured according to the GB/T 2677.10 (1995) standard. The hemicelluloses content was measured as per the TAPPI T223 cm-01 (2001) standard. The content of acid-soluble lignin was measured according to the TAPPI UM 250 (1991) standard. The content of acid-insoluble (Klason) lignin was measured as per the TAPPI T222 om-02 (2002) standard. The whiteness of pulp was measured by CTPE2203 (Technidyne Corp., New Albany, IN, USA) according to the standard ASTM D985 (1997). The intrinsic viscosity of the pulp was measured by dissolving it in cupriethylenediamine in accordance with ASTM D1795-62 standard methods. The Kappa number was measured by TAPPI UM 246 (1991) micro Kappa number test method. The AOX was measured using a Mutil X 2500 AOX analyzer (Jena Analysis Instrument Co., Ltd., Jena, Germany) (Odendahl *et al*. 1990). SPSS 20 Statistics software (IBM Corp., New York, NY, USA) was used to analyze the data and simulate the correlations between whiteness, intrinsic viscosity, and Kappa number to AOX content in wastewater. The coefficient of determination (R^2), F-value, and P-value were used to analysis the model correlations. Eighteen groups of data were randomly selected for model fitting (Table 1), and the remaining six groups of data were used for model verification.

RESULTS AND DISCUSSION

Modeling of AOX Content and the Quality Indices of Bleached Pulp

Correlation analysis between pulp whiteness and wastewater AOX content

The relationship between pulp whiteness and wastewater AOX content based on the experimental data in Table 1 is shown in Fig. 1.

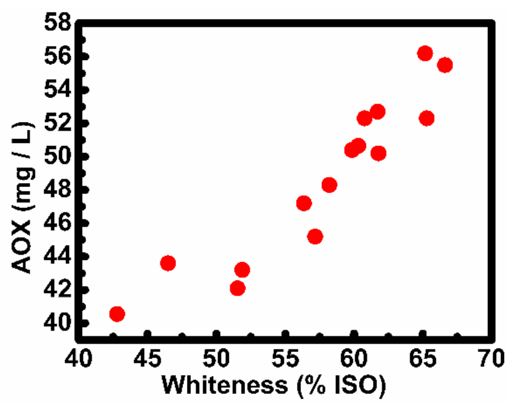

Fig. 1. Correlation between pulp whiteness and wastewater AOX content

As shown in Fig.1, AOX content increased as the whiteness of the bleached pulp increased. The chromophoric groups in pulp are derived from lignin; the lignin content of the pulp in the bleaching process decreases with the aggravation of bleaching conditions (Lehtimaa *et al.* 2010b; Tarvo *et al.* 2010). The whiteness of the bleached pulp increased as the lignin content decreased; the formation of AOX mainly comes from the reaction between lignin and either chlorine or hypochlorous acid generated in-situ from chlorine dioxide (Qin *et al.* 2019). As shown in Fig. 2, as the relative lignin content in the pulp is lowered, the AOX content in the bleaching waste-water increased. Therefore, AOX content increased as the pulp whiteness increased.

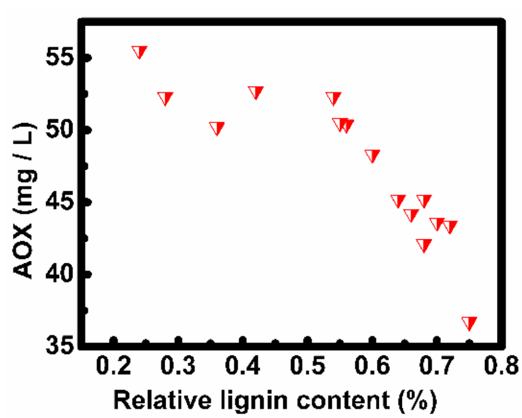

Fig. 2. Correlation between pulp relative lignin content and wastewater AOX content

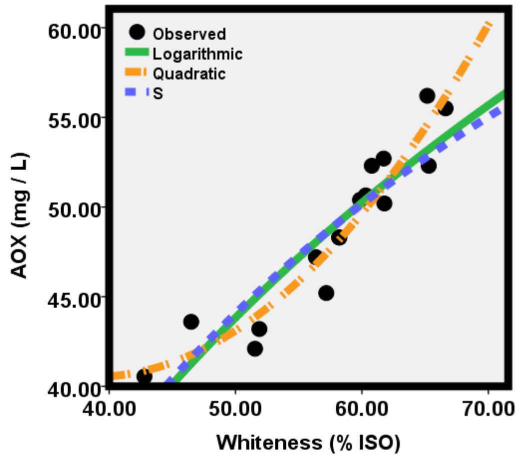

Fig. 3. Model equation relationships between pulp whiteness and wastewater AOX content

Some most suitable models were selected to regress pulp whiteness versus wastewater AOX content (Fig. 3). The results from the model regression analyses are shown in Table 2.

Table 2. Regression Results of Model Equations Relating Whiteness to AOX Content

Relationship	R^2	F-value	Significant P-value
Logarithmic	0.849	84.142	0.000
Quadratic	0.915	74.996	0.000
S-curve	0.835	75.948	0.000

R^2 is the coefficient of determination of a regression model. The closer R^2 is to 1, the better the interpretation of dependent variables by independent variables in regression analysis. All of the significant P-values of F-tests were 0.000, which means that the correlations of chosen curves were significant based on the experiments data. As shown in the table above, R^2 = 0.915 for the quadratic function, which was the largest in the fitting relationship. Therefore, the best model relationship between pulp whiteness and wastewater AOX content was a quadratic equation that is expressed as Eq. 1,

$$y_1 = f_1(x_1) = a_{1.0} + a_{1.1}x_1 + a_{1.2}x_1^2 \tag{1}$$

where $a_{1.0}$ is a constant; $a_{1.1}$, $a_{1.2}$ are the coefficients of the linear and quadratic terms, respectively. The variables x_1 and y_1 are the pulp whiteness (% ISO) and wastewater AOX content (mg/L), respectively.

Correlation analysis between intrinsic viscosity and wastewater AOX content

The relationship between intrinsic pulp viscosity and wastewater AOX content was obtained from the experimental results given in Table 1 and is shown in Fig. 4.

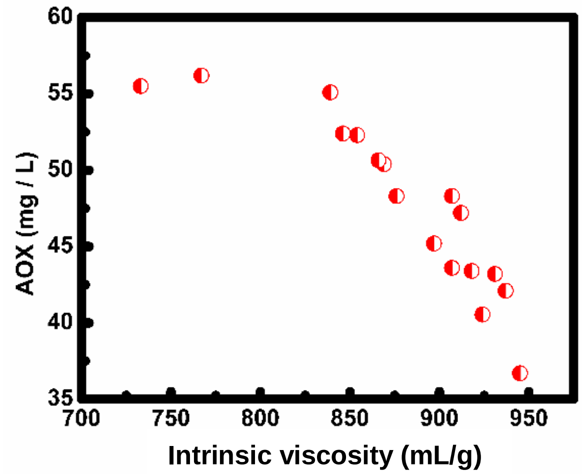

Fig. 4. Relationship between intrinsic pulp viscosity and wastewater AOX content

As shown in Fig. 4, as the intrinsic viscosity increased, the wastewater AOX content trended downward. Lignin and hemicellulose levels in the pulp are related to the AOX levels in the bleach wastewater (Yao *et al.* 2018b; Kaur *et al.* 2019; Yao *et al.* 2019). As the amount of bleaching increased, the amount of lignin and hemicellulose degradation is enhanced, which also increased the relative amount of cellulose. As shown in Fig. 2, as the degradation of lignin increased, the content of AOX in bleaching waste liquid shows an increasing trend. Also, the wastewater AOX content increased as the relative content of the hemicelluloses decreased, as shown in Fig. 5. The acidic hydrolysis mechanism of the hemicelluloses is similar to that of cellulose, which affects the degradation of hemicellulose in the bleaching process, and ultimately the intrinsic viscosity of pulp (Salmen and Olsson 1998). Therefore, as shown in Fig. 6, the AOX content increased when the relative content of cellulose in the pulp increased. Intrinsic viscosity of the pulp showed a decreasing trend as the cellulose was degraded even though the relative cellulose content increased, which was due to the degradation of other pulp constituents (Pikka *et al.* 1999). Therefore, wastewater AOX content decreased as intrinsic pulp viscosity increased.

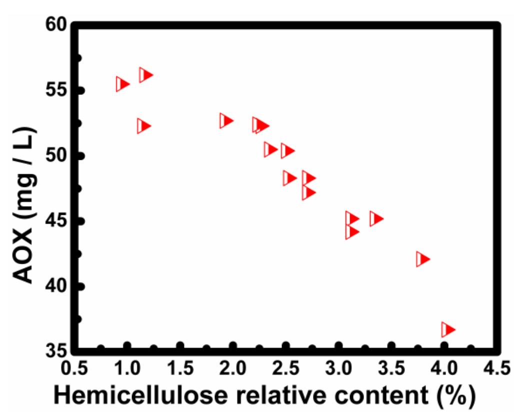

Fig. 5. Correlation between pulp relative hemicellulose content and wastewater AOX content

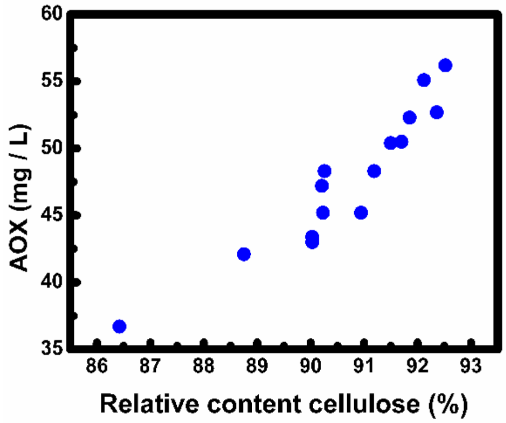

Fig. 6. Correlation between pulp relative cellulose content and wastewater AOX content

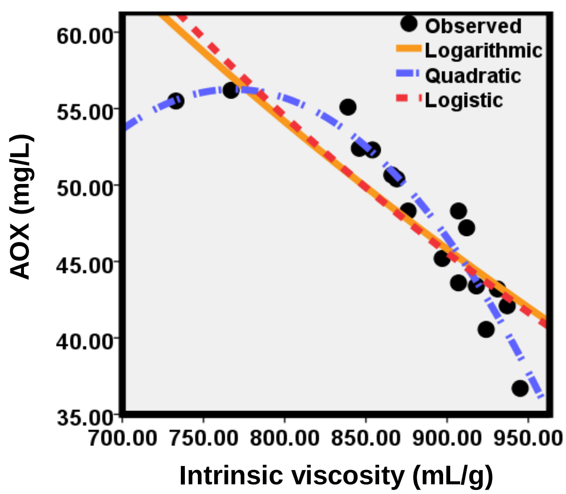

Fig. 7. Model equation correlations between intrinsic pulp viscosity and wastewater AOX content

The most suitable model equations were selected to fit the correlation between intrinsic viscosity and AOX content according to the curve presented in Fig. 7. The results of the regression analyses are shown in Table 3.

Table 3. Regression Results for Model Equations Relating Intrinsic Viscosity to AOX Content

Relationship	R^2	F-value	Significant P-value
Logarithm	0.750	45.034	0.000
Quadratic	0.919	79.904	0.000
Logistic	0.742	43.045	0.000

As shown in Table 3, R^2 = 0.919 and F = 79.904, which are the largest values in all fitting relationships in Table 3. Therefore, the best model relationship between intrinsic pulp viscosity and wastewater AOX content was a quadratic equation that is expressed as Eq. 2,

$$y_2 = f_2(x_2) = a_{2.0} + a_{2.1}x_2 + a_{2.2}x_2^2 \quad (2)$$

where $a_{2.0}$ is a constant, and $a_{2.1}$ and $a_{2.2}$ are the coefficients of the linear and quadratic terms, respectively. The variables x_2 and y_2 are the intrinsic viscosity (mL/g) and AOX content (mg/L), respectively.

Correlation analysis between pulp Kappa number and wastewater AOX content

As shown in Fig. 8, the relationship between the pulp Kappa number and wastewater AOX content was not obvious because the residual lignin content in the pulp after bleaching was low. To analyze the change rule of the two parameters more clearly, a single-factor analysis of the results for each group of experiments was performed, as is shown in Fig. 9.

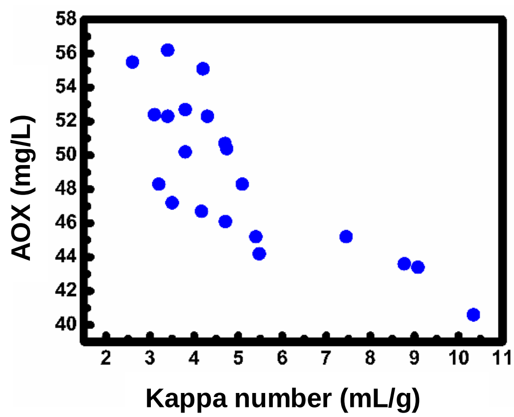

Fig. 8. Relationship between pulp Kappa number and wastewater AOX content

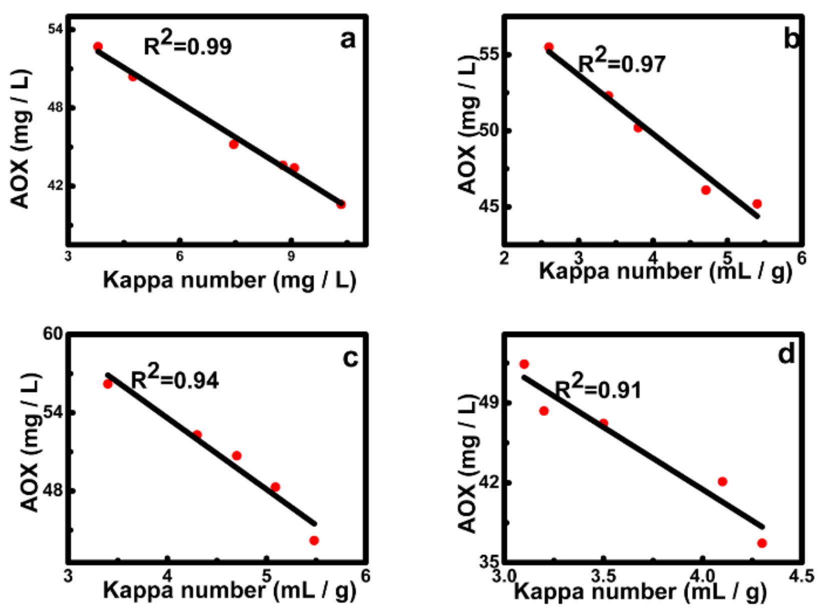

Fig. 9. Correlation between pulp Kappa number and wastewater AOX content at different chlorine dioxide delignification stage conditions (a: dosage of chlorine dioxide 0.7 to 3.2%; b: bleaching temperature 40 to 90 °C; c: bleaching time 35 to 85 min; and d: initial pH of chlorine dioxide stage 3 to 11

There was a linear relationship between the Kappa number and AOX content at different bleaching conditions. The Kappa number indirectly measures the content of residual lignin in the pulp (Fig. 2); the AOX content decreased when the residual lignin content was higher. Therefore, the AOX content decreased when the pulp Kappa number after bleaching was higher. The relationship between the pulp Kappa number and wastewater AOX content is given as,

$$y_3 = f_3(x_3) = a_{3.0} + a_{3.1}x_3 \tag{3}$$

where $a_{3.0}$ is a constant, and $a_{3.1}$ is the coefficient of the linear term. The terms x_3 and y_3 are Kappa number and AOX content, respectively.

Based on Eqs. 1 through 3, a generalized relationship between pulp whiteness (x_1), intrinsic viscosity (x_2), and Kappa number (x_3) to wastewater AOX content (y_4) can be formulated as:

$$y_4 = F\left(x_1, x_2, x_3\right) = a_0 + a_1x_1 + a_2x_1^2 + a_3x_2 + a_4x_2^2 + a_5x_3 \tag{4}$$

Based on Eq. 4, 18 groups of experimental data were randomly selected for model regression. The results from regression yielded the values for the equation parameters (a_0 to a_5):

$$y_4 = -4.07284x_1 + 0.037399x_1^2 + 0.962606x_2 - 0.00059x_2^2$$
$$- 1.08094x_3 - 224.699 \tag{5}$$

Model Verification

Verification of soft sensor model based on pulp quality indices

The wastewater AOX values calculated from the model (Eq. 5) were compared with the experimental values to evaluate the accuracy of the model, as show in Fig.10. Goodness of fit between the experimental value of AOX content and the calculated value was $R^2 = 0.92$. The residual distribution diagram of the AOX experimental value and calculated value is shown in Fig. 11. The residual error was randomly distributed in the range of (-2 to +2), which means that the selected model was reasonable.

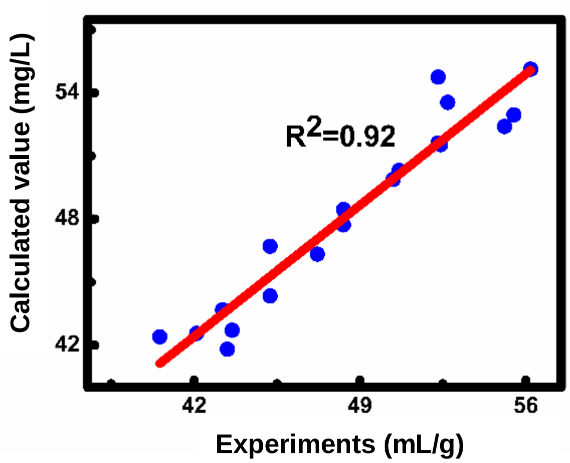

Fig. 10. Correlation between the experimental values and the model's calculated values

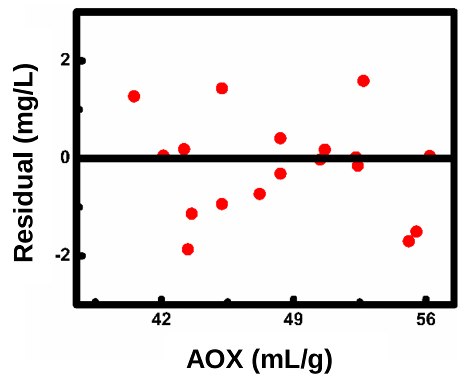

Fig. 11. Residuals of calculated values to experimental values for wastewater AOX content

The remaining six experimental data sets were used to verify the model, as well as to evaluate the model's measurement adaptability and accuracy. The analysis results of the experimental and calculated values are shown in Table 4. The residual absolute values of the verification data sets were all small; the results showed that the soft measurement model had good applicability and accuracy.

Table 4. Analysis of Experimental and Model Calculated Results with the Verification Data Sets

Serial	Measured AOX (mg / L)	Calculated AOX (mg / L)	Residual Absolute Value (mg/L)
3	43.60	44.30	0.7
7	50.20	53.59	3.39
10	44.20	46.52	2.32
12	55.10	52.40	2.7
13	55.50	52.95	2.55
17	45.20	46.70	1.5

Results of the comparison of models based on quality indices and pulp components

The established soft measurement model was verified; however, the verification of a single model is not enough to prove the reliability of the established model. To verify the reliability of the model, the relationship between AOX and post-bleaching pulp components (cellulose, hemicellulose, and lignin) were fitted by the similar method considering the strong correlation between AOX and pulp composition. Then, the AOX values calculated based on the quality index model were compared with the results of regression models based on the pulp compositions, as shown in Fig. 12.

As shown in Fig. 12, the coefficient of determination was R^2 = 0.96 between the calculated value of AOX soft measurement model based on pulp quality indices and the calculated value of AOX soft measurement model based on pulp composition. The value indicates that the calculation of the two models had a high correlation, and the deviation of the calculated results was small. The result demonstrates that the soft measurement model of AOX content based on pulp quality index was reasonable. The feasibility of the soft measurement model for AOX content has been verified. Typically, the index parameters need to be measured frequently during the bleaching process. Considering the adaptability and operability of the model, the soft measurement of AOX based on indices parameters is more feasible.

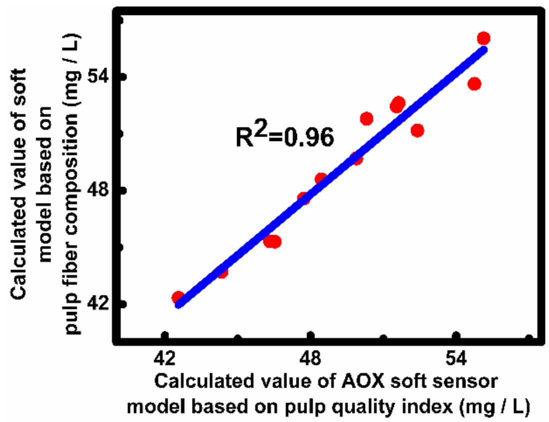

Fig. 12. Correlation between the calculated value of AOX with the soft senor model based on pulp quality indices and calculated value of AOX with the model based on pulp fiber composition

CONCLUSIONS

1. Both pulp whiteness and intrinsic viscosity can be correlated to AOX content in bleaching wastewater by a quadratic equation, whereas kappa number has linear correlation.
2. Verification of the models based on the correlation between pulp quality indices and pulp fiber constituents can accurately predict the AOX content of the bleaching wastewater. In this paper, a soft measurement model for wastewater AOX content was established:

$$y_4 = -4.07284x_1 + 0.037399x_1^2 + 0.962606x_2 - 0.00059x_2^2$$
$$- 1.08094x_3 - 224.699$$

3. In this paper, the AOX soft measurement model provided a new method for the measurement of AOX content. The obtained AOX soft measurement model, combined with the quality indices model, achieved the comprehensive optimization objective of reducing AOX discharge on the premise of meeting the quality requirements after bleaching pulp. At the same time, due to the establishment of the AOX soft measurement model, with the measurement of quality indicators, the corresponding AOX discharge content can be directly obtained, and also more correlations between various data can be mined, which is conducive to the realization of intelligent control of the bleaching process for achieving balance between quality indices of pulp and environmental impact.

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