Optimization of Oxidative Degradation of HexA during Chlorine Dioxide Delignification of Bagasse Pulp

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Hexenuronic acid (HexA) not only influences delignification, but it is also one of the major factors producing absorbable organic halogens (AOX) during the chlorine dioxide bleaching of pulps. The efficient removal of the HexA from cooked pulp is important to minimize the need for bleaching and the pollution load from the mill effluent. Response surface analysis (RSA) was applied to determine the optimal oxidative degradation conditions for HexA in bagasse pulp. Based on the previous single-variable test results, reaction temperature, pH, and reaction time were chosen as the independent variables, with the amount of degradation of HexA being the response value in the RSA. According to the central composite experimental design principles, the type of response surface methodology with three factors and three levels was adopted and analyzed to determine the significant factors and the strength of interactions between factors. The optimal conditions determined were as follows: a reaction temperature of 94.7 °C, a pH of 3.7, and a reaction time of 124 min, which resulted in the amount of degradation of HexA at 10.5 μmol/g.

Keywords: Bagasse kraft pulp; Chlorine dioxide delignification; Hexenuronic acid (HexA); Response surface analysis (RSA); Oxidation degradation

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INTRODUCTION

4-Deoxy-β-L-threo-hex-4-enopyranosyluronic acid (HexA) is formed during kraft pulping by a β-methanol elimination reaction with 4-O-methylglucuronic acid on the side chain of hemicellulose under strong alkali conditions (Andrew *et al.* 2009). HexA concentrations are approximately 35.7 to 45.7 μmol/g pulp to 45.5 to 55.5 μmol/g pulp for hardwoods (Shatalov and Pereira 2009; Eugenio *et al.* 2010), 21.8 μmol/g pulp for softwoods (Nguyen *et al.* 2008), 15.8 μmol/g pulp to 23.7 μmol/g pulp for bagasse (Nie *et al.* 2015), and 53.1 to 58.1 μmol/g pulp for kenaf (Andreu and Vidal 2014). Lignin-HexA-xylan complexes are also formed during kraft pulping processes (Jiang *et al.* 2006). Whereas the degree of sulfation has little effect on the HexA concentration in the pulp, the cooking temperature, dosage of soda, and heat preservation time all have a significant influence on the concentration of HexA. Li *et al.* (2016) optimized the cooking conditions to minimize the amount of HexA found in the pulp.

The HexA are chromophoric compounds that contain unsaturated double bonds, which can react with and consume bleaching chemicals, such as chlorine (Cl_2),

hypochlorous acid (HClO), ozone (O_3), *etc.*, used in the subsequent delignification stages. In addition, permanganate ($KMnO_4$) can also react with the carbon-carbon double bonds (C=C) under the highly acidic conditions of the Kappa number test (Li and Gellerstedt 1997; McDonough *et al.* 2009). The resulting oxalic acid binds to calcium ions (Ca^{2+}) to form a precipitate, which can result in lime scaling in the reaction system. HexA contains auxochromic groups, such as carboxyl and hydroxyl, which can degrade bleached pulp brightness; however, pulp's photochemical reactions occur when the carboxyl groups are catalyzed with heavy metal ions (Sevastyanova *et al.* 2006; Eiras *et al.* 2008). Therefore, the selective removal of HexA in the pulp significantly improves the brightness stability (Cadena *et al.* 2010a, 2010b). The HexA in the pulp reacts with HClO to form absorbable organic halogens (AOX) in the chlorine dioxide delignification of bagasse pulp (Lehtimaa *et al.* 2010b; Nie *et al.* 2015). Bjorklund *et al.* (2004) indicated that HexA in the pulp forms more AOX than lignin does. Thus, the removal of HexA allows bleaching to occur more easily and reduces the pollution load of bleaching wastewater.

Acid or enzymatic hydrolysis of kraft pulps can hydrolyze HexA to produce 2-furoic and 5-formyl-2-furoic acid (Sevastyanova *et al.* 2006; Valls and Roncero 2009), thus increasing the brightness and viscosity of the pulp (Eugenio *et al.* 2010). However, the HexA in pulps cannot be entirely removed by the above method (Fatehi *et al.* 2009; Clavijo *et al.* 2012). Clavijo *et al.* (2012) focused on the hydrolysis kinetics of HexA, and the results showed that the reaction follows first order reaction kinetics with respect to HexA. The reaction rate increases as the pH decreases in the reaction mixture, for which the reaction rate is maximized at a pH of 3. In addition to the removal of HexA from the pulp, acid hydrolysis also removes lignin (Andrew *et al.* 2009). Acid hydrolysis carried out at 125 °C for 180 min removed as much as 98% of the HexA (Andrew *et al.* 2009). Xylanase, a type of hemicellulase, mainly hydrolyzes the xylan to remove HexA. Compared to the control pulp, HexA content can be reduced by 27.9% with a 3.0 IU/g xylanase treatment prior to chlorine dioxide delignification of kraft eucalyptus pulp (Valls *et al.* 2010), whereas HexA content can be reduced by 39.6% with 25 IU/g xylanase treatment of bagasse pulp (Nie *et al.* 2015). The AOX are formed during the bleaching of kraft pulp, which with chlorine and chlorine dioxide bleaching agents, and they are commonly present in measurable quantities in pulp mill effluent (Taghipour and Evans 1996). Free chlorine is produced from chlorine dioxide when it reacts with residual lignin and HexA to produce AOX. Bjorklund *et al.* (2004) found that the AOX includes two categories: the unstable part of the AOX is linearly dependent on the amount of HexA from the pulp and the amounts of stable AOX in the pulp were related to the Klason lignin content of the pulp. The AOX content of bleaching effluent can be reduced 27.9% for chlorine dioxide bleached hardwoods, and 21.4% to 26.6% for chlorine dioxide bleached bagasse pulp when the HexA could be reduced by 39.6% after prehydrolysis (Lehtimaa *et al.* 2010a; Nie *et al.* 2015).

It was observed that a mild hot acid treatment used before chlorine dioxide delignification (A/D) of the birch decreased the HexA content and reduced the dose of chlorine dioxide needed (Mcdonough *et al.* 2009). The initial pH value is the main factor affecting the removal of HexA in pulp, and it can be effectively hydrolyzed when the initial pH value is 3. At low pH, more AOX was formed during chlorine dioxide treatment (Nie *et al.* 2014). High temperature chlorine dioxide delignification (D_{HT}) has the same effects as the acid treatment on the degradation of HexA, and sometimes even the D_{HT} has more effects than the acid treatment (Ragnar and Backa 2004). The D_{HT} stage is carried out at higher temperature and longer retention time than the conventional chlorine dioxide

bleaching (Ragnar and Backa 2004). The D_{HT} stage has been reported to have a positive effect on the degradation of HexA and the reduction of AOX (Nie *et al.* 2015). Chlorine dioxide reacts faster with lignin than HexA does (Clavijo *et al.* 2012). This suggests that D_{HT} is feasible through the initial oxidation step of chlorine dioxide with lignin, followed by the removal of HexA at high temperatures under acidic conditions (Ventorim *et al.* 2005). It is beneficial to remove HexA from pulps, which can reduce the AOX contents in bleaching effluents.

In the current study a response surface analysis (RSA) procedure was carried out to optimize the conditions (reaction temperature, pH, and reaction time) for the oxidation degradation of HexA in bagasse pulp. Furthermore, the significance of each of the influencing factors was explored to determine the best reaction conditions and to make validating experiments on the model. In the research for this paper, the conditions were optimized for HexA removal in the process of chlorine dioxide delignification and a reliable theoretical and experimental basis was provided for clean pulp bleaching technology, especially in terms of AOX reduction.

EXPERIMENTAL

Materials

The unbleached pulp and chlorine dioxide were taken from the pulp mill of Yong Xin (Guangxi, China). The Kappa number, brightness, viscosity, and HexA content of unbleached pulp were 8.7, 43.24% ISO, 1095 mL/g, and 15.31 μmol/g, respectively. The chlorine dioxide solution was stored in a brown bottle, wherein the concentration of available chlorine was 21.16 g/L. All other chemicals used in this study were purchased from Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China), and all of the chemicals were of analytical grade.

Experimental design- Single-factor experiments

The bagasse pulp (10 g bone dry) was mixed with deionized water in plastic bags, and the pulp consistency was kept at 10% during the oxidation degradation experiment. The pH was adjusted to between 2.2 and 4.2 with 2 $mol \cdot L^{-1}$ sulfuric acid (H_2SO_4); then chlorine dioxide was added. The reaction time was recorded when the reaction temperature reached the demand. The pulp was kneaded every 5 min during the reaction until the end point, and then the amount of HexA was tested.

Selection of response factors and Box-Behnken design

An experiment was performed with the Box-Wilson Central Composite Design (CCD) using the response surface design method, which can be applied to fit the response surface model with minimal experimentation. In this experiment, reaction temperature (A), pH (B), and reaction time (C) were selected as the three independent variables with five-levels each. The software Design-Expert (Version 8.0.6, Stat-Ease, Minneapolis, MN USA) was used to analyze the data and build the response models. The selected range of each variable is shown in Table 1. The regression analysis was performed on the collected data and integrated into the a posteriori second-order polynomial model, which is shown as Eq. 1 (Nie *et al.* 2013),

$$Y = b_{0k} + \sum_{i=1}^{4} b_{ik}X_i + \sum_{i=1}^{4} b_{iik}X_i^2 + \sum_{j=2}^{4}\sum_{i=1}^{i<j} b_{ijk}X_iX_j \quad (1)$$

where Y is the predicted response variable (HexA content) (μmol/g), X_i and X_j are the independent factors that affect Y, b_{0k} is the absolute term, and b_{ik}, b_{iik}, and b_{ijk} are the coefficients for the linear, quadratic, and interaction terms, respectively.

Table 1. Levels of Parameter Variables Used in RSA Design for the Degradation Reaction of HexA

Factors	Levels				
	-1.68	-1	0	1	1.68
Reaction Temperature (A, °C)	82	85	90	95	98
pH Values (B)	2.2	2.6	3.2	3.8	4.2
Reaction Time (C, min)	23	50	75	100	127

Methods

The content of HexA in the pulp was detected by using a spectrophotometric method (TAPPI T282 om-13 (2013)) (Zhu *et al.* 2014). The pulp was hydrolyzed using a mercury chloride solution and sodium acetate at 65 °C for 30 min. The absorbance was measured with a UV-Vis spectrometer (Analytik-Jena, Jena, Germany) at 260 nm and 290 nm, and the HexA content was calculated as shown in Eq. 2,

$$C_{HexA}(\mu\text{mol}/g) = 0.287 \times \frac{(A_{260} - 1.2A_{290}) \cdot V(mL)}{w(g)} \quad (2)$$

where C_{HexA} is the HexA content in the pulp (μmol/g), A_{260} and A_{290} are the absorbance values determined at 260 nm and 290 nm, respectively, V is the hydrolysis solution volume (mL), and w is the pulp dry weight (g).

RESULTS AND DISCUSSION

Impact of Single-factor on HexA Removal

Based on how the dosage of the chlorine dioxide influences the efficiency of delignification, the AOX content in the bleaching effluent, pulp viscosity, and cost, using 2.5% active chlorine is optimal in oxidation degradation reactions (Nie *et al.* 2013). Because there are many factors that influence HexA oxidative degradation, the effect of a single factor was tested by controlling the other factors. Each factor had a set of experiments in which the values of the other factors were kept constant.

Impact of reaction temperature on HexA removal

The effect of reaction temperature on HexA oxidation degradation was investigated under the conditions of a reaction time of 125 min and a pH of 3.8, as shown in Fig. 1. As shown, the amount of HexA removal decreased first then increased, as the reaction temperature was increased from 80 °C to 95 °C. The amount of HexA removal remained almost unchanged when the reaction temperature was over 95 °C, which took into account that too high a reaction temperature can cause degradation of carbohydrates, the best reaction temperature was 95 °C.

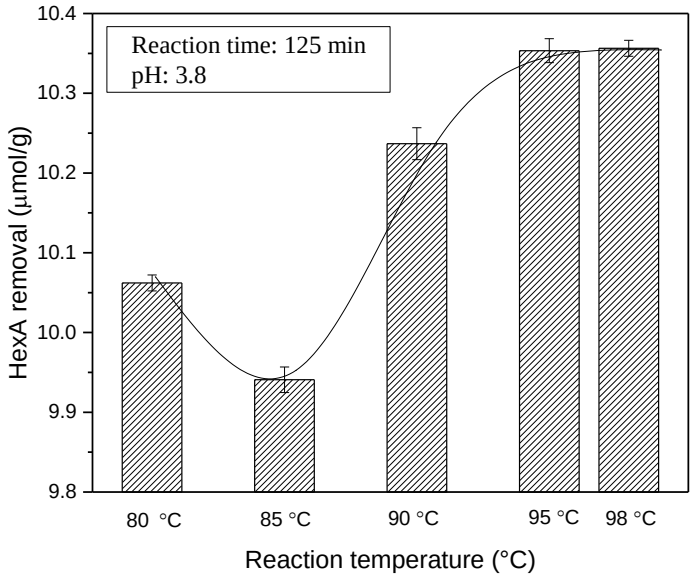

Fig. 1. Impact of reaction temperature on HexA removal

Impact of reaction time on HexA removal

The effect of reaction time on HexA oxidation degradation was studied under the conditions of a reaction temperature of 95 °C and a pH of 3.8, as shown in Fig. 2. The results showed that the amount of HexA removal gradually increased then remained almost unchanged after 125 min. Considering that a too long reaction time can cause the degradation of carbohydrates, brightness reversion of pulp, and so on, the chosen reaction time was 125 min.

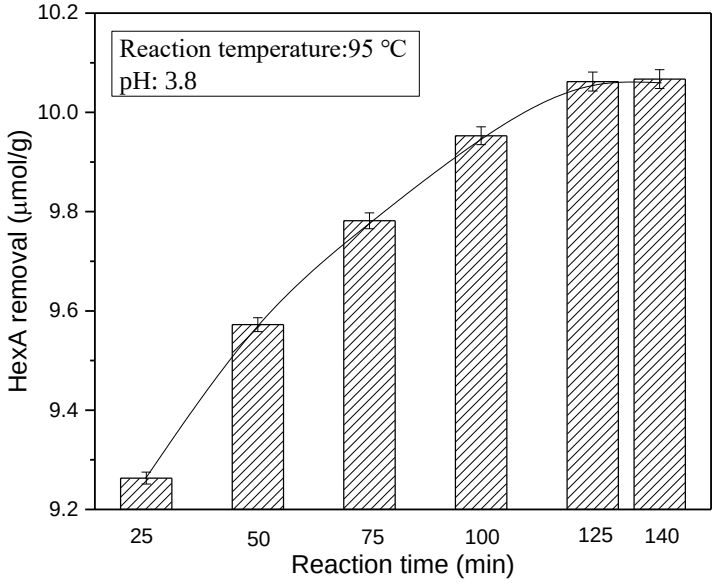

Fig. 2. Impact of reaction time on HexA removal

Impact of pH on HexA removal

The effect of pH on HexA oxidation degradation was investigated under the conditions of a reaction temperature of 95 °C and a reaction time of 125 min, as shown in Fig. 3. As shown, the amount of HexA removal first increased and then decreased later as the pH increased from 2.6 to 4.2. The HexA reached its maximum level at a pH of 3.8. Therefore, the ideal choice of pH was 3.8.

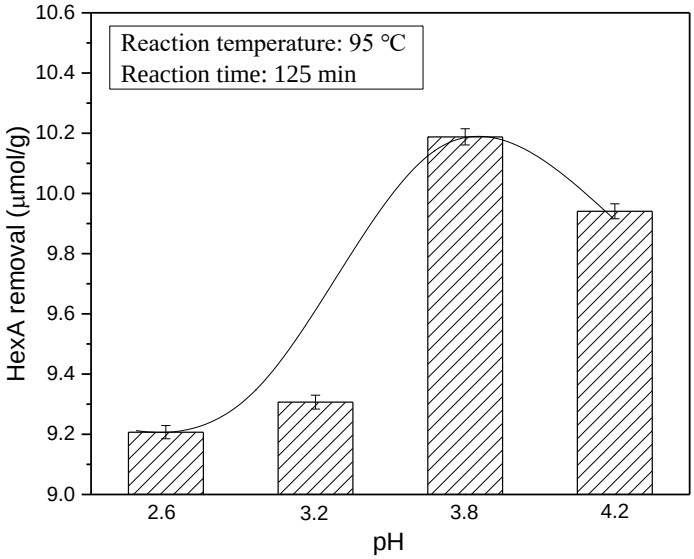

Fig. 3. Impact of pH on HexA removal

Table 2. Box-Behnken Design and the Response Data for HexA Removal

Run No.	Coded Levels			Response Values
	A (°C)	B	C (min)	HexA Removal (μmol/g)
1	-1	1	1	9.9408
2	-1.68	0	0	8.4471
3	0	0	0	9.7351
4	0	0	-1.68	9.9431
5	1	1	1	10.3534
6	0	0	0	9.7356
7	1.68	0	0	10.1304
8	-1	1	-1	8.5414
9	0	-1.68	0	9.1379
10	-1	-1	-1	8.7172
11	1	1	-1	8.8362
12	0	0	0	9.7354
13	1	-1	1	10.3557
14	0	0	0	9.7355
15	0	0	0	9.73559
16	0	0	1.68	9.9948
17	0	1.68	0	9.9351
18	0	0	0	9.735
19	1	-1	-1	9.1695
20	-1	-1	1	9.3069

HexA Degradation Model and the Significance Test

Using these second-order models, the coefficient parameters were evaluated *via* a multiple linear regression analysis, using the Box-Behnken Design (BBD) of the Design Expert 8.0.6 software. The BBD and the results of the experiments for evaluating the HexA removal are presented in Table 2.

Multiple regression was utilized to analyze the experimental values of HexA removal to match the second-order regression equation. The second-order quadratic model for encoding independent variables A, B, and C is shown in Eq. 3:

$$HexA\ content\ (\mu mol/g) = 9.73 + 0.37A + 0.11B + 0.56C - 0.099AB + 0.089AC + 0.14BC - 0.13A^2 - 0.045B^2 - 0.19C^2 \quad (3)$$

The variance analysis and model coefficients of the above model were tested for significance. The model's *F*-value (15.79) and *P*-value were less than 0.0001, and the *F*-value (1.26) and *P*-value of the lack of fit value were more than 0.05, indicating that the model was highly significant and exhibited a good fit (Chen *et al.* 2016), as shown in Table 3. The fitting results can be used to show that the model was a good prediction of HexA degradation in bagasse pulp in high temperature chlorine dioxide delignification.

Table 3. Analysis of Variance for Regression Model for HexA Content

Source	Sum of Squares	df	Mean Square	*F*-Value	*P*-Value ($F > Fa$)	Significant
Model	5.88	9	0.65	15.79	< 0.0001	Highly significant
A	1.86	1	1.86	44.91	< 0.0001	Highly significant
B	0.16	1	0.16	3.79	0.0803	
C	2.83	1	2.83	68.41	< 0.0001	Highly significant
AB	0.08	1	0.08	1.90	0.1980	
AC	0.06	1	0.06	1.54	0.2429	
BC	0.16	1	0.16	3.93	0.0756	
A^2	0.25	1	0.25	6.06	0.0336	Significant
B^2	0.03	1	0.03	0.71	0.4205	
C^2	0.32	1	0.32	7.72	0.0195	Significant
Residual	0.41	10	0.04			
Lack of fit	0.41	5	0.08	1.26	0.0786	Highly significant
Pure Error	3.29	5	6.58			
Correlation Total	6.30	19				

In this research, the value of R^2 was 0.9343, implying that 93.43% of the variations can be explained by the fitted model (Chen *et al.* 2016), indicating a high degree of correlation between the observed and predicted values. According to the *P*-values in this model, the variables *A* and *C* affected the HexA removal with high significance, and the quadratic terms A^2 and C^2 were also significant to the response. Conversely, others terms were insignificant to the response. The results also showed that the relative importance of effects of the independent variables on HexA removal were as follows: $A \geq C > B$.

Analysis of Response Surface and Optimization

The response surface is a three-dimensional spatial surface constructed by the regression equation, which is the result of the response value under the interactions of the experimental factors. It can predict and test the response value of the variable and determine the relationship between the independent variables. The effect of the other two

factors and their interactions on the HexA content was determined when one factor of either the reaction temperature, reaction time, or pH was fixed. Figures 4 through 6 show the response surface and the contours of the model.

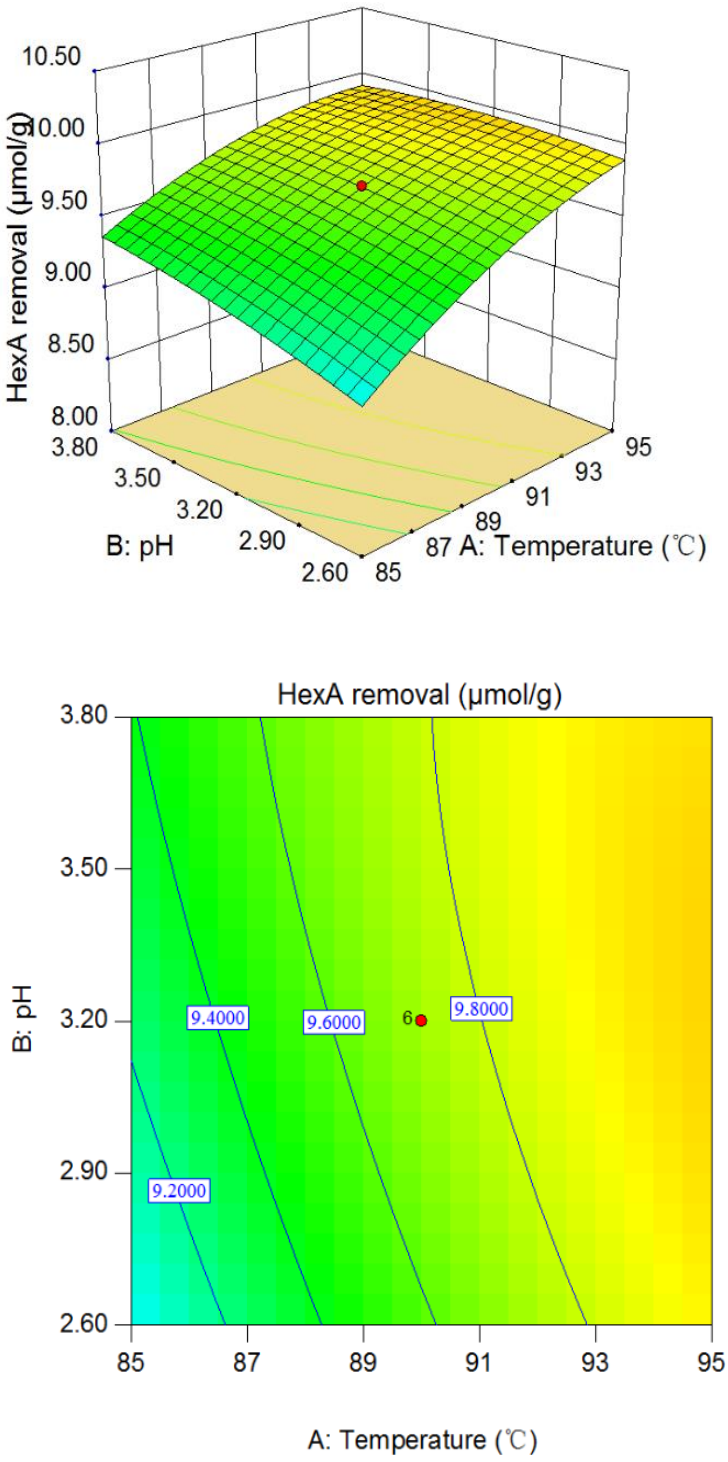

Fig. 4. Three-dimensional response surface plot and isopleth diagram for HexA removal based on reaction temperature and pH

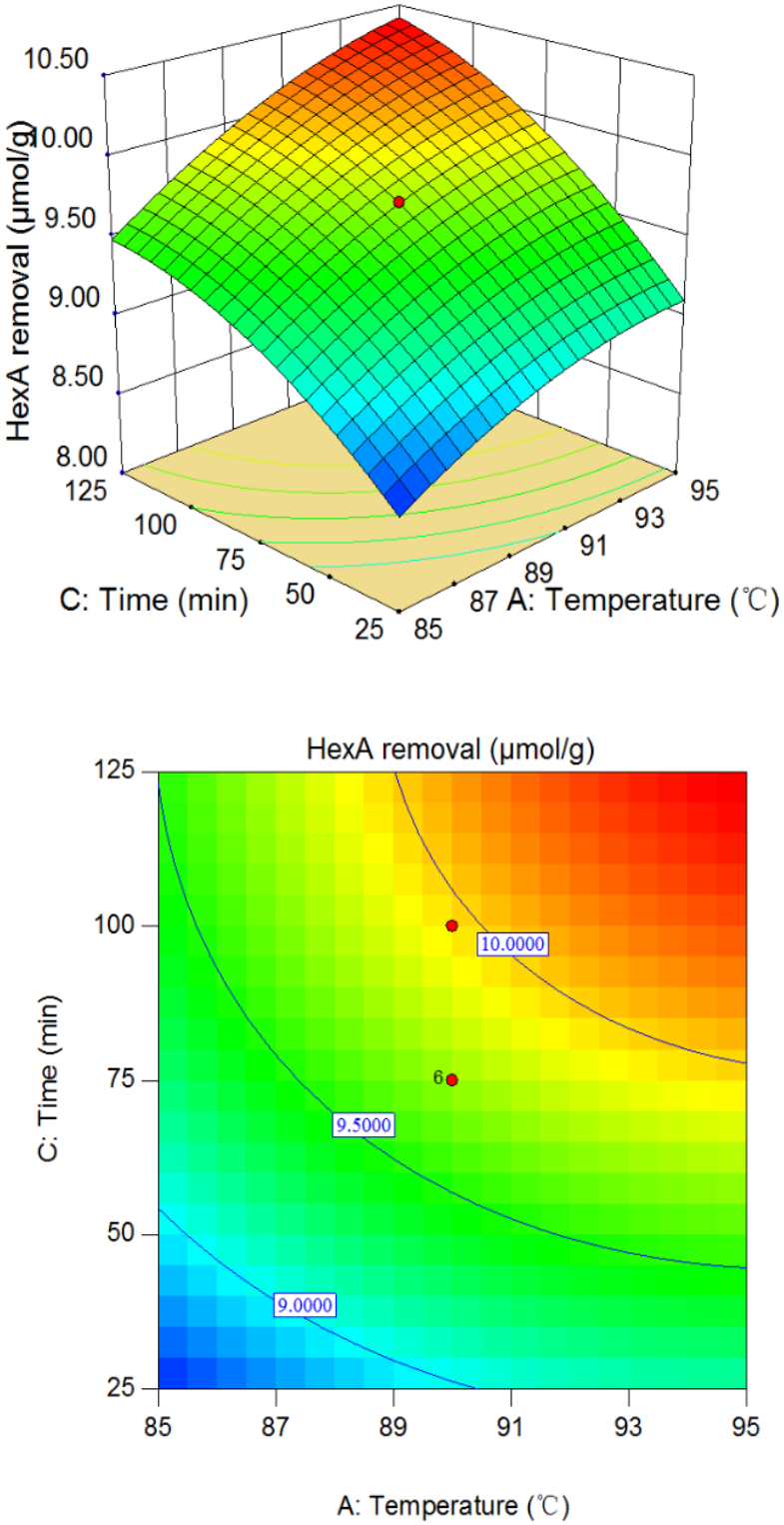

Fig. 5. Three-dimensional response surface plot and isopleth diagram for HexA removal based on reaction temperature and reaction time

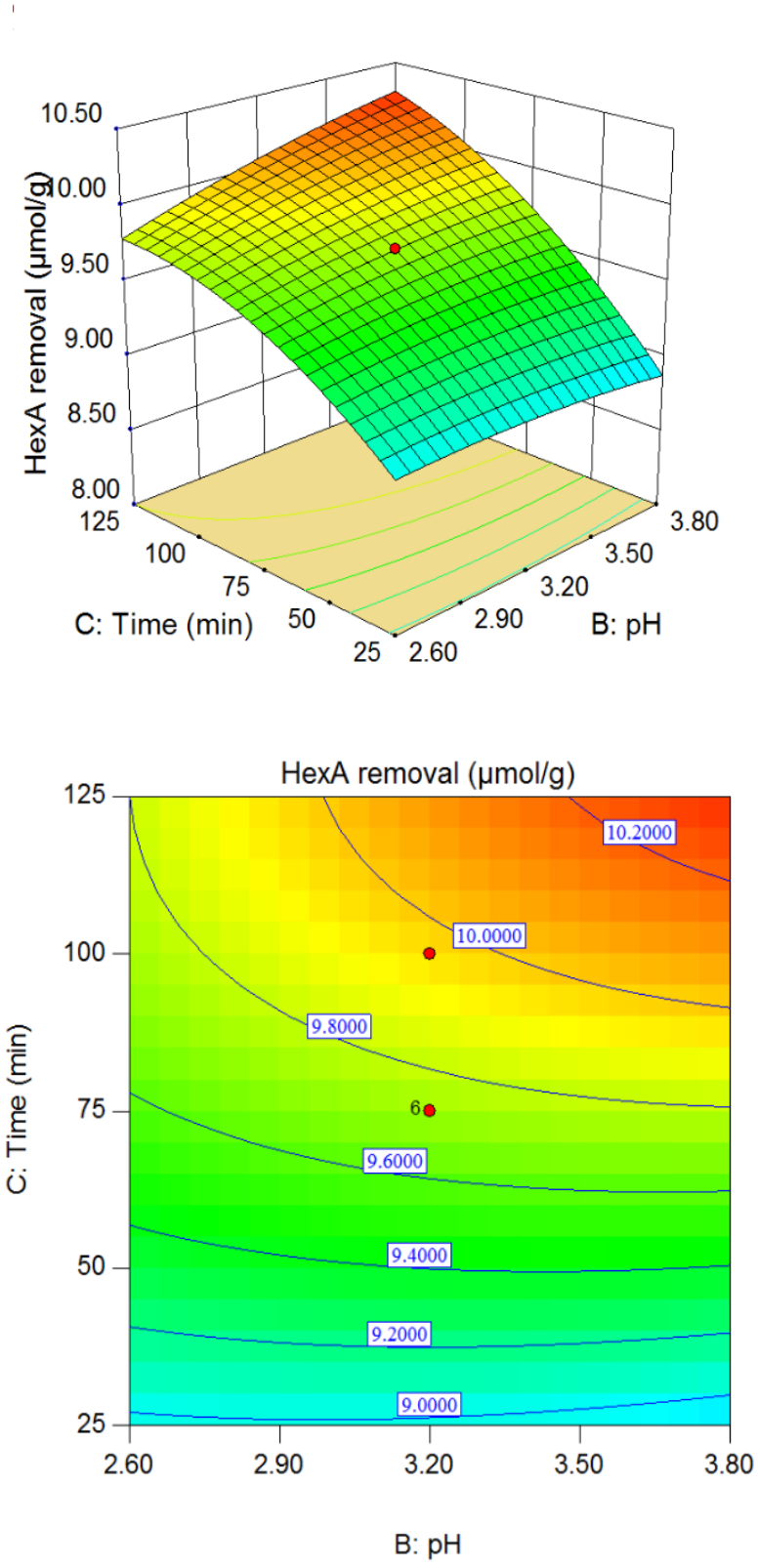

Fig. 6. Three-dimensional response surface plot and isopleth diagram for HexA removal based on pH and reaction time

As shown in the response surface plot, the amounts of HexA removal increased with the extension of the reaction temperature. As the temperature reached a certain point, HexA content increased at a more and more gradual rate. As the pH increased from 2.6 to 3.8, the HexA removal content also increased with the increase of the reaction temperature. Based on the steepness of the response surface, it can be concluded that the reaction temperature and reaction time of high temperature chlorine dioxide delignification had significant effects on HexA removal content in bagasse. This was consistent with the results of the variance analysis.

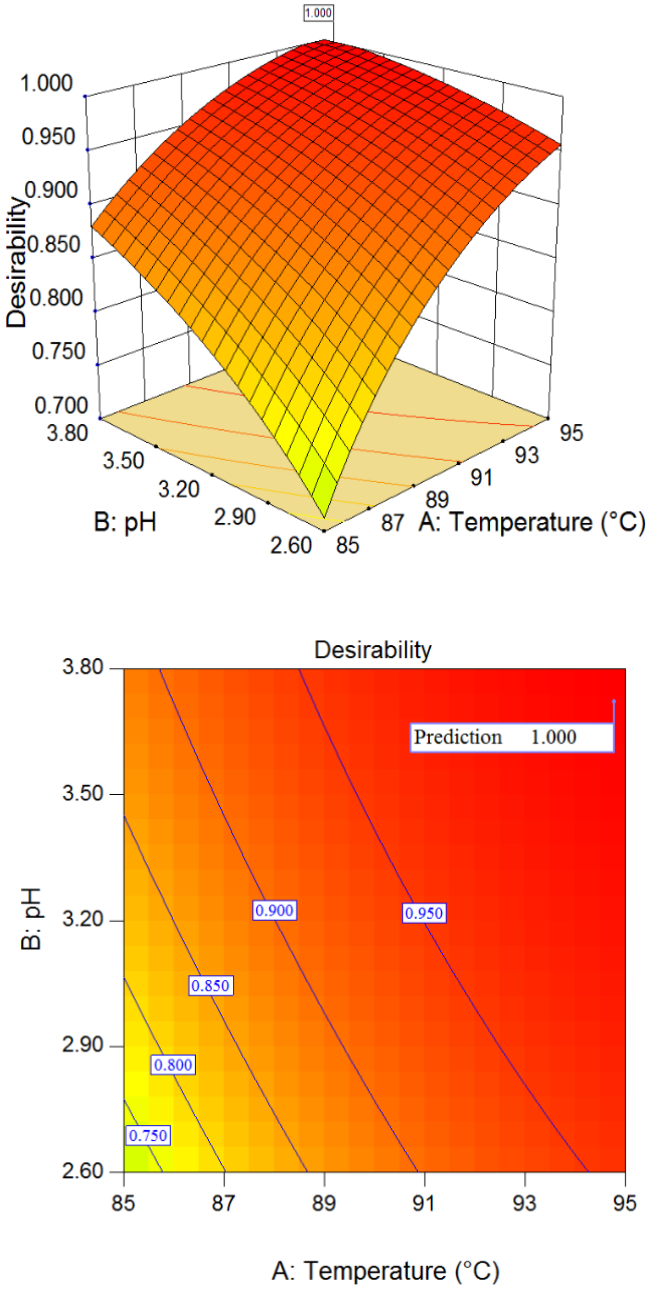

Fig. 7. Three-dimensional response surface plot and isopleth diagram for desirability of HexA removal based on reaction temperature and pH

The shape of the contour plot can reflect the strength and significance of the interaction between the reaction time and reaction temperature. In Fig. 5, the contours are elliptical. The reaction temperature had an obvious effect on HexA removal content at a low pH and short reaction time, and the curve in the corresponding response surface is steep. This implied that the HexA in bagasse was reduced *via* increased reaction temperature when the pH was lower and, in the reactions with a shorter time. However, the effect of reaction temperature on HexA removal content was not obvious when pH was high and the reaction time was long.

The reaction time had a significant effect on the HexA removal content at a low pH and reaction temperature, and the curve in the corresponding response surface was steep. This showed that the reaction time was significant when the pH and the reaction temperature were low, which reduced the HexA content in bagasse. These results suggested that the HexA content in the bagasse was significantly reduced at a low pH and reaction temperature situation when prolonging the reaction time. The effect of reaction time on HexA removal content was not significant when the pH and the reaction temperature were high. In particular, when the temperature was ≥ 95 °C, the curve in the corresponding response surface tended to be horizontally straight, which showed that the HexA content in bagasse was almost unchanged when the reaction temperature was high. However, the effect of pH on HexA removal content was not obvious when the reaction time and reaction temperature changed, as the curve in the corresponding response surface was gentle.

As shown in Fig.7, the maximum expected value of the response surface was 1 > 0.99. The optimal reaction conditions were as follows: a reaction temperature of 94.7 °C, a pH of 3.7, and a reaction time of 124 min, for which the maximum amount of HexA removal was 10.50 μmol/g.

Validation Experiments

The model was validated through the experimental conditions of the reaction with temperature between 80 °C and 95 °C, pH between 2.6 and 3.8, and reaction time between 25 min and 125 min. As seen in Table 4, the experimental values for the responses were highly close to the predicted values.

Table 4. Predicted and Tested Values of Variables during the Validation Experiment

Tested HexA Content (μmol/g)	Predicted HexA Content (μmol/g)	Relative Error	Desirable
8.45	8.73	0.28	0.9556
8.54	8.58	0.04	0.9530
8.72	8.44	-0.27	0.9462
8.84	8.94	0.10	0.9906
9.13	9.41	0.28	0.9940
9.16	9.21	0.05	0.9937
9.30	9.10	-0.21	0.9937
9.73	9.71	-0.02	0.9950
9.92	9.76	-0.16	0.9962
9.94	9.80	-0.14	0.9970
9.94	9.94	0.00	0.9996
9.98	10.10	0.12	0.9998
10.13	9.96	-0.17	0.9997
10.35	10.50	0.16	1.0000
10.35	10.21	-0.15	0.9999

Figure 8 shows the fitting results between the actual HexA removal and the predicted HexA removal. As shown in Fig. 8, the response surface model can be used in the process of chlorine dioxide delignification based on the test parameters in Table 4. The amount of HexA removal in the pulp was well predicted and highly significant ($R^2 > 0.90$). Therefore, it was practical and reliable to use the Box-Behnken center combination test to optimize the optimal conditions for the degradation of HexA in bagasse pulp.

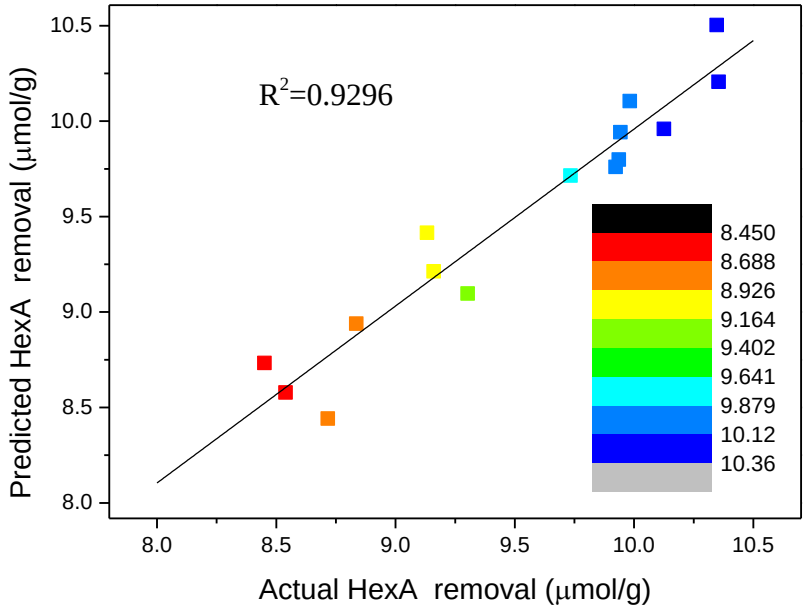

Fig. 8. Plotted relation between the predicted and actual values of HexA removal based on response surface model

CONCLUSIONS

1. The effect of reaction temperature, pH, and reaction time on the oxidative degradation of HexA in kraft bagasse pulp was studied by single factor experiments, and the range of parameters was obtained.
2. Based on the response surface analysis, the model of HexA removal was established by using the design BBD. The variance analysis showed that $P < 0.001$, which established that the model was highly significant. The relative influence of each factor on the degradation of HexA was as follows: reaction temperature ≥ reaction time > pH. Additionally, there was a significant interaction between the reaction temperature and reaction time.
3. The maximum expected value of the response surface was 1 > 0.99 when the reaction conditions were optimized. The optimal reaction conditions were as follows: a reaction temperature of 94.7 °C, a pH of 3.7, and a reaction time of 124 min, for which the maximum degradation of HexA was 10.5044 μmol/g.
4. The experimental results showed that the actual value and the predicted value were minimally different, which indicated that the response surface model predicted the HexA removal well in the chlorine dioxide delignification of bagasse pulp.

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