Kinetics of Adsorbable Organic Halides (AOX) Reduction in Laccase-Aided Chlorine Dioxide Bleaching of Bagasse Pulp

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This paper presents a kinetic model of the laccase-aided chlorine dioxide bleaching of bagasse pulp. The kinetic model was based on the rate of reduction of adsorbed organic halogen (AOX). The effects of the laccase enzyme dosage, the mediator 1-hydroxybenzotriazole (HBT) dosage, and the reaction temperature on the AOX content of the bleaching effluent are discussed. Good fits were obtained for the experimental data obtained from the different laccase enzyme dosages, HBT dosages, and reaction temperatures, indicating the feasibility of the kinetic model as a means of predicting the optimal operation conditions for the laccase-aided chlorine dioxide bleaching of bagasse pulp in the future.

Keywords: Kinetic model; Laccase; AOX; ECF; Bagasse soda pulp

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INTRODUCTION

In recent years, elemental chlorine-free (ECF) bleaching technology has undergone rapid development because of new environmental protection standards (Lehtimaa *et al.* 2010a,b). Chlorine dioxide is the most important bleaching chemical used in the ECF bleaching of pulp (Nie *et al.* 2013). It has exhibited a number of critical benefits compared with traditional bleaching chemicals (Bajpai *et al.* 2006; Nie *et al.* 2014a). ECF bleaching can restrain the formation of adsorbabled organic halogens (AOX) and other chlorine compounds relative to other traditional bleaching (Li *et al.* 2014). AOX level is generally regarded as one of the most important criteria for assessing the composition of a bleaching effluent (Yetis *et al.* 1996; Nie *et al.* 2014b). Many governments have set emission standards for these compounds, especially AOX. The Chinese government, for example, has established a limit on AOX discharge, stipulating that the AOX content of a bleaching effluent discharged must not exceed 12 mg/L (Zhang *et al.* 2012). Conceivably, there is a close relationship between AOX content and chlorine dioxide dosage, as related studies have reported (Bjorklund *et al.* 2002; Nie *et al.* 2014b). Reducing the use of chlorinated bleaching chemicals is crucial for decreasing the discharge of AOX within bleaching effluents; therefore, considerable attention has recently been shifted to exploring cost-effective and environmentally friendly bleaching technologies for the reduction of AOX generation (Sharma *et al.* 2014).

There are many methods of treating organic materials in wastewater. The advanced oxidation processes (AOPs) includes Fenton reagent oxidation, photocatalytic oxidation, supercritical water oxidation, ultrasonic oxidation, ozone oxidization, electrocatalytic oxidation, and wet oxidation. Advanced oxidation has attracted more and more extensive attention because of its higher ability to remove the organic materials in wastewater (Soares *et al.* 2016). However, AOPs can cause secondary pollution. In the context of environmentally friendly bleaching technologies, biobleaching with enzymes has shown tremendous potential for decreasing the use of chlorinated bleaching chemicals (Singh *et al.* 2008; Dai *et al.* 2016). Laccase is a biological enzyme used for pulp bleaching and an effective lignin degrader (Knezevic *et al.* 2013a,b). It can selectively degrade the lignin of paper fibers (Call and Mucke 1997; Qiu and Chen 2012; Quintana *et al.* 2015), imposes little damage on the cellulose of paper fibers (Bourbonnais *et al.* 1995), and has been used in labs and at the pilot scale (Euring *et al.* 2011; Goncalves *et al.* 2014; Martin-Sampedro *et al.* 2015). Laccase-aided bleaching can reduce the use of chlorine dioxide in ECF bleaching and reduce the formation of organic chlorine compounds in the bleaching effluent (Bajpai *et al.* 2006). Laccase-aided bleaching also can improve pulp yield and lower capital investment (Bajpai *et al.* 2006). Sharma *et al.* (2014) reported a 35% ClO_2 reduction and a 34% AOX content reduction following ECF bleaching with enzymatic pre-treatment of eucalyptus kraft pulp.

However, the process of laccase-aided chlorine dioxide bleaching is subject to many complex factors that may interact with each other (Paice *et al.* 2002). Therefore, many transfers and chemical reactions can occur in laccase-aided chlorine dioxide bleaching (Radeva *et al.* 2009). At present, the most accepted reaction mechanism can be concisely described as a consequence of redox cycles (Balakshin *et al.* 2001b). Although the reaction mechanism of the laccase-mediator system (LMS) has been researched since laccase was first used for biobeaching (Balakshin *et al.* 2001b), important problems, including the reaction mechanism and the kinetics of the LMS on AOX reduction, have not been studied thoroughly. Of the number of experiments exploring the reaction mechanism of LMS, few kinetic studies have been conducted (Balakshin *et al.* 2001b). Macro kinetics can be used to explore the key variables influencing the impact of biobleaching, and can quantitatively describe the effects of these variables (Pei *et al.* 2016). Balakshin *et al.* (2001b) constructed a kinetic study on kappa number reduction and the dioygen uptake of pine-kraft-AQ pulp. They determined that the fast formation of the oxidized mediator species was the critical reason for the fast rate of delignification. Another kinetic investigation of kraft unbleached pulp showed that the action of the LMS could be explained using an exponential kinetic equation (Radeva *et al.* 2009).

The objective of this work was to establish a macro kinetic model of AOX reduction in the context of the laccase-aided chlorine dioxide bleaching of bagasse pulp. The model will promote the understanding of AOX formation in the laccase-aided chlorine dioxide bleaching of bagasse pulp, which could benefit the pulp and paper industry as well as the natural environment.

EXPERIMENTAL

Materials

The unbleached bagasse pulp (brightness, 38.97% ISO; viscosity, 1280.86 mL/g; and kappa number, 12.51) used in the bleaching experiments was obtained from the Pumiao paper mill (Guangxi, China). The laccase was supplied by Shanghai Yongye bio-technology Co., Ltd. (Shanghai, China). The laccase had a laccase activity of 2000 U/g. The chlorine dioxide solution, which was stored in a brown bottle, was also obtained from the Pumiao paper mill (Guangxi, China) (available chlorine concentration, 21.58 g/L). The ceramic wool and activated carbon were procured from Analytik-Jena instrument company (Jena, Germany), and all other chemicals used in this study were purchased from Aladdin reagent (Shanghai) Co., Ltd. All of the chemicals were of analytical grade, unless otherwise mentioned.

Methods

The laccase activity was determined by monitoring the oxidation of 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) as increased absorbance at 420 nm. The reaction mixture contained 2.5 mL of sodium acetate buffer (pH 4.5), 0.1 mL of the enzyme sample, and 0.4 mL of 1 mM ABTS, in a final volume of 3.0 mL. 1 U was defined as the amount of enzyme that would convert 1 µmol of substance in one minute under the described conditions at 25 °C (Bajpai *et al.* 2006).

Unbleached bagasse pulp, an appropriate amount of laccase and HBT, surfactant (Tween® 80), and acetate buffer (pH 4.5) were mixed thoroughly and reacted in a micro-reactor. Other constant parameters needed in this biobleaching treatment were as follows: surfactant (Tween® 80), 0.05%; pulp consistency, 10%; oxygen pressure, 0.4 MPa; and rotating speed, 60 rpm. The laccase enzyme biobleaching treatment of the unbleached bagasse pulp was carried out in a micro-reactor at an appropriate temperature. After the laccase enzyme biobleaching treatment, the pulps were washed with distilled water until reaching a neutral pH. The washed pulps were then used for the chlorine dioxide bleaching.

The washed pulps, chlorine dioxide solution, and sulfuric acid solution were mixed in a plastic bag at a pulp consistency of 10%. Other parameters used during the chlorine dioxide bleaching were a chlorine dioxide dosage of 3.7% and a sulfuric acid solution pH value of 4.5. Then, the bags were heated in a water bath at 70 °C for 1 h with kneading every 15 min. After bleaching, the pulps were washed with distilled water until they reached a neutral pH. The bleached pulps were placed in a lab environment held at constant temperature and constant humidity for 24 h and then subjected to characterization. In the control experiment, the laccase enzyme biobleaching treatment of the unbleached bagasse pulp was replaced with the buffer solution alone, and the subsequent conditions used for chlorine dioxide bleaching were the same as those for the experimental samples. All of the experiments were conducted in triplicate, and the mean values were recorded.

The AOX content was measured using a Multi X 2500 halide analyzer (Jena, Germany). The process was as follows: first, the diluted bleaching effluent was passed through an activated carbon column, where the organic chlorine of the bleaching effluent was adsorbed by the activated carbon; second, the adsorbed inorganic chlorine in the activated carbon column was washed with sodium nitrite; finally, the activated carbon column was burned in a combustion furnace, after which the AOX content was calculated using the micro Coulomb titration method (Nie *et al.* 2013, 2014b, 2015).

RESULTS AND DISCUSSION

Mathematical Model of the Kinetic Equation

The relationship between the actual AOX reduction and the reaction time is shown in Fig. 1. The reaction was conducted at a laccase emzyme dosage of 15 U/g, a HBT dosage of 1.5%, and a reaction temperature of 323 K. Notably, the AOX reduction calculated represented the relative AOX reduction, and was calculated as follows,

$$W = \frac{AOX_1 - AOX_0}{AOX_0} \tag{1}$$

where AOX_1 is the AOX content of the biobleaching experiments and AOX_0 is the AOX content of the control experiment.

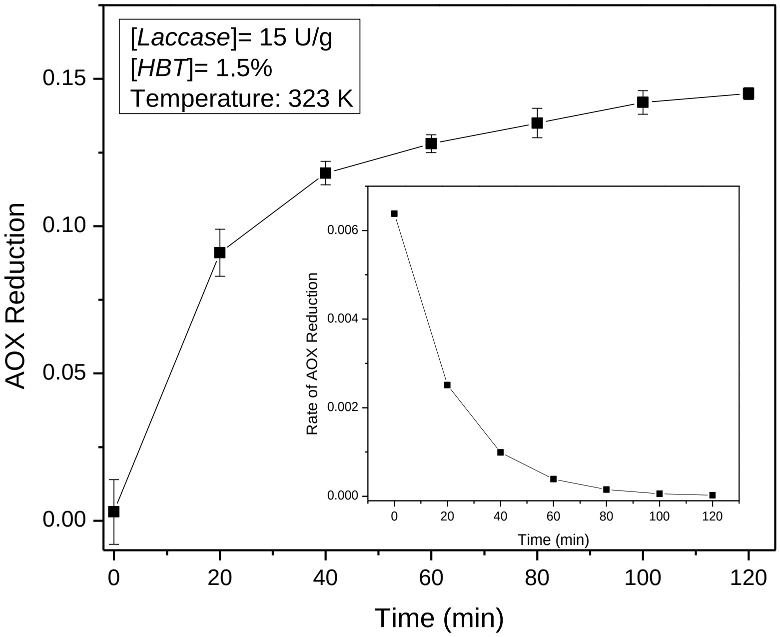

Fig. 1. Relationship between AOX reduction and reaction time

From Fig. 1 it can be seen that the AOX reduction increased as the reaction progressed. The rate of AOX reduction, however, decreased as the reaction progressed. This was expected, as, if the reaction time is too short, the residual lignin will not be as thoroughly degraded, whereas if the reaction time is too long, the reaction results in dehydrogenetive polymerization of the degraded residual lignin molecules (Balakshin *et al.* 2001a). These results are similar to those of the sequential enzymatic treatment studied by Sharma *et al.* (2014). Kinetics has been used to investigate the effects of key variables on the reaction rate (Balakshin *et al.* 2001b; Roncero *et al.* 2003). The kinetic model describing AOX reduction in the context of laccase-aided chlorine dioxide bleaching of bagasse pulp was represented as Eq. 2,

$$dW/dt = k \cdot [Laccase]^a \cdot [HBT]^b \cdot W^c \tag{2}$$

where *dW/dt* is the rate of AOX reduction, *W* is the AOX reduction, *t* is the biobleaching time (min), *k* is the reaction rate constant of AOX reduction, *[Laccase]* is the dosage of the laccase enzyme (U/g), and *[HBT]* is the dosage of the mediator HBT (%). The constants a, b, and c are the reaction orders of laccase, HBT, and AOX reduction, respectively.

To facilitate the calculation, Eq. 2 was transformed into its logarithmic form (Eq. 3):

$$log(dW/dt) = log(k) + a \cdot log[Laccase] + b \cdot log[HBT] + c \cdot log\ (W) \tag{3}$$

Supposing that $M_1 = \log(k) + a \cdot \log[Laccase] + b \cdot \log[HBT]$ when the laccase enzyme dosage of 15 U/g, the HBT dosage of 1.5%, and the reaction temperature of 323 K were held constant, Eq. 3 could be used to explore the changes in AOX reduction over time, so it was rewritten as Eq. 4,

$$\log(dW/dt) = M_1 + c \cdot \log(W) \tag{4}$$

where *log(dW/dt)* is the y-coordinate, M_1 is the intercept, *c* is the slope, and *log(W)* is the x-coordinate.

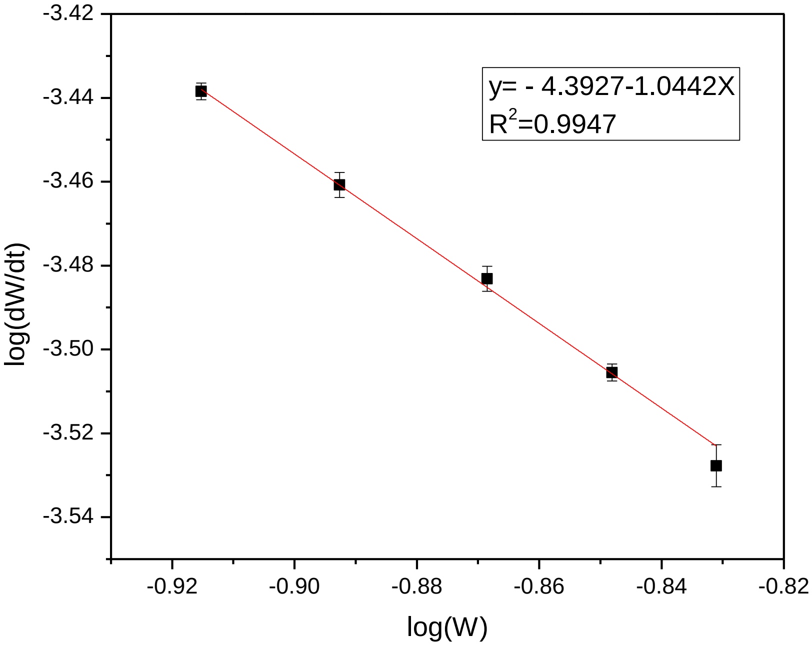

Fig. 2. Linear relationship between log(d*W*/d*t*) and log(*W*)

Through linear fitting, a regression equation was obtained, as shown in Fig. 2. The equation was in strong accordance with the experimental results, with R^2 = 0.9947. The value of M_1 was -4.3927, and the value of *c* was equal to -1.0442.

When the laccase enzyme dosage of 15 U/g and the reaction temperature of 323 K were held constant and the HBT dosage was changed, Eq. 3 was rewritten as Eq. 5 to explore the AOX reduction changes over time under different HBT dosages,

$$\log(dW/dt) + 1.0442 \cdot \log(W) = M_2 + b \cdot \log[HBT] \tag{5}$$

where $M_2 = \log(k) + a \cdot \log[Laccase]$.

Through linear fitting, five regression equations under five different reaction times were obtained, as shown in Fig. 3. Each equation was in strong accordance with their experimental results, with R^2 values corresponding to 0.9751, 0.9819, 0.9813, 0.9858, and 0.9927, respectively. The slope average of the five fitted linear models was recorded as the value of *b*, so the value of *b* is equal to 0.4910.

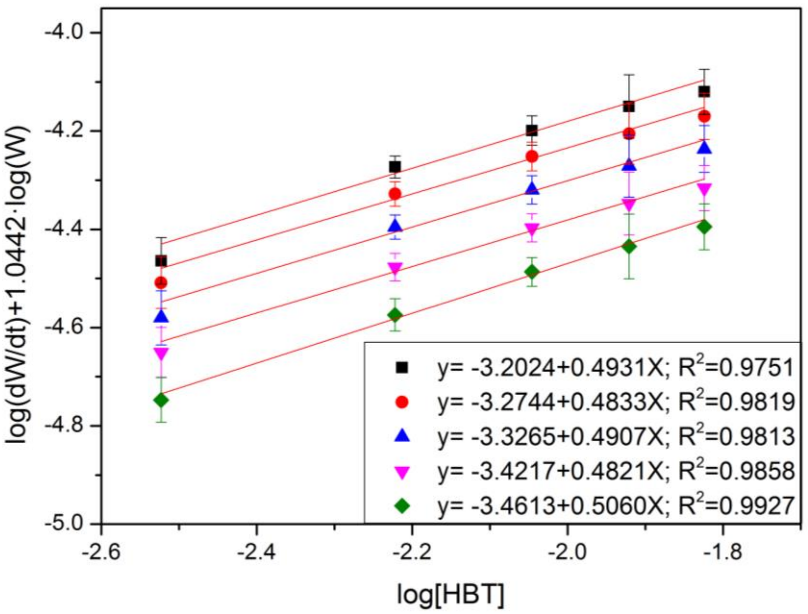

Fig. 3. Linear relationship between log(dW/dt) +1.0442 • log(W) and log[HBT]

When the HBT dosage of 1.5% and the reaction temperature of 323 K were held constant, while the laccase enzyme dosage was changed, Eq. 3 was rewritten as Eq. 6 in order to explore the changes in AOX reduction over time under five different laccase enzyme dosages,

$$\log(dW/dt) + 1.0442 \cdot \log\ (W) = M_3 + a \cdot \log[Laccase] \tag{6}$$

where $M_3 = \log(k) + b \cdot \log[HBT]$.

Using univariate regression, five regression equations were obtained under five different reaction times, as shown in Fig. 4. Each equation was in strong accordance with the experimental results, with all R^2 values greater than 0.9. In the same way as before, the slope average of the five fitted linear models was recorded as the value of *a*, so the value of *a* was equal to 0.6946. In accordance with the Arrhenius law, the relationship between the reaction rate constant of the AOX reduction and the reaction temperature can be represented as follows,

$$k = A \cdot e^{-E/R \cdot T} \tag{7}$$

where *A* is the pre-exponential factor, *E* is the apparent activation energy for the AOX reduction (KJ/mol), *R* (equal to 8.314 J/(mol • K)) is the ideal-gas constant, and *T* is the thermodynamic temperature (K).

Equation 3 can be represented as Eq. 8:

$$\log(k) = \log(dW/dt) - a \cdot \log[Laccase] - b \cdot \log[HBT] - c \cdot \log\ (W) \tag{8}$$

In this case, the reaction temperature was changed, while the laccase enzyme dosage of 15 IU/g and the HBT dosage of 1.5% were held at a constant value. Figure 5 shown the relationship between AOX reduction and reaction time when the temperatures ranged from 303 to 323 K.

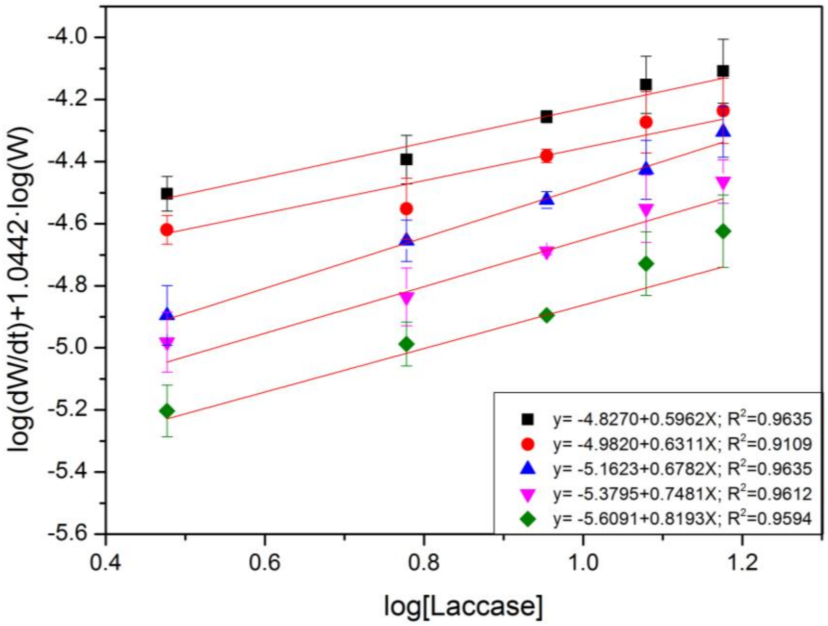

Fig. 4. Linear relationship between *log(dW/dt) + 1.0442·log(W)* and *log[Laccase]*

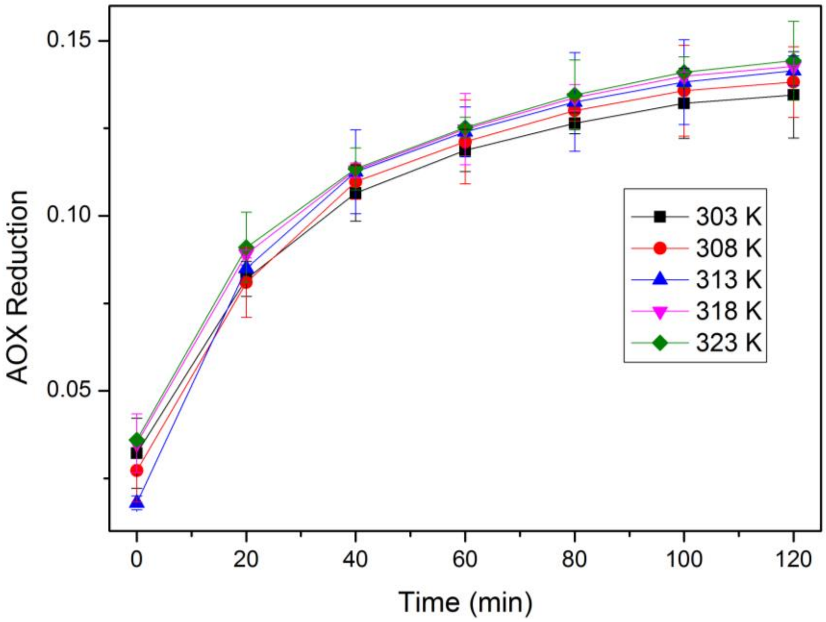

Fig. 5. Relationship between AOX reduction and reaction time at five different temperatures

In accordance with the relationship between the AOX reduction and the reaction time (Eq. 5), the calculated values of *a*, *b*, and *c*, as well as the laccase enzyme dosage and the HBT dosage, were substituted into Eq. 7. Similarly, the AOX reductions at five different times for five different temperature (Eq. 5) were also substituted into Eq. 8. Finally, under the five different reaction temperatures, the value of *log(k)* was obtained. In addition, Eq. 7 was transformed into its logarithmic form (Eq. 9):

$$log(k) = log(A) - E/RT \quad (9)$$

A fitted linear model, y=-2.9391-435.0967x, was obtained using linear regression analysis in accordance with the relationship between *log(k)* and *1/T* (Fig. 6). The value of *log(A)* was equal to -2.9391, which was obtained from the intercept of the fitted linear model. Similarly, based on the slop of the fitted linear model, the value obtained for *–E/RT* was -435.0967. Finally, the value of *A* (pre-exponential factor) was calculated to be 0.001151, and the value of *E* (apparent activation energy) was calculated to be 3.6157 kJ/mol. Thus, the final value of the reaction rate constant of the AOX reduction, *k*, was 0.001151 • $e^{-435.0967/T}$.

This implies that the apparent activation energy for AOX reduction in the laccase-aided chlorine dioxide bleaching of bagasse pulp was low. In other words, the reaction speed between laccase and bagasse pulp was fast and accelerated the formation of the AOX.

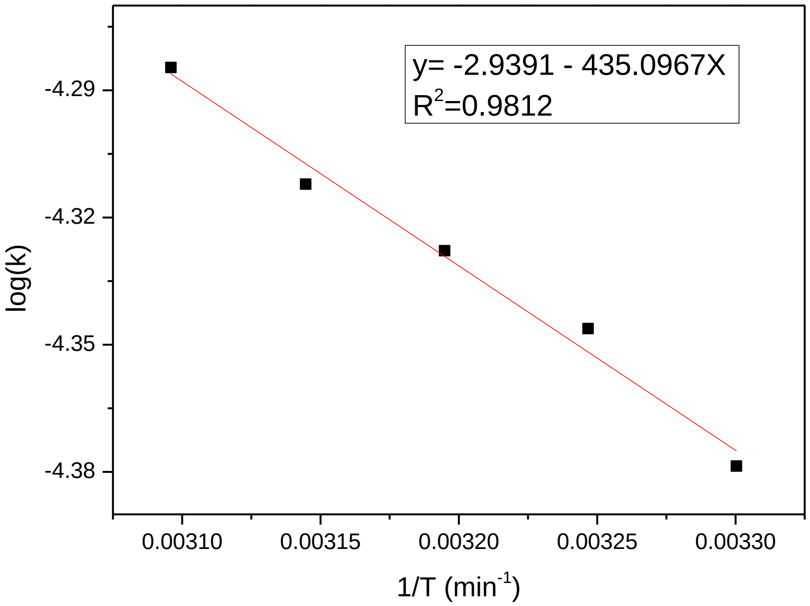

Fig. 6. Linear relationship between log(*k*) and 1/*T*

Because the reaction orders of the laccase enzyme dosage (*a*) and HBT dosage (*b*), as well as the pre-exponential factor (*A*) and the activation energy (*E*), were known, a complete kinetic model of AOX reduction was obtained as follows:

$$dW/dt = 0.001151 \cdot e^{-435.0967/T} \cdot [Laccase]^{0.6946} \cdot [HBT]^{0.4910} \cdot W^{-1.0442} \quad (10)$$

Thus, in the future, it will be convenient for paper mills to be able to predict the rate of AOX reduction during the laccase-aided chlorine dioxide bleaching of bagasse pulp by reference to this new kinetic model.

Figure 7 shows the close relationship between the actual values of the AOX reduction and the calculated values from Eq. 10. As can be seen, the points of the scatterplot are distributed in the proximity of the straight line of 45°, indicating that the new kinetic model accurately predicted the rate of AOX reduction in the laccase-aided chlorine dioxide bleaching of bagasse pulp.

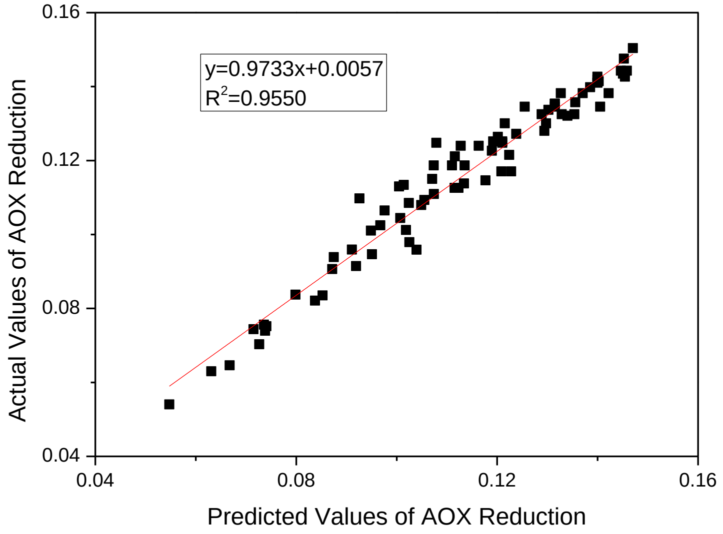

Fig. 7. Relationship between the actual values and the calculated values of the AOX reduction

Effect of Laccase Dosage and HBT Dosage on the Rate of AOX Reduction

From the kinetic model (Eq. 10) describing the laccase-aided chlorine dioxide bleaching of bagasse pulp, it is not hard to see that the reaction order values of the kinetic model are not integers. The AOX reduction is a multi-stage and complex reaction, rather than a single simple reaction. Because of the macromolecular structure of lignin, it is too hard to figure out the molecular structure of the lignin clearly. Hence, numerous complex redox reactions occurred on the lignin, and many of the intermediates were formed during the redox reactions.

When the laccase enzyme dosage, the HBT dosage, and the reaction temperature were held at a constant values, the AOX reduction increased from 0.05 to 0.14. The rate of the AOX reduction ($\gamma_{0.14}/\gamma_{0.05}$) was as folows:

$$\gamma_{0.14}/\gamma_{0.05}=\frac{0.001151\cdot e^{-435.0967/T}\cdot[Laccase]^{0.694566}\cdot[HBT]^{0.491024}\cdot 0.14^{-1.04416}}{0.001151\cdot e^{-435.0967/T}\cdot[Laccase]^{0.694566}\cdot[HBT]^{0.491024}\cdot 0.05^{-1.014416}}=0.3413 \tag{11}$$

Based on Eq. 11, the rate of the AOX reduction was reduced with the increase in AOX reduction in the context of laccase-aided chlorine dioxide bleaching of bagasse pulp. The model also indicated that the LMS oxidation of lignin was very fast at the beginning of the biobleaching. In other words, most of the AOX was formed at the beginning of the biobleaching stage.

When the laccase enzyme dosage and the reaction temperature were held at a constant value, the HBT dosage increased from 0.003 to 0.015. The rate of the AOX reduction (γ_2/γ_1) was as follows:

$$\gamma_2/\gamma_1=\frac{0.001151\cdot e^{-435.0967/T}\cdot[Laccase]^{0.694566}\cdot 0.015^{0.491024}\cdot W^{-1.04416}}{0.001151\cdot e^{-435.0967/T}\cdot[Laccase]^{0.694566}\cdot 0.003^{0.491024}\cdot W^{-1.014416}}=2.204 \tag{12}$$

When the HBT dosage and the reaction temperature were held at a constant value, the laccase enzyme dosage increased from 3 U/g to 15 U/g. The rate of the AOX reduction (γ_4/γ_3) was as follows from Eq. 13:

$$\gamma_4/\gamma_3=\frac{0.001151\cdot e^{-435.0967/T}\cdot 15^{0.694566}\cdot [HBT]^{0.491024}\cdot W^{-1.04416}}{0.001151\cdot e^{-435.0967/T}\cdot 3^{0.694566}\cdot [HBT]^{0.491024}\cdot W^{-1.014416}}=3.059 \tag{13}$$

Based on Eqs. 12 and 13, the AOX reduction increased noticeably with the increase in the HBT dosage and with increase in laccase enzyme dosage. Because of its low redox potential (Bourbonnais *et al.* 1998) and large size (Morozova *et al.* 2007), laccase alone has little impact on lignin. However, the combination of laccase and mediators resulted in the fast degradation of lignin (Morozova *et al.* 2007). Therefore, an appropriate laccase enzyme dosage and HBT dosage are essential for increasing the degradation of lignin and the AOX reduction.

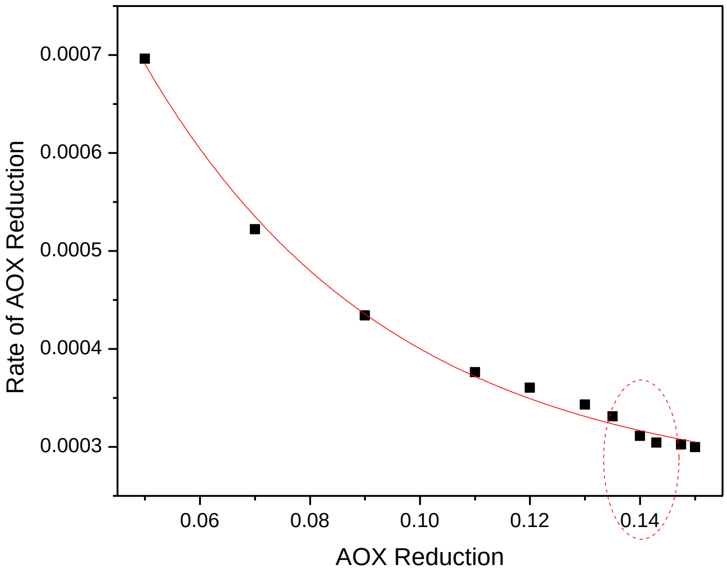

Fig. 8. Relationship between the rate of AOX reduction and AOX reduction

Effect of AOX Reduction on the Rate of AOX Reduction

Based on the relationship between AOX reduction and the reaction time (Fig. 1) and on the kinetic model (Eq. 10), the relationship between the rate of AOX reduction and AOX reduction was obtained (Fig. 8).

Here, the laccase enzyme dosage was 15 U/g, the HBT dosage was 1.5%, and the reaction temperature was 323 K. From Fig. 8, it can be seen that the rate of AOX reduction decreased noticeably when the AOX reduction was less than 0.14. When the AOX reduction was more than 0.14, the change in the rate of AOX reduction was small. This was similar to the results obtained in previous studies (Balakshin *et al.* 2000, 2001a; Fillat and Roncero 2009), which revealed that the reaction of AOX reduction could be separated into two stages. In the initial stage, when the AOX reduction was less than 0.14, the lignin was degraded rapidly. In the final stage, when the AOX reduction was more than 0.14, degradation of lignin was much slower.

The equation can predict the rate of AOX reduction conveniently under the different LMS condition. It could optimize the level of AOX to meet the regulation limits.

CONCLUSIONS

1. A macro kinetic model of the AOX reduction in the context of the laccase-aided chlorine dioxide bleaching of bagasse pulp was developed.
2. The effects of the laccase enzyme dosage, the HBT dosage, and the reaction temperature on the rate of AOX reduction were illustrated using a macro kinetic model.
$$dW/dt = 0.001151 \cdot e^{-435.0967/T} \cdot [Laccase]^{0.6946} \cdot [HBT]^{0.4910} \cdot W^{-1.0442}$$
   The reaction order values of the kinetic model were not integers, indicating that the AOX reduction was a multi-stage and complex reaction, rather than a single simple reaction.
3. The reaction of AOX reduction was shown to take place in two stages. In the initial stage, when the AOX reduction was less than 0.14, the lignin was degraded rapidly. In the final stage, when the AOX reduction was more than 0.14, the degradation of lignin was much slower.

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