Kinetics of AOX Formation in Chlorine Dioxide Bleaching of Bagasse Pulp

Shuangxi Nie,[a,b] Shuangquan Yao,[a] Chengrong Qin,[a] Kecheng Li,[b] Xinliang Liu,[a]
Lijun Wang,[a] Xueping Song,[a,b,]* and Shuangfei Wang [a,]*

In this paper, a kinetic model of the first chlorine dioxide bleaching stage (D_0) in an elemental chlorine-free (ECF) bleaching sequence is presented for bagasse pulps. The model is based on the rate of adsorbable organic halogen (AOX) formation. The effects of the chlorine dioxide dosage, the sulfuric acid dosage, and the reaction temperature on the AOX content of wastewater are examined. The reaction of AOX formation could be divided into two periods. A large amount of AOX was formed rapidly within the first 10 min. Ten minutes later, the AOX formation rate significantly decreased. The kinetics could be expressed as: $dW/dt = 660.8 \cdot e^{-\frac{997.98}{T}} \cdot [ClO_2]^{0.877} \cdot [H_2SO_4]^{0.355} \cdot W^{-1.065}$, where W is the AOX content, t is the bleaching time (min), T is the temperature (K), $[ClO_2]$ is the dosage of chlorine dioxide (kg/odt), and $[H_2SO_4]$ is the dosage of sulfuric acid (kg/odt). The fit of the experiment results obtained for different temperatures, initial chlorine dioxide dosages, initial sulfuric acid dosages, and AOX content were very good, revealing the ability of the model to predict typical mill operating conditions.

Keywords: Bagasse pulp; Chlorine dioxide bleaching; Adsorbable organic halogens (AOX); Kinetics; Modeling

*Contact information: a: College of Light Industry and Food Engineering, Guangxi University, Nanning, 530004, PR China; b: Department of Chemical Engineering, University of New Brunswick, Fredericton, E3B5A3, Canada; *Corresponding authors: sx_ping@sina.com; wangsf@gxu.edu.cn*

INTRODUCTION

In recent years, there has been increasing interest in elemental chlorine-free (ECF) bleaching as a means to minimize the generation of absorbable organic halogens (AOX) (Lehtimaa *et al.* 2010; Nie *et al.* 2014). Chlorine dioxide is the main oxidant used in the ECF bleaching of bagasse. AOX is formed during the bleaching process, and it is seen as the most generally useful parameter to assess the potential environmental impacts of bleaching effluents (Yetis *et al.* 1996; Liu *et al.* 1997). Many techniques to decrease the emission of AOX from a bleaching mill have been researched. Many studies have focused on process operations both before and in the plant itself (Barroca *et al.* 2001). Juuti *et al.* (1996) and Yuan *et al.* (2011) have noted that the ECF bleaching process will have an impact on the environment due to the significant ecological toxicity of AOX, which can seriously inhibit the effectiveness of the biological treatment of wastewater. Related studies have pointed out that the amount of AOX formed is closely related to the unbleached kappa number of the pulp and the dosage of chlorine dioxide (Johansson and Fletcher 1994; Tsai *et al.* 1994; Yin *et al.* 1994; Bjorklund *et al.* 2002; Garcia *et al.* 2010). At the same time, some AOX is eliminated when the filtrates from D_0 and E_1 (or (EO) or (EOP)) are mixed together prior to being sewered and sent to effluent treatment (McDonough *et al.* 1998; Courchene and McDonough 1993).

In the ECF bleaching of pulp, a series of complex chemical reactions and mass transfer occurs in a solid phase (pulp) and a liquid phase (chemicals) (Tarvo *et al.* 2008; Tarvo 2010; Tarvo *et al.* 2010; Brogdon *et al.* 2012). This process is subject to many complex factors. There are interactions between several factors (Loureiro *et al.* 2011). Macro kinetics is employed to study the target variable of the bleaching process, which is quantitative description of influence that the process variables on the bleaching. Chlorine dioxide as the primary bleaching agent of ECF has been widely employed in pulp bleaching. Tessier and Savoie (2000) have studied the kinetics of chlorine dioxide bleaching of hardwood kraft pulp. They determined the optimal range of the kappa factor (KF) and temperature by constructing a mathematics model. Jain *et al.* (2009) constructed a kinetic model for ECF of wood pulp, providing guidance for chlorine dioxide bleaching for softwood and hardwood pulps. Barroca and Castro (2003) established the kinetics of the D_0 brightening stage of the ECF bleaching of eucalyptus pulps, and the equation becomes a useful guidance for plant operation conditions (Brogdon *et al.* 2012). At the same time, a chlorine dioxide delignification stage was also studied in the bleaching of hardwood pulps (Barroca *et al.* 2001).

Recently, we have investigated the AOX formation of the bagasse pulp during ECF bleaching. The AOX formation process was minimized for a soda AQ bagasse pulp in the first chlorine dioxide stage (D_0) (Nie *et al.* 2013); also, the oxidation kinetics of lignin model compounds with chlorine dioxide has been studied (Nie *et al.* 2014). The aim of the present work is to establish a macro-kinetic equation for AOX formation during ECF bleaching. This model will provide a reference for the control of AOX formation during the chlorine dioxide bleaching of bagasse pulp.

EXPERIMENTAL

Materials

Sodium chlorite, hydrochloric acid, sodium hydroxide, sulfuric acid, potassium iodide, and sodium thiosulfate were obtained from Cheng du Kelon Chemical Reagent Factory (Cheng du, China). Activated carbon and ceramic cotton were purchased from Analytik Jena AG (Jena, Germany), and all other chemicals employed in this work were obtained from Chongqing Changyuan Chemical Corp. Ltd. (Chongqing, China). All chemicals used were of analytical grade.

The unbleached bagasse pulp came from a pulp mill located in Guangxi China. The soda pulping conditions were as follows: 15% sodium hydroxide, 0.05% AQ (anthraquinone), 4.5:1 liquor-to-bagasse ratio, maximum cooking temperature of 155 °C for 40 min, and 120 min to rise to the cooking temperature. The bagasse brownstock had a yield of 58.5%, a kappa number of 10.1, a brightness of 32.77% ISO, and an intrinsic viscosity of 1021 mL/g. The pulp was well-washed and was stored at 2 to 4 °C until needed.

Methods

Bleaching operation

Bagasse pulp (20 g bone dry) and a certain amount of deionized water were placed into a three-neck flask. Then sulfuric acid was added to adjust the initial pH to make sure it remained at 3 to 4. The reaction was allowed to take place for 10 min beyond the time when the reaction temperature reached the set point. Chlorine dioxide was added to the pulp slurry once the reaction temperature was reached. The reaction unit was rapidly sealed and shielded from light exposure. A timer was started with the addition of chlorine dioxide. The reaction temperature was held constant when bleaching; the amount of AOX in the bleaching effluent was measured by regular sampling of the reactor during bleaching.

AOX content analysis

The AOX determinations were measured using an AOX analyzer instrument (multi X® 2500, Analytik Jena AG, Jena, Germany). AOX from the effluent sample was adsorbed onto activated carbon according to the method of Yuan *et al.* (2012). The basic method and process were as follows. Organic chloride of the bleaching effluent was adsorbed by the activated carbon column. Sodium nitrate was used in the washing of the activated carbon column. The activated carbon column was burnt in the combustion furnace. The AOX content could then be calculated though the micro-coulomb titration method given by Nie *et al.* (2013).

RESULTS AND DISCUSSION

AOX Formation and Mechanism Model Development

A typical AOX generation versus time profile for the chlorine dioxide stage is shown in Fig. 1. It was obtained at a temperature of 333 K, a pulp consistency of 10%, an initial chlorine dioxide charge of 30 kg/odt, and a sulfuric acid charge of 2 kg/odt. Figure 1(A) shows that the initial increase in AOX was extremely fast.

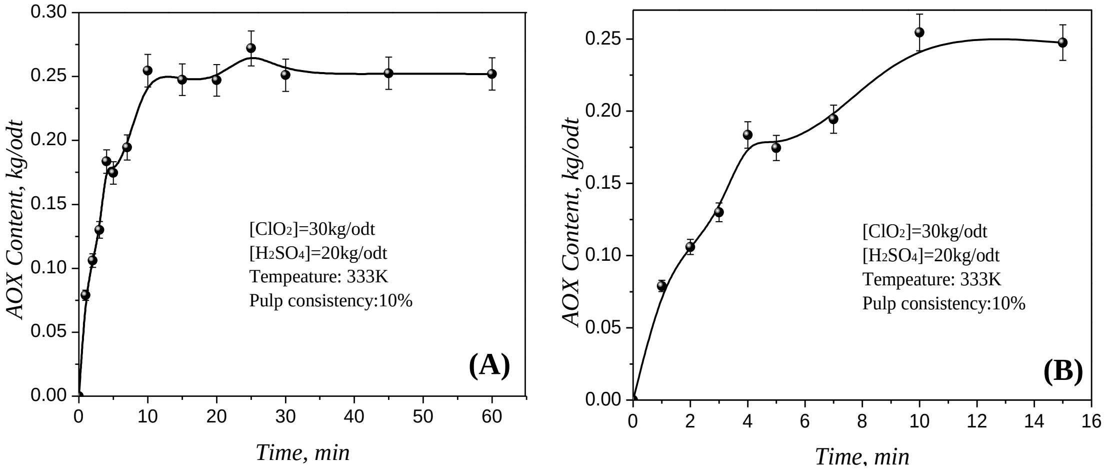

Fig. 1. Relationship between AOX content and reaction time

Within the first 10 min, the AOX content increased from 0 to 0.235 kg/odt. This suggested that some components of the pulp are very reactive towards chlorine dioxide under the acidic conditions (Hart and Hsieh 1993). As the reaction continued, the AOX content reached an asymptotic level. Obviously this phenomenon cannot be explained in the light of depletion of chlorine dioxide, as its concentration remained constant. Alternatively, it is possible that this apparent limit of AOX generation can be explained based on an assumption that the generation of AOX is from the *in-situ* generation of hypochlorous acid (HOCl) as the chlorine dioxide is reduced from the +4 state to the -1 state (chloride). The HOCl reacts very rapidly with the pulp. Once the HOCl is consumed, no more AOX is generated (Kolar *et al.* 1983; Ni *et al.* 1992; Hart and Hsieh 1993; Ni *et al.* 1994; Tarvo 2010; Tarvo *et al.* 2010). Thus, it can be seen that the formation of AOX during the chlorine dioxide bleaching of bagasse pulp was a very fast process. Figure 1(B) shows how rapidly AOX was generated during the first 15 min of bleaching.

Mathematical Model of the Kinetics Equation

Chemical reaction kinetics has been employed to study the reaction rate and the impacts of various factors of the reaction system (Roncero *et al.* 2003). To achieve the purpose of degradation process controlling, the reaction mechanisms are learned and a realistic process of the reaction is proposed though the determination of the kinetic equation (Tarvo 2010; Yuan *et al.* 2012). Many recent studies have focused on the pulp bleaching kinetics (Dence and Reeve 1996; Barroca *et al.* 2003; Tessier *et al.* 2000; Tarvo *et al.* 2008; Jain *et al.* 2009; Tarvo, 2010; Hart and Rudie 2012; Tarvo *et al.* 2012). The kinetic model for AOX generation during the chlorine dioxide bleaching of bagasse pulp can be expressed as,

$$\frac{dW}{dt} = k \cdot [ClO_2]^a \cdot [H_2SO_4]^b \cdot W^n \tag{1}$$

where dW/dt is the reaction rate, *W* is the AOX amount (kg/odt), *t* is the bleaching time (minutes), k is the AOX formation rate constant, $[ClO_2]$ is the chlorine dioxide dosage (kg/odt), and $[H_2SO_4]$ is the sulfuric acid dosage (kg/odt). The parameters *a, b,* and *n* are the reaction orders of chlorine dioxide, sulfuric acid, and AOX, respectively. Equation (1) can also be expressed in its logarithmic form:

$$log(dW/dt) = log(k) + a \cdot log[ClO_2] + b \cdot log[H_2SO_4] + n \cdot log(W) \tag{2}$$

Supposing that $M_1 = log(k) + a \cdot log[ClO_2] + b \cdot log[H_2SO_4]$, under constant reagent dosages (chlorine dioxide and sulfuric acid), Eq. 2 can be rewritten as,

$$log(dW/dt) = M_1 + n \cdot log(W) \tag{3}$$

where $log(dW/dt)$ is the *y*-coordinate, $log(W)$ is the *x*-coordinate, M_1 is the linear *y*-intercept and *n* is the slope. In Fig. 2, the value of *n* can be obtained as -1.065.

The value of a can be determined when the dosage of chlorine dioxide is changed while the other conditions held constant. Supposing that $M_2 = log(k) + b \cdot log[H_2SO_4]$; then, Eq. (2) can be rearranged to yield Eq. 4:

$$log(dW/dt) - n \cdot log(W) = M_2 + a \cdot log[ClO_2] \tag{4}$$

Thus, the value of a can be obtained by using univariate regression; the slope from the fitted line of Fig. 3(A), 0.877, is equal to a. Similarly, when the dosage of sulfuric acid is changed while the other conditions are held constant, the value of b can be determined. In this scenario, $M_3 = log(k) + a \cdot log[ClO_2]$ is substituted into Eq. (2), which is rearranged to yield Eq. 5:

$$log(dW/dt) - n \cdot log(W) = M_3 + b \cdot log[H_2SO_4] \tag{5}$$

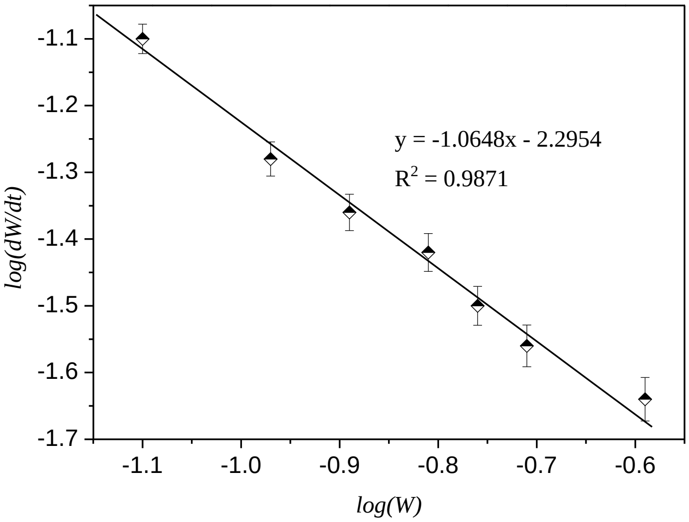

Fig. 2. Linear relationship between $log(dW/dt)$ and $log(W)$

The value of b can be determined using univariate regression, as shown in Fig. 3(B); the slope of the fitted line afforded a value of b of 0.355.

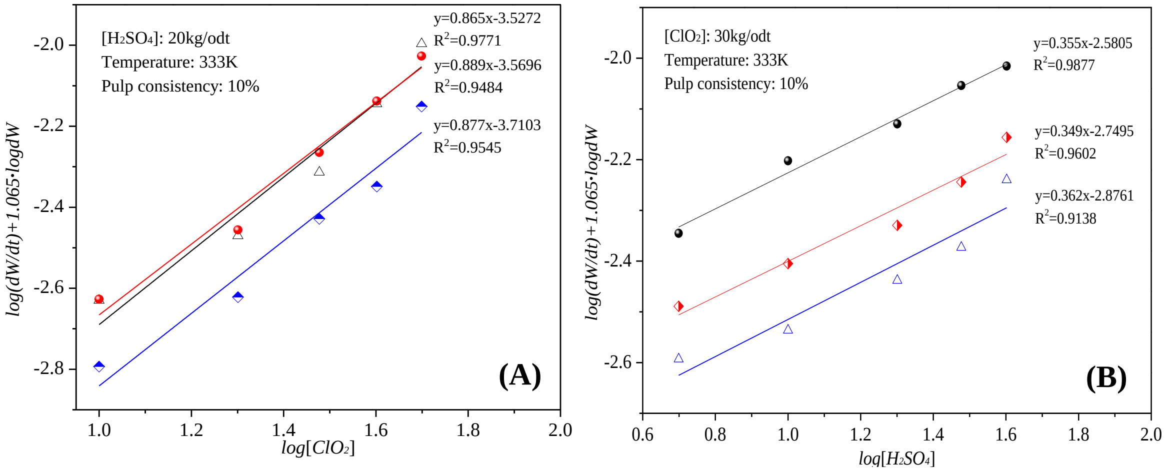

Fig. 3. Linear relationship between $log(dW/dt) + 1.065 \cdot log(W)$ and log[reagent]

The relationship between the reaction rate constant of Eq. (1) and reaction temperature was assumed to follow Arrhenius' law,

$$k = A \cdot e^{-E/R \cdot T} \tag{6}$$

where A is the frequency or pre-exponential factor, E is the activation energy (J/mol), R is the ideal-gas constant (8.314 J/(mol·K)), and T is the temperature (K). Chemicals were held at a constant value. The relationship between AOX generation and the reaction time at five different temperatures are shown in Fig. 4. Eq. (1) can be rewritten as:

$$log(k) = log(dW/dt) - a \cdot log[ClO_2] - b \cdot log[H_2SO_4] - n \cdot log(W) \tag{7}$$

The determined values of *a*, *b*, and *n*, as well as the concentration of the reactants, were substituted into Eq. 7. The AOX content at different time for each temperature from Fig. 4 were also substituted into Eq. 7. The value of *log*(*k*) for different reaction temperatures were thus calculated. From Eq. 2, Eq. 6 can be rewritten as:

$$log(k) = log(A) - {}^{E}/_{RT} \qquad (8)$$

An analysis of *log*(*k*) versus 1/*T* (Fig. 5) was carried out using univariate regression. The value of $-E/R$ was determined from the slope of Fig. 5, which was -997.98; the value of *log*(*A*) was determined from the *y*-intercept, which was 2.8201. Thus, the activation energy *E* was calculated to be 8.297 kJ/mol, and the pre-exponential factor *A* was calculated to be 660.8. The rate constant of AOX generation, *k*, was determined to be equal to $607.5 \cdot e^{-2269.2/T}$. This indicated that the activation energy of AOX generation during the chlorine dioxide bleaching of bagasse pulp is low, which means that the speed of chlorine dioxide reacting with bagasse pulp is fast, and that AOX forms quickly.

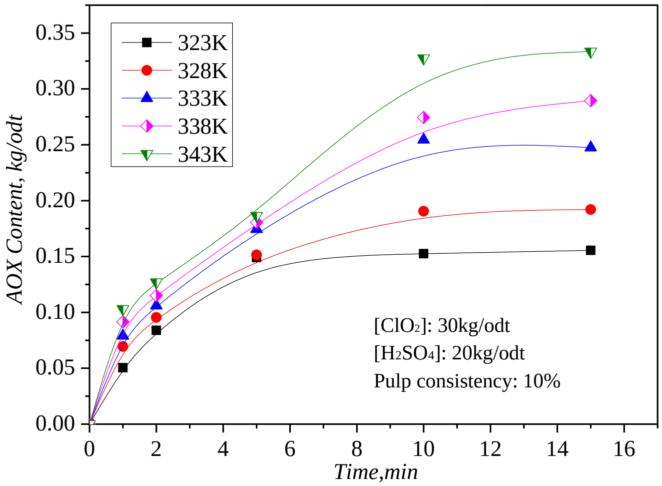

Fig. 4. Relationship between AOX content and time for different reaction temperatures

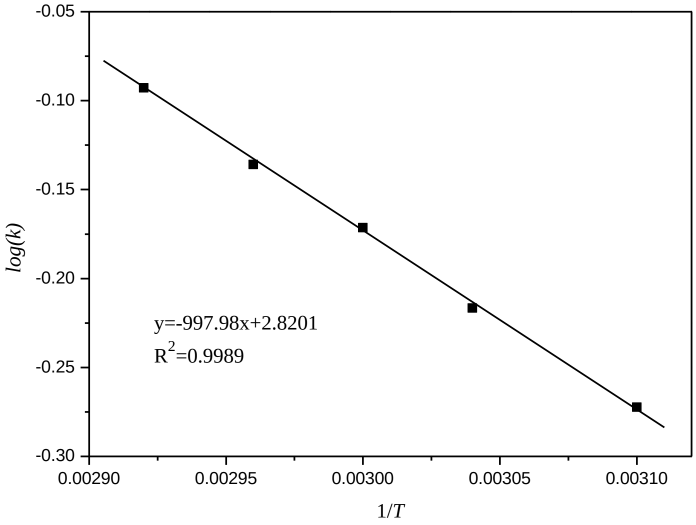

Fig. 5. Linear relationship between *log*(*k*) and 1/*T*

Because the reaction orders with respect to chlorine dioxide and sulfuric acid dosages are known, as is the activation energy, one can can obtain the complete rate equation of AOX formation as follows:

$$dW/dt = 660.8 \cdot e^{-\frac{997.98}{T}} \cdot [ClO_2]^{0.877} \cdot [H_2SO_4]^{0.355} \cdot W^{-1.065} \tag{9}$$

With this new kinetic model, it is possible to predict the content of AOX generation during the chlorine dioxide bleaching of bagasse pulp. Figure 6 shows the values of the AOX content determined experimentally versus those calculated from Eq. (9). It is apparent that the data fell around a 45° straight line, which indicates that developed kinetic model accurately predicted the rate of AOX generation during chlorine dioxide bleaching of bagasse pulp.

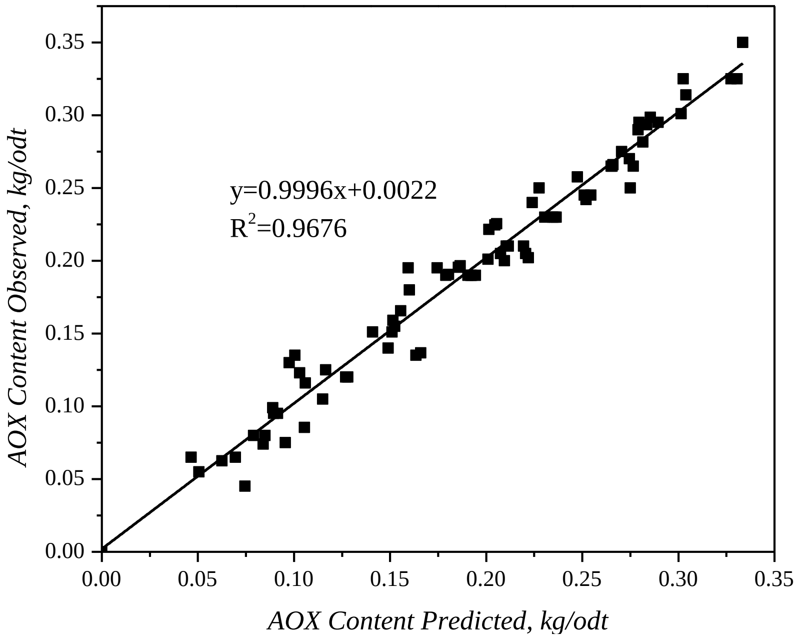

Fig. 6. Plot of experimentally determined versus kinetic model-predicted AOX content

Effect of Reagent Dosages on the AOX Formation Rate

As can be seen from the reaction order and kinetics equation of AOX generation during chlorine dioxide bleaching, all of the reaction order values were not whole integers. This indicates that the AOX formation was not a single primitive reaction, but rather complex and multi-stage. The substrate, lignin, is poorly characterized, and the inorganic reactions with chlorine dioxide and its intermediates are very complex due to numerous redox reactions that occur from +4 (ClO_2) to -1 (Cl^-) oxidation states. (Gellerstedt *et al.* 1995).

When the reaction temperature, pH, and concentration of the chemicals were held constant, the AOX generated increased from 0.05 kg/odt to 0.3 kg/odt. From these values, the AOX formation rate ratio ($\gamma_{0.3}/\gamma_{0.05}$) can be calculated:

$$\gamma_{0.3}/\gamma_{0.05} = \frac{k \cdot [ClO_2]^{0.877} \cdot [H_2SO_4]^{0.355} \cdot 0.3^{-1.065}}{k \cdot [ClO_2]^{0.877} \cdot [H_2SO_4]^{0.355} \cdot 0.05^{-1.065}} = 0.148 \tag{10}$$

It is clear that the formation rate of AOX was sharply reduced with the degradation of lignin in the chlorine dioxide bleaching of bagasse pulp. It is also apparent that the chlorine dioxide oxidation of lignin is very fast. The AOX generated is formed at the beginning of the bleaching process.

When the bleaching temperature is held constant while the chlorine dioxide dosage is increased from 10 kg/odt to 30 kg/odt and sulphuric acid dosage is increased from 0.5 kg/odt to 2 kg/odt, the AOX reaction rate ratio (γ_2/γ_1) can be calculated as:

$$\gamma_2/\gamma_1 = \frac{k \cdot 30^{0.845} \cdot 2^{0.369} \cdot W^{-1.081}}{k \cdot 10^{0.845} \cdot 0.5^{0.369} \cdot W^{-1.081}} = 4.22 \qquad (11)$$

From this analysis, it becomes obvious that the amount of AOX generated significantly increased with the increased charge of chlorine dioxide and sulfuric acid. The Tarvo *et al*. (2010) and Tarvo (2010) works indicate that as the amount of chlorine dioxide is increased, so increases the amount of the intermediate HOCl formed, which is the primary species involved in chlorinating the lignin and hexenuronic acids, which results in the increase in AOX generation. This has been well established in the chlorine dioxide delignification literature for the past 30+ years.

Effect of AOX content on the AOX formation rate

The research presented here has determined the rate equation of AOX generation during the chlorine dioxide bleaching of bagasse pulp. The relationship between AOX content and reaction time, as well as the relationship between AOX formation rate and AOX content, are shown in Fig. 1(A) and Fig. 7, respectively. In these cases, the bleaching stage began with initial dosages of sulfuric acid and chlorine dioxide of 2 kg/odt and 30 kg/odt, respectively, and at a temperature of 333 K (60 °C).

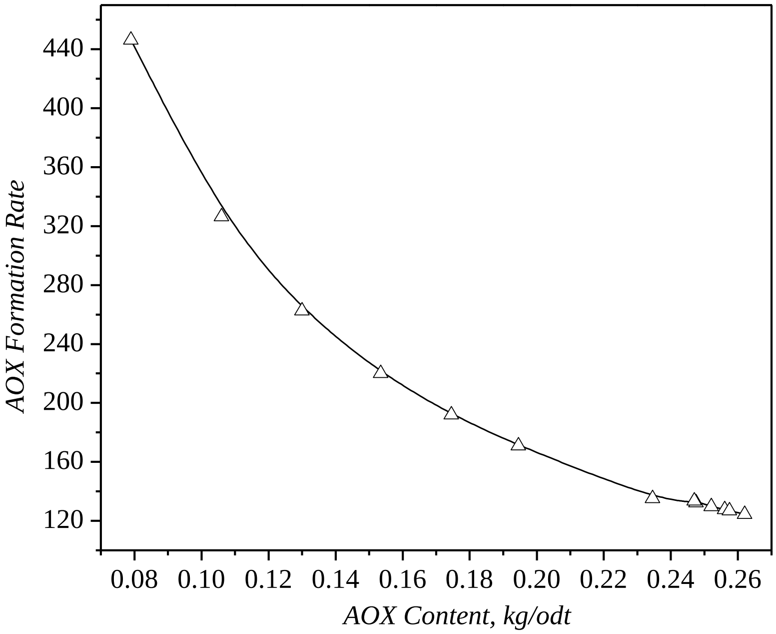

Fig. 7. Relationship between AOX formation rate and AOX content

Figure 7 shows that the reaction rate of AOX formation sharply decreased at AOX levels less than 0.235 kg/odt; afterwards, the downward trend tended to be gentler when the AOX levels were greater than 0.235 kg/odt. This indicated that within the range of this study, the reaction of AOX generation could be divided into two stages. The initial stage during the first 10 min is where a large amount of AOX is rapidly formed. The latter stage occurred 10 min later and is where the AOX formation rate significantly decreased. In this latter stage, part of the intermediate products formed in the initial stage continued to react with chlorine dioxide, which resulted in additional AOX generation in the bleaching effluent.

CONCLUSIONS

1. A macro-kinetic model of AOX generation was developed by analyzing the effect of the chlorine dioxide dosage, the sulfuric acid dosage, and the reaction temperature on the AOX formation rate from experimental data. The fit of the proposed model with the experiment results is excellent, and the deviations are within the experiment error.
2. Within the range of examined in this study, the reaction of AOX generation could be divided into two stages. The initial stage during the first 10 min is where a large amount of AOX is rapidly formed. The latter stage occurred 10 min later and is where the AOX formation rate markedly decreased. In this latter stage, part of the intermediate products formed in the initial stage continued to react with chlorine dioxide, which resulted in additional AOX generation in the bleaching effluent.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the Innovation Project of Guangxi Graduate Education (YCBZ2012003), the Scientific Research Foundation of Guangxi University (Grant No.XJZ13066), and the Guangxi Natural Fund (2012GXNSFAA053023 & 2013GXNSFFA019005).

REFERENCES CITED

Barroca, M. J. M. C., Seco, I. M., Fernandes, P. M. M., Ferreira, L. M. G. A., and Castro, J. A. A. M. (2001). "Reduction of AOX in the bleach plant of a pulp mill," *Env. Sci. Technol.* 35(21), 4390-4393.

Barroca, M. J. M. C., Simões, R. M. S., and Castro, J. A. A. M. (2001). "Kinetics of chlorine dioxide delignification of a hardwood pulp," *Appita J.* 54(2), 190-195, 202.

Barroca, M. J. M. C., Simões, R. M. S., and Castro, J. A. A. M. (2001). "Effect of unbleached kappa number on the kinetics of chlorine dioxide delignification," *Appita J.* 54(6), 532-535.

Barroca, M. J. M. C., and Castro, J. A. A. M. (2003). "Kinetics of the first chlorine dioxide bleaching stage (D_1)of a hardwood kraft pulp," *Ind. Eng. Chem. Res.* 42(18), 4156-4161.

Bjorklund, M., Germgard, U., Jour, P., and Forsstrom, A. (2002). "AOX formation in ECF bleaching at different kappa numbers - Influence of oxygen delignification and hexenuronic acid content," *TAPPI J.* 1(9), 20-24.

Brogdon, B. N. (2012). "Multistage bleach plant modeling and optimization," In: *The Bleaching of Pulp*, Hart, P. W., and Rudie, A. W. (eds.), 5th Edn., TAPPI Press, Atlanta, pp. 327-368.

Courchene, C. E., and McDonough, T. J. (1993). "Regression models to predict levels of AOX generation," Inst. of Paper Sci. and Technology, Project 3826, report 1. 1-22.

Dence, C. W., and Reeve, D. W. (1996). *Pulp Bleaching: Principles and Practice,* TAPPI Press, Atlanta, 1996.

Garcia, J. C., Lopez, F., Perez, A., Pelach, M. A., Mutje, P., and Colodette, J. L. (2010). "Initiating ECF bleaching sequences of eucalyptus kraft pulps with Z/D and Z/E stages," *Holzforschung* 64(1), 1-6.

Gellerstedt, G., Lindfors, E.-L., Pettersson, M., and Robert, D. (1995). "Reactions of lignin in chlorine dioxide bleaching of kraft pulps," *Res. Chem. Intermediat.* 21(3), 441-456.

Hart, P.W., and Hsieh, J. S. (1993). "Competing/parallel reaction of chlorine and chlorine dioxide during kraft pulp bleaching," *Chemical Engineering Communication*. 126(1), 27-41.

Hart, P. W., and Rudie, A. W. (2012). *The Bleaching of Pulp*, 5th Edn., *TAPPI Press*, Atlanta.

Juuti, S., Vartiainen, T., and Ruuskanen, J. (1996). "Formation of organochlorine compounds in kraft pulp bleaching processes," *Chemosphere* 33(12), 2431-2440.

Jain, S., Mortha, G., and Calais, C. (2009). "Kinetic models for all chlorine dioxide and extraction stages in full ECF bleaching sequences of softwoods and hardwoods," *TAPPI J.* 8(11), 12-21.

Johansson, N. G., and Fletcher, D. E. (1994). "Optimization of bleaching sequences in order to help meet environmental regulations," in: *Proceedings, International Non-Chlorine Bleaching Conference*, Miller Freeman, San Francisco, March 1994.

Kolar, J. J., Lindgren, B. O., and Petterson, B. (1983). "Chemical reactions in chlorine dioxide stages of pulp bleaching," *Wood Sci. Technol*. 17, 117-128.

Lehtimaa, T., Tarvo, V., Kuitunen, S., Jaaskelainen, A.-S., and Vuorinen, T. (2010). "The effect of process variables in chlorine dioxide prebleaching of birch kraft pulp. Part 2. AOX and OX formation," *J. Wood Chem. Technol.* 30(1), 19-30.

Liu, H.-W., Liss, S. N., and Allen, D. G. (1997). "The influence of anoxic conditioning of sludge on enhanced AOX (adsorbable organic halogen) removal in aerobic biological treatment systems," *Water Sci. Technol.* 35(2-3), 77-84.

Loureiro, P. E. G., Evtuguin, D. V., and Carvalho, M. G. V. S. (2011). "The final bleaching of eucalypt kraft pulps with hydrogen peroxide: Relationship with industrial ECF bleaching history and cellulose degradation," *J. Chem. Technol. Biotechnol.* 86(3), 381-390.

McDonough, T. J., Baromès, J. C., Carter, B. R., and Courchene, C .E. (1998). "Effects of washer efficiency on characteristics of effluents from D(EPO)D bleaching of a softwood kraft pulp," In: *Proceedings, TAPPI 1998 Environmental Conference, TAPPI Press*, Atlanta, pp. 85-92.

McDonough, T. J., Courchene, C. E., and Wiegand, P. S. (1998). "Predicting AOX generation and discharge rates at bleached kraft pulp mills," in: Proceedings, *TAPPI 1998 Cluster Rule Symposium*, TAPPI Press, Atlanta, 1998, pp. 157-170.

Ni, Y., Kubes, G. J., and van Heiningen, A. R. P. (1992). "Rate processes of chlorine species distribution during chlorine dioxide prebleaching of kraft pulp," *Nord. Pulp Pap. Res. J.* 7(4), 200-204.

Ni, Y., Shen, X., and van Heiningen, A. R. P. (1994). "Studies on the reactions of phenolic and non-phenolic lignin model compounds with chlorine dioxide," *J. Wood Chem. Technol.* 14(2), 243.

Nie, S., Liu, X., Wu, Z., Zhan, L., Yin, G., Yao, S., Song, H., and Wang, S. (2014). "Kinetics study of oxidation of the lignin model compounds by chlorine dioxide," *Chem. Eng. J.* 241(1), 410-417.

Nie, S., Wu, Z., Liu, J., Liu, X., Qin, C., Song, H., and Wang, S. (2013). "Optimization of AOX formation during the first chlorine dioxide bleaching stage (D_0) of soda AQ bagasse pulp," *APPITA J.* 66(4), 306-312.

Roncero, M. B., Torres, A. L., Colom, J. F., and Vidal, T. (2003). "Effect of xylanase on ozone bleaching kinetics and properties of *Eucalyptus* kraft pulp," *J. Chem. Technol. Biotechnol.* 78(10), 1023-1031.

Tarvo, V. (2010). "Modeling chlorine dioxide bleaching of chemical pulp," Ph.D. Dissertation, Aalto University School of Science and Technology, Espoo, Finland.

Tarvo, V., Kuitunen, S., and Lehtimaa, T. (2008). "Modeling of chemical pulp bleaching," *Nord. Pulp Paper J.* 23(1), 91-101.

Tarvo, V., Lehtimaa, T., Kuitunen, S., Alopaeus, V., Vuorinen, T., and Aittamaa, J. (2010). "A model for chlorine dioxide delignification of chemical pulp," *J. Wood Chem. Technol.* 30(3), 230-268.

Tessier, P., and Savoie, M.(2000). "Chlorine dioxide bleaching kinetics of hardwood kraft pulp," *TAPPI J.* 83(6), 1-13.

Tsai, T. Y., Renard, J. J., and Phillips, R. B. (1994). "Formation of polychlorinated phenolic compounds during high chlorine dioxide substitution bleaching, Part 1: Laboratory investigation," *TAPPI J.* 77(8), 149-157.

Yetis, U., Selcuk, A., and Gokcay, C. F. (1996). "Reducing chlorinated organics, AOX, in the bleachery effluents of a Turkish pulp and paper plant," *Water Sci. Technol.* 34(10), 97-104.

Yin, C., Renard, J. J., and Phillips, R. B. (1994). "Formation of polychlorinated phenolic compounds during high chlorine dioxide substitution bleaching, Part 2: Biotreatment of combined bleach plant effluents," *TAPPI J.* 77(8), 158-162.

Yuan, R., Ramjaun, S. N., Wang, Z., and Liu, J. (2011). "Effects of chloride ion on degradation of Acid Orange 7 by sulfate radical-based advanced oxidation process: Implications for formation of chlorinated aromatic compounds," *J. Hazard. Mater.* 196, 173-179.

Yuan, R., Ramjaun, S. N., Wang, Z., and Liu, J. (2012). "Photocatalytic degradation and chlorination of azo dye in saline wastewater: Kinetics and AOX formation," *Chem. Eng. J.* 192, 171-178.

Article submitted: May 5, 2014; Peer review completed: July 3, 2014; Revised version received and accepted: July 18, 2014; Published: July 28, 2014.