

Kinetics of Adsorbable Organic Halogen Formation During the First Chlorine Dioxide Bleaching Stage of Eucalyptus Kraft Pulp

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The emission standard for adsorbable organic halogen (AOX) has been adjusted as a mandatory assessment indicator in the papermaking industrial pollutants emission standards of China. To provide a theoretical basis to reduce AOX formation, a kinetic model of the first chlorine dioxide bleaching stage (D_0) is presented for elemental chlorine-free (ECF) bleaching of eucalyptus kraft pulp. The kinetics of the D_0 stage can be expressed as $dW/dt = 314.6e^{-20.53/RT}[H^+]^{0.21}[ClO_2]^{0.41}K^{0.98}$, where the reaction series for lignin, chlorine dioxide dosage, and H^+ concentration are 0.98, 0.41, and 0.21, respectively. The reaction activation energy was 20.53 kJ.mol⁻¹. R^2 was greater than 0.9, which means that the model was shown to have high prognostic ability and feasibility. In the D_0 stage, mostly lignin was removed and the reaction was fast. Much AOX was formed at the beginning of bleaching, and the reaction rate was primarily determined by the lignin content and chlorine dioxide dosage. H^+ existed primarily as a catalyst and had little influence on AOX formation. The AOX formation occurs easily, as the reaction activation energy is less than 30 kJ.mol⁻¹.

Keywords: Eucalyptus Kraft pulp; ECF bleaching; Kinetic model; AOX; First chlorine dioxide bleaching stage

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INTRODUCTION

Chlorine dioxide (ClO_2) is the main bleaching agent in elemental chlorine-free (ECF) bleaching technology. It has good selectivity for lignin removal, but there will be some adsorbable organic halogen (AOX) formed in the bleaching process (Nakamata *et al.* 2010; Bajpai 2012). AOX contains over 300 different organic chlorides, some of which are toxic because they are lipophilic and demonstrate bioaccumulation; this part of the AOX encompasses the most persistent organic pollutants (POPs) in the ECF bleaching process (Mckague *et al.* 1988; Suntio *et al.* 1988). Pulp bleaching wastewater pollution problems have become increasingly prominent with increasing environmental safety requirements, which has spurred more interest by researchers (Watanabe *et al.* 2014). The AOX content of pulp and paper wastewater has been subjected to mandatory assessment in pollutant emission standards for the papermaking industry in China (Chen *et al.* 2012).

Researchers generally study the ClO_2 bleaching stage to understand the causes of AOX formation, as the vast majority of AOX comes from the first ClO_2 bleaching stage in the ECF bleaching process (Tuula *et al.* 2010). In the global pulp and paper industry, ClO_2 has become one of the most basic ECF bleaching agents, and it is primarily used to

remove lignin from the pulp (Bajpai 2015). Svenson *et al.* (2006) found that the pH requirement for the ClO_2 oxidation of lignin was higher than other conditions, and the reaction mostly took place in the aromatic ring of lignin under acidic conditions, making it easy to produce AOX. However, the side chains of lignin were mostly oxidized under alkaline conditions, and AOX was rarely formed under these conditions. Chlorite and hypochlorite were produced when the phenolic lignin was oxidized by ClO_2 , while only chlorite was formed when non-phenolic lignin was oxidized (Hoigné and Bader 1994). Meanwhile, at the beginning of the ClO_2 bleaching, lignin, after oxidation, exists in two forms: small and large fragments. The vast majority of lignin is oxidized by ClO_2 into small fragments (Pei *et al.* 2016).

Brage *et al.* (1991) pointed out that ClO_2 oxidation of lignin could be explained using single electron transfer theory, based on studies of ClO_2 -oxidized phenolic and non-phenolic lignin model compounds. The rate-determining step of the benzene oxidation process was the formation of a charge transfer complex. Joncourt *et al.* (2000) proposed that AOX forms primarily because ClO_2 produces hypochlorous acid (HClO) when it reacts with lignin in the process of ClO_2 bleaching. With a low pH, HClO can rapidly become a chlorine molecule (Cl_2) and then promote the production of large quantities of AOX. They further verified the rationality of this inference by varying the bleaching process. Björklund (2004) studied the hypochlorous acid root and AOX formation in the process of birch ECF bleaching. It was pointed out that the AOX formation, which with stable structure, was related to the content of Klason lignin in the pulp in the D_0 stage, thus offering a theoretical foundation for follow-up studies of AOX reduction technology. The relationship between AOX formation and Cl_2 and ClO_2 dosage has been studied by Gonzalez and Zaror (2000) using Chile pine and eucalyptus unbleached kraft pulp. Experimental results showed that AOX generation was decreased as ClO_2 was substituted for Cl_2 as a bleaching agent. It was concluded that AOX formation was greatly influenced by the lignin content in the pulp, and the relationship between AOX formation and Cl_2 and ClO_2 dosage was deduced. Tessier and Savoie (2000) studied the kinetics of chlorine dioxide bleaching of hardwood kraft pulp. They determined the optimal range of the Kappa factor and temperature by constructing a mathematical model.

This paper explores AOX formation by establishing an AOX formation relationship curve over time. The corresponding mathematical model was established on the basis of existing experimental results to provide a basis for the study of the reaction mechanism of AOX formation from eucalyptus pulp.

EXPERIMENTAL

Materials

Sodium hydroxide, sulfuric acid, and hydrogen peroxide (H_2O_2) were obtained from Cheng du Kelon chemical reagent factory (Cheng du, China). ClO_2 solution was obtained from the Pumiao Paper Mill (Guangxi, China). The eucalyptus kraft pulp came from a pulp mill located in Guangxi China. One pulp's Kappa number was 12.5, the viscosity was $1222.8 \text{ mL}\cdot\text{g}^{-1}$, and the brightness was 42.28 % ISO, and another pulp's Kappa number, viscosity, and brightness were 16, $1286.6 \text{ mL}\cdot\text{g}^{-1}$ and 41.53 % ISO, respectively.

Methods

The method for testing Kappa number was referencing TAPPI Useful Method U M 246, the viscosity was tested using a DP-02 type pulp viscosity tester, and the brightness was tested using a YQ-Z-48A brightness and color tester.

The bleaching reaction was carried out in a sealed polyethylene bag using the process D₀E_pD₁; 10 g of unbleached bone dry pulp was mixed with bleaching fluid, and the pulp concentration was adjusted to 10% in a sealed bag (Du *et al.* 2015). Mixing was allowed to take place for 5 min, after which the sealed bag was placed in a constant temperature water bath. Waste liquid was collected when the reaction time achieved the set point; 5 mL of the effluent was pipetted out to dilute it 200 times and adjust the pH value.

The D₀E_pD₁ bleaching conditions remained constant throughout the experiments. The pulp concentration was 10%. In the D₀ stage, the ClO₂ dosage was 2.8%, pH was 2.5, temperature was 60 °C, and time was 60 min. In the E_p stage, the H₂O₂ dosage was 1.25%, the dosage of NaOH was 2.5%, temperature was 65 °C, and time was 105 min. In the D₁ stage, the ClO₂ dosage (available chlorine) was 0.2%, pH was 4.5, temperature was 60 °C, and time was 55 min.

The content of AOX in the bleaching effluent was measured using a Multi X2500 type total organic halogen analyzer (Analytik Jena AG, Jena, Germany). Processing and analysis of AOX from the effluent sample were performed according to the methods of Yuan *et al.* (2012) and Nie (2013). The temperature was controlled by a HH - SY21 - NI4C thermostatic water bath.

RESULTS AND DISCUSSION

Establishment of Kinetics Model

In the process of ClO₂ bleaching, chloride and HClO were produced by ClO₂ reacting with lignin. Subsequently, halogenated organic molecules were produced from the reaction between HOCl and lignin. It is generally believed that lignin can react with HOCl, which is more easily oxidized and contains less aromatic structures than other lignin in the pulp (Gunnarsson and Ljunggren 1996; Joncourt *et al.* 2000). Most of the HOCl was consumed by non-aromatic structures. As a result, less chlorinated aromatic compounds were generated. A typical reaction was HOCl reacting with a double bond to generate chlorohydrin. It is easier to remove chlorine in the chlorohydrin than the ClO₂ products in the alkali extraction (Elder 1998; Zeng *et al.* 2010).

Many recent studies have focused on pulp bleaching kinetics (Hart and Rudie 2012; Nie *et al.* 2014). Therefore, there were only three main factors considered in this paper: the effects of ClO₂, H⁺, and lignin on the formation of AOX. Referring to chemical reaction kinetics and the basis of existing research (Tarvo *et al.* 2010; Nie *et al.* 2014), the kinetic model for AOX formation during the ClO₂ bleaching of eucalyptus kraft pulp can be expressed as Eq. 1,

$$dW/dt=k[H^+]^\alpha[ClO_2]^\beta K^\gamma \quad (1)$$

where dW/dt is the reaction rate, W is AOX formation (kg.t⁻¹), k is the AOX formation rate constant, t is the bleaching time (minutes), and K is the Kappa number of pulp.

The parameters α , β , and γ are the reaction orders of H^+ , ClO_2 , and lignin, respectively, in the lignin removal reaction. Equation (1) also can be expressed in its logarithmic form:

$$\lg(dW/dt)=\lg(k [H^+]^\alpha [ClO_2]^\beta K^\gamma)=\lg k + \alpha \lg[H^+] + \beta \lg[ClO_2] + \gamma \lg[K] \quad (2)$$

Effect of pH on AOX Formation

Up to this point, experimental data for studying reaction mechanisms has been primarily obtained through two ways (Bansal *et al.* 2009; Papari and Hawboldt 2015). The first method uses isolated variables, measuring how the concentration of a reactant changes with time in the process of reaction, while the concentration of other reactants remain unchanged. However, such an approach may not produce an exact rate of reaction due to the fact that large differences exist between experiments and practical production, and the concentrations of other reactants are not constant in the actual production.

The second way is called the initial concentration method, changing the initial concentration of one reactant and measuring how the concentration of the reactant changes over time in the process of reaction. While the initial concentrations of other reactants are specified, they also will be changing with time in the process of reaction. The bleaching conditions here are close to actual production conditions. Therefore, the second way was adopted for this article, to simulate industrial bleaching conditions as much as possible. First, a corresponding relationship between AOX formation and time was determined by the kinetic experiments with various initial concentrations. Then, the corresponding initial rate was obtained by plotting.

In this study, as the initial pH was changed from 2 to 3, AOX formation with time was measured, and the results are shown in Fig. 1.

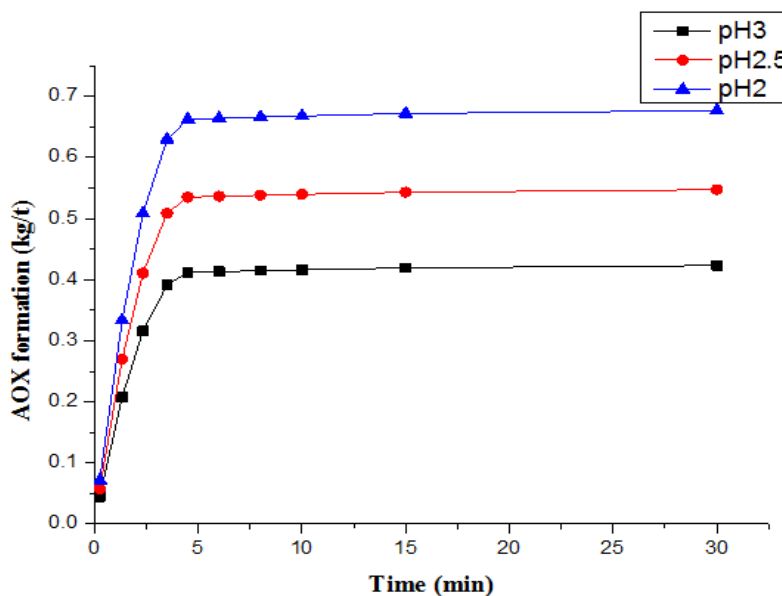


Fig. 1. AOX formation with time under various pH conditions

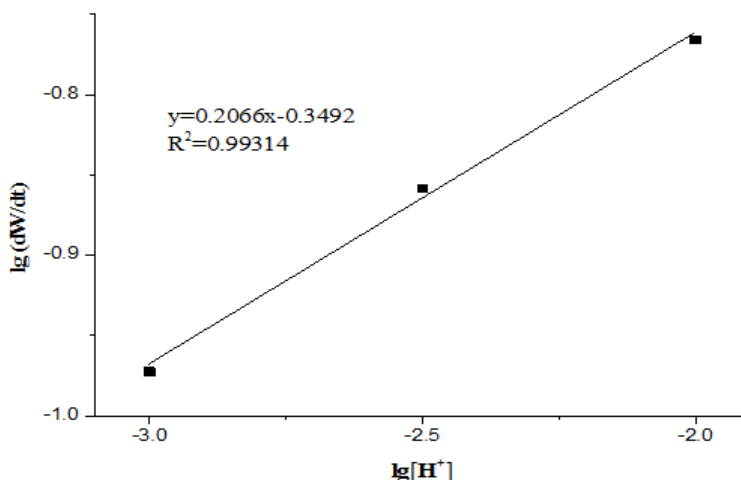


Fig. 2. Linear relationship between $\lg(dW/dt)$ and $\lg[H^+]$

The initial rate of AOX formation at various pH values was obtained by plotting; the results are shown in Fig. 2, where the linear regression equation can be written as Eq. 3:

$$\lg(dW/dt) = \lg(k[\text{ClO}_2]^\beta K^\gamma) + \alpha \lg([H^+]) \quad (3)$$

The determination coefficient R^2 was 0.99, which shows that the fit with the data was excellent. The value of α was 0.21, according to the slope of Fig. 2. As shown in Fig. 1, AOX formation was 0.663 kg.t^{-1} pulp at pH 2 after 5 min, and it was 0.677 kg.t^{-1} pulp at 30 min. The experimental results showed the order of H^+ reaction was smaller, which indicates that H^+ plays a catalytic role in the reaction.

H^+ concentration has an influence on AOX formation (Nie *et al.* 2014). AOX formation increased from 0.42 to 0.68 kg.t^{-1} pulp when the H^+ concentration increased from pH 3 to pH 2. This indicates that the activity of the bleaching solution and the reaction pathway were influenced by H^+ concentration.

Effect of ClO_2 Dosage on AOX Formation

In this study, the dosages of ClO_2 were 0.7%, 1.4%, and 2.8%. The change in AOX formation with time is shown in Fig. 3.

The initial rate of AOX formation at various ClO_2 dosages could be calculated by a plotting method. The $\lg(dW/dt)$ was the y-coordinate and $\lg(\text{ClO}_2)$ was the x-coordinate, as shown in Fig. 4. The linear regression equation was obtained as Eq 4:

$$\lg(dW/dt) = \lg(k[H^+]^\alpha K^\gamma) + \beta \lg([\text{ClO}_2]) \quad (4)$$

The determination coefficient R^2 was 0.98, so the fit with the data was good. The value of β was calculated to be 0.41 using the slope. As shown in Fig. 3, when the ClO_2 dosage was 2.8%, AOX formation was 0.535 kg.t^{-1} pulp after 5 min; after 30 min, AOX formation was 0.547 kg.t^{-1} pulp.

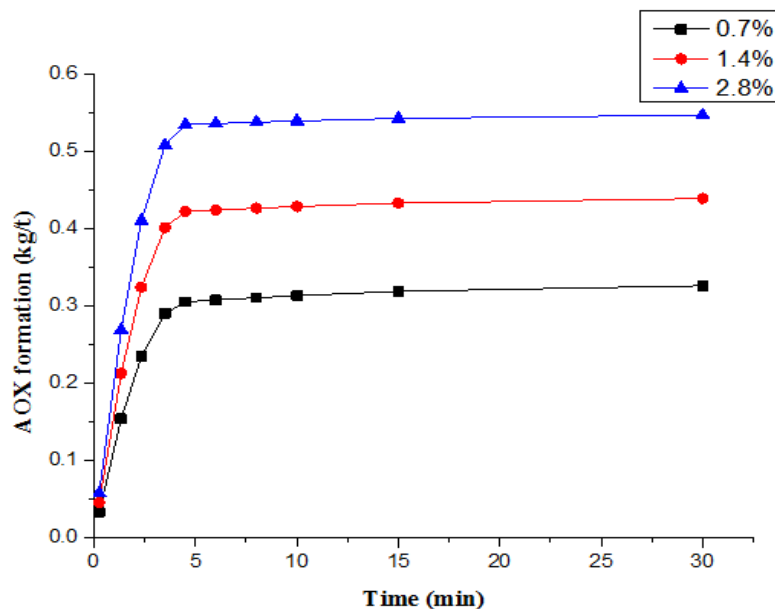


Fig. 3. AOX formation with time under various ClO_2 dosage conditions

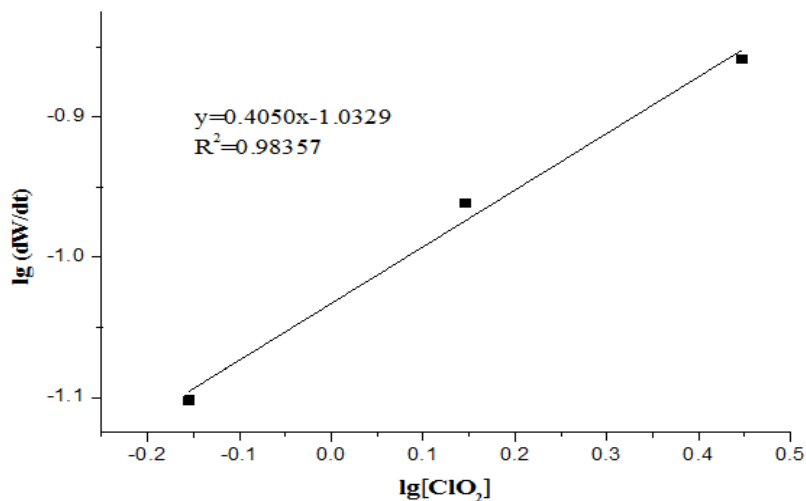


Fig. 4. Linear relationship between $\lg(dW/dt)$ and $\lg[\text{ClO}_2]$

ClO_2 dosage has a great influence on AOX formation (Tarvo *et al.* 2010). As the ClO_2 dosage was increased from 0.7% to 2.8%, AOX formation increased from 0.33 to 0.55 $\text{kg}\cdot\text{t}^{-1}$ pulp. Compared with the reaction order with respect to H^+ concentration, ClO_2 dosage reaction order was larger. One possible reason was that the main reactant content directly determines the number of active factors in the reaction, which affects the reaction rate.

Effect of Kappa Number on AOX Formation

The effect of time on AOX formation with various Kappa numbers (9, 12.5, and 16) was studied; the results are shown in Fig. 5.

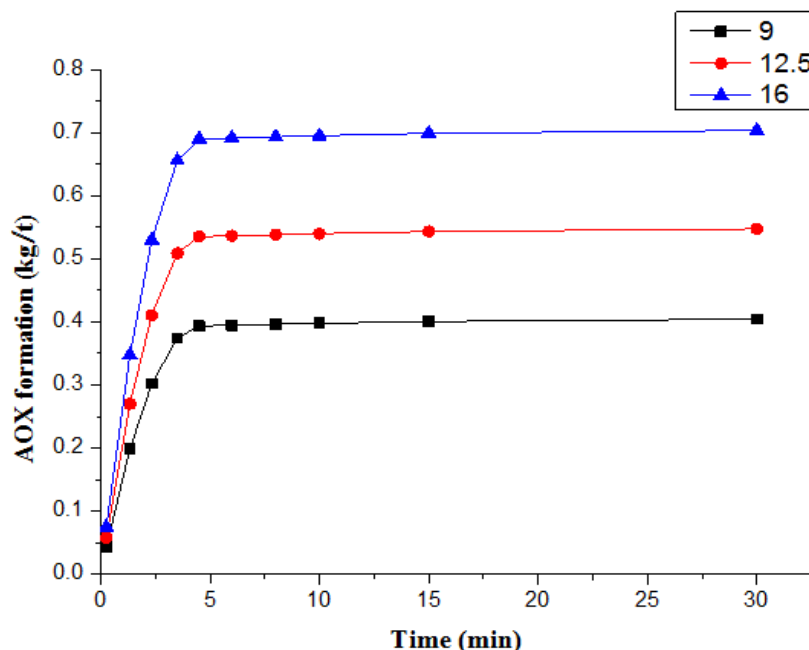


Fig. 5. AOX formation with time under various Kappa number conditions

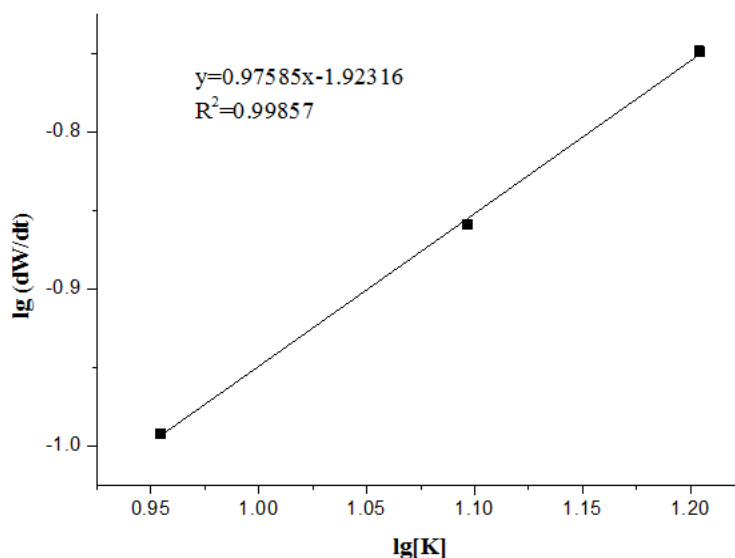


Fig. 6. Linear relationship between $\lg(dW/dt)$ and $\lg[K]$

The initial rate of AOX formation at various Kappa numbers was calculated using plotting. The $\lg(dW/dt)$ was the y-coordinate, and $\lg(K)$ was the x-coordinate, as shown in Fig. 4. The linear regression equation was calculated as Eq. 5:

$$\lg(dW/dt) = \lg(k[H^+]^\alpha [ClO_2]^\beta) + \gamma \lg K \quad (5)$$

The determination coefficient R^2 was 0.99, which shows that the fit with the data was good, and γ was obtained as 0.98. In Fig. 5, when the Kappa number was 16, AOX formation was 0.690 kg.t^{-1} pulp 5 min after the beginning of reaction, but it was 0.704 kg.t^{-1} pulp at 30 min.

AOX formation was affected by Kappa number. It increased from 0.40 kg.t⁻¹ pulp to 0.70 kg.t⁻¹ pulp as the Kappa number increased from 9 to 16. Compared with the reaction order of H⁺ concentration and ClO₂ dosage, the reaction order of Kappa numbers was the highest. This indicated that the difficulty of ClO₂ reaction and the easy removal lignin were determined by the total lignin content, which has a great influence on the reaction rate.

Effect of Temperature on AOX Generation

According to the Arrhenius equation, the relationship between temperature and reaction constant k is represented by Eq 6,

$$k = Ae^{-Ea/RT} \quad (6)$$

where A is the pre-exponential factor, E is the reaction activation energy (kJ.mol⁻¹), R is the gas constant (8.314 J.mol⁻¹), and T is absolute temperature (K). AOX formation at various temperatures (50, 60, and 70 °C) with time is shown in Fig. 7.

In Fig. 8, R^2 was 0.99, so the fit with the data was suitable. The activation energy of AOX formation reaction and the exponential factor were calculated as 20.53 kJ.mol⁻¹ and 314.6 s⁻¹, respectively.

As shown in Fig. 7, when the temperature was 70 °C, AOX formation was 0.664 kg.t⁻¹ pulp after 5 min; after reaction for 30 min, AOX formation was 0.677 kg.t⁻¹ pulp.

The reaction activation energy of the D₀ stage was low, indicating that the chemical reaction can be carried out at room temperature without heating or adding catalyst. The rate of reaction in the bleaching effluent was determined at various temperatures, and AOX formation increased from 0.44 kg.t⁻¹ to 0.68 kg.t⁻¹ pulp when the temperature increased from 50 to 70 °C. In summary, the activation energy of AOX formation was low. This indicated that AOX was easy to generate in the initial stage of the ClO₂ bleaching process.

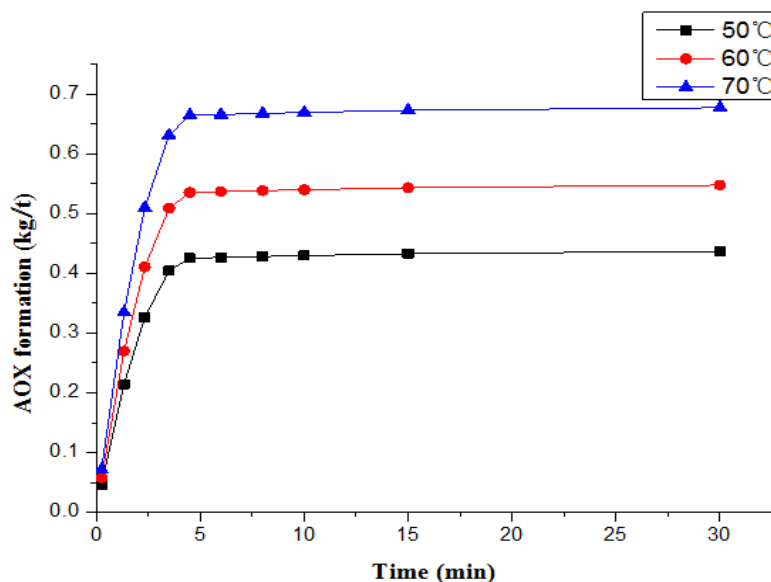


Fig. 7. AOX formation with time under various temperature conditions

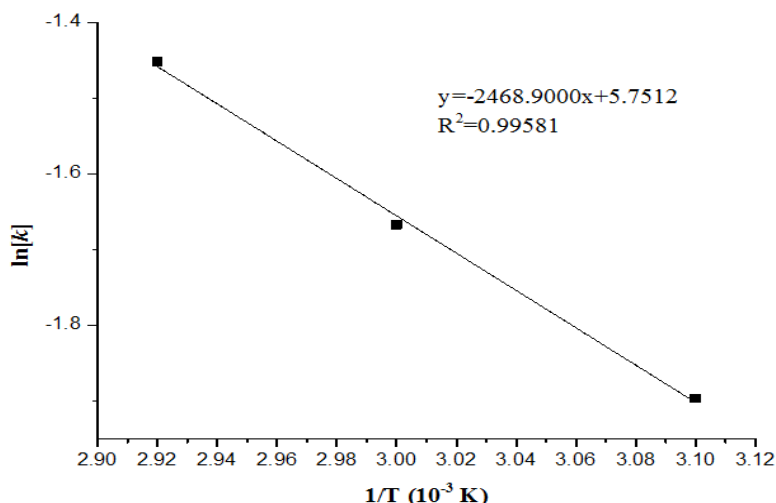


Fig. 8. Linear relationship between $\lg[k]$ and $1/T$

CONCLUSIONS

1. The D_0 stage kinetic model of AOX formation in the ECF bleaching process can be expressed as $dW/dt = Ae^{-20.53/RT}[H^+]^{0.21}[ClO_2]^{0.41}K^{0.98}$. The exponents of reaction to lignin, chlorine dioxide content, and H^+ concentration were 0.98, 0.41, and 0.21, respectively. The activation energy of the reaction was $20.53 \text{ kJ}\cdot\text{mol}^{-1}$. The model prediction value and the experimental value have a perfect linear correlation, with a correlation coefficient $R > 0.9$. This illustrates that the forecasting model has high accuracy and can be used for predictions of AOX formation from eucalyptus kraft pulp during ECF bleaching.
2. In the D_0 stage, a large amount of lignin was removed and the reaction rate was extremely fast. More than 97% of the AOX was produced at the beginning 5 min of the bleaching stage, and the reaction rate was primarily determined by the amount of lignin in the pulp and ClO_2 dosage. H^+ played a catalytic role in the reaction and has less influence on the formation of AOX. The activation energy of the D_0 stage was less than $30 \text{ kJ}\cdot\text{mol}^{-1}$, which indicates that the reaction is easy to carry out.

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