ELSEVIER

Chemical Engineering Journal 108 (2005) 101–108

Chemical Engineering Journal

www.elsevier.com/locate/cej

Kinetic modeling of the promoted and unpromoted wet oxidation of debarking evaporation concentrates

Svetlana Verenich[a,*], Kati Roosalu[b], Marjaana Hautaniemi[b], Arto Laari[b], Juha Kallas[b]

[a] *NCRC, North Carolina State University, 2401 Research Drive, Raleigh, NC 27695-8301, USA*
[b] *Department of Chemical Technology, Lappeenranta University of Technology, P.O. Box 20, 53850 Lappeenranta, Finland*

Received 19 April 2004; received in revised form 22 December 2004; accepted 11 January 2005

Abstract

In the present study, the wet oxidation (WO) of a debarking evaporation concentrate was studied at a temperature range of 383–473 K. To improve the oxidative process, the pH level of the wastewater was in some experiments set to 13 using a sodium hydroxide solution. Additionally, in some experiments H_2O_2, in amounts of 0.2 g per 1 g of COD was introduced into the reaction system as a promoter. All three cases, unpromoted WO, hydrogen peroxide promoted WO and WO in alkaline media, were modeled. In order to explain the experimental data, the model by Verenich and Kallas [S. Verenich, J. Kallas, Wet oxidation of concentrated wastewaters: the kinetic modelling, in: Proceedings of the IWA 2nd International Conference on Oxidation Technologies for Water and Wastewater Treatment, Clausthal-Zellerfeld, Germany, 2000] was modified and the kinetic parameters, the activation energies and frequency factors, were estimated along with the sensitivity analysis, a study on the cross-correlation and identification of the parameters. The recast model explains the experimental data well. The addition of hydrogen peroxide reduced the activation energies of the oxidative reactions.

Keywords: Debarking; Wet oxidation; Acceleration; Hydrogen peroxide; Kinetics; Modeling

---

1. Introduction

Industrial activity has been recognized as causing water pollution through atmospheric depositions and wastewater discharge. The pulp and paper industry is the world's sixth largest polluter (after the oil, cement, leather, textile, and steel industries), as it discharges a variety of liquid wastes into the environment [2]. The primary wood treatment process or wood debarking is almost totally ignored in environmental studies. However, the effluent produced in this process is currently one of the most toxic wastewaters in the papermaking industry. The wastewaters from the debarking process are heavily contaminated by fatty and resin acids, tannins, lignins and their derivatives. The presence of lignins and their derivatives, as well as of polymerized tannins, causes these wastewaters to be also highly colored. Tannins are highly toxic polar phenolic polymers, which contribute as much as up to 50% of the chemical oxygen demand (COD) of the wastewater [3]. Previously, the treatment of debarking process water using ozone [4] and a combination of chemical flocculation and activated sludge [5] led to a large dose of the oxidant being consumed or to a decrease in the efficiency of the treatment with the increase in the concentration of the organic matter. Oxidative polymerization is a way of neutralizing the toxicity of the debarking effluent constitutes, but it does not, however, eliminate the pollutants from the aqueous solution. In this work, wet oxidation (WO) is considered as a suitable method for the elimination of contaminants from such effluents.

WO is a well-established method for the purification of industrial wastewaters that cannot be treated using traditional purification processes because of their high concentration of organic matter and/or their toxicity [6,7]. The WO process involves the use of oxygen as the oxidizing agent for

---

* Corresponding author. Tel.: +1 919 513 4778; fax: +1 919 515 4556.
E-mail address: svetlana_verenich@ncsu.edu (S. Verenich).

1385-8947/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2005.01.003

Nomenclature

Biodegradability	BOD/COD × 100 (%)
c_{A}	concentration of organics in lump A (mol/m^3)
$c_{\mathrm{A,e}}$	concentration of unoxidized organics in lump A at 383–473 K (mol/m^3)
$c_{\mathrm{A,o}}$	initial concentration of organics in lump A (mol/m^3)
c_{B}	concentration of organics in lump B (mol/m^3)
$c_{\mathrm{B,e}}$	concentration of unoxidized organics in lump B at 383–473 K (mol/m^3)
$c_{\mathrm{B,o}}$	initial concentration of organics in lump B (mol/m^3)
$c_{\mathrm{H_2O_2}}$	concentration of hydrogen peroxide in solution (mol/m^3)
$c_{\mathrm{O_2}}$	concentration of oxygen in solution (mol/m^3)
c_{OH}	concentration of hydroxyl ions in solution (mol/m^3)
E_{a}	activation energy (kJ/mol)
k	reaction rate constant (min^{-1})
k^0	frequency factor (min^{-1})
K^0	frequency factor defined in Eq. (6) (min^{-1})
K^0_{mean}	frequency factor defined by Eq. (8) (min^{-1})
R	gas constant (8.314 J mol^{-1} K^{-1})
t	reaction time (min)
T	temperature (K)
T_{mean}	mean temperature between the lowest and the highest temperatures used in the estimation (K)

Subscripts

i	reaction pathways, 1, 2 or 3

Superscripts

n	oxygen reaction order for the reaction pathways of 1, 2 or 3

the removal of pollutants in the liquid phase under elevated conditions (0.5–20 MPa and 398–573 K). WO is, however, a complex process, especially if it involves the oxidation of industrial streams that contain large numbers of organic compounds. The oxidative process proceeds along complex reaction pathways and leads to the formation of different intermediates. It is impossible to trace all the chemical transformations that take place in industrial wastewaters. However, merging different compounds, which have similar properties or structures, into certain lumps allows for the oxidation process of multicomponent systems to be described. Takamatsu et al. [8], Foussard et al. [9], Li et al. [10], Donlagic and Levec [11], Verenich and Kallas [12], etc. have lumped organic compounds according to their solubility and evaporative properties, biodegradability, ability to be oxidized to carboxylic acids that are the most resistant to oxidation substances. Since WO requires rather high temperatures, the addition of a catalyst to mitigate the operating conditions and attempts to simulate this process have been also undertaken. Belkacemi et al. [13] and Zhang and Chuang [14] have proposed models that could fairly describe catalytic WO.

The present study focuses on the modeling of the hydrogen peroxide promoted and unpromoted WO of a debarking concentrate. Hydrogen peroxide decomposes in aqueous solution with the formation of hydroxyl radicals that, in turn, react with organic substances, catalyzing or promoting the WO process. Moreover, some reactions were conducted under alkaline conditions, as the phenolic compounds present in the studied wastewater in large amounts are oxidized much faster at high pH values than at neutral (original) pH [15]. The lumped model developed by Verenich and Kallas [1] was applied and recast for this particular case.

2. Kinetic model

In the model developed by Verenich and Kallas [1], the reaction system was divided into lumps with respect to the biodegradability of the organic substances. The first lump, A, includes the compounds that are difficult to oxidize biologically and was obtained by subtracting the biochemical oxygen demand ($\mathrm{BOD_5}$) from the COD. As can be seen from Fig. 1, the further oxidation of A leads to the formation of a biodegradable compound, B, and to the reaction end-products. Lump B is characterized via BOD analysis and usually incorporates the products of partial oxidation, such as carboxylic acids, aldehydes, alcohols or other substances, that can be utilized by microorganisms. The latter (lump B) also undergoes further oxidation into carbon dioxide and water.

This reaction system is expressed mathematically as follows:

$$-\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} = (k_1 + k_2)c_{\mathrm{A}} \tag{1}$$

$$-\frac{\mathrm{d}c_{\mathrm{B}}}{\mathrm{d}t} = -k_2 c_{\mathrm{A}} + k_3 c_{\mathrm{B}} \tag{2}$$

where

$$k_{\mathrm{i}} = k_{\mathrm{i}}^0 \exp\left(-\frac{E_{\mathrm{ai}}}{RT}\right) c_{O_2}^{\mathrm{ni}} \tag{3}$$

At "zero" time, the concentrations of lumps A and B are the concentrations of $c_{\mathrm{A,0}}$ = [COD minus $\mathrm{BOD_5}]_0$ and $c_{\mathrm{B,0}} = [\mathrm{BOD_5}]_0$, respectively.

Due to the recalcitrant properties of the studied wastewater (as can be seen further from experimental results), Eqs. (1)

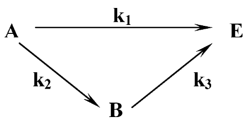

Fig. 1. The wet oxidation reaction network [1].

and (2) can be rewritten, according to Foussard et al. [9], as Eqs. (4) and (5)

$$-\frac{dc_A}{dt} = (k_1 + k_2)(c_A - c_{A,e}) \tag{4}$$

$$-\frac{dc_B}{dt} = -k_2(c_A - c_{A,e}) + k_3(c_B - c_{B,e}) \tag{5}$$

where $c_{A,e}$ and $c_{B,e}$ are quantities of organic compounds that cannot be oxidized at given temperature range.

The activation energies and frequency factors for the above model were obtained using a parameter estimation procedure. The computations were performed using the MODEST software package [16] that is designed for various tasks of model building such as simulation, parameter estimation, sensitivity analysis and optimization. The software consists of a FORTRAN 95/90 library of objective functions, solvers and optimizers that are linked to model problem-dependent routines and the objective function.

The parameters were estimated from the systems of differential equations using the least squares method. The differential equations were solved by means of linear multistep methods implemented in ODESSA that is based is on the LSODE software [17].

Along with common indicators, such as the regression coefficient, R^2, the standard error and correlation matrix, Ω, a graphical sensitivity analysis was performed. The two-dimensional sensitivity contour plots produce a "landscape" of the regression coefficient for the identification of the probable region of the optimum values. The more centered the contours are, the better the parameters are identified.

3. Experimental

3.1. Materials

For the present research, an evaporation concentrate of debarking process water was obtained from a Finnish paper mill. It had a very dark brown color and the dry-solid content was about 20–25%. More than half (61–62%) of the solid matter present in the concentrate consisted of organic compounds. The obtained concentrate had the following characteristics: 47–60 g/L of COD; 15–25 g/L of dissolved organic carbon (DOC); 30–40% of biodegradability; 30–55 Pt–Co color unit of color; 5.5–9 g/L of soluble tannin/lignin, and pH of 5.5–7.0.

3.2. Experimental procedure

The experimental runs were conducted in a 300-ml high-pressure autoclave (Parr Instrument Co., Moline, IL) made of a nickel–chromium–molybdenum alloy. The reactor was equipped with a gas inlet and a liquid sampling tube, a gas release valve and a four-bladed turbine type impeller. A rotation speed of 900 min^{-1} was maintained to ensure proper interfacial oxygen transfer. An external heating jacket, thermal sensors and a cooling loop implemented inside the reactor permitted the reaction temperature to be maintained within ±1 K from a set value.

Debarking concentrate (175 ml) at a pre-adjusted pH, if necessary, was placed in the reactor. After the reactor was sealed, it was heated to the desired reaction temperature. When the set temperature was achieved, pure oxygen was introduced into the reactor via the gas inlet line. For hydrogen peroxide promoted wet oxidation (PWO), oxygen inlet line was opened immediately after the injection of hydrogen peroxide by nitrogen gas via a liquid-charging pipette. Six liquid

Table 1
Relative concentration of organic material (COD_t/COD_o) observed during the experimental runs and predicted by the models

Time (min)	COD_t/COD_0: experimental/predicted		
	383 K	423 K	453 K
Unpromoted wet oxidation			
0	1.0/1.0	1.0/1.0	1.0/1.0
60	0.94/0.97	0.87/0.86	0.80/0.81
120	0.89/0.93	0.81/0.80	0.74/0.79
	383 K	423 K	443 K
Wet oxidation in alkaline media			
0	1.0/1.0	1.0/1.0	1.0/1.0
60	0.82/0.88	0.74/0.68	0.66/0.66
120	0.81/0.80	0.72/0.65	0.61/0.66
	383 K	423 K	443 K
H_2O_2 promoted wet oxidation in alkaline media			
0	1.0/1.0	1.0/1.0	1.0/1.0
60	0.78/0.80	0.72/0.71	0.70/0.69
120	0.75/0.76	0.70/0.67	0.66/0.69

samples were extracted periodically during the 2-h reaction period and analyzed for their COD and BOD_5 characteristics, color and pH. After 2 h, the oxidative reaction was stopped by closing the oxygen inlet line and cooling the autoclave rapidly with chilled water.

The COD analysis was performed by means of the closed reflux dichromate method [18] using a COD reactor (Hach Company, Loveland, CO) and a direct-reading spectrophotometer DR/2000. The BOD analysis was assessed with the help of a SensorBOD device developed by Dr. Lange & Co. (Germany), which allows for BOD values identical to BOD_5 to be obtained. A more detailed procedure of the analysis can be obtained elsewhere [12]. The apparent color of the samples was measured using the HACH direct-reading spectrophotometer DR/2000 at a wavelength of 455 nm.

4. Results

4.1. Unpromoted WO

The WO experiments were conducted at a temperature range of 383–473 K and oxygen partial pressure of 1 MPa for 2 h. The measurement of COD indicated the resistant nature of the organic material present in the wastewater (see Table 1). At 443 K, the amount of organics (COD) remained at as constant value of about 74.6% of the initial COD after a reaction time of 2 h. These results prompted us to employ the approach by Foussard et al. [9] in order to simulate the experimental data using the model by Verenich and Kallas [1]. It was observed that the unoxidized fraction of lump A, or $c_{A,e}$, is temperature-independent and equals to about 0.72 of $c_{A,o}$ or, in other words, is 72% of the initial concentration of lump A (see the kinetic model description); meanwhile, $c_{B,e}$, which could be interpreted as the accumulation of partially oxidized compounds in lump B, was dependent on the reaction temperature. Its minimum value of 0.93 $c_{B,o}$ was observed at 473 K and, afterwards, this value was inserted into the model as $c_{B,e}$ for the temperature range of 383–473 K.

Since lump A consists of large and toxic compounds [12], tannins, which are present in large quantities in the debarking concentrate, can be attributed to this group. A study of the results of the color measurements, in Fig. 2, shows that the color increased with the increase in temperature; however, at higher temperatures the color intensity lessened. In other words, these observations can be explained by the polymerization of tannins to a higher degree where they became insoluble and precipitate causing a reduction in coloration [19,20]. At initial stage, oxidative process causes polymerization rather promotes the formation of the end-products or lump E. Hence, the pathway “one” from the reaction network in Fig. 1 was eliminated and the frequency factors and activation energies were estimated for reactions “two” and “three” only.

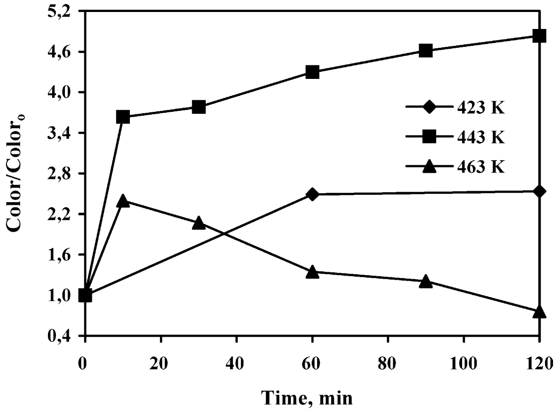

Fig. 2. The effect of temperature on the color of the debarking concentrate during the 2-h reaction time.

The activation energies, E_{ai}, and frequency factors, K_i^0, were estimated from the Arrhenius equation (6), where k_i^0 was merged with $c_{O_2}^{ni}$ to give K_i^0.

$$k_i = K_i^0 \exp\left(-\frac{E_{ai}}{RT}\right) \tag{6}$$

However, the Arrhenius equation, in its traditional form (Eq. (6)), has two strongly correlating parameters, E_{ai} and K_i^0. By suitably increasing the values of both K_i^0, and E_{ai}, k_i could remain virtually unchanged. Therefore, a new parameterization of Eq. (6) should be performed, and this can be written in the following form [16]:

$$k_i = K_{mean,i} \exp\left(-\frac{E_{ai}}{R}\left(\frac{1}{T} - \frac{1}{T_{mean}}\right)\right) \tag{7}$$

where

$$K_{mean,i} = K_i^0 \exp\left(-\frac{E_{ai}}{RT_{mean}}\right) \tag{8}$$

and T_{mean} is the mean temperature between the lowest and the highest temperatures used in the estimation. Later on, $K_{mean,i}$ have to be recalculated from Eq. (8) to receive the values of the original frequency factors, K_i^0. The estimated activation energies are presented in Table 2. It is also worth noting that the regression coefficient, R^2, of the estimation using a simplified reaction network was high, up to 99%.

A sensitivity analysis was performed by presenting a global picture of the identifiability of the parameters in the form of contour plot of R^2 for the pairs K_{mean2}–E_{a2} and K_{mean3}–E_{a3}. Fig. 3 illustrates the typical shape of the contour lines observed during the estimation of the kinetic parameters. As can be seen, the contour lines are well centered around the most probable minimum point. Furthermore, the correlation matrix, Ω_1 (9), confirms that the estimated parameters are not strongly cross-correlated. Its elements were far from the values of −0.9 or 0.9, which would indicate a strong interdependency between the two parameters.

Table 2
Evaluated kinetic parameters for conventional, alkaline media and promoted wet oxidation processes

Reaction pathways	Frequency factor, K_{mean} (min^{-1})	95% Confidence interval for K_{mean} (min^{-1})	Activation energy, E_a (kJ/mol)	95% Confidence interval for E_a (kJ/mol)	Regression coefficient R^2 (%)
Unpromoted wet oxidation					
2	0.0225	±0.0066	33.6	±13	99
3	0.0871	±0.0570	65.1	±26	
Wet oxidation in alkaline media					
1	0.0173	±0.0031	53.8	±12	95
2	0.0088	±0.0024	41.6	±18	
Promoted wet oxidation in alkaline media					
1	0.0399	±0.0071	24.3	±11	97
2	0.0158	±0.0039	9.1	±15	

$$\Omega_1 = \begin{array}{c|cccc} & K_{mean2} & K_{mean3} & E_{a2} & E_{a3} \\ \hline K_{mean2} & 1 & & & \\ K_{mean3} & -0.55 & 1 & & \\ E_{a2} & -0.34 & -0.05 & 1 & \\ E_{a3} & -0.23 & -0.62 & -0.36 & 1 \end{array} \qquad (9)$$

4.2. WO in alkaline media

Alkaline media are used in industry, particularly in the pulp and paper industry, to remove unwanted phenolic compounds such as lignin and its derivatives. High pHs are able to increase the rate of phenol oxidation by up to 10^7 times [15]. The studied debarking concentrate is an example of wastewater enriched with phenolic (polymeric) substances.

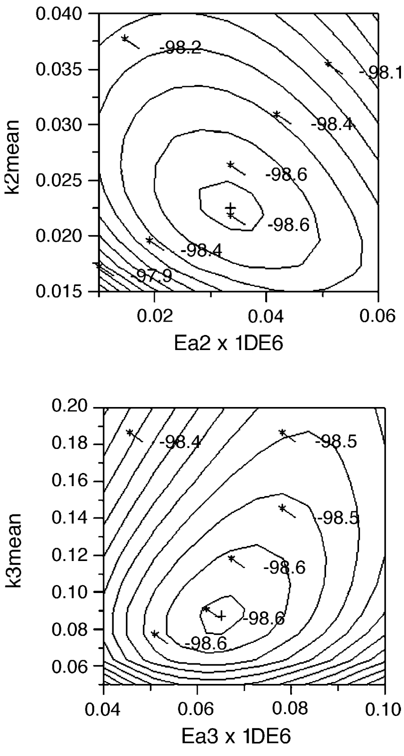

Fig. 3. The sensitivity contour plot of R^2 for the pairs E_{a2}–K_{mean2} and E_{a3}–K_{mean3} of the kinetic model for unprompted wet oxidation.

Therefore, it was found that expediently treating the debarking concentrate in an alkaline media lessened the concentration of major toxic compounds such as tannin. The WO runs in alkaline media were conducted at a pH level pre-adjusted to 13 using a sodium hydroxide solution, operation temperatures of 383–443 K and an oxygen partial pressure of 1 MPa.

To model the process, the reaction network on Fig. 1 was recast again for the considered conditions. Due to the relative stability of the aliphatic compounds in the alkaline media, which mostly incorporated in lump B, it is expected that there would be no, or very slow, conversion to carbon dioxide, i.e. to lump E. Then, reaction pathway “three” can be excluded from the reaction scheme (Fig. 1) and all the products of partial oxidation then accumulate in lump B. Thus, the reaction network is simplified and the oxidation proceeds according to the model by Zhang and Chuang [14]. However, the products of partial oxidation (lump B) were characterized with BOD_5. Such an oxidative process can be described using the system of ODEs as follows:

$$-\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} = (k_1 + k_2)(c_{\mathrm{A}} - c_{\mathrm{A,e}}) \qquad (10)$$

$$-\frac{\mathrm{d}c_{\mathrm{B}}}{\mathrm{d}t} = -k_2(c_{\mathrm{A}} - c_{\mathrm{A,e}}) \qquad (11)$$

where $c_{\mathrm{A,e}}$ was found experimentally and is equal to 0.25 of $c_{\mathrm{A,o}}$ for a temperature interval of 383–443 K and k_{i} is expressed via Eq. (6); however, K_{i}^0 now is additionally merged with a concentration of OH ions.

The result of the modeling is presented in Tables 1 and 2. The sensitivity analysis for the parameter pairs E_{a1}–K_{mean1} and E_{a2}–K_{mean2} suggests that the parameters are well-identified (Fig. 4) and only weakly correlated, Ω_2 (12).

$$\Omega_2 = \begin{array}{c|cccc} & K_{mean1} & K_{mean2} & E_{a1} & E_{a2} \\ \hline K_{mean1} & 1 & & & \\ K_{mean2} & 0.73 & 1 & & \\ E_{a2} & 0.25 & 0.24 & 1 & \\ E_{a3} & 0.21 & 0 & 0.69 & 1 \end{array} \qquad (12)$$

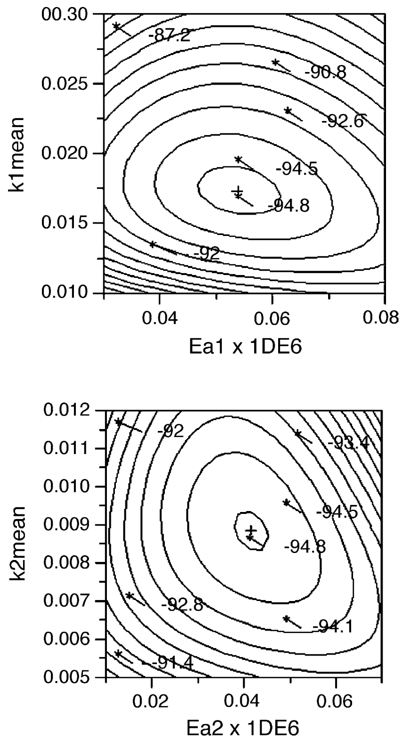

Fig. 4. The sensitivity contour plot of R^2 for the pairs E_{a1}–K_{mean1} and E_{a2}–K_{mean2} of the kinetic model for wet oxidation process in alkaline media.

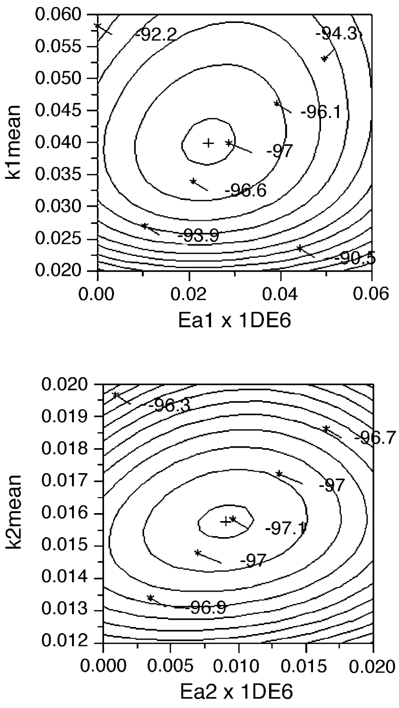

Fig. 5. The sensitivity contour plot of R^2 for the pairs E_{a1}–K_{mean1} and E_{a2}–K_{mean2} of the kinetic model for hydrogen peroxide promoted wet oxidation process in alkaline media.

4.3. Hydrogen peroxide promoted WO in alkaline media

Hydrogen peroxide decomposes in aqueous solution producing two hydroxyl radicals, which have a strong oxidative capability. The OH radicals can be formed during the course of oxidation [10] or can also be introduced with the addition of a H_2O_2 solution, thus providing an additional source of OH radicals and accelerating the oxidative process. To achieve a promoting effect, 0.2 g of H_2O_2 per 1 g of COD was added into the remaining alkaline solution in the same temperature range of 383–443 K, at an oxygen partial pressure of 1 MPa for a treatment time of 2 h.

The WO with the addition of H_2O_2 was modeled using the same reaction network as in the previous chapter, i.e. Eqs. (10) and (11). However, the frequency factors, K_i^0 (Eq. (6)), combine not only c_{O_2} and c_{OH} but also the concentration of hydrogen peroxide in the aqueous solution, $c_{H_2O_2}$.

The factor of $c_{A,e}$ was observed to be 0.38 from $c_{A,o}$. The apparent activation energies and frequency factors, as well as some statistical parameters, such as the standard error and regression coefficient of estimation, are presented in Table 2. The COD_t/COD_0 ratios obtained experimentally and with the estimated kinetic parameters are depicted in Table 1.

The contours of the R^2 for the pairs E_{a1}–K_{mean1} and E_{a2}–K_{mean2} imply that the kinetic parameters are well-identified as the contour lines are centered around the most probable point (Fig. 5). The correlation matrix, Ω_3 (15), confirms that the estimated parameters are not strongly cross-correlated.

$$\Omega_3 = \begin{array}{c|cccc} & K_{mean1} & K_{mean2} & E_{a1} & E_{a2} \\ \hline K_{mean1} & 1 & & & \\ K_{mean2} & 0.83 & 1 & & \\ E_{a2} & 0.19 & 0.16 & 1 & \\ E_{a3} & 0.16 & 0.20 & 0.83 & 1 \end{array} \qquad (13)$$

5. Discussions

Many industrial processes, especially in pulp and paper mills, deal with alkaline streams. Therefore, the recast model is applicable for cases of the oxidative treatment of alkaline effluents. The model uses characteristics such as COD and BOD, which can be easily determined. Both parameters are often used to determine the concentration of pollutants in industrial effluents and the ability of microorganisms to utilize organics during biological treatment, which is commonly applied as a final treatment for wastewater. Biodegradability, defined as the ratio of BOD to COD, is an important parameter to be ascertained before feeding the stream into bio-oxidation. The model used in this work also permits the observation of the BOD/COD ratios of the stream after the WO processes. Fig. 6 depicts the results of modeling compared with those obtained experimentally.

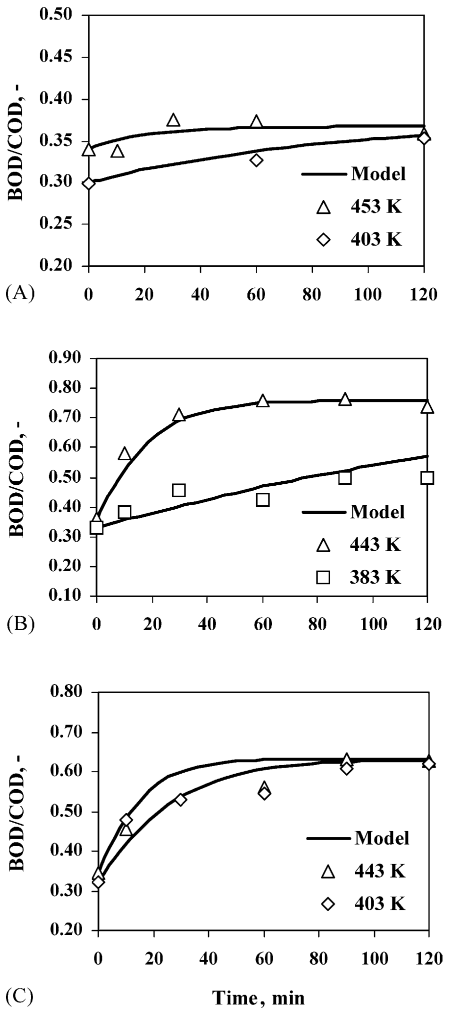

Fig. 6. The performance of the model for the experimental data observed under the following conditions: (A) conventional wet oxidation at 1 MPa of oxygen partial pressure; (B) wet oxidation in alkaline media at 1 MPa of oxygen partial pressure; (C) H_2O_2 promoted wet oxidation in alkaline media at 1 MPa of oxygen partial pressure.

It is necessary to point out that each effluent considered for WO treatment has to be carefully studied in terms of the modeling procedure, because the lumped models published in literature might be just a general description of the oxidative process and not applicable for a particular case. Thus, two different reaction pathways were eliminated from the model by Verenich and Kallas [1] in order to obtain data (BOD and COD) similar to that obtained experimentally during the WO of the debarking evaporation concentrate at neutral and alkaline pHs.

The addition of hydrogen peroxide injected in a dose of 0.2 g per 1 g of COD did reduce the energy barrier to the production of oxidation products or, in other words, played the role of reaction accelerator. The activation energy for the formation of products of partial oxidation decreased by 4.6 times, while that for direct oxidation to carbon dioxide was reduced by 2.2 times (Table 2).

6. Conclusions

In this work, a debarking concentrate was studied. The results showed a recalcitrant nature of this wastewater. The conventional and promoted oxidative processes resulted in maximum 40% of removal of pollutants. However, WO in alkaline media and hydrogen peroxide prompted WO converted resistant wastewater to biodegradable by raising the COD/BOD ratios from 0.32–0.34 to about 0.7–0.75.

To model the WO process for the debarking concentrate, the general form of the model by Verenich and Kallas [1] had to be recast. Firstly, the term of the unoxidizable fraction, $c_{A,e}$ and $c_{B,e}$, was introduced and, secondly, some reactions were removed from the reaction network. These modifications resulted in the high values—as high as 95–99%—of the regression coefficient, and a sensitivity analysis confirmed that the estimated kinetic parameters, activation energies and frequency factors, are well-identified and not cross-correlated. The promoting effect of hydrogen peroxide was evident, as the activation energy, E_{a2}, for the formation of partially oxidized compounds decreased from 41.6 to 9.1 kJ/mol and the energy required for the formation of carbon dioxide, E_{a1}, fell from 53.8 to 24.3 kJ/mol.

Acknowledgements

The authors would like to acknowledge the financial support provided for this research by the Graduate School in Chemical Engineering (GSCE), Maj and Tor Nessling Foundation (Finland), and Academy of Finland, project numbers 203947 and 808.

References

[1] S. Verenich, J. Kallas, Wet oxidation of concentrated wastewaters: the kinetic modelling, in: Proceedings of IWA 2nd International Conference on Oxidation Technologies for Water and Wastewater Treatment, Clausthal-Zellerfeld, Germany, 2000.
[2] M. Ali, T.R. Sreekrishnan, Aquatic toxicity from pulp and paper mill effluents: a review, Adv. Environ. Res. 5 (2) (2001) 175–196.
[3] J.A. Field, M.J.H. Leyendeckers, R. Sierra-Alvarez, G. Lettinga, L.H.A. Habets, The methanogenic toxicity of bark tannins and the anaerobic biodegradability of water soluble bark matter, Water Sci. Technol. 20 (1988) 219–240.
[4] S. Korhonen, T. Tuhkanen, Effect of ozone on resin acids in thermomechanical pulp and paper mill circulation waters, Ozone Sci. Eng. 22 (2000) 575–584.
[5] R. Saunamäki, M. Savolainen, Effluent-free drum debarking, Pulp Pap. Can. 100 (1999) 27–30.
[6] S.H. Lin, S.J. Ho, Treatment of high-strength industrial wastewater by wet oxidation—a case study, Waste Manage. 17 (1997) 71–78.
[7] J. Donlagic, J. Levec, Comparison of catalyzed and noncatalyzed oxidation of azo dye and effect on biodegradability, Environ. Sci. Technol. 32 (9) (1998) 1294–1302.
[8] T. Takamatsu, I. Hashimoto, S. Sioya, Model identification of wet air oxidation process thermal decomposition, Water Res. 4 (1) (1970) 33–59.

[9] J.N. Foussard, H. Debellefontaine, V.J. Besombes, Effective elimination of organic liquid wastes: wet air oxidation, Environ. Eng. 115 (1989) 367.

[10] L. Li, P. Chen, E.F. Gloyna, Generalized kinetics model for wet oxidation of organic compounds, AIChE J. 37 (11) (1991) 1687–1697.

[11] J. Donlagic, J. Levec, Oxidation of an azo dye in subcritical aqueous solutions, Ind. Eng. Chem. Res. 36 (1997) 3480–3486.

[12] S. Verenich, J. Kallas, Wet oxidation lumped kinetic model for water biodegradability prediction, Environ. Sci. Technol. 36 (15) (2002) 3335–3339.

[13] K. Belkacemi, F. Larachi, A. Sayari, Lumped kinetics for solid-catalyzed wet oxidation: a versatile model, J. Catal. 193 (2000) 224–237.

[14] Q. Zhang, K.T. Chuang, Lumped kinetic model for catalytic wet oxidation of organic compounds in industrial wastewater, AIChE J. 45 (1) (1999) 145–150.

[15] R.J. Rivas, S.T. Kolaczkowski, F.J. Beltran, D.B. McLurgh, Development of a model for wet air oxidation of phenol based on a free radical mechanism, Chem. Eng. Sci. 53 (14) (1998) 2575–2586.

[16] H. Haario, Modest User Manual, ProfMath Oy, Helsinki, Finland, 1994.

[17] A.C. Hindmarsh, A Systematized Collection of Ode-Solvers, Lawrence Livermore Laboratory of Scientific Computing, North-Holland Publishing Company, Amsterdam, 1983.

[18] Standard Methods for the Examination of Water and Wastewater, seventh ed., American Public Health Association (APHA)/American Water Works Association/Water Pollution Control Federation, Washington, DC, 1989.

[19] J. Araña, E. Tello Rendón, J.M. Doña Rodrígez, J.A. Herrera Melián, O. González Díaz, J. Pérez Peña, Highly concentrated phenolic wastewater treatment by the photo-fenton reaction, mechanisms study by FTIR-ATR, Chemosphere 44 (5) (2001) 117–123.

[20] J.A. Field, B.V. Pacques, Methods for Purifying Wastewaters, Patent, EP 0238148, 1987.