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Kinetic model for oxygen concentration dependence in the supercritical water oxidation of an industrial wastewater

J. Sánchez-Oneto [a,*], F. Mancini [b], J.R. Portela [a], E. Nebot [a], F. Cansell [b], E.J. Martínez de la Ossa [a]

[a] *Department of Chemical Engineering, Food Technologies and Environmental Technologies, Faculty of Sciences, University of Cádiz, 11510 Puerto Real, Spain*

[b] *Institut de Chimie et de la Matière Condensée de Bordeaux, CNRS-UPR 9048, Universite BORDEAUX 1, 87 avenue du Docteur Albert Schweitzer, 33608 Pessac Cedex, France*

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Abstract

The objective of this work was the determination of a global rate expression for the kinetics of the supercritical water oxidation (SCWO) of cutting fluid wastes generated in metal industries. SCWO experiments were carried out in a continuous flow reactor system using pure oxygen as the oxidant at a constant pressure of 25 MPa. The temperature effect was studied in the range 673–773 K. Oxygen excess coefficient was varied from $n = 0.4$ (60% of stoichiometric oxygen) to $n = 1.2$ (20% oxygen excess) to determine the reaction order for O_2. The effectiveness of the process was monitored in terms of COD removal.

The rate equation parameters were obtained by fitting of experimental data to the differential equation obtained using the Runge–Kutta algorithm. The kinetic model proposed allows the prediction of the COD conversion with respect to oxygen supply to optimize the operating conditions and to minimize investment and operating costs.

Keywords: Supercritical water oxidation; Supercritical hydrothermal oxidation; Kinetics; Modelling; Industrial wastewater; Cutting fluids; Cutting oils; Runge–Kutta algorithm

1. Introduction

Hydrothermal oxidation in supercritical conditions, denoted supercritical water oxidation (SCWO), has proved to be an effective process to treat a wide variety of industrial wastes [1,2]. SCWO essentially consists of oxidation in an aqueous medium at high temperature and pressure, above the critical point for pure water, usually ranging from 673 to 923 K and from 25 to 35 MPa, respectively.

Above its critical point ($T = 647$ K, $P = 22.1$ MPa) water exhibits unique physical–chemical properties that make it an effective reaction medium for the oxidation of organic and inorganic compounds [3]. The reaction occurs in a homogeneous phase, meaning that interface mass transfer limitations are avoided and high reaction efficiencies can be achieved in short residence times [4]. From an environmental perspective, the resulting effluent complies with the strictest environmental regulations and can be disposed of without further treatment [5]. The two main challenges facing SCWO – corrosion and salt deposition – are being solved through technical solutions such as the use of special construction materials and the development of new reactor designs that are able to soften the conditions that the materials must support [6,7].

The majority of the global rate expressions reported in the literature was for the SCWO of model compounds. The objective of this work was the determination of a global rate expression for the kinetics of SCWO of a complex waste, specifically, cutting fluid wastes generated in a metalworking industry.

Cutting fluids are widely used in this type of industries and the main functions of these fluids are lubrication, refrigeration and evacuation of filings. The composition of these fluids is variable and depends on the requirements of the mechanical process in which they are used. The main components present in cutting oil are: refrigerant (water), lubricants (mineral oils, vegetable oils, synthetic oils), surfactants (anionic,

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[*] Corresponding author. Tel.: +34 956 016 458; fax: +34 956 016 411.
E-mail address: jezabel.sanchez@uca.es (J. Sánchez-Oneto).

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Table 1
Properties of cutting fluid waste from a metalworking industry (with confidence level of 95%)

Waste	pH	Conductivity (mS cm^{-1})	COD (g l^{-1})
Cutting fluid	8.6 ± 0.2	3.5 ± 0.9	160 ± 30

cationic or non-ionic), inhibitors for corrosion (amines, borates, nitrites), humectants/stabilizers, biocides, and additives consisting of high pressure and antifoaming compounds [8]. Habitually, cutting oils are commercialized in a concentrated formula and this is diluted *in situ* with deionized water, normally between 2 and 10%, to give the corresponding cutting fluid. Depending on the relative percentages of refrigerant, lubricant and additives, the cutting oils can be classified into different types: synthetic, semi-synthetic and oil emulsion types.

Semi-synthetic cutting fluids are the most commonly used systems in the metalworking company studied (Delphi Automotive Systems) and these normally contain 20–50% of water, 10–40% of synthetic oil and 20–60% of additives. The cutting fluid studied in this work is a semi-synthetic type and its commercial name is Biocut® (Houghton Ibérica S.A., Spain). This fluid is normally diluted between 2 and 10% v/v with deionized water to obtain a stable and homogeneous emulsion that is used in the tooling machines to dissipate heat and to provide lubrication between the face of the cutting tool and the metal being cut.

After a long period of use, the cutting fluids lose their properties and accumulate physical, chemical or biological contaminants and they must therefore be replaced. The cutting fluid wastes generated are complex oily aqueous wastes, the properties of which depend on the types of cutting fluids used, the dilutions employed and the metalworking operations carried out in the different machines. Some of the main properties for a mixture of cutting fluid wastes generated in the company studied are shown in Table 1 [9].

Under most of the current legislation, used cutting fluids are considered as hazardous waste and their safe collection and disposal must be ensured [10]. Since conventional treatment methods (evaporation, phase separation, filtration) are often inefficient or environmentally unacceptable, the development and application of new technologies is a great necessity.

In our previous studies we successfully applied SCWO to the treatment of different cutting fluids [9,11–13]. In these studies we performance several analysis of the samples, COD concentration, TOC concentration, gas composition, etc., and the carbon mass balance was applied successfully in each experiments. The composition of gas samples were mainly CO_2 and CO and a little proportion of CH_4. Little differences between COD and TOC removal were found. In all cases, experiments were carried out with an excess of oxygen so it was reasonable to assume a zero order for oxygen concentration. Kinetic models obtained are suitable to design and to describe the behaviour of a SCWO industrial plant working with similar reaction conditions to those used in the kinetic study, i.e. with excess oxygen. However, the assumption of zero order for oxygen concentration seriously limits the application of these kinetic parameters for the scale-up or the simulation of the process, since it does not predict that the reaction rate decreases when the oxygen concentration diminishes. Moreover, from an industrial point of view, where it is necessary to optimize the operating conditions needed to obtain a high depurative degree with the minimum of investment and operating costs, the optimization of the oxygen consumption is very important.

Usually, multi-linear regression is the method used for the determination of oxygen order on the oxidation rate of organic compounds. Another method applied to experimental data analysis is based on the Runge–Kutta algorithm. Mateos et al. [14] compared both methods and concluded that the Runge–Kutta algorithm for experimental data treatment, when compared to the multi-linear regression method, presented some advantages due to the possibility of fitting together all experimental data obtained at the same temperature and the suppression of experiments with the same amount of oxygen at any given residence time. In this work, we applied the Runge–Kutta algorithm to determine the kinetic parameters for the SCWO of the industrial wastewater studied.

2. Experimental

2.1. Materials

Biocut® from Houghton Ibérica, S.A. (Spain) is the commercial name of the semi-synthetic cutting oil studied in this work. Some of the properties of this oil are shown in Table 2. This concentrated oil is diluted *in situ* with water, normally between 2 and 6%, to generate the corresponding cutting fluid.

Pure oxygen (99.99% pure) was used as the oxidising agent and was obtained from an oxygen cylinder connected to a Haskel compressor.

2.2. Equipment and procedure

A schematic drawing of the apparatus used in this work is shown in Fig. 1 [15]. This is a continuous flow system able to treat 2.8 kg/h of aqueous waste in a temperature range of 473–873 K at pressures up to 30 MPa. The main units in this equipment were connected to a data acquisition and control unit controlled by Labview software. The aqueous feed solution is pressurized by a high pressure pump (LEWA). Before entering the reactor, the feed is preheated by an electric heater (1.5 kW) along 9 m of 316 SS tubing with an internal diameter of 1.6 mm. The oxidant feed consists of pure oxygen pressurized

Table 2
Properties of the semi-synthetic cutting oil in the concentrated formula (with confidence level of 95%)

	Biocut®
Elemental analysis (wt.% dry basis)	
C	70.10 ± 0.42
H	16.54 ± 2.61
N	0.26 ± 0.05
S	0.36 ± 0.04
Others (rest to 100%)	12.74
COD (g O_2 g^{-1} concentrated cutting oil)	2.264 ± 0.041

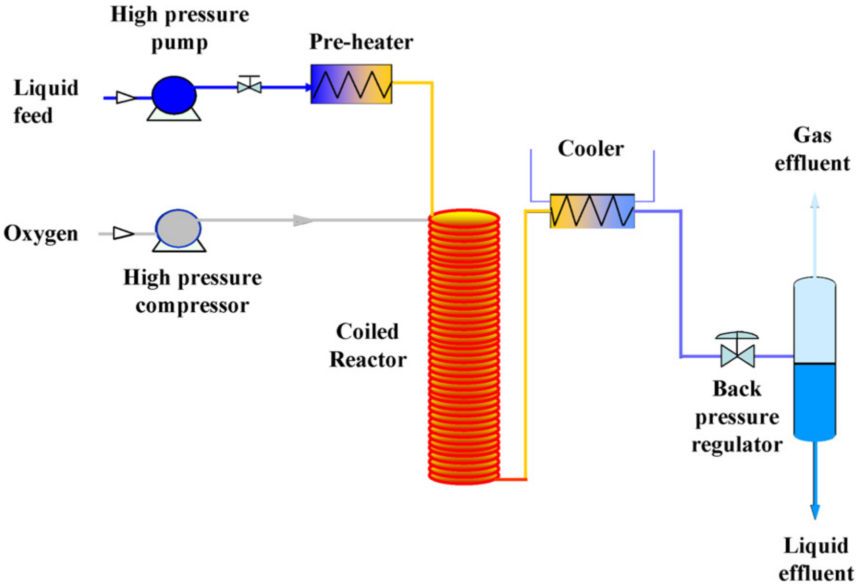

Fig. 1. Schematic diagram of the continuous flow reactor system.

by a Haskel compressor, which injects the oxygen at 25 MPa, without preheating, at the input of the reactor. A massflow meter (Brooks 5850S) allowed the selection and control of the desired flowrate in the range 0–100 g/h. The reactor was made from a 42 m length of 1/8 in. Inconel 625 tubing. Twenty-eight thermocouples were attached to the external surface. The working reaction temperature assigned to an experiment is taken as the mean temperature measured in those twenty-eight thermocouples. This reaction temperature was controlled by three external electrical heaters (1.5 kW each) connected to a PID controller, and was kept in the desired value along the tubular reactor typically with a maximum difference between all thermocouples of ±3 °C. The reactor was isolated with a calcite jacket. On exiting the reactor, the effluent was cooled rapidly in a counter current heat exchanger and the system pressure was then reduced using a back-pressure regulator. The product stream was then separated into liquid and vapour phases. More specific details of the experimental apparatus and procedure are well described in previous studies [14,15,18].

2.3. Analytical methods

Since the cutting fluids are a complex mixture of several compounds, the efficiency of the oxidation process was followed in terms of the reduction in chemical oxygen demand (COD). The COD concentration measurements in liquid samples were obtained according to standard methods [16]. All COD measurements were performed minimum in duplicate. The accuracy for the COD measurements was around ±3%.

3. Results and discussion

3.1. Experiments with different oxygen concentrations

All experiments were carried out under supercritical conditions at a constant pressure of 25 MPa. The experiments were carried out under isothermal conditions at different temperatures ranging between 673 and 773 K, which enabled the influence of temperature to be studied. These experiments were carried out with a moderate oxygen excess of 20% (oxygen excess coefficient, $n = 1.2$). The oxygen excess was calculated over the theoretical amount of oxygen required for complete oxidation. Moreover, at a constant temperature of 723 K, several experiments were carried out with different oxygen concentrations ranging from oxygen default ($n = 0.4$) to a moderate oxygen excess ($n = 1.2$). The initial concentrations of cutting fluid in the feed stock solution were around 10 g/l in terms of COD. The rate of COD (gO_2/h) entering the system was calculated from the aqueous waste massflow, assuming the density of water at room temperature. That value was then used to calculate the mass flow of pure oxygen (gO_2/h) needed to reach the desired oxygen excess coefficient (n). All experiments were performed in duplicate. The operation conditions of the experiments and the results obtained for COD reduction are shown in Table 3. Data are presented with a 95% confidence level.

3.2. Determination of kinetic parameters using the Runge–Kutta algorithm

The global rate for the transformation of organic compounds in CO_2 by hydrothermal oxidation can be expressed as follows:

$$r_{\mathrm{COD}} = -\frac{\mathrm{d[COD]}}{\mathrm{d}\tau} = k[\mathrm{COD}]^{\alpha}[\mathrm{O_2}]^{\beta}[\mathrm{H_2O}]^{\gamma} \qquad (1)$$

where α, β and γ are the reaction orders for organic matter, oxygen and water, respectively. Assuming an Arrhenius temperature dependence, the reaction rate coefficient can be expressed as

$$k = A \exp\left(-\frac{E_a}{RT}\right) \qquad (2)$$

where A is the pre-exponential factor ($(\mathrm{mol\,l^{-1}})^{1-\alpha-\beta-\gamma}\,\mathrm{s^{-1}}$), E_a is the apparent activation energy ($\mathrm{J\,mol^{-1}}$), R is the universal

Table 3
Reaction conditions and results obtained in SCWO experiments on a semi-synthetic cutting fluid (with 95% confidence level)

Temperature (K)	Oxygen excess coefficient (n)	$[\mathrm{COD}]_0$[a] (mg/l)	$[\mathrm{O}_2]_0$[a] (mg/l)	Residence time (s)	COD removal (%)
673	1.2	10127	12571	20	51.0 ± 1.8
	1.2	10388	12897	29	58.6 ± 2.5
	1.2	10388	12572	48	68.2 ± 2.7
	1.2	10388	12589	91	71.5 ± 2.1
698	1.2	10552	13188	17	57.0 ± 3.6
	1.2	10384	11102	24	68.8 ± 0.02
	1.2	10323	12093	35	67.8 ± 2.9
	1.2	10485	11989	50	77.6 ± 0.1
	1.2	10323	12973	68	75.3 ± 1.8
723	0.4	10117	4021	20	31.8 ± 0.5
	0.4	10371	3908	22	35.8 ± 3.0
	0.6	10360	5499	15	39.1 ± 3.0
	0.6	10363	6000	22	40.2 ± 5.7
	0.8	10072	8035	19	52.0 ± 1.2
	0.8	10364	7958	22	57.1 ± 2.4
	0.8	10371	7420	30	69.4 ± 5.6
	1.0	10360	9052	15	52.7 ± 4.3
	1.0	10601	10018	21	64.6 ± 5.1
	1.0	10371	9015	30	72.5 ± 3.4
	1.0	10449	9713	64	89.4 ± 0.5
	1.2	10417	12135	15	57.5 ± 5.2
	1.2	10233	12162	20	67.4 ± 0.4
	1.2	10371	11913	30	76.3 ± 1.5
	1.2	10449	12374	63	90.8 ± 1.2
748	1.2	10514	12704	13	61.4 ± 3.3
	1.2	10526	12307	18	75.0 ± 0.02
	1.2	10312	12317	27	81.4 ± 2.2
	1.2	10576	12077	36	83.5 ± 0.2
	1.2	10312	13208	49	88.2 ± 1.9
773	1.2	10415	12853	12	75.2 ± 3.6
	1.2	10541	12206	16	88.0 ± 0.1
	1.2	10250	12126	21	91.2 ± 0.5
	1.2	10275	12036	25	90.4 ± 0.8
	1.2	10305	13746	48	95.8 ± 0.3

The pressure in all experiments was maintained in 25 MPa

[a] $[\mathrm{COD}]_0$ and $[\mathrm{O}_2]_0$ concentrations are referred at room temperature.

gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K). As already published, the reaction order of organic compounds in hydrothermal oxidation treatment can be assumed as equal to unity ($\alpha = 1$) [17]. In addition, in a reaction medium containing more than 90% water, the reaction order for water can be considered as equal to zero ($\gamma = 0$). These two considerations mean that Eq. (1) can be simplified as follows:

$$r_{\mathrm{COD}} = -\frac{\mathrm{d}[\mathrm{COD}]}{\mathrm{d}\tau} = k[\mathrm{COD}][\mathrm{O}_2]^{\beta} \tag{3}$$

Moreover, the oxygen concentration at any given time can be expressed as a function of the initial oxygen concentration and the reduction in COD concentration as follows:

$$[\mathrm{O}_2] = [\mathrm{O}_2]_0 - ([\mathrm{COD}]_0 - [\mathrm{COD}]) \tag{4}$$

Taking into account Eqs. (3) and (4) the global rate for COD disappearance is represented in Eq. (5)

$$\begin{aligned} r_{\mathrm{COD}} &= -\frac{\mathrm{d}[\mathrm{COD}]}{\mathrm{d}\tau} = k[\mathrm{COD}]([\mathrm{O}_2]_0 - ([\mathrm{COD}]_0 - [\mathrm{COD}]))^{\beta} \\ &= f([\mathrm{COD}, \tau]) \end{aligned} \tag{5}$$

where $[\mathrm{COD}]_0$ and $[\mathrm{O}_2]_0$ corresponded to $\tau = 0$. This differential equation was solved numerically using the Runge–Kutta method, determining the kinetic parameters (k and β) that produce the best fitting of experimental and calculated data. In this algorithm, the integration interval from 0 to the global residence time (τ_{N}) was divided into N subintervals with $h = \tau_{\mathrm{N}}/N$. This method is called "one step" because the determination of the function on point $N+1$ only requires the differential equation and information corresponding to the variables in the preceding point N. More specifically we used the Runge–Kutta-fourth order, which adopts the following form:

$$[\text{COD}]_{n+1} = [\text{COD}]_n + \frac{h}{6}(p_1 + 2p_2 + 2p_3 + p_4)$$
$$N = 0, ..., N - 1 \tag{6}$$

where

$$p_1 = f(\tau_n, [\text{COD}]) \tag{7}$$

$$p_2 = f\left(\tau_n + \frac{h}{2}, [\text{COD}] + \frac{h}{2}p_1\right) \tag{8}$$

$$p_3 = f\left(\tau_n + \frac{h}{2}, [\text{COD}] + \frac{h}{2}p_2\right) \tag{9}$$

$$p_4 = f(\tau_n + h, [\text{COD}] + hp_3) \tag{10}$$

Starting with initial values for the kinetic parameters, k and β, and knowing the initial concentration at $\tau = 0$ for COD and O_2, i.e. $[\text{COD}]_0$ and $[O_2]_0$, respectively, the application of Eqs. (5)–(10) allow $[\text{COD}]_1$ to be determined for a residence time $\tau_1 = 1 \cdot \tau_N/N$. Using this value and again using the equations of the algorithm, Eqs. (5)–(10), it is possible to calculate $[\text{COD}]_2$ for $\tau_2 = 2 \cdot \tau_N/N$ and, in a similar way, successive values until the calculation of $[\text{COD}]_N$. Finally, these estimated $[\text{COD}]_N$ values were compared with the corresponding experimental COD concentration value, $[\text{COD}]_{N-\text{EXP}}$, and an adjustment of both k and β values was performed in order to minimize the difference between the calculated $[\text{COD}]_N$ and experimental values.

This method has been used successfully by other authors to model pollutants [14]. For example, Mateos et al. [14] developed a Fortran program based on the Runge–Kutta algorithm for the determination of kinetic parameters for the hydrothermal oxidation of three model compounds: acetic acid, methanol and phenol. These kinetics parameters were used successfully by Portela et al. [18] for the simulation of an SCWO process for highly concentrated feeds. In the present work, the Runge–Kutta algorithm has been specifically developed using an MS Excel® spreadsheet and the s*olver* tool, with the *objective* being the minimization of the following function:

$$\text{Objetive function} = \sum_{0}^{N}\left([\text{COD}]_N - [\text{COD}]_{N-EXP}\right)^2 \tag{11}$$

In order to determine the kinetic parameters the following procedure was used: in the first instance, with experiments carried out at 723 K, we determined the reaction order for oxygen, β, and the reaction rate coefficient corresponding to this temperature, $k_{723\,\text{K}}$. Having obtained the β value we used the experiments carried out at 673, 698, 748 and 773 K to determine the corresponding value for the reaction rate coefficients, $k_{673\,\text{K}}$, $k_{698\,\text{K}}$, $k_{748\,\text{K}}$, and $k_{773\,\text{K}}$. The results obtained for the kinetic parameters with a 95% confidence level are presented in Table 4.

The prediction profiles using the kinetic parameters obtained and the corresponding experimental data are shown in Fig. 2. It can be observed that there is quite good agreement between the predicted COD profiles and the experimental ones.

Table 4
Kinetic parameters for the removal of COD in the SCWO of cutting fluids at 25 MPa

Temperature (K)	k (mg O_2/l)$^{-b}$ s^{-1}	β
673	$1.37 \times 10^{-4} \pm 0.42 \times 10^{-4}$	0.579 ± 0.014
698	$2.10 \times 10^{-4} \pm 0.61 \times 10^{-4}$	
723	$3.16 \times 10^{-4} \pm 0.38 \times 10^{-4}$	
748	$3.86 \times 10^{-4} \pm 0.62 \times 10^{-4}$	
773	$7.48 \times 10^{-4} \pm 1.65 \times 10^{-4}$	

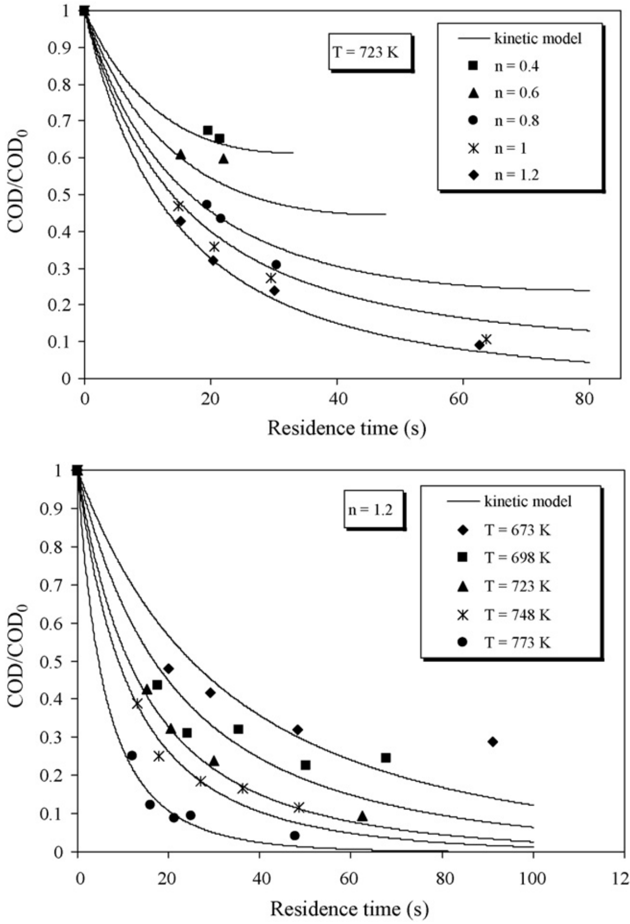

Fig. 2. Effect of oxygen excess and temperature in the SCWO of a semi-synthetic cutting fluid. The oxygen excess coefficient is unity ($n = 1$) when the quantity of initial oxygen corresponds to the required stoichiometric amount.

Having estimated k at different temperatures, these values were fitted to an Arrhenius plot in order to determine the corresponding parameters (Fig. 3). The values obtained for A and E_a are given in Table 5.

Table 5
Arrhenius parameters obtained for the removal of COD in the SCWO of cutting fluids

Temperature range (K)	A (mg O_2/l)$^{-b}$ s^{-1}	E_a (kJ/mol)	r^2
673–773	35 ± 25	70 ± 15	0.976

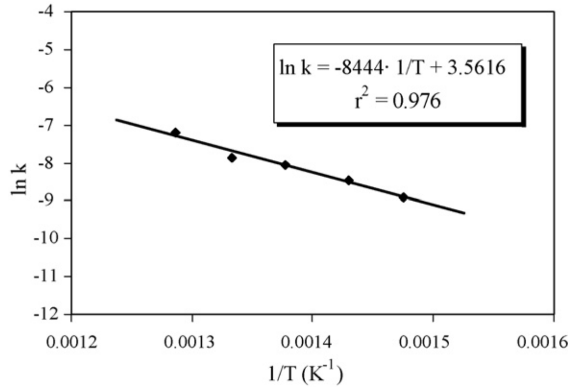

Fig. 3. Arrhenius plot for the *k* values calculated by the Runge–Kutta algorithm.

Finally, the global rate expression for the SCWO of the semi-synthetic cutting fluid was expressed as follows:

$$r_{\mathrm{COD}} = -\frac{\mathrm{d[COD]}}{E\tau} = 35\exp\left(-\frac{70000}{RT}\right)[\mathrm{COD}][\mathrm{O}_2]^{0.579} \quad (12)$$

where the residence time, τ, is expressed in seconds, the temperature, T, in Kelvin, the universal gas constant, $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$, and COD and O_2 concentration in $\mathrm{mg\,l^{-1}}$.

On using this equation, and knowing the operation conditions for the reactor, it is possible to obtain the COD concentration of the effluent and therefore the COD conversion, X_{COD}, can be obtained.

$$X_{\mathrm{COD}} = \frac{[\mathrm{COD}]_0 - [\mathrm{COD}]}{[\mathrm{COD}]_0} \quad (13)$$

The experimental conversions obtained in each experiment are plotted against the conversion predicted by the kinetic model in Fig. 4. The data were fitted using a linear regression analysis. The slope obtained is close to unity and there is a low dispersion of the data from the diagonal, which indicates that the kinetic model obtained is in good agreement with the experimental conversions.

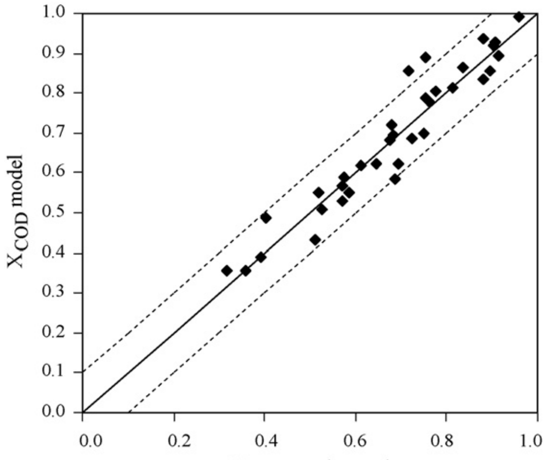

Fig. 4. Comparison between experimental conversions and those predicted by the kinetic model.

4. Conclusions

Cutting fluid wastes has been treated by Supercritical Water Oxidation at 25 MPa of pressure and temperature ranging from 673 to 773 K. Runge–Kutta algorithm, developed using an MS Excel® spreadsheet and *solver* tool, has been used for experimental data analysis and the kinetic parameters determination. The kinetic equation obtained is able to predict the COD conversion for different oxygen concentrations, getting an order $\beta = 0.58$ for oxygen concentration, and as such is suitable for designing and describing the behaviour of a SCWO industrial plant. The main advantages of Runge–Kutta algorithm for experimental data treatments were: (i) the possibility of fitting together all experimental data obtained at the same temperature and (ii) the suppression of experiments with the same amount of oxygen at any residence time. Thus, a lower number of total experiments are required to obtain a satisfactory kinetic model.

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