Kinetic study of glyphosate degradation in wet air oxidation conditions

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Abstract

Glyphosate is one of the most widely used herbicides in the world against perennial and annual weeds. It has been reported to be a micro pollutant, and its degradation in different wastewater treatment processes must be studied. For that purpose, the kinetics of wet air oxidation of glyphosate was studied in an autoclave reactor at a temperature range of 423-523 K and under a total pressure of 15 MPa. Oxidation reactions obeyed the first-order kinetics with respect to glyphosate concentration. The activation energy for glyphosate oxidation was found to be equal to 68.4 kJ mol^{-1}. Furthermore, the possible reaction intermediates and main end products of glyphosate degradation in the wet air oxidation process were identified and quantified using UV-spectrophotometry and liquid chromatography coupled to high resolution mass spectrometry. A degradation pathway for glyphosate oxidation was proposed.

Keywords: Glyphosate; wet air oxidation; kinetics; emerging contaminant

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1 Introduction

Glyphosate (*N*-(phosphonomethyl)glycine), a synthetic phosphonate compound, is a broad-spectrum, post-emergence and non-selective organophosphate herbicide (Manassero et al., 2010; Gill et al., 2017). Glyphosate is one of the most widely used herbicides in the world against perennial and annual weeds and the active ingredient of Roundup (Baylis, 2000; Chen and Liu, 2007). Due to the numerous uses of glyphosate, it has been widely detected in the aquatic environment with potential toxicity to non-target aquatic life (Guilherme et al., 2010; Sandy et al., 2013). Therefore, it has attracted much attention in recent years in order to avoid further risks and effectively avoid it in the environment.

Various conventional methods have been applied to treat glyphosate-containing wastewater, such as precipitation, membrane filtration, adsorption and biodegradation (Xie et al., 2010; Liu et al., 2013; Herath et al., 2016; Firdous et al., 2017). However, these processes may cause secondary pollution, such as the generation of sludge (Wang et al., 2016). The safe disposal of sludge is another issue in wastewater treatment. Furthermore, biological treatment generally needs a long residence time to obtain high glyphosate removal efficiency up to 90% (Fan et al., 2012; Hadi et al., 2013). Thus, more efficient technology for glyphosate degradation is needed to be developed. In this work, the conditions to use wet air oxidation (WAO) as an efficient process were studied. This process would be more dedicated to treating effluents from the pesticides industry, or other types of effluents with rather high pollutants concentration, before their release in the environment. The first industrial development of this process was in the 60's.

The principal of WAO is to oxidize organic pollutants at high temperature and pressure through the generation of active oxygen species, such as hydroxyl radicals. It has been proven to be a potential treatment technology for wastewaters containing a high content of organic contaminants or toxic pollutants when direct biological treatment is unfeasible (Levec and Pintar, 2007). Typical conditions of WAO are 398-573 K for temperature and 0.5-20 MPa for pressure (Debellefontaine and Foussard, 2000; Lefevre et al., 2012; Lefèvre et al., 2011a, 2011b). By using oxygen or air as the oxidizing agent, WAO method can effectively converts organic pollutants to CO_2 and H_2O and usually less toxic oxidation intermediates up to short-chain acids (Hu et al., 2001; Luck, 1999; Mishra et al., 1995). For a further degradation of short-chain acids, such as acetic acid, supercritical water or a catalytic system is needed, or a biological process (Watanabe et al., 2001). Under high temperatures and pressures, the solubility of oxygen is enhanced in aqueous solutions, which provides a strong driving force for oxidation (Demirel and Kayan, 2012). For industrial applications, the design of bubble columns working at high pressure and high temperature has been yet studied (Feng et al., 2019; Leonard et al., 2019, 2015).

Table S1 summarizes available studies on the treatment of pollutants by WAO process. It is shown that WAO technology could achieve high removals of organic compounds and of total organic carbon (TOC). The performance of WAO can be affected by three main parameters: temperature, oxygen partial pressure (and also total pressure) and reaction time. With the increase of temperature, the removal efficiency of organic compounds generally increases (García-Molina et al., 2007; Lefèvre et al.,

65 2011a; Lei et al., 2007; Mantzavinos et al., 1996). For instance, the removal of 4-
66 chlorophenol ranges from 1.1% to 99.5% with temperature increasing from 423 to 463
67 K (García-Molina et al., 2007). The partial pressure of oxygen is part of the driving
68 force for mass transfer, thus the removal efficiency increases with the increase in
69 oxygen amount (Lei et al., 2007; Mantzavinos et al., 1996). However, if the
70 stoichiometric quantity of oxygen is achieved, the oxygen partial pressure is not a
71 significant factor for organic compounds degradation (Kim and Ihm, 2011; Lei et al.,
72 2007). With increasing reaction time, more free radicals are generated, which promotes
73 the degradation rate (Demirel and Kayan, 2012; Lefèvre et al., 2011a; Shende and
74 Levec, 1999). Although WAO technology has been frequently used for the treatment of
75 organic pollutants, most studies focus on phenolic compounds. Little literature studies
76 the degradation of glyphosate via WAO technology. Only Xing et al. (2018) reports that
77 100% glyphosate removal and over 93% organic phosphorus removal (containing 200-
78 3000 mg L^{-1} glyphosate) is achieved for real glyphosate wastewater by catalytic wet
79 oxidation using modified activated carbon as a catalyst. The reactor is a co-current
80 upflow fixed bed reactor at 383-403 K and under 1.0 MPa with a residence time of 4.8
81 h. There is no literature focuses on the kinetics of glyphosate oxidation by WAO
82 technology, which is necessary for the design of WAO reactor.

83 Several studies show two possible oxidation pathways of glyphosate under other
84 oxidation conditions, such as photodegradation (Chen et al., 2007; Echavia et al., 2009),
85 manganese oxidation (Barrett and McBride, 2005) and H_2O_2/UV oxidation (Manassero
86 et al., 2010): (1) glyphosate transfers to aminomethylphosphonic acid (AMPA) through

87 the cleavage of C-N bond; (2) glyphosate converts to sarcosine through the direct
88 cleavage of C-P bond. AMPA may be further oxidized to methylamine, formaldehyde,
89 NH_4^+, NO_3^- and PO_4^{3-}. Sarcosine could be further oxidized to glycine, formaldehyde,
90 and NH_4^+. Studies on oxidation pathways of glyphosate by WAO process is rare. Only
91 Xing et al. (2018) suggest the AMPA pathways for glyphosate degradation by catalytic
92 wet oxidation.

93 Therefore, this work investigates the wet air oxidation of glyphosate synthetic
94 solutions up to 1 $g.L^{-1}$ in an autoclave batch reactor under three temperatures (423, 473
95 and 523 K) and a pressure of 15 MPa. The kinetics of glyphosate degradation by WAO
96 process is carried out at the three temperatures, to enable the determination of the
97 removal efficiencies, the rate constants and the activation energy of the oxidation
98 reaction. A kinetic model is determined to represent the experimental data for
99 glyphosate. Some possible transformation products of glyphosate are also searched and
100 measured by using UV-spectrophotometry and liquid chromatography coupled to high
101 resolution mass spectrometry, in order to identify the main by-products formed and to
102 propose a possible oxidation pathway of glyphosate by WAO process.

103

104 ## 2 Materials and methods

105 ### 2.1 Chemicals

106 Glyphosate is purchased from Leap Labchem Co., Limited, China with a purity
107 higher than 95%. AMPA and glyoxylic acid are obtained from Sigma-Aldrich (Saint
108 Quentin Fallavier, France). Aqueous stock solutions (1 $g.L^{-1}$) are prepared in

polypropylene bottles, as well as standards and injection solutions. All other chemicals and solvents used are also obtained from Sigma-Aldrich. The synthetic air (purity higher than 99.999%) used as oxidant is bought from Air Liquid, France.

2.2 Experimental procedure

In order to study the kinetics of glyphosate degradation, the experiments are conducted in a batch reactor (Top Industrie, France). The experimental apparatus for WAO in the batch reactor is shown schematically in Fig. S1. The autoclave with an internal volume of 202 mL can reach a maximum pressure and temperature of 30 MPa and 623 K, respectively. The temperature in the reactor is regulated by a hot (electric power)/cold (double jacket with air or water) regulating system. The stirring device is a rushton type mixer with 8 blades, with a hollow shaft allowing recirculation of the gas phase into the liquid phase. Experimentally, the reactor is first pressurized with an amount of nitrogen, which value is estimated from thermodynamic calculations using the Soave-Redlich-Kwong equation of state (Lefèvre et al., 2011b), in order to reach desired final pressure and temperature. To evaluate the influence of the temperature on glyphosate oxidation by WAO process, reactions with an initial glyphosate concentration of 1 g L^{-1} are conducted at three temperatures (423, 473 and 523 K). This concentration of glyphosate is in the range of glyphosate concentration measured in industrial wastewaters (Heitkamp et al., 1992; Xing et al., 2017). The initial pressure of nitrogen is 7.78, 6 and 2.15 MPa with respect to the temperature of 423, 473 and 523 K, respectively. 120 mL glyphosate solution is injected into the reactor and then the

reactor is isolated. When the set temperature is reached, the air is injected into the reactor to achieve the required pressure of 15 MPa and the reaction begins (t=0). An excess of oxygen of 70%, in comparison to the stoichiometry, is fixed at the beginning of the reaction for each tested temperature, i.e. air ratio of 1.7 (Lefèvre et al. 2011a, 2011b). The agitation speed is set at 1000 rpm, which could permit to overcome mass transfer limitations (Lefèvre et al., 2011a). The samples are collected at regular intervals for glyphosate and TOC concentration analysis. The experiments at 473 and 523 K with a reaction time of 15 and 30 min are repeated three times in order to obtain the standard error.

2.3 Analytical methods

pH determined by pH meter (HACH Sension+ PH3). TOC concentration is calculated from the difference between total carbon concentration and inorganic carbon concentration measured by a TOC-L SHIMADZU analyser.

The possible organic intermediates of glyphosate degradation reported in the literature are AMPA, glyoxylic acid, sarcosine and formaldehyde (Aquino Neto and de Andrade, 2009; Balci et al., 2009; Echavia et al., 2009; Lan et al., 2013; Xing et al., 2018). The detection of sarcosine is performed by a specific test kit (Biovision kit Sarcosine, K636-100) with the maximum absorption wavelength (λ) of 570 nm. HCHO is measured by UV-vis spectrophotometry by Spectroquant® test kit (1.14678.0001, Merch Chemicals) at λ=565 nm.

The concentrations of glyphosate, AMPA and glyoxylic acid are determined by

153 LC/MS analysis. LC/MS analyses are performed using an Agilent 1290 Infinity system
154 coupled to an Agilent 6530 Q-TOF tandem mass spectrometer equipped with an Agilent
155 jet stream ion source. Instrument control, data analysis, and processing are performed
156 using Mass Hunter workstation software B4.00. The analysis method is adapted from
157 Yoshioka et al. (2011). Briefly, 1 µL of sample is injected and separation is performed
158 by using an Obelisc N column (150 mm x 2.1 mm internal diameter, 5µm) distributed
159 by SIELC Technologies (Interchim, France). The mobile phase is composed of
160 acetonitrile/water (20/80, v/v) acidified with 0.1% formic at a flow rate of 0.2 mL.min^{-1}
161 ^{1}. The column is kept at 40°C in the column oven. Mass calibration first performs pre-
162 acquisition using ESI-L low concentration tuning mix, provided by Agilent
163 technologies. Mass correction is performed by continuous calibration with hexakis (1H,
164 1H, 3H, tetrafluoropropoxy) phosphine and purine at m/z 922.0098 and m/z 121.0509
165 amu. After LC separation, the solution is introduced into the atmospheric pressure
166 ionization source and ionizes by electrospray in negative ion mode (ESI-) leading to
167 the formation of the [M - H]- ions of the analytes. Source parameters are set as follows:
168 fragmentor 140 V, capillary 3000 V, skimmer 65 V, and nitrogen is used as the drying
169 (350 °C, 10 L.min^{-1}), nebulizing (30 psi) and sheath (350 °C, 8 L.min^{-1}) gas. Scanning
170 is performed from m/z 50 to 1000 amu with 10,038 transients per spectrum.

171 For quantification of the three targeted analytes, Extracted Ion Current
172 chromatograms were used. Retention times, mass of deprotonated molecules and
173 Extracted Ion Current target molecular weight ranges shown between brackets are as
174 follows: glyoxylic acid (3.400 min, 72.9943 amu, [72.8-73.2 amu]), AMPA (3.695 min,

110.0032 amu, [109.8-110.2 amu]) and glyphosate (7.455 min, 168.0111 amu, [167.8-168.2 amu]). The quantification of glyphosate, AMPA and glyoxylic acid concentrations are based on linear regression (R^2>0.999) obtained by injecting standard solutions containing the three analytes with concentrations ranging from 5-200 $\mu g.mL^{-1}$. Instrumental QC is performed by regular analyses of solvent blanks and random injection of standards. Measured values are not deviating more than 15% from the theoretical values. A rough estimation of the concentrations of other phosphorylated by-products identified is performed by using the linear curve obtained for AMPA.

A screening of by-products is performed by working in Total Ion Current - MS mode in order to determine molecular ions m/z. The chromatograms and their mass spectra are inspected for transformation products known from the literature and for unknown compounds. It should be underlined that none of the degradation products is detected in the blank and standard. The elemental compositions are further calculated, the maximum deviation was set to 10 ppm and C, H, N, O, P were selected as possible present elements.

PO_4^{3-}, NH_4^+, and NO_3^- are reported as possible inorganic degradation by-products of glyphosate (Aquino Neto and de Andrade, 2009; Manassero et al., 2010; Lan et al., 2013; Ndjeri et al., 2013). PO_4^{3-} is quantified by UV-vis spectroscopy through using Spectroquant® test kit (1.00798.0001, Merck Chemicals) at λ=690 nm. NH_4^+ is detected by UV-vis spectrophotometry through using Spectroquant® test kit (1.14752.0001, Merck Chemicals) at λ=690 nm. NO_3^- is measured by UV-vis spectroscopy (Spectroquant® test kit 1.09713.0001, Merck Chemicals) with λ=340 nm.

3 Results and discussion

3.1 Glyphosate degradation

In order to check the possible thermal degradation of glyphosate under the three temperatures, the glyphosate concentrations are measured when the required temperature is achieved and before oxygen injection. Different thermal degradations of glyphosate under the three temperatures are found. The glyphosate concentration after thermal degradation decreases from 1000 to 915.56, 754.00 and 459.00 mg L^{-1}, in correspondence with TOC decreasing from 213 to 210.5, 178.1 and 159.3 mg L^{-1}, under temperatures of 423, 473 and 523 K, respectively. Thus, the initial concentrations of glyphosate and TOC for oxidation under the three temperatures are revised to the concentration after thermal degradation. Then the glyphosate and TOC removal (oxidation) is calculated by the following equation:

$$Removal\ (\%) = \frac{(C_0 - C_t)}{C_o} \times 100\% \quad (1)$$

where C_0 is the initial concentration of glyphosate or TOC after revision (mg L^{-1}) and C_t is the concentration at time t (mg L^{-1}).

The experimental results of glyphosate removal with time under three temperatures are shown in Fig. 1. At 523 K, during the first 5 min of reaction, the temperature in the cell increases up to 2 to 3°C due to exothermicity and then stabilizes at 523 K thanks to the regulation system. The reaction temperature has a major effect on the degradation of glyphosate. The glyphosate removal significantly increases with an increase in temperature. At 523 K, complete glyphosate removal is obtained after 30 min. However, the removal of glyphosate is 87.6% and 21.4% after 60 min at 473 and

423 K, respectively. Furthermore, the results show that glyphosate is quickly degraded at 473 and 523 K, but slowly at 423 K, indicating that there seems to be a threshold between 423 and 473 K due to the significant gap in terms of degradation.

As some intermediate products appear during the oxidation of glyphosate to CO_2, it would be convenient for WAO design purposes to present its lumped parameter, i.e., TOC. The effect of the temperature on the TOC removal is shown in Fig. 1. During the reaction time, the TOC decreases following the same pattern as for glyphosate removal. For instance, after 60 min, the TOC removal is 4.5%, 14% and 54% at 423, 473 and 523 K, respectively. At the same reaction time, the TOC removal is smaller than glyphosate removal. This is attributed to the formation of low-molecular-weight and refractory intermediates, which remain in the solution and are not oxidized (Mishra et al., 1995; Vicente et al., 2002), especially at temperature below 473 K. Between 473 and 523 K, there is a considerable performance gap for TOC abatement, indicating that the intermediates of glyphosate are more degradable at 523 K than that at 473 K.

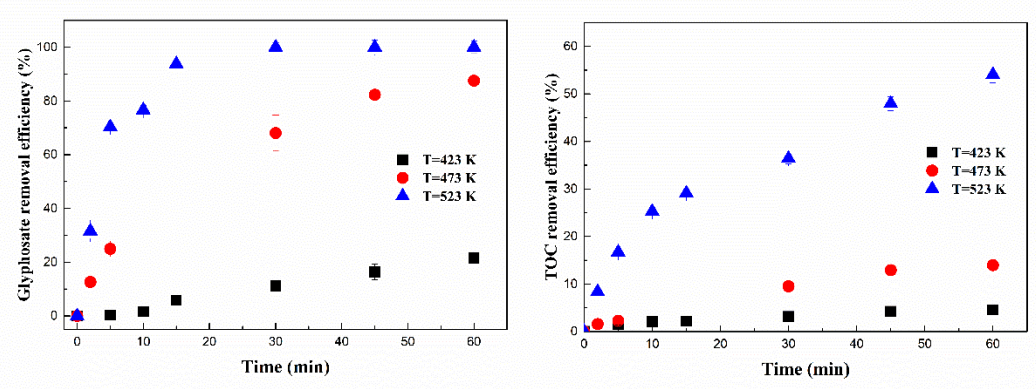

Fig. 1 Effect of temperature on glyphosate and TOC removal efficiencies at 15 MPa

Regarding reaction intermediates, the formation of oxidation by-products of glyphosate in WAO process is further confirmed by the effluent pH. During glyphosate

oxidation by WAO process, the pH increases from 2.5 to 2.6, 3.0 and 4.1 after 60 min at 423, 473 and 523 K, respectively. The increase of pH after oxidation is also found by Xing et al. (2018). The highest pH value is obtained for the highest temperature, indicating a faster elimination of glyphosate and its intermediates. This trend is opposite to other literature dealing with other compounds, which found a pH decrease with the increase in temperature caused by the formation of organic acids as reaction intermediates (García-Molina et al., 2007; Suárez-Ojeda et al., 2007). In our case, this is probably due to the generation of PO_4^{3-} during glyphosate oxidation as confirmed by UV-vis spectrometry. For instance, the concentration of PO_4^{3-} ranged from 5.9 to 99.8 mg L^{-1} with the temperature increasing from 423 to 523 K after 30 min. PO_4^{3-} presents alkaline properties in aqueous solution, causing the increase of pH.

3.2 Kinetic modelling

The global kinetic model tested, considering the concentration of organic compounds and oxygen, has been validated by other authors for the treatment of organic compounds and different wastewaters by WAO process (Lefèvre et al., 2011a; Li et al., 1991; Rivas et al., 1998; Shende and Levec, 1999). The resulting mass balance in the batch reactor is given through Equation 2.

$$r = -\frac{dC}{dt} = kC^n C_{O_2}^m \quad (2)$$

where C is the concentration of organic compound; C_{O_2} is the concentration of oxygen dissolved in the liquid phase; n and m are the partial orders; k is the rate constant, which depends on Arrhenius equation (Equation 3).

$$k = k_o e^{-Ea/RT} \quad (3)$$

where k_o is the pre-exponential factor; E_a is the activation energy for the reaction (kJ mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K).

In most cases for the oxidation of organic compounds by WAO process, a first order with respect to the organic compound is found (Li et al., 1991; Shende and Levec, 1999). Thus, in this study, the order with respect to glyphosate is assumed to be first order. Moreover, it is reported that if an excess oxygen is maintained at a constant partial pressure in the reactor, the zero-order is respected for oxygen and the oxygen terms may be assumed as a constant (Li et al., 1991; Kolaczkowski et al., 1997; García-Molina et al., 2007; Suárez-Ojeda et al., 2007). In this study, the air ratio is 1.7, ensuring that oxygen is in excess. Thus, Equation 2 can be transferred to Equation 4.

$$r = -\frac{dC}{dt} = kC \quad (4)$$

Equation 4 can be integrated to give Equation 5 to obtain the rate constant, k.

$$\ln (C/C_0) = kt \quad (5)$$

Then, Equation 3 is transformed with logarithm to obtain the following expression:

$$lnk = lnk_o - Ea/RT \quad (6)$$

Thus, through linear regression, k_o and E_a are obtained. In this study, C_0 and C represent the initial concentration of glyphosate and glyphosate concentration at time t (mM).

Table 1 Estimations of rate constant, pre-exponential factor and activation energy for glyphosate oxidation

T (K)	k (min^{-1})	R^2	k_0 (min^{-1})	Ea (kJ mol^{-1})
423	0.0042	0.991		
473	0.035	0.995	1212.3	68.4
523	0.17	0.954		

Table 1 shows that the first-order kinetic reaction fits well the glyphosate degradation. The apparent reaction constants are presented in Table 1. It indicates that glyphosate degradation rate increases significantly with an increase in temperature, which is corroborated by the literature (Lei et al., 2007; Lin et al., 1996). Furthermore, the apparent reaction constants are found to well agree with the Arrhenius equation (Fig. S2) with R^2 of 0.99. The activation energy for glyphosate oxidation is estimated through Arrhenius equation at 68.4 kJ mol^{-1} , which is in the upper range of those published for WAO treatment of other organic compounds (33.1-77.8 kJ mol^{-1}) (Helling et al., 1981; Joglekar et al., 1991; Lefèvre et al., 2011a; Pruden and Le, 1976; Suárez-Ojeda et al., 2007). However, this value is well below those found in the literature for some small organic molecules, such as acetic acid (167.7 kJ mol^{-1}), formic acid (121.3 kJ mol^{-1}), or oxalic acid (129.4-133.8 kJ mol^{-1}) (Foussard Jean-Noël et al., 1989; Shende and Mahajani, 1997, 1994). For most WAO process, organic compounds is inclined to oxidize to these small molecules instead of CO_2 and H_2O (Lei et al., 2007). In this study, the low activation energy indicates that glyphosate is more likely to be oxidized to various intermediates.

A comparison of the glyphosate concentrations as a function of time obtain from the results of kinetic experiments with those calculated from the kinetic models is presented in Fig. 2. It can be seen that for the three temperatures studied, the model shows a good fit to the experimental points.

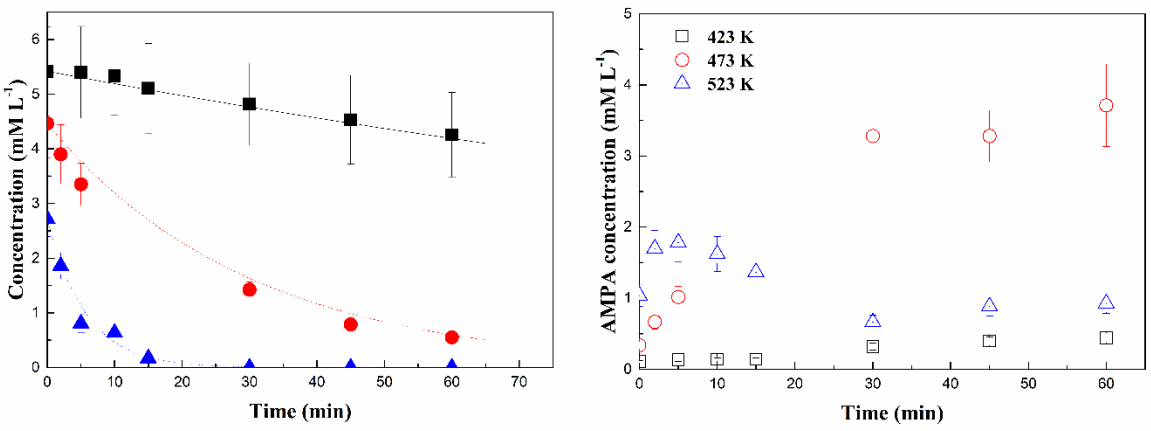

Fig. 2 Experimental and simulated concentration of glyphosate (left) and experimental generated AMPA concentration (right) during the experimental process: (1) ■: Experimental glyphosate concentration at 423 K; (2) ●: Experimental glyphosate concentration at 473 K; (3) ▲: Experimental glyphosate concentration at 523 K; (4) Solid line (—): Simulated glyphosate concentration at 423 K (5) Dash line (---): Simulated glyphosate concentration at 473 K; (6) Dot line (···): Simulated glyphosate concentration at 523 K; (7) □: AMPA concentration at 423 K; (8) ○: AMPA concentration at 473 K; (9) △: AMPA concentration at 523 K.

3.3 Formation of by-products

To further understand the reaction mechanisms involved for glyphosate degradation by WAO process, by-product evaluation is required. Due to the complex variety of oxidation products, it is difficult to identify and quantify all the intermediates. However, some major stable oxidation by-products are measured to propose a possible degradation pathway of glyphosate via WAO. Some oxidation by-products of glyphosate in WAO process are confirmed by LC-MS or UV-vis spectrophotometry. Sarcosine is not detected in the samples by UV-vis spectrophotometer. AMPA, a most

frequently detected primary by-product of glyphosate in water, soil and oxidation treatments (Assalin et al., 2009; Echavia et al., 2009; Xing et al., 2018), is also detected in our study by using LC/MS analysis at the m/z ratio of 110.0032 amu. The concentrations of AMPA generated under three temperatures are presented in Fig. 2. It shows that at 423 K, low removal of glyphosate is obtained with little AMPA formed; at 473 K, high removal of glyphosate is achieved and almost all removed glyphosate is transformed into AMPA; complete glyphosate degradation is achieved and the AMPA generated at the beginning of the reaction is further degraded into other by-products over time at 523 K.

To further understand the relationship between glyphosate degradation and AMPA formation, glyphosate degradation, AMPA yield and relative yield of AMPA (described as the ratio of the molar quantity of AMPA generated, divided by the molar quantity of glyphosate removed) are calculated by equations 7-9.

$$\text{Glyphosate degradation (\%)} = \frac{n^0_{GLY} - n^t_{GLY}}{n^0_{GLY}} \times 100 \quad (7)$$

$$\text{AMPA yield (\%)} = \frac{n_{AMPA}}{n^0_{GLY}} \times 100 \quad (8)$$

$$\text{Relative yield (\%)} = \frac{n_{AMPA}}{n^0_{GLY} - n^t_{GLY}} \times 100 \quad (9)$$

where n^0_{GLY} is the initial glyphosate quantity (mol, with respect to the initial concentration of 1 $g.L^{-1}$); n^t_{GLY} is the glyphosate quantity at time t (mol); n_{AMPA} is the AMPA quantity at time t (mol).

The results of glyphosate degradation, AMPA yield and relative yield of AMPA under three temperatures are shown in Fig. 3. This figure shows that AMPA yield increases with respect to the increase of glyphosate degradation at 423 and 473 K, while

it first increases then decreases at 523 K. This indicates that AMPA is the primary product of glyphosate and can be further degraded at high temperature. Moreover, the relative yield of AMAP is close to 70% at 473 K, demonstrating that AMPA is the major transformation product of glyphosate at this temperature. The decrease of the relative yield to 15% at 523 K shows that by-products other than AMPA and containing the element P are mainly formed at this latter temperature.

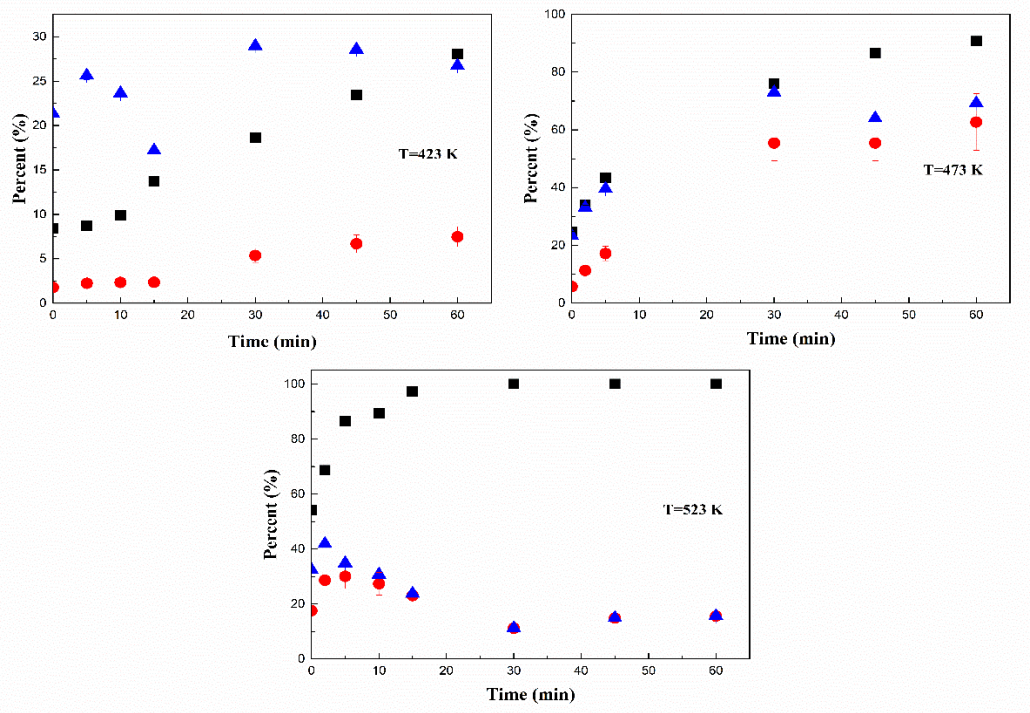

Fig. 3 Glyphosate degradation (■), AMPA yield (●) and relative yield of AMPA (▲) during oxidation process at 423-523 K

Furthermore, in order to further confirm the degradation of AMPA at 523 K, some kinetic experiments of AMPA degradation by WAO process are conducted using the same experimental procedure as for glyphosate (see section 2.2), with an initial AMPA concentration of 658 mg L^{-1} corresponding to the same molar quantity as an initial glyphosate concentration of 1 g L^{-1}. The rate constant of AMPA degradation by WAO

process at 523 K is 0.01 mM min^{-1} with the half-life of 69.3 min (Fig. S3). After 60 min, the removal efficiency of AMPA is 45.7%, which is lower than glyphosate removal for the same conditions, indicating that AMPA is more resistant to degradation than glyphosate, which is consistent with Xing et al. (2018).

The LC-MS analysis also reveal the presence of glyoxylic acid with m/z of 72.9943 amu. Fig. 4 shows the formation of glyoxylic acid during WAO degradation of glyphosate. A low but almost constant concentration of glyoxylic acid is measured at 423 K, while at 473 and 523 K, its concentration first increases and then decreases until it tends towards 0; this fall being particularly fast at 523 K. This suggests a quick further oxidation of glyoxylic acid at higher temperatures. It was indeed reported that glyoxylic acid can be further oxidized into formic acid (HCOOH) and finally mineralized into CO_2 (Balci et al., 2009; Echavia et al., 2009).

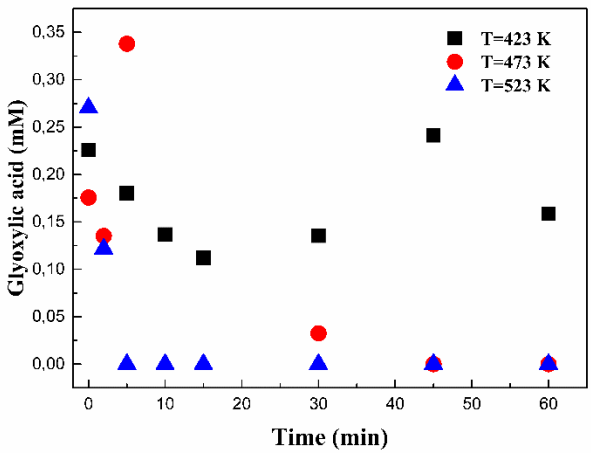

Fig. 4 The formation of glyoxylic acid in WAO degradation of glyphosate.

375 Table 2 Concentration of by-products of glyphosate in the WAO process under three

376 temperatures after 30 min

T (K)	AMPA (mg L^{-1})	PO_4^{3-} (mg L^{-1})	NH_4^+ (mg L^{-1})	NO_3^- (mg L^{-1})	HCHO (mg L^{-1})
423	35.4	5.9	-	2.7	3.1
473	364.0	41.1	-	2.5	42.2
523	73.4	99.8	9.2	2.6	35.4

377 Table 2 shows the concentration of other by-products from glyphosate, such as
378 PO_4^{3-}, NH_4^+, NO_3^-, and HCHO, in WAO conditions under three temperatures after 30
379 min. It indicates that the concentration of PO_4^{3-} increases with reaction temperature,
380 which is inconsistent with the destruction of glyphosate, implying that PO_4^{3-} is not
381 transformed directly from glyphosate, but rather from AMPA. Considering the element
382 N in AMPA, NH_4^+ (Echavia et al., 2009; Ndjeri et al., 2013; Xing et al., 2018), which
383 is frequently reported as one of the final mineralization product of AMPA, is only
384 formed at 523 K. But the mass of N in the produced NH_4^+ is not equal to the mass of N
385 in the AMPA degraded, indicating the presence of reaction intermediates between
386 AMPA and NH_4^+. From recent literature (Annett et al., 2014; Fu et al., 2017),
387 methylamine (CH_3NH_2) has been reported as the intermediate during the degradation
388 of AMPA to NH_4^+, which is also possible in our case, but this is not confirmed by
389 measuring it. The concentrations of NO_3^- under three temperatures are almost the same
390 and equal to the initial glyphosate solution, indicating that NO_3^- is not the final
391 mineralization product of glyphosate in our experiments. It is probably due to the short
392 reaction time, which is not enough to further oxidize the generated NH_4^+ into NO_3^-.
393 Furthermore, the concentration of HCHO increased significantly with the increase in

reaction temperature from 423 K to 473 K. As for each mole of glyphosate decomposed, the yield of AMPA and HCHO is not equivalent, it is supposed that glyphosate was not directly degraded into HCHO. The concentration of HCHO is approximately the same as the concentration of PO_4^{3-}. This equality may indicate that HCHO and PO_4^{3-} are directly formed through the degradation of AMPA, which is consistent with the results obtained by Xing et al. (2018). When the temperature further increases to 523 K, the concentration of HCHO decreases, indicating that HCHO can be further oxidized to other by-products at the highest temperature. HCOOH intermediate and final mineralization into CO_2 has been previously reported (Manassero et al., 2010; Xing et al., 2018; Yang et al., 2018).

3.4 Proposed degradation pathway

A degradation pathway of glyphosate in WAO conditions (Fig. 5) is proposed considering the evaluation of major intermediates and final products based on experimental data. Previous studies have reported that glyphosate oxidation often follows two mechanisms, which are related to the cleavage of C-N and C-P bonds to generate AMPA and sarcosine, respectively (Barrett and McBride, 2005; Manassero et al., 2010; Paudel et al., 2015; Yang et al., 2018). In this work, the existence of AMPA and glyoxylic acid and the absence of sarcosine indicate that the glyphosate degradation by WAO conditions followed the mechanism of C-N bond cleavage. First, the C-N bond of glyphosate promoted by OH attack is broken and yield to AMPA, and glyoxylic acid. Glyoxylic acid is further oxidized into HCOOH. Then C-P bond cleavage of AMPA generated PO_4^{3-}, HCHO, and methylamine (CH_3NH_2). Methylamine is further oxidized

into NH_4^+ and HCHO. WAO conditions generally involve the oxidation of NH_4^+ into NO_3^- and the oxidation of HCHO into HCOOH, and further into CO_2 and H_2O. As these final products were not detected in this work, these transformations are reported with dotted arrow on the pathway scheme of Fig. 5.

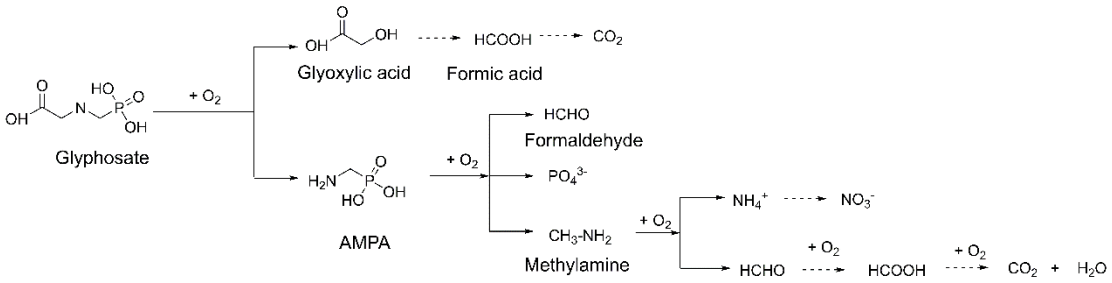

Fig. 5 A proposed degradation pathway of glyphosate for WAO conditions

4 Conclusions

WAO process is an effective technique to treat effluents containing glyphosate since complete glyphosate removal and 54% of TOC reduction was obtained at 523 K and 15 MPa after 60 min. The glyphosate oxidation obeys first-order kinetics with respect to glyphosate concentration. The degradation rate is faster when increasing the reaction temperature. The activation energy is 68.4 kJ mol^{-1}. Some possible by-products of glyphosate in WAO process are identified and a degradation pathway is proposed. This study proposes a kinetic scheme which can be easily implemented in a WAO process simulation in order to obtain a first evaluation of the process functioning. Further work to consider the kinetic scheme with by-products of glyphosate should be studied to have more accurate information on WAO process.

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