

DEGRADATION OF CHLOTHIANIDIN FROM DANTUTSO 50WG IN ELECTROCHEMICAL PROCESS: KINETICS AND ROLE OF REACTIVE SPECIES

Nguyen Tien Hoang*

The University of Danang - University of Science and Education

*Corresponding author: nthoang@ued.udn.vn

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Abstract - The kinetic degradation of clothianidin (CLO) (in Dantuso 50 WG) during electrochemical oxidation (EO) process using sulfate- and chloride-supporting electrolytes was comprehensively investigated. The degradation of CLO was not due to direct electron oxidation, but was mainly due to $\bullet\text{OH}$ and other radicals generated from supporting electrolytes. The degradation of CLO was significantly inhibited when increasing the concentration of nitrobenzene (NB), methanol (MeOH) and benzoic acid (BA). The second-order rate constant of $\bullet\text{OH}$ toward CLO was determined to be $3.23 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ using competition kinetics method. When SO_4^{2-} and Cl^- were used as supporting electrolytes, the degradation of CLO by $\bullet\text{OH}$ was the same with $k_{\text{CLO}} = 0.0084 \text{ min}^{-1}$. Meanwhile, the higher removal of CLO in SO_4^{2-} -supporting electrolyte was due to the contribution of ($\text{SO}_4^{\bullet-}/\text{S}_2\text{O}_8^{\bullet-}$) more than that of ($\text{Cl}^{\bullet}/\text{HClO}/\text{ClO}^{\bullet}$).

Key words - Clothianidin; the second-order rate constant; electrochemical degradation; kinetic degradation; competition kinetics method.

1. Introduction

Pesticides, the organic compounds, have been commonly used in the agriculture to kill insects and pests. However, the widespread use of pesticides cause the serious problems to human health and ecological balance. It becomes of great interests to scientists and motivates them to find ways to deal with pesticides. Among them, CLO ([E]-1-[2-chloro-1,3-thiazol-5-yl-methyl]-3-methyl-2-nitroguanidine) is a new pesticide, which is classified in the neonicotinoid group [1]. Its structure contains an open long chain of nitroguanidine with a thiazole ring (Figure 1).

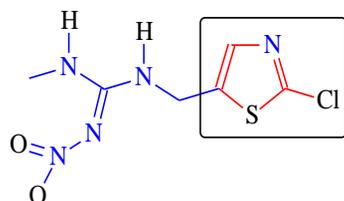
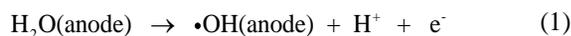


Figure 1. Structural formula of CLO

Because of CLO's long-term stability in different environments, its long lifetime in surface water and groundwater was determined with a half-life of up to 545 days in the soil [2], even up to 6931 days in soil [3]. In advanced oxidation processes (AOPs), EO was considered to be a promising technology for the removal of various types of organics: pesticides, pharmaceuticals and others [4]. The EO mechanism is mainly attributed to hydroxyl radical ($\bullet\text{OH}$, $E^0 = 2.74 \text{ V}$, Eq. (1)) formed at the anode surface, thereby oxidizing the organics in solution [5]. Besides, sulfate radical ($\text{SO}_4^{\bullet-}$, $E^0 = 2.5\text{-}3.1 \text{ V}$, Eqs. (2-3)) formed from the electron transfer at the anode also

contributes to the degradation of organics if sulfate anions are used as the supporting electrolyte [6].



Additionally, the electrochemical activation of persulfate was also an alternative EO to improve the efficiency of process [4]. This can be activated through the direct electron transfer at the cathode (Eq. (3)). Also, the efficiency of organics degradation was dependent on types of electrolyte: Cl^- , NO_3^- , $\text{HCO}_3^-/\text{CO}_3^{2-}$, etc [7].



The purpose of this study was to: (1) Determine the limitation detection of CLO by HPLC and UV-Vis; (2) Investigate the kinetic degradation of CLO in different types of electrolyte; (3) Determine the role of reactive species on the CLO degradation.

2. Materials and methods

2.1. Reagents

Dantutso 50 WG (contains 50% of CLO by weight in powder form) was purchased from market in Vietnam. CLO (99.5%) was of analytical grade from Merck. Methanol (MeOH), acetone, TBA (*tert*-butanol), BA (benzoic acid), acetic acid and other chemicals are of analytical grade, were purchased from Sigma-Aldrich. The solutions were prepared using distilled water.

2.2. Experimental procedures

The experiments were conducted in a 250 mL glass using a DC power at room temperature ($t_{\text{emp.}} = 25^\circ\text{C}$) and under rotation speed (700 rpm). The anode (boron-doped diamond, BDD, $2 \text{ cm} \times 2 \text{ cm}$) and the cathode (Pt, $1.5 \text{ cm} \times 1 \text{ cm}$) were placed at distance of 2 cm (see Figure S5, SI). The solution containing CLO was initially filtered by Whatman paper (9.0 cm dia; pore size $0.4 \mu\text{m}$) to eliminate the residues before starting analytical procedures and/or electrochemical degradation of CLO. Note that CLO accounted for 50% in Dantutso 50 WG and the impurities did not cause any interference in solution. The solution pH was adjusted using 0.05 M NaOH and 0.05 M H_2SO_4 . The volume of the treated solution was 150 mL. All experiments were conducted in duplicate.

2.3. Analytical methods

CVs measurement

The CV curves of BDD in the presence of $20 \mu\text{M}$ CLO were recorded between -1.0 V to 2.0 V (E^0 vs SCE) at

different scan rates using Metrohm Autolab installed by Nova 2.1 software for electrochemical interface.

UV-vis measurement

The optical absorption property for CLO was measured using a UV-Vis spectrometer (Jasco, V730) in the wavelength region between 200 and 350 nm. For each measurement, the quartz cuvette was rinsed with distilled water to make sure no residue remained for the new run.

Concentration of persulfate (PS, $S_2O_8^{2-}$) was measured in a UV-Vis spectrophotometer (V730, Jasco, Japan) at wavelength of 287 nm based on the potassium iodide method [8]. The PS standard solutions were prepared in the range of 0.1, 0.2, 0.3, and 0.4 mM. The KI/NaHCO₃ solution was prepared with a KI/NaHCO₃ ratio of (15 g L⁻¹ KI):(5 g L⁻¹ NaHCO₃). 500 μ L of PS standard solutions or the treated solutions were added into 5 mL KI/NaHCO₃ solution. After that, the mixture was shaken by hand for 15 min before measuring at 287 nm in a UV-Vis spectrophotometer.

The concentration of active chlorine (HOCl/OCl) was calculated using DPD colorimetric method [9]. The reaction between active chlorine and DPD (N,N-diethyl-1,4-phenylenediamine sulfate) results in the pinkish color that can be measured at 515 nm using a UV-Vis spectrophotometer.

HPLC measurement

Concentrations of the standard CLO solution were measured using a HPLC system (Aligent) equipped with a Eurospher 100 5 C8, 250 mm \times 4.6 mm column and a UV-Vis detector at the temperature column of 40°C. The mobile phase consisted of acetonitril/water (50/50, v/v), pH = 3, at a flow rate of 0.8 mL min⁻¹, with a detection wavelength of 254 nm. The inject volume was 10 μ L.

3. Results and discussion

3.1. Stability of CLO and CVs test for direct oxidation of CLO in EO process

Obviously, CLO was reported to be very stable in aqueous solution and in soil [3]. To clarify the durability of CLO in pesticide Dantutso 50 WG, the stability of CLO in different pHs was again tested within 18 to 20 days (Figure 2). As predicted, we did not see any loss in CLO within 18 to 20 days, indicating that CLO is highly stable under different pH conditions.

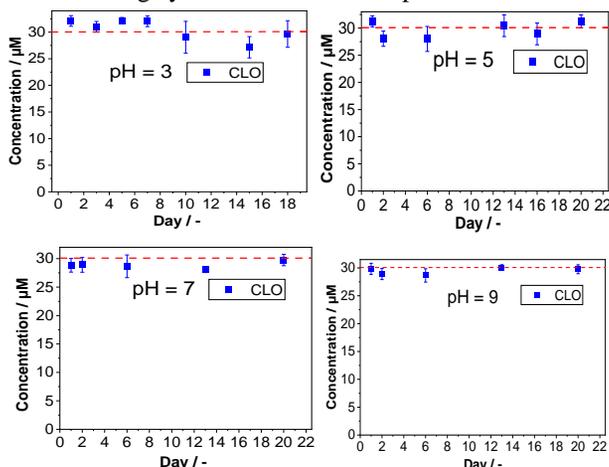


Figure 2. Durability of CLO at different pHs 3, 5, 7, and 9. [CLO] = 30 μ M

The direct oxidation of a compound involves the electron transfer on the surface of electrode. This process undergoes two steps: (i) Diffusion of organic matter from the solution to the electrode surface; (ii) Oxidation of organic matter at the surface. Generally, the direct oxidation is also classified in two ways: Partially oxidation and electrochemical combustion. If the oxidation peaks can be observed in the CVs during forward scanning [10], the degradation of organic is attributed to direct oxidation. The contribution of direct oxidation was much less than that of indirect oxidation [11]. However, there was no oxidation peak in the CV, indicating that the degradation of CLO by direct oxidation was negligible. Therefore, the degradation of CLO was mainly attributed to reactive radicals (i.e., \bullet OH, $SO_4^{\bullet-}$, Cl^{\bullet} , etc.).

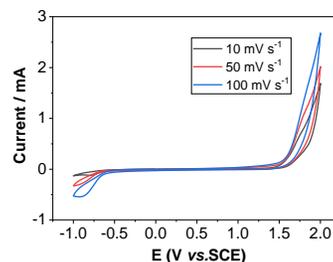


Figure 3. CVs of CLO at different scan rates. [Na₂SO₄] = 0.05 M, [CLO] = 20 μ M

3.2. Degradation of CLO in different electrolytes

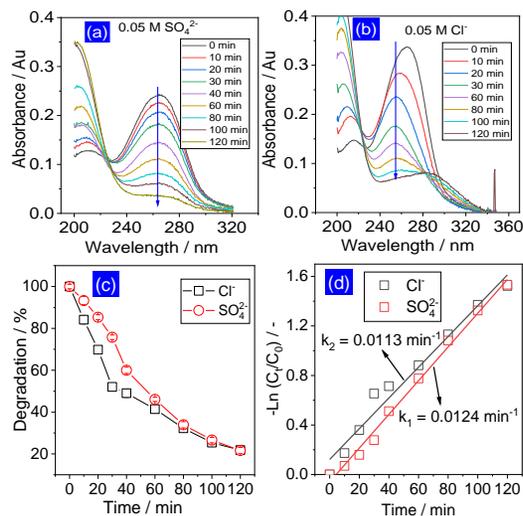


Figure 4. The degradation of CLO in electrochemical process. **a, b** Spectrum of CLO versus electrolysis time in Cl^- and SO_4^{2-} , respectively. **c** Degradation of CLO in electrolytes. **d** The first-order degradation rate constant of CLO.

Experimental conditions: [CLO] = 200 μ M, [Cl⁻] = [SO₄²⁻] = 0.05 M, j = 10 mA cm⁻², BDD (anode), Pt (cathode), no pH adjustment (pH about 6.7), 700 rpm

It is well-known that the degradation efficiency of organics was highly dependent on the type of electrolytes [7], because it was related to the generated reactive species, which contributed to the degradation of organics. Among them, Cl⁻ and SO₄²⁻ are considered to be the common and effective supporting electrolytes [10], [12]. Therefore, they were selected in this study for comparison. As seen in Figure 4a-b, the peak for CLO gradually decreased during the electrolysis time. There was no difference in the degradation efficiency of CLO in case of Cl⁻ and SO₄²⁻, about 80% of CLO was

removed after 120 min (Figure 4c). The degradation of CLO well fitted the first-order rate constant with $k_1 = 0.0124 \text{ min}^{-1}$ (in SO_4^{2-}) and $k_2 = 0.0113 \text{ min}^{-1}$ (in Cl^-) (Figure 4d).

In EO process, active chlorine (AC) ($\text{HOCl}/\text{ClO}^\cdot$) (Figure S3) and persulfate (PS, $\text{S}_2\text{O}_8^{2-}$) (Figure S4) was formed. These oxidants might contribute to the degradation of some organics, as reported in previous studies [1], [13]. The formation mechanisms of AC and PS can be seen in Figures (4-6).



The accumulation of AC and PS during electrolysis time is displayed in Figure 5 (the spectra for their detection are displayed in Figs. S(3-4), SI). As seen in Figure 5, the accumulation of AC reached 0.05 mM after 120 min meanwhile that of PS was 0.06 mM. The previous studies have also detected the formation of active chlorine in electrochemical process [14], [15]. To test the degradation possibility of CLO by AC/PS, the degradation of CLO was conducted in a water solution containing AC/PS with the same concentrations at 120 min in the EO process (see Figure 5). As a result, the degradation of CLO by AC and PS was insignificant (data was not shown), indicating that the contribution of AC/PS in EO was negligible. However, the kinetic degradation of CLO in EO process should take into account such oxidants.

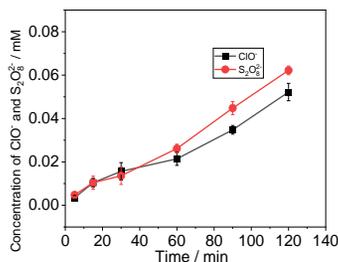


Figure 5. AC and PS concentrations in case of 0.05 M NaCl and 0.05 M Na_2SO_4 during electrochemical oxidation. Experimental conditions:

$[\text{CLO}] = 200 \mu\text{M}$, $[\text{Cl}^-] = [\text{SO}_4^{2-}] = 0.05 \text{ M}$, $j = 10 \text{ mA cm}^{-2}$, BDD (anode), Pt (cathode), no pH adjustment (pH about 6.7), 700 rpm

3.3. Role of reactive species to CLO degradation in EO process

As discussed above, the direct oxidation and AC/PS were not involved in the degradation of CLO. Therefore, this degradation was mainly attributed to the reactive radicals (i.e., $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, Cl^\cdot , etc.). To determine the contribution of those radicals to CLO degradation, the quenching studies were performed [4], [11]. In Sulfate-EO process (the process was conducted using sulfate as the supporting electrolyte), MeOH was used to capture both $\cdot\text{OH}$ ($k_{\cdot\text{OH},\text{MeOH}} = 9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and $\text{SO}_4^{\cdot-}$ ($k_{\text{SO}_4^{\cdot-},\text{MeOH}} = 1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) [16], [17]. In Chloride-EO process (the process was conducted using chloride as the supporting electrolyte), BA was used to scavenge both $\cdot\text{OH}$ and Cl^\cdot ($k_{\cdot\text{OH},\text{BA}} = 5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{Cl}^\cdot,\text{BA}} = 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [18]. For both cases, NB was used to scavenge $\cdot\text{OH}$ ($k_{\cdot\text{OH},\text{NB}} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) because NB was resistant to other radicals [19].

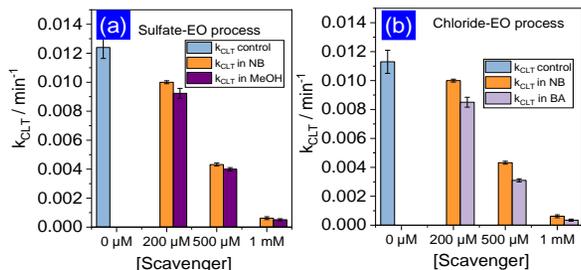
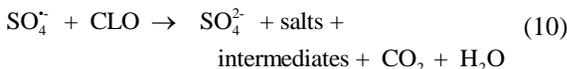
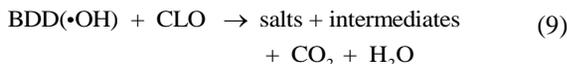


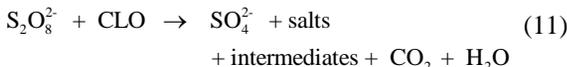
Figure 6. CLO degradation in the presence of NB, MeOH and BA in Sulfate-EO and Chloride-EO processes. Experimental conditions: $[\text{CLO}] = 200 \mu\text{M}$, $[\text{Cl}^-] = [\text{SO}_4^{2-}] = 0.05 \text{ M}$, $j = 10 \text{ mA cm}^{-2}$, BDD (anode), Pt (cathode), no pH adjustment (pH about 6.7), $t = 120 \text{ min}$, 700 rpm

In Sulfate-EO process

As seen in Figure 6a, k_{CLO} decreased by 20% and 25% when adding 200 μM of NB and MeOH, respectively. When increasing the concentration of NB and MeOH to 1 mM, k_{CLO} significantly decreased by 95%. This is due to the scavenging effect of NB/MeOH toward $\cdot\text{OH}/\text{SO}_4^{\cdot-}$. Therefore, $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ were the dominant radicals contributing to the degradation of CLO in Sulfate-EO process (see their mechanism in Eqs. (9-10)) [20]. The the formation mechanism of those radicals can be seen in Eqs. (7-8).



If PS contributes to CLO degradation, then:



The kinetic degradation of CLO in this process can be expressed as follow:

$$-\text{Ln}\left(\frac{[\text{CLO}]_t}{[\text{CLO}]_0}\right) = k_{d,\text{CLO}} + k_{\cdot\text{OH},\text{CLO}}[\cdot\text{OH}] + \quad (12)$$

$$k_{\text{SO}_4^{\cdot-},\text{CLO}}[\text{SO}_4^{\cdot-}] + k_{\text{S}_2\text{O}_8^{2-},\text{CLO}}[\text{S}_2\text{O}_8^{2-}]$$

where $k_{d,\text{CLO}}$ represents the degradation of CLO by direct oxidation. This value was negligible as discussed above, therefore, Eq. (12) can be simplified as:

$$-\text{Ln}\left(\frac{[\text{CLO}]_t}{[\text{CLO}]_0}\right) = k_{\cdot\text{OH},\text{CLO}}[\cdot\text{OH}] + \quad (13)$$

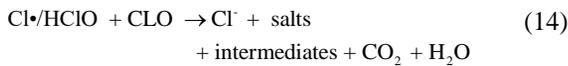
$$k_{\text{SO}_4^{\cdot-},\text{CLO}}[\text{SO}_4^{\cdot-}] + k_{\text{S}_2\text{O}_8^{2-},\text{CLO}}[\text{S}_2\text{O}_8^{2-}]$$

where $k_{\cdot\text{OH},\text{CLO}}$ and $k_{\text{SO}_4^{\cdot-},\text{CLO}}$ were the second-order rate constants of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ toward CLO, respectively, $\text{M}^{-1} \text{ s}^{-1}$; $[\cdot\text{OH}]$ and $[\text{SO}_4^{\cdot-}]$ were the steady-state concentration of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$, respectively (M); $k_{\text{S}_2\text{O}_8^{2-},\text{CLO}}[\text{S}_2\text{O}_8^{2-}]$ is the degradation rate of CLO by PS, min^{-1} .

In Chloride/EO process

Similarly, in Chloride-EO process, k_{CLO} decreased by 12% and 25% when adding 200 μM of NB and BA. When increasing the concentration of NB and BA to 1 mM, k_{CLO}

significantly decreased by 95% and 97%, respectively. This is due to the scavenging effect of NB/BA toward $\bullet\text{OH}/\text{Cl}\bullet$. Therefore, $\bullet\text{OH}$ and $(\text{Cl}\bullet/\text{HClO})$ were the dominant radicals contributing to the degradation of CLO in Chloride-EO process. The mechanism formation of free chlorine can be seen in Eqs. (4) and (5). The mechanism degradation of CLO by $(\text{Cl}\bullet/\text{HClO})$ can be expressed in Eq. (14).



The kinetic degradation of CLO in Chloride-EO process can be expressed as follow:

$$-\text{Ln}\left(\frac{[\text{CLO}]_t}{[\text{CLO}]_0}\right) = k_{d,\text{CLO}} + k_{\bullet\text{OH},\text{CLO}}[\bullet\text{OH}] + k_{\text{Cl}\bullet,\text{CLO}}[\text{Cl}\bullet] \quad (15)$$

$$+ k_{\text{HClO}/\text{ClO}^-,\text{CLO}}[\text{HClO}/\text{ClO}^-]$$

where $k_{d,\text{CLO}}$ represents the degradation of CLO by direct oxidation. This value was negligible as discussed above, therefore, Eq. (15) can be simplified as:

$$-\text{Ln}\left(\frac{[\text{CLO}]_t}{[\text{CLO}]_0}\right) = k_{\bullet\text{OH},\text{CLO}}[\bullet\text{OH}] + k_{\text{Cl}\bullet,\text{CLO}}[\text{Cl}\bullet] \quad (16)$$

$$+ k_{\text{HClO}/\text{ClO}^-,\text{CLO}}[\text{HClO}/\text{ClO}^-]$$

where $k_{\bullet\text{OH},\text{CLO}}$ and $k_{\text{Cl}\bullet,\text{CLO}}$ were the second-order rate constants of $\bullet\text{OH}$ and $\text{Cl}\bullet$ toward CLO, respectively, $\text{M}^{-1}\text{s}^{-1}$; $[\bullet\text{OH}]$ and $[\text{Cl}\bullet]$ were the steady-state concentration of $\bullet\text{OH}$ and $\text{Cl}\bullet$, respectively (M).

3.4. Contribution of reactive species to CLO degradation

According to Eqs. (13) and (16), to determine the contribution of $\bullet\text{OH}$, $(\text{SO}_4^{\bullet-}/\text{S}_2\text{O}_8^{2-})$ and $(\text{Cl}\bullet/\text{HClO}/\text{ClO}^-)$ to CLO degradation, the second-order rate constants of radicals toward CLO and the steady-state concentration of radicals should be considered: i.e., $k_{\bullet\text{OH}/\text{SO}_4^{\bullet-}/\text{Cl}\bullet,\text{CLO}}$ and [radical].

Therefore, $k_{\bullet\text{OH},\text{CLO}}$ and $[\bullet\text{OH}]$ should be calculated. The contribution of the rest radicals was $\text{SO}_4^{\bullet-}$ or $\text{Cl}\bullet/\text{HClO}/\text{ClO}^-$, which could be not necessary to determined once we know the contribution of $\bullet\text{OH}$ to CLO degradation to simplify the calculation of each radicals in EO process. The first step: $k_{\bullet\text{OH},\text{CLO}}$ was determined based on the competition kinetics method [21], [22], in which both CLO and NB was degraded in UV/ H_2O_2 system. It was determined in section “**Determination of the second-order rate constant of $\bullet\text{OH}$ toward CLO ($k_{\bullet\text{OH},\text{CLO}}$)**”. The second step: calculate the steady-state concentration of $\bullet\text{OH}$ ($[\bullet\text{OH}]$) in Sulfate-EO and Chloride-EO processes, which was determined in section “**Calculating the $[\bullet\text{OH}]$ in Sulfate-EO and Chloride-EO processes**”.

Determination of the second-order rate constant of $\bullet\text{OH}$ toward CLO ($k_{\bullet\text{OH},\text{CLO}}$)

The second-order rate constant of CLO reacting with $\bullet\text{OH}$ can be determined using UV/ H_2O_2 :

$$k_{\text{CLO}} = k_{w,\text{CLO}} + k_{\bullet\text{OH},\text{CLO}}[\bullet\text{OH}] \quad (17)$$

$$k_{\text{NB}} = k_{w,\text{NB}} + k_{\bullet\text{OH},\text{NB}}[\bullet\text{OH}] \quad (18)$$

$\bullet\text{OH}$ radical was the dominant radical and contributed mainly to the degradation of pollutants (i.e., CLO and NB) in the UV/ H_2O_2 system [23]. The contribution of UV to

CLO and NB degradation ($k_{w,\text{CLO}}$ and $k_{w,\text{NB}}$) was negligible in the condition: $[\text{CLO}] = [\text{NB}] = 20\ \mu\text{M}$, $[\text{H}_2\text{O}_2] = 1\ \text{mM}$, $t = 20\ \text{min}$, $\text{pH} = 7$, UV fluence rate: $145\ \mu\text{W cm}^{-2}$. Then $k_{\bullet\text{OH},\text{CLO}}$ can be determined according to Eq. (19):

$$k_{\bullet\text{OH},\text{CLO}} = \frac{k_{\text{CLO}}}{k_{\text{NB}}} \times k_{\bullet\text{OH},\text{NB}} = \frac{\ln([\text{CLO}]_0/[\text{CLO}]_t)}{\ln([\text{NB}]_0/[\text{NB}]_t)} \times k_{\bullet\text{OH},\text{NB}} \quad (19)$$

$$\text{or } \ln([\text{CLO}]_0/[\text{CLO}]_t) = \frac{k_{\bullet\text{OH},\text{CLO}}}{k_{\bullet\text{OH},\text{NB}}} \ln([\text{NB}]_0/[\text{NB}]_t) \quad (20)$$

According to Eq. (20), the plots of $\ln([\text{CLO}]_0/[\text{CLO}]_t)$ vs $\ln([\text{NB}]_0/[\text{NB}]_t)$ has a straight line with slope of $k_{\bullet\text{OH},\text{CLO}}/k_{\bullet\text{OH},\text{NB}}$ that was applied to calculate $k_{\bullet\text{OH},\text{CLO}}$

with the known $k_{\bullet\text{OH},\text{NB}} = 3.9 \times 10^9\ \text{M}^{-1}\text{s}^{-1}$, as shown in

Figure 7. As a result, $k_{\bullet\text{OH},\text{CLO}}$ was determined to be $3.23 \times 10^9\ \text{M}^{-1}\text{s}^{-1}$, which was consistent with the reactivity of $\bullet\text{OH}$ toward organics (their second-order rate constant in the range of 10^9 - $10^{10}\ \text{M}^{-1}\text{s}^{-1}$) [23].

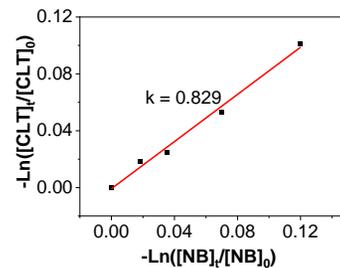


Figure 7. Competition kinetics of NB and CLO with hydroxyl radical ($\bullet\text{OH}$). Experimental conditions: $[\text{CLO}] = [\text{NB}] = 20\ \mu\text{M}$, $[\text{H}_2\text{O}_2] = 1\ \text{mM}$, $\text{pH} = 7$, UV intensity ($145\ \mu\text{W cm}^{-2}$), $t = 20\ \text{min}$, $\text{temp.} = 25^\circ\text{C}$

Calculating the $[\bullet\text{OH}]$ in Sulfate-EO and Chloride-EO processes

As argued above, NB was degraded only by $\bullet\text{OH}$ in EO-process and the degradation of NB by electron transfer was negligible. Therefore, it was used to determine the $[\bullet\text{OH}]$ [11]. The kinetic degradation of NB in EO process is expressed as:

$$k_{\text{NB}} = k_{\bullet\text{OH},\text{NB}}[\bullet\text{OH}] \quad (21)$$

where k_{NB} (min^{-1}) was the first-order degradation rate constant of NB in EO process; $[\bullet\text{OH}]$ was the steady-state concentration of $\bullet\text{OH}$ (M), $k_{\bullet\text{OH},\text{NB}} = 3.9 \times 10^9\ \text{M}^{-1}\text{s}^{-1}$. Therefore:

$$[\bullet\text{OH}] = k_{\text{NB}} / k_{\bullet\text{OH},\text{NB}} \quad (22)$$

Figure 8 displays the k_{NB} in Sulfate-EO process and Chloride-EO process for calculating the $[\bullet\text{OH}]$ in those processes. Therefore, $[\bullet\text{OH}]$ was calculated to be $2.6 \times 10^{-12}\ \text{M}$.

The contribution of reactive radicals to CLO degradation can be observed in Figure 9. When using SO_4^{2-} and Cl^- as supporting electrolytes, k_{CLO} by $\bullet\text{OH}$ was the same ($0.0084\ \text{min}^{-1}$) because the $[\bullet\text{OH}]$ was the same. k_{CLO} by $\bullet\text{OH}$ accounted for 68% and 74% in Sulfate-EO and Chloride-EO processes, respectively. The differences in k_{CLO} was mainly due to the contribution of $(\text{SO}_4^{\bullet-}/\text{S}_2\text{O}_8^{2-})$ and $(\text{Cl}\bullet/\text{HClO}/\text{ClO}^-)$ groups. It can be concluded that the generation of $\bullet\text{OH}$ was rather dependent on the type of

electrodes and the concentration of supporting electrode [7], [11], [24]. Because BDD was used as anode for this investigation and the concentrations of supporting electrolytes were the same. Therefore, there was no difference in $[\bullet\text{OH}]$. In contrast, k_{CLO} by $(\text{SO}_4^{\bullet-}/\text{S}_2\text{O}_8^{2-})$ was higher than that of $(\text{Cl}\bullet/\text{HClO}/\text{ClO}^-)$ probably due to two reasons: (1) the strong oxidation capability of $\text{SO}_4^{\bullet-}$ compared to $\text{Cl}\bullet$; (2) $\text{SO}_4^{\bullet-}$ was generated more than $\text{Cl}\bullet$. Similarly, some organics could be more effectively degraded in the Sulfate-EO process than in Chloride-EO process, as can be seen elsewhere [25]. The generation of reactive species in two processes is illustrated in Figure 10.

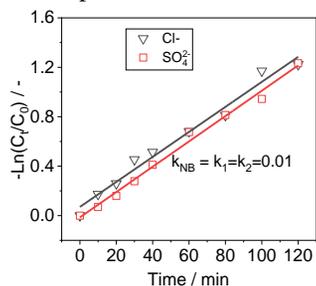


Figure 8. The first-order rate constant of NB in EO process.

Experimental conditions: $[\text{NB}] = 200 \mu\text{M}$,

$[\text{Cl}^-] = [\text{SO}_4^{2-}] = 0.05 \text{ M}$, $j = 10 \text{ mA cm}^{-2}$, BDD (anode),

Pt (cathode), no pH adjustment (pH about 6.7), 700 rpm

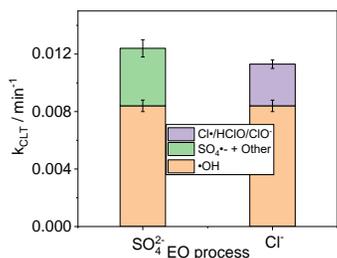


Figure 9. The kinetic degradation of CLO in electrochemical

process. Experimental conditions: $[\text{CLO}] = 200 \mu\text{M}$,

$[\text{Cl}^-] = [\text{SO}_4^{2-}] = 0.05 \text{ M}$, $j = 10 \text{ mA cm}^{-2}$, BDD (anode),

Pt (cathode), no pH adjustment (pH about 6.7), 700 rpm

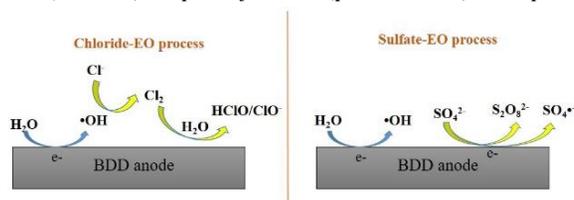


Figure 10. Schematic illustration for the mechanism of reactive species generation

4. Conclusion

The kinetic degradation of CLO (in Dantuso 50 WG) with the supporting electrolytes of sulfate and chloride ions was comprehensively studied. The study indicated that the degradation of CLO was not by direct oxidation by electron, but mainly by $\bullet\text{OH}$ and radicals available from supporting electrolytes. As a part of study, the second-order rate constant of $\bullet\text{OH}$ toward CLO was calculated to be $3.23 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. In the presence of SO_4^{2-} and Cl^- , the degradation of CLO by $\bullet\text{OH}$ was the same, $k_{\text{CLO}} = 0.0084 \text{ min}^{-1}$. Whereas, the higher removal of CLO in SO_4^{2-} was due to the higher contribution of

$(\text{SO}_4^{\bullet-}/\text{S}_2\text{O}_8^{2-})$ compared with $(\text{Cl}\bullet/\text{HClO}/\text{ClO}^-)$.

Conflicts of interest: The author confirm that there are no conflict to declare.

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SUPPORTING INFORMATION (SI):

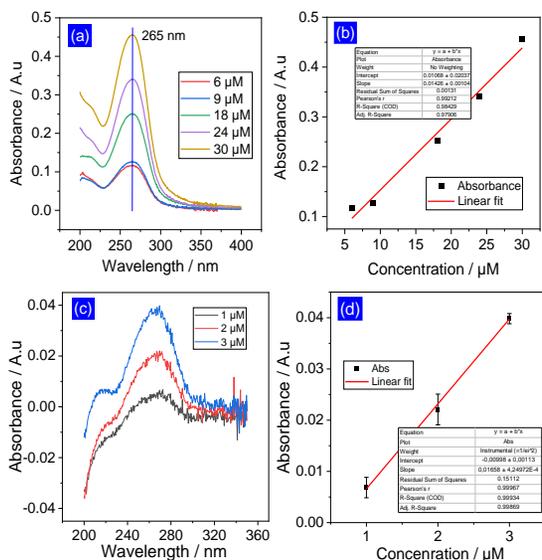


Figure S1. a) UV-vis spectrum of CLO at different concentrations (6–30 μM) in deionized water. b) Linear fit for absorption peaks of CLO. c) UV-vis spectrum of CLO at the low concentration range from 1–3 μM . d) Linear fit for absorption peaks of CLO at the range of 1–3 μM

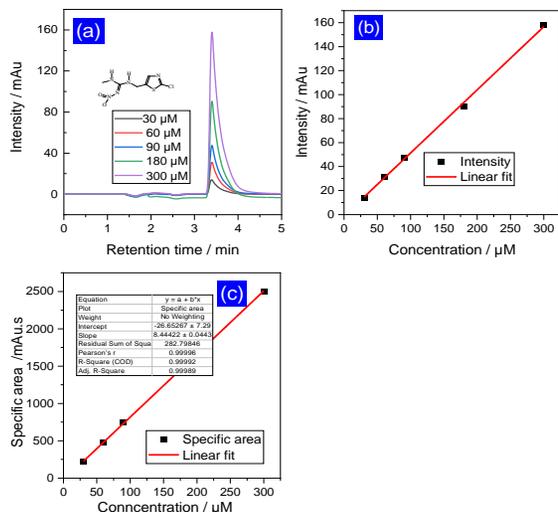


Figure S2. a) HPLC spectrum for CLO at different concentrations. b) Linear fit based on the HPLC intensity of CLO. c) Linear fit based on the specificity area of CLO

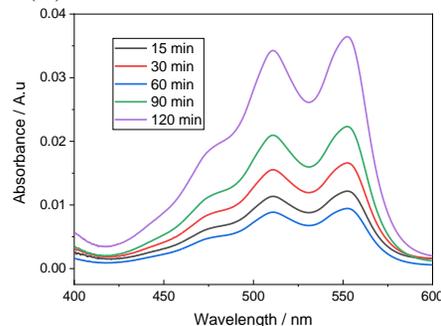


Figure S3. UV-Vis spectrum of DPD with free chlorine in EO process. Experimental conditions: $[\text{CLO}] = 200 \mu\text{M}$, $[\text{Cl}^-] = 0.05 \text{ M}$, $j = 10 \text{ mA}\cdot\text{cm}^{-2}$, BDD (anode), Pt (cathode), no pH adjustment (pH about 6.7)

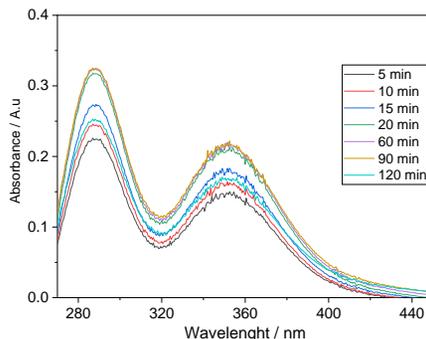


Figure S4. UV-Vis spectrum for determining PS in EO process. Experimental conditions: $[\text{CLO}] = 200 \mu\text{M}$, $[\text{SO}_4^{2-}] = 0.05 \text{ M}$, $j = 10 \text{ mA}\cdot\text{cm}^{-2}$, BDD (anode), Pt (cathode), no pH adjustment (pH about 6.7). Take 1 mL treated solution + 5 mL (5 g/L NaHCO_3 + 15 g/L KI), then incubate for 15 min before measuring in U-Vis

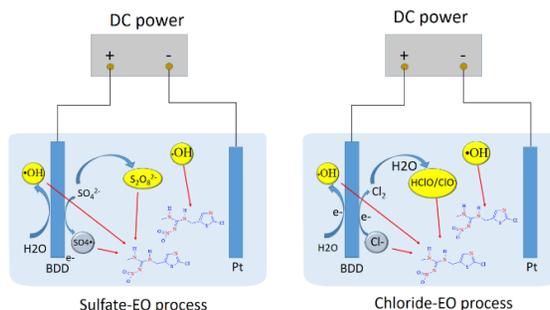


Figure S5. Experimental setup in EO-process