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Enhanced degradation of 2,4-dichlorphenoxyacetic acid herbicide by CaO_2 activated by Fe(II) and ultrasound irradiation: Practical insight and mineralization

Akbar Eslami*,**,†, **Fayyaz Mahdipour****, **Hajar Sharifi Maleksari****, **Gamze Varank*****, **Seyed Mehdi Ghasemi******, **Parisa Nejatian*******, **Amin Bagheri****, and **Soheila Madihi-Bidgoli********,†

*Environmental and Occupational Hazards Control Research Center, Shahid Beheshti University
of Medical Sciences, Tehran, Iran
**Department of Environmental Health Engineering, School of Public Health and Safety,
Shahid Beheshti University of Medical Sciences, Tehran, Iran
***Yildiz Technical University, Faculty of Civil Engineering, Department of Environmental Engineering,
34220 Istanbul, Turkey
****Deputy of Health, Babol University of Medical Sciences, Babol, Iran
*****Deparment of Agricultral Extension and Education, Bu-Ali Sina University, Hamedan, Iran
******Research Center for Environmental Contaminants (RCEC), Abadan University of Medical Sciences, Abadan, Iran

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Abstract−CaO_2 was activated by Fe(II) and ultrasound (US) irradiation to degrade 2,4-dichlorphenoxyacetic acid (2,4-D) for the first time. Among transition metals (Fe, Cu, Mn and Co), Fe(II) had the best performance for the activation of CaO_2. The impact of pH, CaO_2 and Fe(II) concentration was studied, and under optimal situation ~91% of 2,4-D was degraded during 60 min reaction time. The quenching experiments showed that the hydroxyl radical was the main factor for the destruction of 2,4-D while superoxide anions had a minor role. The bicarbonate ions and acid humic exhibited a strong inhibitory effect on the performance of CaO_2/US/Fe(II) process. Carbon and chlorine mineralization of 2,4-D degradation was investigated; around 41% of C and 35% of Cl were mineralized during 60 min reaction time. The function of CaO_2/US/Fe(II) process was studied on real drainage and other organic pollutants, and the results showed that the CaO_2/US/Fe(II) process can be practical for water treatment. Finally, intermediates of 2,4-D degradation were identified, a pathway was proposed, and the toxicity of intermediates was assessed by ECOSAR software.

Keywords: Herbicide, Fenton Oxidation, Mineralization, Calcium Peroxide, Toxicity Evaluation

INTRODUCTION

As an effective herbicide, 2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the most commonly used and is applied all over the world. However, the International Agency for Research on Cancer (IARC) has recognized 2,4-D as a teratogen and carcinogenic chemical [1]. 2,4-D not only pollutes water resources and soil, but also it can be hazardous for humans and animals. Accordingly, the World Health Organization (WHO) recommends 70 μg/L for 2,4-D as the maximum permissible concentration in drinking water [1,2]. High concentration of 2,4-D has been detected in agricultural drainage (3.24 mg/L), which can be toxic for aquatic life [2]. It should be noted that 2,4-D is classified as an endocrine disruptor since it changes hormonal levels. Moreover, it has the half-life period of 170 days in the environment. Due to chemical and biological stability, 2,4-D accounts for a refractory pollutant that conventional processes are not able to remove it completely from water environment [3,4]. Advanced oxidation processes have been extensively used for the degradation of refractory organic pollutants. Fenton oxidation (H_2O_2+Fe^{2+}) is perhaps the most common and effective process for the degradation of organic pollutant. In this way, hydrogen peroxide is catalyzed by iron to generate hydroxyl radicals ($HO^{\bullet}$) as strong and powerful reactive oxygen species (ROS) (Eqs. (1)-(2)) [5].

$$Fe^{2+}+H_2O_2 \rightarrow HO^{\bullet}+Fe^{3+}+HO^{-} \qquad k=67\ M^{-1}\ s^{-1} \tag{1}$$

$$Fe^{3+}+H_2O_2 \rightarrow HO_2^{\bullet}+Fe^{2+}+H^{+} \qquad k=0.02\ M^{-1}\ s^{-1} \tag{2}$$

Several studies have focused on finding a substitute for hydrogen peroxide since it is an unstable oxidant and excess H_2O_2 may result in the reduction of Fenton efficiency [6]. Moreover, H_2O_2 is a liquid hazardous oxidant in which its shipping and storage is a big problem in industrial scale. It is worth mentioning that storage of hydrogen peroxide needs several considerations such as container material, volume of container and ventilation. Hence, the cost of operation and maintenance for H_2O_2 application is relatively high [7]. In recent years, CaO_2 has been introduced as an alternative for hydrogen peroxide. CaO_2 is a stable oxidant which has good thermal stability, easy transportation, and storage and it is non-toxic [7,8]. CaO_2 as a solid source of H_2O_2 releases H_2O_2 slowly into water in which its decomposition is dependent on the temperature and the solution pH (Eqs. (3)-(4)). Moreover, CaO_2 may release oxygen to the solu-

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†To whom correspondence should be addressed.
E-mail: akbar_eslami@yahoo.com, S.madihi8@gmail.com

tion, which is a good source for the generation of superoxide anion (Eq. (5)) [7].

$$CaO_2+2H_2O\rightarrow H_2O_2+Ca(OH)_2 \qquad \Delta G=-49.2\ kJ/M \tag{3}$$

$$CaO_2+H_2O\rightarrow 0.5O_2+Ca(OH)_2 \qquad \Delta G=-20.7\ kJ/M \tag{4}$$

$$Fe^{2+}+O_2\rightarrow Fe^{3+}+O_2^{\bullet -} \tag{5}$$

As the most important disadvantage of Fenton-oxidation, the regeneration of Fe(II) through the reaction of Fe(III) with H_2O_2 is very slow. Several strategies have been used to overcome this problem in Fenton-based processes, including the use of reductant and chelating agent and high energy input (UV and Ultrasound (US) irradiation) [9]. US irradiation can lead to the thermal dissociation of water to form radical species through the collapse of the cavitation bubbles. US irradiation can regenerate Fe(II) from Fe(III) to improve H_2O_2 activation [10,11]. In addition, US irradiation cleaves O-O bond of hydrogen peroxide to generate hydroxyl radicals [12]. Hence, the combination of US and Fe(II) for activation of CaO_2 may enhance the efficiency of Fenton-like oxidation.

In the last decades, several studies have been conducted on the application of CaO_2 for the degradation of organic pollutants. Zhao et al. found a rapid degradation of dye by CaO_2/Fe^{2+}/MoS [7]. Aniline [13] and several pharmaceutical compounds [14] were effectively degraded by CaO_2/UV. Another study utilized Fe^{2+}/oxalic acid/CaO_2 for dye degradation [15]. To the best of our knowledge, CaO_2 has not been coupled by US irradiation in Fenton-like process. CaO_2/US/Fe(II) is probably the first study for CaO_2 activation in AOPs for the degradation of a refractory organic pollutant such as 2,4-D. In this work, a systematic investigation was conducted on the CaO_2/US/Fe(II) process. First, the effect of various transition metals (Fe, Cu, Mn and Co) was studied on CaO_2/US process and the best ones (Fe) were chosen for consequent experiments. The effects of pH, Fe concentration and CaO_2 dosage were studied on 2,4-D degradation. The effect of water matric, including chloride, phosphate, bicarbonate and humic acid, was also studied. The scavenging experiment was carried out to determine the role of ROS ($HO^\bullet$, $^1O_2$ and $O_2^{\bullet -}$). The efficiency of CaO_2/US/Fe(II) process was evaluated on real drainage and other pollutants. Carbon and chlorine mineralization of 2,4-D were also assessed. Finally, the intermediates formed were recognized and a pathway was proposed.

MATERIALS AND METHODS

1. Chemicals

2,4-Dichlorophenoxyacetic acid ($C_8H_6Cl_2O_3$, >98%) was purchased from Merck company. CaO_2 was Provided from Sigma-Aldrich. Sodium chloride (NaCl, >99%), and sodium bicarbonate ($NaHCO_3$, >99%) were purchased from Fluka Company. Hydrogen peroxide (30%), sodium hydroxide, iron (II) sulfate heptahydrate ($FeSO_4\cdot 7H_2O$>99%), cobalt (II) sulfate heptahydrate ($CoSO_4\cdot 7H_2O$>99%), copper (II) sulfate pentahydrate ($CuSO_4\cdot 5H_2O$>99%), manganese (II) sulfate monohydrate ($MnSO_4\cdot H_2O$>99%) and sulfuric acid (96%) were obtained from Merck Company. Ethanol (EtOH) was provided from Razi Company. Methanol and water with HPLC grade were provided from Samchun Inc. The real agricultural drainage was collected from Ahvaz city (Iran) and characteristics are presented in Table S1.

2. Experimental Setup

A beaker (600 mL) was used for CaO_2/US/Fe(II) process in which 400 mL 2,4-D solution (0.1 mM) was introduced into it. A known amount of CaO_2 and Fe(II) was added the solution. The solution pH was adjusted by sulfuric acid (0.1 M) and sodium hydroxide (1%). For sonolysis of the solution, a sonotrode was placed in the beaker to generate low frequency ultrasound (20 kHz) with 100 W power (Hielscher ultrasound-UP 400S). The ultrasound device was performed at 50% duty cycle (1s on/1s off). 2,4-D degradation was stated by turn on the ultrasound device. A water circulating jacket was used to avoid temperature effects while the temperature of the solution was 23-25 °C. 2 mL of sample was withdrawn from the beaker at defined time intervals.

3. Analytical Methods

The concentration of 2,4-D was determined using high-performance liquid chromatography (HPLC) (KNAUER, Germany) equipped with ultraviolet (UV) detector. The wavelength of 280 nm was used for the 2,4-D. The acetonitrile and water with a ratio of 50 : 50 was utilized as mobile phase. The flow rate of mobile phase was 0.5 mL/min while a C8 column (250 mm×4.6 mm) was used as the stationary phase. The temperature of the column was set at 30 °C. Hydrogen peroxide was measured based on potassium titanium(IV) oxalate method [16]. TOC analyzer was used to elucidate carbon-mineralization (Shimadzu). Chlorine-mineralization was determined by chloride measurement in the solution after reaction time. Bisphenol A, tetracycline and acid red 14 were measured based on previous studies [17]. The Waters mass spectrometer (Quattro micro API) was applied to detect intermediates of 2,4-D degradation. The volume of samples for injection was 0.015 mL. Acetonitrile and water were used as the mobile phase in ration of 60/40. A column temperature of 39.85 °C and a flow rate of 2×10^{-4} L/min were chosen for this phase. The mass spectrometry was performed in negative ionization mode. The toxicity of intermediates was evaluated by ECOSAR program and the acute and chronic toxicities of intermediates of 2,4-D degradation on fish, daphnia and green algae were estimated based on Table S2 and S3.

RESULTS AND DISCUSSION

1. Comparative Evaluation

Fig. 1 depicts the yield of different processes for 2,4-D degradation under fixed conditions. US and CaO_2 indicated low efficiency for the 2,4-D removal due to the lack of free radicals. In the binary system of US/CaO_2, around 50% removal efficiency was observed; this can be ascribed by the generation of hydroxyl radicals by the cleavage of O-O bond of H_2O_2 released and the activation of H_2O_2 by hydrogen radicals ($H^\bullet$) (Eqs. (6)-(8)). Also, oxygen generated during dissociation of CaO_2 may produce hydroxyl radicals under US irradiation (Eq. (9)) [18].

$$US+H_2O_2\rightarrow HO^\bullet+HO^\bullet \tag{6}$$

$$US+H_2O\rightarrow HO^\bullet+H^\bullet \tag{7}$$

$$H^\bullet+H_2O_2\rightarrow HO^\bullet+H_2O \qquad k=9\times10^7\ M^{-1}\ s^{-1} \tag{8}$$

$$H_2O+0.5O_2+US\rightarrow HO^\bullet+HO^\bullet \tag{9}$$

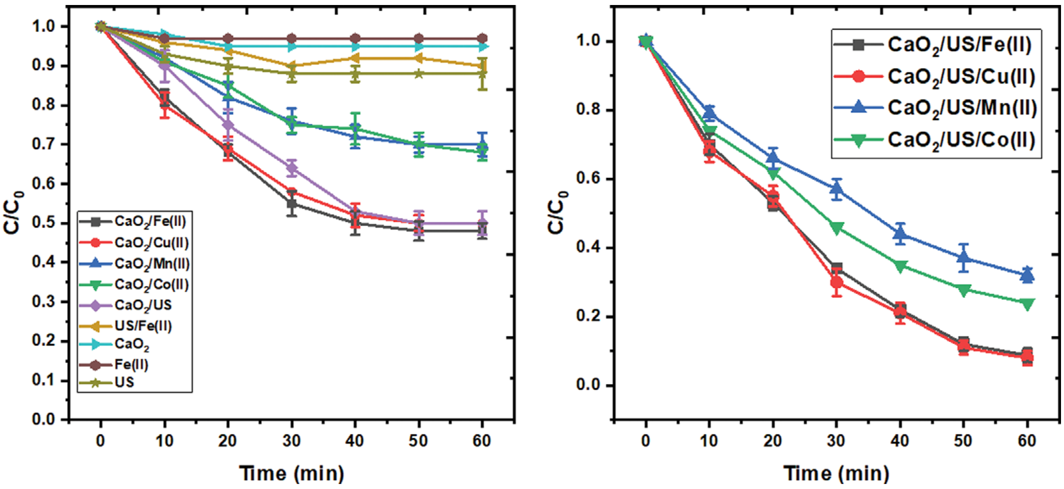

Fig. 1. The 2,4-D degradation by various processes (CaO_2=3 mM, transition metals=0.6 mM and pH=3).

Other binary systems indicated the performance of transition metals for the activation of H_2O_2 released. As can be seen, Cu(II) and Fe(II) had high catalytic activity compared to Mn(II) and Co(II). The 2,4-D degradation efficiencies were 52, 50, 30 and 33% for CaO_2/Fe(II), CaO_2/Cu(II), CaO_2/Mn(II) and CaO_2/Co(II), respectively. It has been reported that Cu(II)/Cu(I) has a similar behavior to Fe(II)/Fe(III). Note that the reaction rate of Cu/H_2O_2 is more than that of Fe/H_2O_2 (Eqs. (10)-(11)) [19].

$$Cu^{2+}+H_2O_2 \rightarrow HO_2^{\bullet}+Cu^{+}+H^{+} \qquad k=460\ M^{-1}\ s^{-1} \tag{10}$$

$$Cu^{+}+H_2O_2 \rightarrow HO^{\bullet}+Cu^{2+}+OH^{-} \qquad k=10{,}000\ M^{-1}\ s^{-1} \tag{11}$$

It should be pointed out that hydrolyzed complexes of $Cu(OH)_2$ for Cu^{2+} and $FeOH(H_2O)^{2+}$ for Fe^{3+} may contribute to the activation of H_2O_2 released, since it has been reported that they are active catalyst for catalyzing H_2O_2 [20]. Although some studies reported that Co(II) has high reactivity for the activation of persulfate anions, the mechanism of H_2O_2 activation is still an unsolved paradigm [21]. Low efficiency of Mn for H_2O_2 activation can be related to the precipitation of Mn in the presence of oxygen in form of MnO_2.

Ternary systems were evaluated on 2,4-D degradation (Fig. 1 right side). The 2,4-D degradation efficiencies were 91.2%, 91.3%, 68.1% and 76% for CaO_2/US/Fe(II), CaO_2/US/Cu(II), CaO_2/US/Mn(II) and CaO_2/US/Co(II), respectively. As expected, CaO_2/US/Fe(II) and CaO_2/US/Cu(II) process had a higher efficacy than CaO_2/US/Co(II) and CaO_2/US/Mn(II). As mentioned, higher catalytic activity of copper and iron for hydrogen peroxide results in more production of free radicals. Moreover, it should be emphasized that US irradiation can regenerate Fe(II) through the Eq. (12) and increase the hydroxyl radical generation significantly [10].

$$Fe\text{-}O_2H^{2+}+))) \rightarrow Fe^{2+}+HO_2^{\bullet} \tag{12}$$

In comparison with transition metals, it is clear that copper and iron had a higher efficiency compared to cobalt and manganese. Apart from the performance and 2,4-D removal efficiency, compared to copper, iron is an inexpensive, non-toxic and environmentally friendly element for the activation of CaO_2. Hence, CaO_2/US/Fe(II) was considered for further experiments.

To clarify the performance of each system, the rate constants (pseudo-first order) of 2,4-D degradation were determined and the results are presented in Fig. S1. As can be seen, CaO_2/US/Fe(II) and CaO_2/US/Cu(II) had the highest rate constant (0.0396 min^{-1}). Also, Fe(II) indicated the highest efficiency in binary systems (transition metal/CaO_2) confirming high catalytic activity of Fe(II) compared to other metals. On the other hand, CaO_2 and US individually were not effective for 2,4-D degradation, while their combination (CaO_2/US) increased the degradation rate of 2,4-D significantly, indicating that US is able to fission O-O bond of H_2O_2. Moreover, it should be noted that sole Fe(II) did not affect 2,4-D removal since coagulation mechanism needs neutral or alkaline conditions.

CaO_2/US/Fe(II) was also compared to H_2O_2/US/Fe(II) for the degradation of 2,4-D and the results are presented in Fig. S2. It is clear that at first 30 min reaction time, 2,4-D degradation rate was fast in H_2O_2/US/Fe(II) system, while after that time the degradation rate dropped. In contrast with H_2O_2/US/Fe(II), 2,4-D degradation rate gradually increased during 60 min reaction time in CaO_2/US/Fe(II) system as previously mentioned. These phenomena can be explained by the scavenging effect of excess hydrogen peroxide in H_2O_2/US/Fe(II) and gradual release of H_2O_2 in CaO_2/US/Fe(II) system.

2. The Effect of pH, CaO_2 Dosage and Fe(II) Concentration of 2,4-D Degradation

The solution pH is a key parameter in all oxidation processes which can be highly influential on the degradation of organic pollutants. Fig. 2(a) shows the effect of pH on 2,4-D removal using CaO_2/US/Fe(II) process. As shown, the increase of solution pH suppressed the 2,4-D elimination by CaO_2/US/Fe(II) process. As the most important of issue, the solubility of Fe(II) was dramatically reduced by the increase of pH. Therefore, iron may be precipitated in the pH>4.0. However, a slight reduction was observed in pH=2 compared to pH=3 in a way that 2,4-D degradations were 77.5% and 83.2% for pH=2 and pH=3, respectively. The existence of high concentration of hydrogen ions (pH=2) may scavenge hydroxyl radicals and generate water molecules (Eq. (13)) [22].

$$H^{+}+HO^{\bullet}+e^{-} \rightarrow H_2O \tag{13}$$

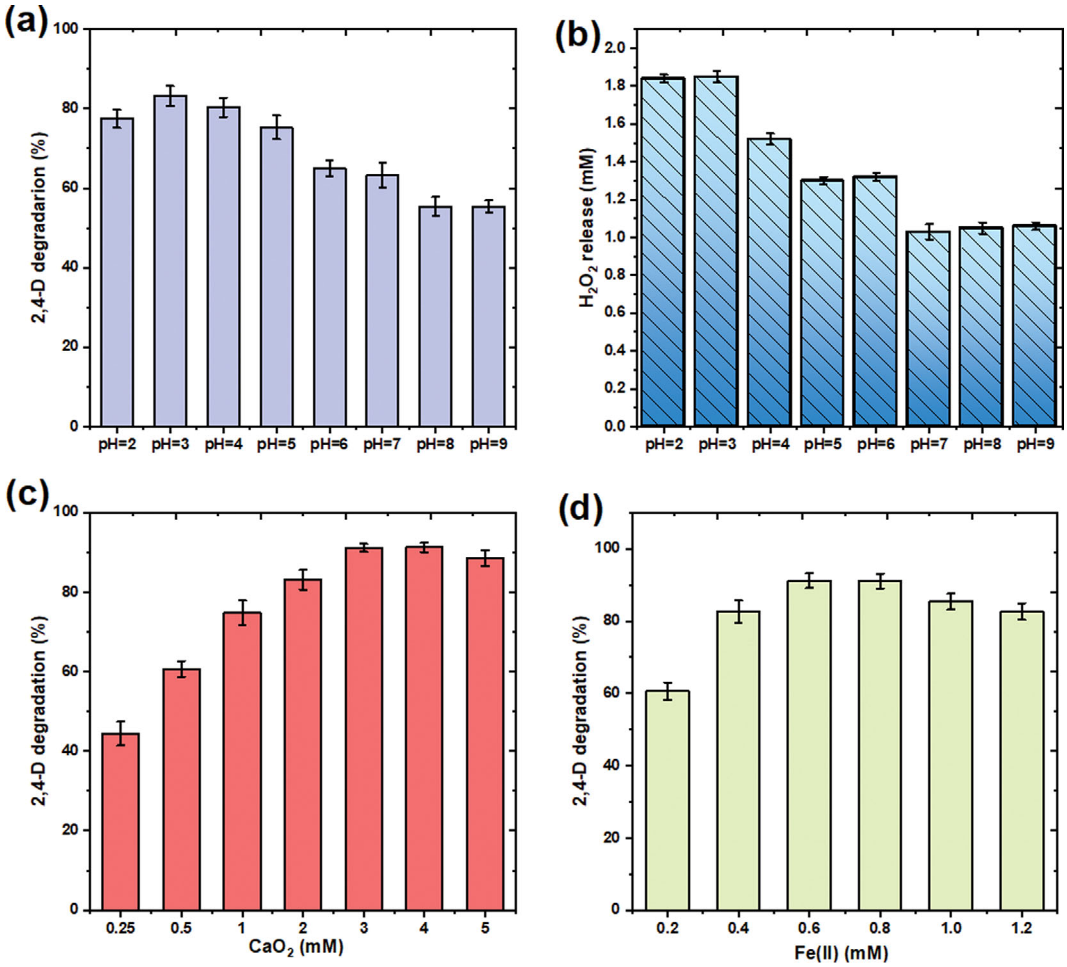

Fig. 2. (a) The effect of pH on 2,4-D degradation (CaO_2=2 mM and Fe(II)=0.6 mM) (b) H_2O_2 release in various pH values (CaO_2=2 mM) (c) The effect of CaO_2 dosage (d) The effect of Fe(II) concentration (pH=3 and CaO_2=3 mM).

Besides, H_2O_2 may be stabilized at pH=2 in the presence of high concentration of hydrogen ions and forms the oxonium cation (Eq. (14)). Oxonium cation has electrophilic behavior reducing its reaction with ferrous ions for the generation of free radicals [23].

$$H^{+}+H_2O_2\rightarrow H_3O_2^{+} \tag{14}$$

In addition, the oxidation power of $HO^{\bullet}$ decreased by the rise of solution pH according to Nernst equation (Eq. (15)). For example, the oxidation power of hydroxyl radicals is 2.38 V at pH=7.0 while its value is 2.68 for pH=2. Hence, the acidic condition improved the 2,4-D degradation significantly [5].

$$E^{0}=E^{0}_{HO^{\bullet}/H_2O}-0.059pH \tag{15}$$

It has been reported that acidic condition is a favorable media for the release of H_2O_2 from CaO_2 [24]. To confirm this issue and the performance of CaO_2/US/Fe(II), H_2O_2 released was monitored at the various pH values and the results are illustrated in Fig. 2(b). As one can see, a remarkable decrease is observable in the reduction of H_2O_2 released when the solution pH was increased. In this way, released H_2O_2 concentration decreased from 1.84 mM to 1.06 mM when the solution pH increased from 2 to 9. This issue supports the performance of CaO_2/US/Fe(II) process for the 2,4-D degradation in acidic conditions in which the highest yield was obtained at the pH=3, which is the best condition for homogeneous Fenton-based processes.

The effect of CaO_2 dosage was investigated on the 2,4-D abatement via CaO_2/US/Fe(II) process (Fig. 2(c)). It is clear that the higher the CaO_2 dosage is, the more hydrogen peroxide can be released in CaO_2/US/Fe(II) process, which in turn enhances the generation of hydroxyl radical. Generally, the dosage of oxidant in AOPs is the most important factor in the amount of free radicals generated; therefore, the increase in CaO_2 dosage promoted the 2,4-D degradation considerably. In this way, the 2,4-D degradation efficiency was 44.5, 60.7, 74.8, 83.2 and 91.2% for CaO_2 dosage of 0.25, 0.5, 1.0, 2.0 and 3.0 mM, respectively. On the other hand, the 2,4-D degradation was slightly reduced in CaO_2 dosages of 4.0 and 5.0 mM. It has been reported that higher concentration of CaO_2 has a deteriorative effect of the production of free radicals. Excess CaO_2 increases H_2O_2 concentration that it can scavenge hydroxyl radicals with high reactivity and produce hydroperoxyl radicals with low oxidation power (Eq. (16)) [25-27]. Meanwhile, at high concentration of free radicals, the recombination of hydroxyl radicals and hydroperoxyl radicals leads to the generation of hydrogen peroxide (Eqs. (17)-(18)), which they have a negative effect on

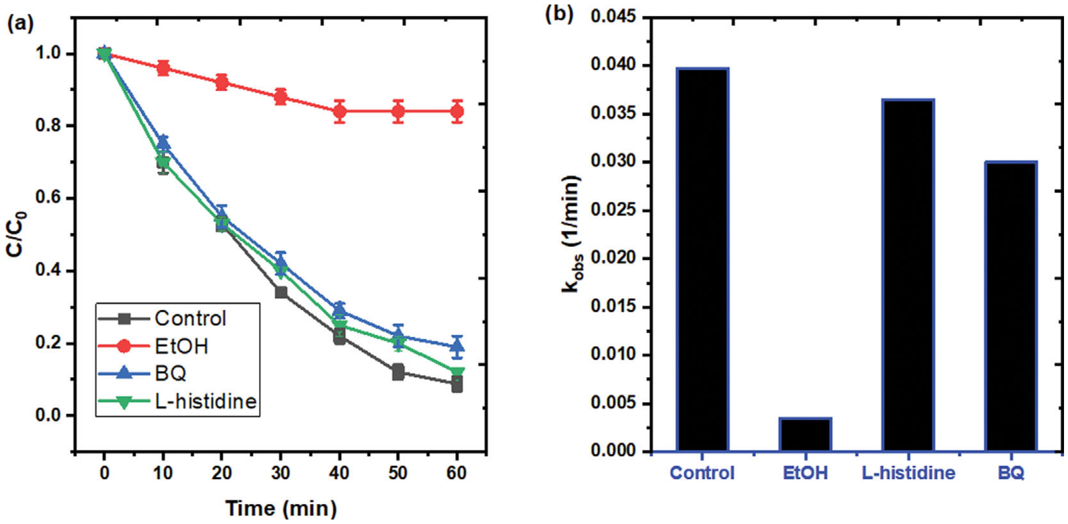

Fig. 3. (a) The effect of various scavengers on 2,4-D degradation (b) the rate constants of various conditions (pH=3, CaO_2=3 mM, Fe(II)=0.6 mM, L-histidine=BQ=2 mM and EtOH=0.1 M).

the destruction of 2,4-D. Also, the interaction between hydroxyl radicals and hydroperoxyl radicals results in the generation of water and oxygen (Eq. (19)) [5,28]. In fact, radical-radical reaction in Fenton chemistry can be a limiting step to the degradation of organic pollutants [28].

$$HO^{\bullet}+H_2O_2 \rightarrow HO_2^{\bullet}+H_2O \qquad k=1.7-4.5\times10^{7}\ M^{-1}\ s^{-1} \tag{16}$$

$$HO^{\bullet}+HO^{\bullet} \rightarrow H_2O_2 \qquad k=4-8\times10^{9}\ M^{-1}\ s^{-1} \tag{17}$$

$$2HO_2^{\bullet} \rightarrow H_2O_2+O_2 \qquad k=0.8-2.2\times10^{6}\ M^{-1}\ s^{-1} \tag{18}$$

$$HO^{\bullet}+HO_2^{\bullet} \rightarrow H_2O+O_2 \qquad k=1.4\times10^{10}\ M^{-1}\ s^{-1} \tag{19}$$

The effect of ferrous ions as catalyzing agent for CaO_2 activation was also investigated on the 2,4-D abatement and the results are illustrated in Fig. 2(d). The increase of Fe(II) concentration from 0.2 to 0.6 mM enhanced the 2,4-D abatement markedly and the removal efficiency was increased from 60.6 to 91.2%. It is obvious that the increase in Fe(II) concentration improved more H_2O_2 decomposition for the generation of free radicals. Moreover, the role of Fe(II) in the generation superoxide anions can be another reason for the improvement of the CaO_2/US/Fe(II) performance. At the higher concentration of Fe(II) (>0.6 mM), a reduction in the efficiency occurred. In this manner, 2,4-D degradation was reduced from 91.2% to 82.6% when ferrous ions increased from 0.6 mM to 1.2 mM. Several studies have mentioned the inverse effect of excess ferrous ions in Fenton-based processes, in which excess ferrous ions scavenge hydroxyl radicals and hydroperoxyl radicals (superoxide anions) based on Eqs. (20)-(21) [29,30]. These results indicated that the optimization of CaO_2 and ferrous ions dosages is a crucial step for the CaO_2/US/Fe(II) process for degrading the organic pollutants. In spite of the performance of the CaO_2/US/Fe(II), the optimization of CaO_2 and Fe(II) decreases the cost of operation and chemicals.

$$HO^{\bullet}+Fe^{2+} \rightarrow Fe^{3+}+HO^{-} \qquad k=2.5-5\times10^{8}\ M^{-1}\ s^{-1} \tag{20}$$

$$HO_2^{\bullet}+Fe^{2+} \rightarrow Fe^{3+}+HO_2^{-} \qquad k=0.72-1.5\times10^{6}\ M^{-1}\ s^{-1} \tag{21}$$

3. The Evaluation of Reactive Oxygen Species in the CaO_2/US/Fe(II) Process

In CaO_2-based processes several reactive oxygen species (ROS) may contribute to the degradation of organic compounds. Hydroxyl radicals, superoxide anions and singlet oxygen are the main ROS in CaO_2-based process, which thr latter is derived from the reaction of superoxide anions and hydroxyl radicals (Eq. (22)) [31]. Hence, both mechanisms (radical and non-radical) may play key roles in the degradation of organic pollutants.

$$HO^{\bullet}+O_2^{\bullet-} \rightarrow HO^{-}+{}^{1}O_2 \qquad k=2.5-5\times10^{8}\ M^{-1}\ s^{-1} \tag{22}$$

To identify the ROS, scavenging tests were applied by some effective scavenger. In this way, EtOH was used to scavenge hydroxyl radicals ($k_{HO^{\bullet}}=2\times10^{9}\ M^{-1}\ s^{-1}$), while the p-benzoquinone (BQ) was utilized for superoxide anions ($k=9.6\times10^{8}\ M^{-1}\ s^{-1}$) [32]. To quench the singlet oxygen, L-histidine was used as a strong scavenger ($k=3.2\times10^{7}\ M^{-1}\ s^{-1}$) [33]. Fig. 3(a) shows the 2,4-D degradation in the presence of various scavengers. A significant inhibition was seen in the presence of EtOH, depicting that the hydroxyl radicals are dominant in the CaO_2/US/Fe(II) process. On the other hand, BQ and L-histidine had a slight inhibition effect on the 2,4-D degradation, proving that superoxide anion and singlet oxygen did not significantly contribute to the degradation of 2,4-D. Accordingly, pseudo-first order model was fitted for the results obtained from Fig. 3(a) and their rate constants are presented in Fig. 3(b) (the plot of pseudo-first-order model is presented in Fig. S3). As control experiment without scavenger, the rate constant was 0.0397 min^{-1}, whereas in the presence of EtOH, BQ and L-histidine reduced the rate constants to 0.0035, 0.030 and 0.0365 min^{-1}. According to Fig. 3(a) and 3(b), it can be concluded that hydroxyl radical is the main agent for the oxidation of 2,4-D and the superoxide anion had a minor role. In case of singlet oxygen, it can be stated that its contribution was almost negligible for the degradation of 2,4-D. These results are in agreement with study of Guo et al. [34] in which the rate constants of 2,4-D with hydroxyl radical and superoxide anion were $5.1\times10^{9}\ M^{-1}\ s^{-1}$ and $8.3\times10^{5}\ M^{-1}\ s^{-1}$, respectively, while

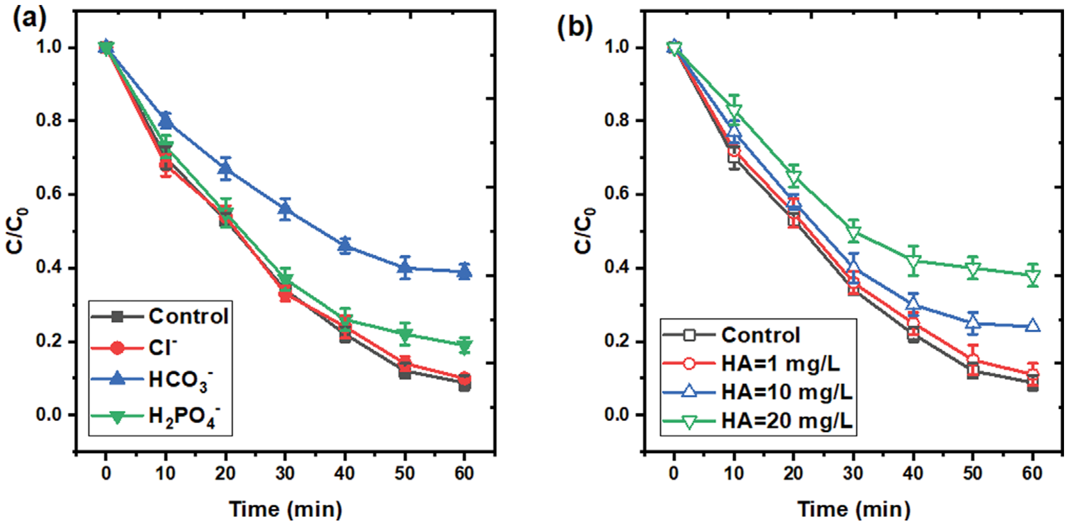

Fig. 4. (a) The effect of anions on 2,4-D degradation (b) The effect of humic acid on 2,4-D degradation (pH=3, CaO_2=3 mM, Fe(II)=0.6 mM and anions=5 mM).

there was no reaction with singlet oxygen. According to the results, the reactivity of 2,4-D with hydroxyl radicals is around 1000 times more than that of superoxide anions. Therefore, hydroxyl radicals had the most contribution to the degradation of 2,4-D using CaO_2/US/Fe(II) process.

4. The Effect of Co-existing Anions and Natural Organic Matter

Several types of inorganic anions including Cl^-, and HCO_3^- and $H_2PO_4^-$ which naturally exist in water resources and municipal and industrial wastewaters, can affect the function of AOPs. The effect of these anions on the degradation efficiency of 2,4-D was tested and the results are presented in Fig. 4(a). The chloride ions did not affect the 2,4-D degradation. The 2,4-D degradation trend in control condition was similar to in presence of chloride ion. In general, chloride ion has high reactivity with free radical and forms chlorine reactive species. These chlorine species are able to oxidize organic pollutants due to high reactivity. The chlorine radical ($Cl^\bullet$) and dichlorine radical ($Cl_2^{\bullet-}$) produced during the chain reactions (Eqs. (23)-(26)), have oxidation potential of E^0=2.47 V and E^0=2.0 V, respectively, indicating their capacity for destructing 2,4-D.

$$HO^\bullet + Cl^- \rightarrow ClOH^{\bullet-} \qquad k=4.3\times10^9\ M^{-1}\ s^{-1} \tag{23}$$

$$ClOH^{\bullet-} + H^+ \rightarrow Cl^\bullet + H_2O \qquad k=2\times10^{10}\ M^{-1}\ s^{-1} \tag{24}$$

$$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet-} \qquad k=6.5\times10^9\ M^{-1}\ s^{-1}-2.1\times10^{10}\ M^{-1}\ s^{-1} \tag{25}$$

$$Cl_2^{\bullet-} \rightarrow Cl^\bullet + Cl^- \qquad k=1.1\times10^5\ s^{-1} \tag{26}$$

There was a slight inhibiting effect on the 2,4-D degradation for dihydrogen phosphate ($H_2PO_4^-$). Phosphate ions exist in various forms (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) in water resources, which are highly dependent on the solution pH (Eq. (27)). At the pH=3, $H_2PO_4^-$ is dominant in the solution since the pK1, pK2 and pK3 are 2.15, 7.2 and 12.33 based on the following equation [35,36]:

$$H_3PO_4 \overset{pK1}{\longleftrightarrow} H_2PO_4^- \overset{pK2}{\longleftrightarrow} HPO_4^{2-} \overset{pK3}{\longleftrightarrow} PO_4^{3-} \tag{27}$$

The presence of $H_2PO_4^-$ can consume hydroxyl radicals (k=2×10^4 M^{-1} s^{-1}) and suppress the performance of CaO_2/US/Fe(II) process [37]. In this way, $H_2PO_4^\bullet$ is produced, which is a weaker oxidant with low reactivity compared to hydroxyl radicals [36]. Moreover, $H_2PO_4^-$ may lead to precipitate the iron species and dismiss Fe(II) from the reaction chain of Fenton oxidation.

Among anions, HCO_3^- indicated a high hindered effect on 2,4-D degradation. Bicarbonate and carbonate ions are powerful scavengers of free radicals (Eqs. (28)-(29)). Carbonate radicals generated are impotent free radical for the degradation of organic bonds.

$$HCO_3^- + HO^\bullet \rightarrow CO_3^{\bullet-} + H_2O \qquad k=8.5\times10^6\ M^{-1}\ s^{-1} \tag{28}$$

$$CO_3^{2-} + HO^\bullet \rightarrow CO_3^{\bullet-} + HO^- \qquad k=3.9\times10^8\ M^{-1}\ s^{-1} \tag{29}$$

On the other hand, bicarbonate ions can directly react with released and generate peroxymonocarbonate (HCO_4^-) (Eq. (30)) [38] decreasing the concentration of H_2O_2 as the main oxidant in CaO_2/US/Fe(II) process. Therefore, HCO_3^- not only scavenged the free radicals, but also it reduced the source of producing free radicals, which in turn significantly suppressed the performance of CaO_2/US/Fe(II) process. In addition, adding bicarbonate ions into solution increased the solution pH to 7.2, reducing the availability of ferrous ions. In fact, bicarbonate ions decreased the active iron for CaO_2 activation in the solution since ferrous ions were precipitated in neutral conditions. Hence, 2,4-D degradation dramatically dropped in the presence of bicarbonate ions.

$$HCO_3^- + H_2O_2 \rightarrow HCO_4^- + H_2O \qquad k_{eq}=0.33\ M^{-1} \tag{30}$$

Natural organic matter (NOM) is an extremely complex mixture of organic compounds with high molecule weight that is found in all water resources. 40-80% of the NOM consists of humic substances (humic acid (HA) and fulvic acid (FA)), which are complex and multicomponent in nature [37]. The effect of humic acid (HA) was studied on the function of CaO_2/US/Fe(II) process for the abatement of 2,4-D (Fig. 4(b)). With increase of HA concentration, the inhibitory effect was markedly enhanced in a way that the removal efficiency reduced from 91.2% to 62.5%. HA has high reactivity with $HO^\bullet$ (k=1.39-2.18$\times10^8$ M^{-1} s^{-1}) and thus HA competes with

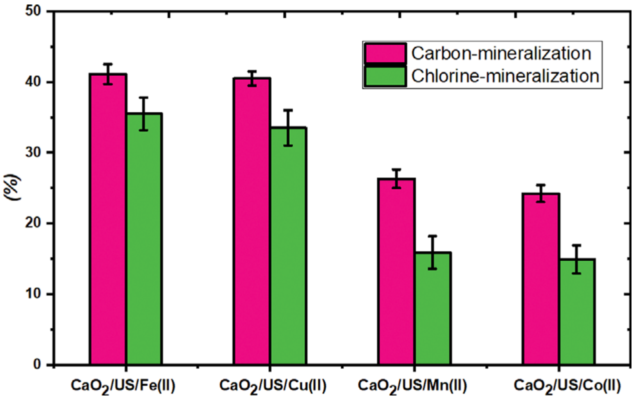

Fig. 5. Carbon and chlorine mineralization of 2,4-D by various processes (pH=3, CaO_2=3 mM and transition metals=0.6 mM).

target pollutant (2,4-D) for the reaction with hydroxyl radicals. Organic compounds with high aromaticity and molecular weight have reactivity for scavenge of hydroxyl radicals (1.9-2.7×10^4 L mg^{-1} s^{-1}) [37].

5. Mineralization Study

To confirm total degradation of target pollutant to mineral and low toxic compounds, mineralization degree was studied on 2,4-D degradation using TOC and chlorine release, and the results are presented in Fig. 5. To better understand the performance of the CaO_2/US/Fe(II) process, other transition metals (Cu, Mn and Co) were also evaluated. As can be seen, as expected, CaO_2/US/Fe(II) process has higher mineralization in terms of carbon and chlorine in a way that 41.1 and 35.5% of carbon and chlorine were, respectively, mineralized by CaO_2/US/Fe(II). Close to this result, CaO_2/US/Cu(II) could mineralize 40.5% of carbon and 33.5% of chlorine during 60 min reaction time. On the other hand, CaO_2/US/Mn(II) and CaO_2/US/Co(II) removed around 25% TOC and released ~15% of chlorine. Overall, to complete mineralization of organic compounds, more hydroxyl radicals and longer reaction time are needed. From these results it can be indirectly stated that higher mineralization, especially for chlorine (as a function group increasing toxicity), resulted in hazardless production.

6. CaO_2/US/Fe(II) Performance for Real Contaminated Water

CaO_2/US/Fe(II) performance was evaluated in a real drainage in which 2,4-D may be found through washing the soil and plants. In this way, 20 mg/L of 2,4-D was spiked into a real drainage (characteristics are presented in Table S1) and CaO_2/US/Fe(II) performance is presented in Fig. 6(a). As can be seen, CaO_2/US/Fe(II) performance declined in the real drainage markedly. The presence of several organic and inorganic compounds in the solution may scavenge free radicals produced ($HO^{\bullet}$ and $O_2^{\bullet-}$). According to Table S1, the simultaneous existence of various anions suppressed the function of CaO_2/US/Fe(II) through the scavenging the free radicals or the formation of Fe(II) complex to reduce activating released H_2O_2.

To study the performance of Ca_2/US/Fe(II), some pollutants were considered to compare with 2,4-D degradation. Bisphenol A (BPA) is an endocrine disruptor chemical which has been frequently studied by different AOPs [39]. Acid red 14 (AR14) as a food dye, which is one of the most applicable dyes in the food industry, and tetracycline (TC) is an antibiotic which has been extensively used for the treatment of a number of infectious [40]. Fig. 6(b) shows the degradation of various pollutants by CaO_2/US/Fe(II) process. Among these pollutants, AR14 was rapidly and completely degraded by CaO_2/US/Fe(II) process during only 30 min reaction time. This indicates that hydroxyl radicals attacked chromophore segment of AR14 to decolorize the solution. On the other hand, 2,4-D and BPA had the same trend in degradation, while TC seems that is resistant to the degradation compared to other pollutants. The removal efficiencies of 2,4-D, BPA, TC and AR14 were 91.2, 93, 82 and 100% respectively. By and large, CaO_2/US/Fe(II) process could be considered for the degradation of a wide range of contaminants in water resources.

7. Pathway of 2,4-D Degradation by CaO_2/US/Fe(II) Process and Toxicity Evaluation

The intermediates of 2,4-D degradation were identified via LC/MS spectrum (Fig. S4) and proposed pathway of 2,4-D degradation is illustrated in Fig. 7. 2,4-D pollutant (P) as parent molecule (m/z=219) was first cleaved from -O- bond via hydroxyl radicals and

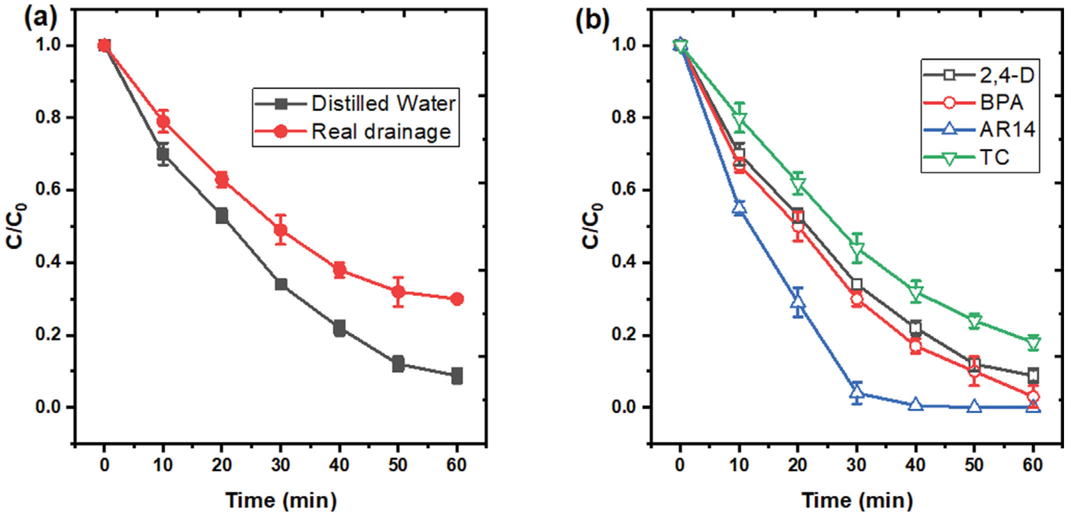

Fig. 6. The function of CaO_2/US/Fe(II) process on (a) real drainage (b) other pollutants (pH=3, CaO_2=3 mM, and Fe(II)=0.6 mM).

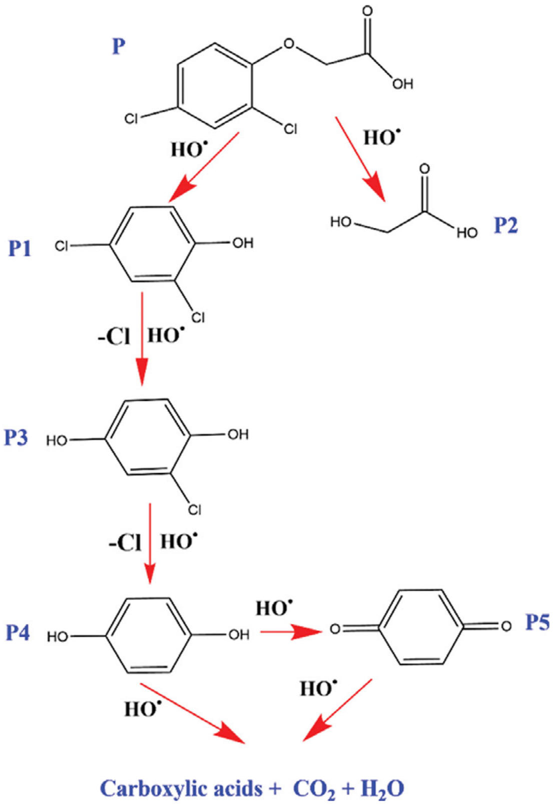

Fig. 7. The proposed pathway of 2,4-D degradation by CaO_2/US/Fe(II) process.

2,4-dichlorophenol (P1, m/z=161) and glycolic acid (P2, m/z=75) were formed. The first step has been reported by several studies [41,42]. The oxidation rate of 2,4-D to 2,4-dichlorophenol is very fast $(5\times10^{9}\ M^{-1}\ s^{-1})$ [42,43]. With more generation of hydroxyl radicals in CaO_2/US/Fe(II) process, further oxidation occurred and 2,4-dichlorophenol was oxidized and chlorine function lost, and chlorohydroquinone (P3, m/z=143) was produced. Chlorohydroquinone lost chlorine function via attacking hydroxyl radicals and hydroquinone (P4, m/z=109) was formed as the first intermediate without chlorine functional group. In this way, hydroquinone was oxidized to benzoquinone (P5, m/z=108) and it is possible to be converted to carboxylic acids through opening aromatic ring. This pathway demonstrated that losing chlorine during the oxidation of 2,4-D was in agreement with chlorine mineralization of 2,4-D.

To investigate the toxicity of the by-products generated during 2,4-D degradation by CaO_2/US/Fe(II) process, ECOSAR program was employed and the results of acute and chronic toxicity of by-products for fish, daphnia and green algae are presented in Table S4. The toxic level of the compounds can be classified into four categories based on the Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Fig. 8 shows the level of toxicity of five intermediates of 2,4-D degradation. Note that 2,4-D has not yet been recognized by the database of ECOSAR. Hence, the data of 2,4-D toxicity is not presented in Fig. 8. Therefore, the toxicity of intermediates (P1-P5) is illustrated in Fig. 8. As can be seen, P2 as a carboxylic acid is a non-toxic compound (not harmful) for fish, daphnia and green algae, while other intermediates are very toxic and toxic in terms of chronic and acute toxicities. The presence of Cl and OH functions in the molecular structure of P1, P3 and P4 increased chronic and acute toxicity. According to the results, the production of carboxylic acids as final organic by-products can be considerable for the reduction of toxicity, whereas

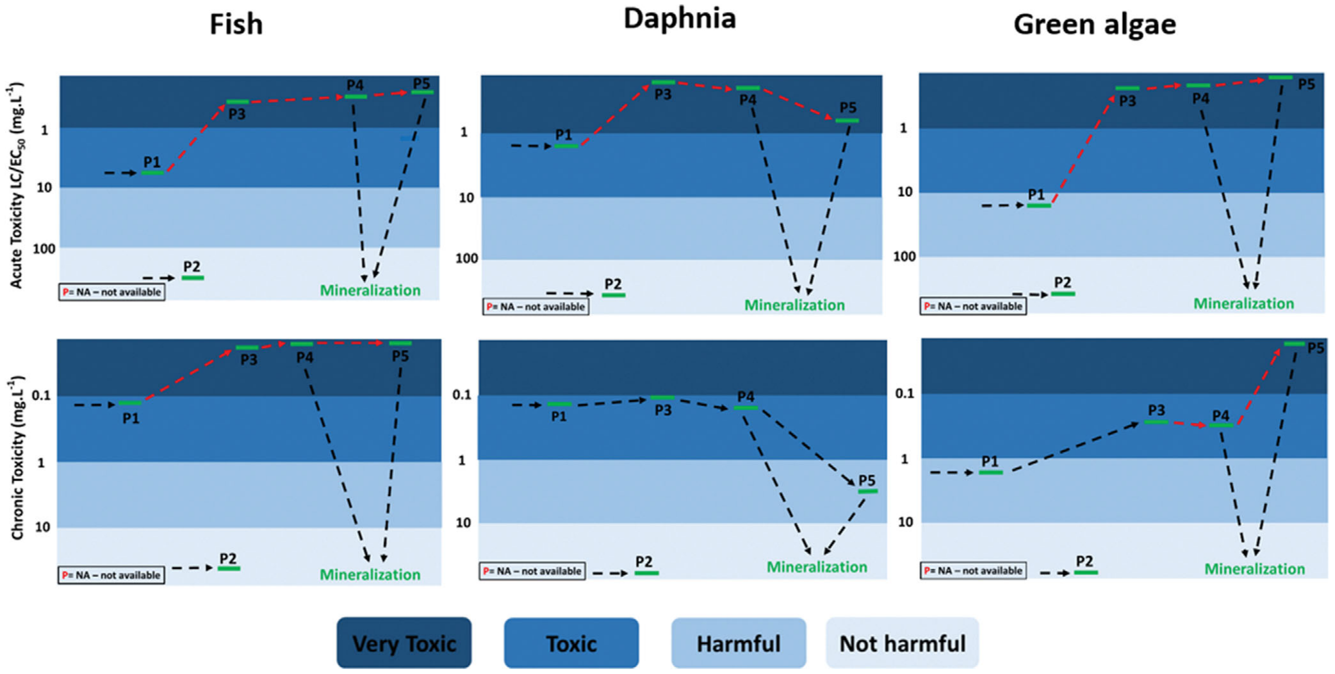

Fig. 8. Predicted concentration for acute and chronic toxicity evaluation of 2,4-D and its by-products via ECOSAR program (The letters from P1 to P5 ascribe to by-products).

aromatic intermediates are toxic and very toxic. Howbeit, the mineralization of 2,4-D (40.5%) can be justified for the performance of CaO_2/US/Fe(II) process for 2,4-D degradation.

Overall, it should have a serious insight into intermediates formed in 2,4-D degradation by AOPs in which toxic intermediates are produced. Hence, to increase the mineralization degree and the reduction of toxic intermediates, a further reaction time is required. However, monitoring the intermediates should be considered during the degradation of herbicides. Moreover, another disadvantage of homogenous Fenton-based process is loss of ferrous ions in which heterogeneous catalysts can be the best alternative for this issue. Note that heterogeneous catalysts can be operated in a wide range of pH, which is preferable to acidic conditions [44,45].

CONCLUSION

This work demonstrates that CaO_2 as alternative of H_2O_2 can be applied for the Fenton reaction. Fe(II) indicates a higher catalytic activity amongst other transition metals. CaO_2/US/Fe(II) process removed 91.2% of 2,4-D during 60 min reaction under optimum condition of CaO_2=3 mM, pH=3.0 and Fe(II)=0.6 mM. Under these situations, 45% carbon mineralization and 35% chlorine mineralization were obtained. High contribution of hydroxyl radicals and low contribution of superoxide anions were the results of scavenging experiments. The effect of water matrix showed that bicarbonate ions and humic acid can hinder the 2,4-D degradation in CaO_2/US/Fe(II) process. The performance of CaO_2/US/Fe(II) process was acceptable for real drainage and other pollutants. The proposed pathway and toxicity evaluation of 2,4-D and its intermediates showed that they may be more toxic than parent molecule. Overall, the CaO_2/US/Fe(II) process can be considered as an alternative of sono-Fenton process for the decontamination of organic pollutants.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Enhanced degradation of 2,4-dichlorphenoxyacetic acid herbicide by CaO_2 activated by Fe(II) and ultrasound irradiation: Practical insight and mineralization

Akbar Eslami[*,**,†], **Fayyaz Mahdipour**[**], **Hajar Sharifi Maleksari**[**], **Gamze Varank**[***], **Seyed Mehdi Ghasemi**[****], **Parisa Nejatian**[*****], **Amin Bagheri**[**], **and Soheila Madihi-Bidgoli**[******,†]

*Environmental and Occupational Hazards Control Research Center, Shahid Beheshti University
of Medical Sciences, Tehran, Iran
**Department of Environmental Health Engineering, School of Public Health and Safety,
Shahid Beheshti University of Medical Sciences, Tehran, Iran
***Yildiz Technical University, Faculty of Civil Engineering, Department of Environmental Engineering,
34220 Istanbul, Turkey
****Deputy of Health, Babol University of Medical Sciences, Babol, Iran
*****Deparment of Agricultral Extension and Education, Bu-Ali Sina University, Hamedan, Iran
******Research Center for Environmental Contaminants (RCEC), Abadan University of Medical Sciences, Abadan, Iran
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Table S1. Characteristics of drainage water

Parameter	Unit	Value
TDS	mg/L	940
COD	mg/L	58
Chloride	mg/L	160
pH		7.2
2,4-D*	mg/L	19.42

*20 mg/L 2,4-D was spiked into drainage water

Table S2. Classification of acute toxicity classes

Toxicity range (mg/L)	Class
$LC/EC_{50} \leq 1$	Very toxic
$1 < LC/EC_{50} \leq 10$	Toxic
$10 < LC/EC_{50} \leq 100$	Harmful
$LC/EC_{50} > 100$	Not harmful

Table S3. Classification of chronic toxicity classes

Toxicity range (mg/L)	Class
$LC/EC_{50} \leq 0.1$	Very toxic
$0.1 < LC/EC_{50} \leq 1$	Toxic
$1 < LC/EC_{50} \leq 10$	Harmful
$LC/EC_{50} > 10$	Not harmful

Table S4. Predicted acute and chronic toxicity of BPA and intermediates products

Compound	Acute toxicity (mg/L)			Chronic toxicity (ChV) (mg/L)		
	Fish (96h-LC50)	Daphnid (48h-LC50)	Green Algae (96h-EC50)	Fish	Daphnid	Green Algae
P	NA	NA	NA	NA	NA	NA
P1	7.7	2.6	11.5	0.37	0.29	2.4
P2	3.55E06	1.52E06	35052	24824.2	6228.5	4886.1
P3	0.156	0.173	0.289	0.01	0.142	0.462
P4	0.13	0.29	0.33	0.012	0.21	0.58
P5	0.095	0.738	0.047	0.009	4.87	0.011

P=NA - not available

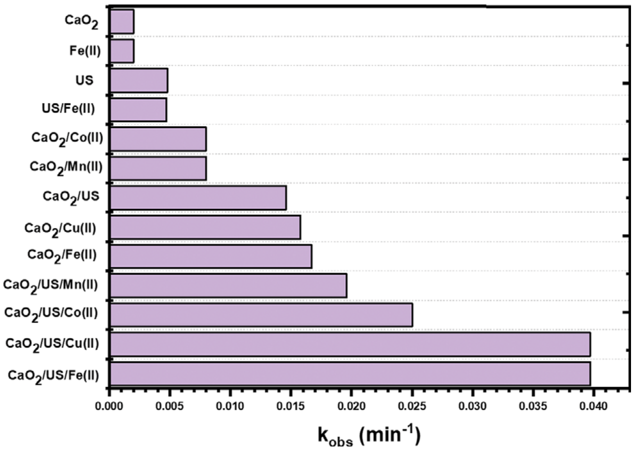

Fig. S1. The rate constant of 2,4-D degradation in various systems.

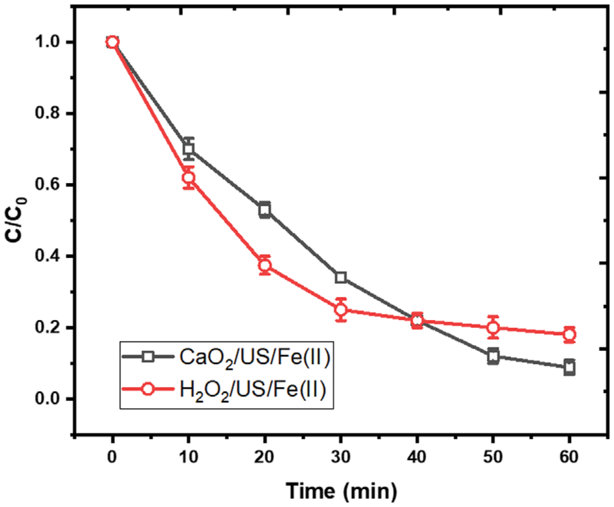

Fig. S2. The 2,4-D degradation by various processes (H_2O_2 and CaO_2= 3 mM, transition metals=0.6 mM and pH=3).

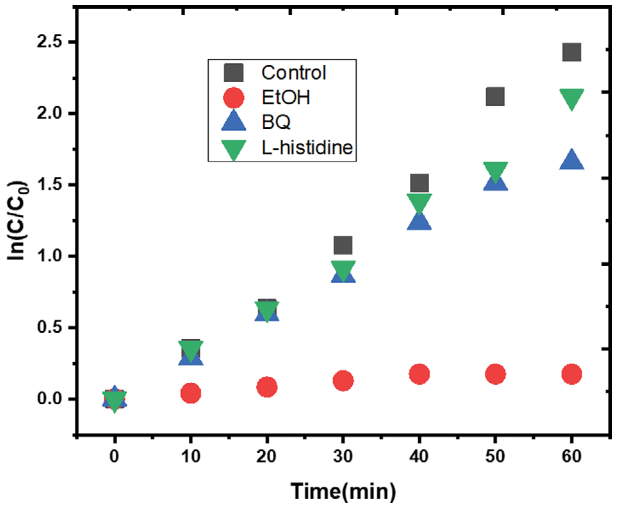

Fig. S3. The plot of ln(C/C_0) *vs* time for pseudo-first order kinetic.

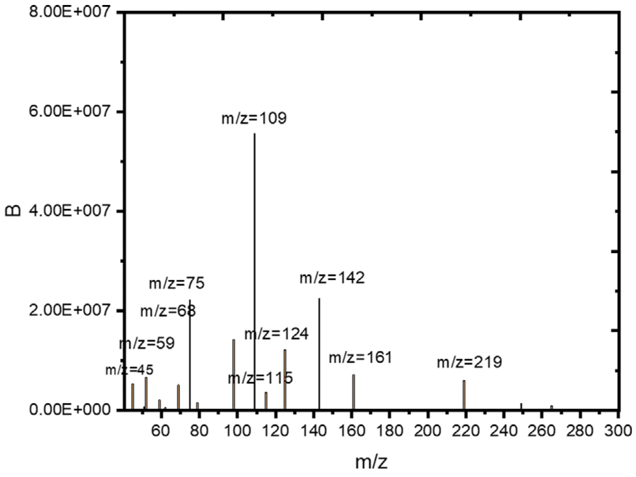

Fig. S4. LC-MS spectrum of 2,4-D degradation.