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A comparative study on oxidative degradation of 2,4-dichlorophenol and 2,4-dichlorophenoxyacetic acid by ammonium persulfate

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ABSTRACT

The degradation of 2,4-dichlorophenol (2,4-DCP) and 2,4-dichlorophenoxyacetic acid (2,4-D) by ammonium persulfate under various activation conditions was investigated. The effect of the initial oxidant concentration, pH, temperature, and Fe^{2+} concentrations were studied. The rate of 2,4-DCP and 2,4-D oxidation was proportional to the concentration of persulfate. The optimal pH for 2,4-DCP degradation was 9.0, while for the 2,4-D, it was 3.0. The effect of temperature on the kinetics of 2,4-DCP and 2,4-D oxidation was examined, and it was demonstrated that increasing the temperature from 25 to 50˚C accelerated the oxidation rate of both contaminants. The effects of Fe^{2+} concentrations and the optimal ratio of persulfate to Fe^{2+} were studied. Synergistic activation of persulfate by heat and Fe^{2+} was also investigated to enhance the oxidation of 2,4-DCP and 2,4-D. Under optimal experimental conditions, when the persulfate to Fe^{2+} molar ratio was 1:2 at 50˚C, the complete oxidation of 2,4-DCP and 2,4-D was achieved after about 45 and 60 min. In any case, the 2,4-DCP was oxidized faster and more efficiently than 2,4-D.

Keywords: 2,4-DCP; 2,4-D; Oxidation; Persulfate

1. Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the most widely used pesticides in the world. It is commonly used as a herbicide to control broad-leaf weeds in cereal crops and aquatic weeds as well as to provide some weed control in forestry, orchards, and farmlands. 2,4-D and its analog 4-chloro-2-metylphenoxyacetic acid have been produced in Poland for fifty years or more in the scale of many thousands of tons per year, which constitutes 5–7% of the world's production [1]. The production technology is based on the reaction of 2,4-dichlorophenol (2,4-DCP) with monochloroacetic acid (Fig. 1) [1].

Furthermore, 2,4-DCP is also the main degradation product of 2,4-D, which causes that these compounds occur in the environment simultaneously. The major source of 2,4-D in drinking water is runoff from herbicide used on crops [2]. Chlorophenols are present in

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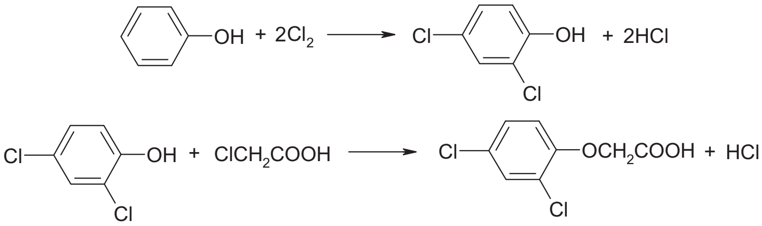

Fig. 1. Reaction for synthesis of 2,4-D.

drinking water as degradation products of 2,4-D, as byproducts of the reaction of hypochlorite with phenolic acids, and as a result of the chlorination of phenols during water disinfection [3]. In drinking water, phenoxy herbicides and chlorophenols emit an unpleasant odor and flavor; the taste and odor threshold of 2,4-D and 2,4-DCP is 3.13 mg/L [3] and 0.3 μg/L [2], respectively. Moreover, both compounds are poisonous to aquatic life, plants, and animals, including humans [4,5]. Therefore, due to their toxicity and persistence, it is very important to reduce the input of these toxic chemicals into the environment and to study the methods of their removal from contaminated sites.

Several methods are currently used in order to remove 2,4-D and 2,4-DCP from aqueous solutions. These methods have been classified in two principal categories: non-destructive processes e.g. adsorption and destructive processes such as oxidation. Adsorption on activated carbon is one of the well-established and effective techniques of removing 2,4-D [6–16] and 2,4-DCP [17–20] from water solution because of its large surface area, high adsorption capacity, and easy availability. Oxidation of chlorophenols [21–25] and phenoxy herbicides [25–27], especially by Advanced Oxidation Processes (AOPs), is also a very effective method of their degradation in water. In AOPs, oxidation of organic pollutants occurs primarily through reactions with hydroxyl radicals produced by photolysis, heterogeneous catalysis, ozone (e.g. O_3/H_2O_2, UV/O_3) and hydrogen peroxide-related processes (e.g. H_2O_2/O_3, H_2O_2/UV, Fenton-like processes) [21]. These methods, although very effective, are limited by the short lifetime of hydrogen peroxide and ozone in water environment.

In view of recent studies, an interesting alternative to AOP methods seems to be the oxidation of organic contaminants by persulfate. Persulfate ($S_2O_8^{2-}$) is one of the strongest inorganic oxidants known in an aqueous solution. The standard *redox* potential (E_0) of the persulfate ion (Eq. (1)) is 2.1 V [28], which is only slightly higher than that of ozone (2.07 V), but much higher than those and oxygen (1.2 V), permanganate (1.7 V) or hydrogen peroxide (1.8 V) [28].

$$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^- \tag{1}$$

Moreover, persulfate can be activated by heat, UV light (Eq. (2)), or transition metal ions (Eq. (3)) [29] to produce very reactive sulfate radicals (E_0 = 2.60 V):

$$S_2O_8^{2-} + \text{heat/UV} \rightarrow 2SO_4^{\cdot -} \tag{2}$$

$$S_2O_8^{2-} + Me^{n+} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + Me^{n+1} \tag{3}$$

In addition to its oxidizing strength, persulfate radical offers some of the advantages of $^{\cdot}OH$. It is non-selectively reactive. Moreover, the sulfate radical is more stable than the hydroxyl radical, and therefore can be delivered considerable distances in the subsurface [30].

In recent years, persulfate salts (sodium, potassium or ammonium persulfate) have been used as oxidants for the degradation of various organic contaminants including chlorinated ethenes [30], methyl *tert*-butyl ether [31], trichloroethylene [32], lindane [33], polyvinyl alcohol [34], 2,4-dinitrotoluene [35], methylene blue [36], diuron [37], phenol [38], bisphenol A [39], *p*-chloroaniline [40], polychlorinated biphenyls [41], and polycyclic aromatic hydrocarbons [42]. Rastogi et al. [43] evaluated the effectiveness of different chelating agents on Fe^{2+}-mediated activation of peroxymonosulfate, persulfate, and hydrogen peroxide at neutral pH conditions. The methods were applied for oxidative degradation of 4-chlorophenol, 2,4-DCP, 2,4,6-trichlorophenol, and 2,3,4,5-tertachlorophenol. Zhao et al. [44] developed a method for degradation of 4-chlorophenol by the combination of zero-valent iron and persulfate under near neutral pH conditions. They investigated concentration of zero-valent iron loading, solution pH, and the reaction mechanism. The authors concluded that Fe^0 and persulfate for wastewater treatment provides a promising alternative as a new technology for contaminants elimination. Recently, Liang et al. [45] described the applicability of various activated persulfate processes for oxidation of 2,4-D. The 2,4-D degradation effectiveness under different persulfate activations, including persulfate at 20°C, thermally activated persulfate at 70°C, iron-activated persulfate at 20°C, hydrogen peroxide-activated persulfate at 20°C, and sodium hydroxide-activated persulfate at 20°C was studied. The authors reported that all persulfate-activated processes are susceptible to the 2,4-D degradation.

The objective of the present study was to comparatively evaluate the kinetics and efficiency of 2,4-DCP and 2,4-D oxidation by ammonium persulfate. 2,4-DCP and 2,4-D were chosen as the target contaminants because they are commonly found in drinking water. In addition, 2,4-DCP is the primary substrate for the 2,4-D synthesis and the main byproduct of its degradation. Although the oxidation of 2,4-DCP and 2,4-D by persulfate were described, not all the factors affecting their degradation were examined. In addition, it is difficult to compare the kinetics and efficiency of their oxidation because the studies were conducted in various laboratory conditions. The effect of initial persulfate concentration, pH, temperature, and Fe^{2+} ions on the kinetics and effectiveness of 2,4-DCP and 2,4-D oxidation were examined.

2. Materials and methods

2.1. Chemicals

2,4-DCP, >99%, (2,4-DCP) and 2,4-D, 98%, (2,4-D) were obtained from Sigma-Aldrich (St. Louis, MO, USA). HPLC-grade acetonitrile, acetic acid, sulfuric acid, sodium hydroxide, ammonium persulfate, and iron(II) sulfate heptahydrate were purchased from Avantor Performance Materials (Gliwice, Poland).

2.2. Experimental procedures

The degradation experiments were conducted in a 10 mL glass volumetric flasks. Stock solutions of 2,4-DCP (0.5 mmol/L) and 2,4-D (0.5 mmol/L) were prepared in deionized water and stored at 4°C. The ammonium persulfate (1 mol/L) and $FeSO_4 \cdot 7H_2O$ (1 mol/L) solutions were freshly prepared before the use. Before the experiment, the 2,4-DCP and 2,4-D solutions were diluted to the designated initial concentration of 0.1 mmol/L by deionized water. All of the experiments were carried out in two replicates, the mean values of which are reported.

To investigate the effect of the initial persulfate concentration to glassy flasks containing 0.1 mmol/L of 2,4-DCP or 2,4-D, some appropriate amounts of ammonium persulfate (1 mol/L) were added. The initial concentration of persulfate was 1, 5, 10, and 20 mmol/L, respectively. The mixtures were diluted to the volume of 10 mL with deionized water, and kept at room temperature. The initial pH of the 2,4-DCP and 2,4-D water solutions was 6.0 and 3.5, respectively. At selected time intervals, 20 μL sample from each duplicate flask was collected for 2,4-DCP and 2,4-D determination.

In the experiments of the effect of pH on the 2,4-DCP and 2,4-D degradation, the initial pH was adjusted by 0.1 mol/L H_2SO_4 or 0.1 mol/L NaOH before adding persulfate to the solution. The pH of the solutions (3.0, 5.0, 7.0, and 9.0) was adjusted by potentiometric titrations. The experiments were conducted at room temperature, the initial concentration of 2,4-DCP and 2,4-D was fixed at 0.1 mmol/L, and the initial persulfate concentration was 20 mmol/L.

To examine the effect of temperature on the oxidation of both contaminants by persulfate, the temperature was maintained at 25, 30, 40, and 50°C. The initial pH of the 2,4-DCP and 2,4-D mixtures were adjusted to 9.0 and 3.0, respectively. 2,4-DCP or 2,4-D to persulfate molar ratio was 1:200.

To investigate the effect of Fe^{2+} on the persulfate oxidation of chosen chloroorganic compounds, different amounts of iron(II) sulfate heptahydrate were added to the 2,4-DCP or 2,4-D solutions before being completely mixed with the persulfate solution in the flask. The initial molar ratio of 2,4-DCP or 2,4-D to persulfate was 1:10. To obtain the optimal persulfate ratio to Fe^{2+}, the experiments were carried out under various $S_2O_8^{2-}$ to Fe^{2+} molar ratios (10:1, 10:5, 10:10, and 10:20).

To evaluate the kinetics of 2,4-DCP and 2,4-D oxidation by persulfate, the experimental data were fitted to a first-order rate model:

$$\ln\left(\frac{C_t}{C_0}\right) = -k_1 t \tag{4}$$

where C_t and C_0 are the concentrations at time t and the initial concentration of 2,4-DCP or 2,4-D (mmol/L), respectively. Values of k_1 were calculated from the plots $\ln\left(\frac{C_t}{C_0}\right)$ vs. t. Half-life time ($t_{1/2}$) of 2,4-DCP or 2,4-D degradation was calculated by Eq. (5):

$$t_{1/2} = \frac{\ln(2)}{k_1} \tag{5}$$

2.3. Analytical methods

2,4-DCP and 2,4-D were quantified by Shimadzu LC-20 series HPLC (Kyoto, Japan) equipped with a diode-array detector using a Phenomenex Luna C18

(2.0 × 150 mm, 3 μm) column thermostated at 40˚C. The mobile phase consisted of acetonitrile and water adjusted to pH 3.0 with acetic acid (50/50, v/v). The flow rate was 0.25 mL/min and the elution was monitored at wavelength of 284 nm. 20 μL of the sample was injected into the chromatographic column. The calibration curves were constructed by plotting the peak area vs. 2,4-DCP or 2,4-D concentration, and the curves were fitted by least-squares linear regression analysis. The calibration plots for 2,4-DCP and 2,4-D were linear in the range tested (0.005–0.1 mmol/L) with correlation coefficients (R^2) better than 0.999 for both analytes. The regression equations ($n = 3$) were $y = 420.05x - 2.19$ for 2,4-DCP, and $y = 181.61x + 1.25$ for 2,4-D.

3. Results and discussion

3.1. Effect of initial persulfate concentration

The removal of 2,4-DCP and 2,4-D by the oxidative process was studied at constant 2,4-DCP and 2,4-D concentration (0.1 mmol/L) and with variable persulfate concentration (1, 5, 10 and 20 mmol/L). The results have been depicted in Fig. 2. Although the experiment was conducted in deionized water at ambient temperature (without persulfate activation), significant quantities of 2,4-DCP and 2,4-D have been oxidized. The initial persulfate concentration causes an important effect to the degradation efficiency and after 6 h of reaction time, when persulfate concentration increases, the oxidation efficiency does as well and is varied from 2.9 to 37.1% for 2,4-DCP and from 0.1 to 24.9% for 2,4-D, respectively. In both cases, as the molar ratio of persulfate to pollutant is increased, more oxidants are available to attack the aromatic structure, and therefore the degradation reaction efficacy increases.

3.2. Effect of initial pH

The pH of the solution is a very important parameter in the oxidation with persulfate because its activation may be initiated by alkaline conditions (Eqs. (6)–(8)) [45].

$$S_2O_8^{2-} + 2H_2O \rightarrow HO_2^- + 2SO_4^{2-} + 3H^+ \quad (6)$$

$$HO_2^- + S_2O_8^{2-} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + H^+ + O_2^{\cdot -} \quad (7)$$

$$SO_4^{\cdot -} + OH^- \rightarrow SO_4^{2-} + {}^{\cdot}OH \quad (8)$$

The effect of pH on degradation efficiency of 2,4-DCP and 2,4-D was studied in the range of 3.0–9.0, and the required data are presented in Table 1. As can be seen, degradation of 2,4-DCP and 2,4-D with persulfate is strongly pH dependent. The results of the experiment demonstrate an increase in 2,4-DCP degradation with increasing pH from 13.6% at pH 3.0 to 60% at pH 9.0. Calculated degradation constants (Table 1) increase from 0.024 1/h at pH 3.0 to 0.149 1/h at pH 9.0. Efficiency of 2,4-D oxidation decreases with an increase in the solution pH (from 21.8% at pH 3.0 to 5.9% at pH 9.0). The first-order rate constants were 0.042, 0.029, 0.013, and 0.010 1/h for the initial solution pH of 3, 5, 7, and 9, respectively.

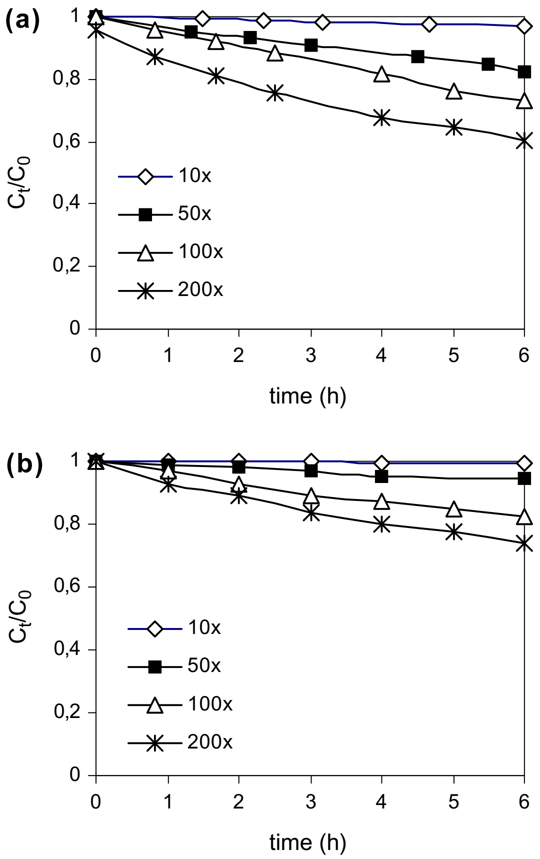

Fig. 2. Effect of persulfate excess on 2,4-DCP (a) and 2,4-D (b) degradation in deionized water at 25˚C.

The effectiveness of 2,4-D degradation under sodium hydroxide-activated persulfate (pH 13.1) has been documented by Liang et al. [45]. However, in these studies, under much milder conditions (pH 3–9), the increase in the alkalinity causes a decrease in the conversion degree of the 2,4-D. Alkaline environment favored the formation of hydroxyl radicals (Eqs. (6)–(8)). Both $SO_4^{\cdot -}$ and ${}^{\cdot}OH$ are possibly responsible for the destruction of organic contaminants, but in the presence of ${}^{\cdot}OH$ excess (which takes place at high

Table 1
Effect of pH on 2,4-DCP and 2,4-D degradation at 25°C (2,4-DCP and/or 2,4-D to persulfate molar ratio 1:200)

pH	k_1 (1/h)	$t_{1/2}$ (h)	R^2	% of degradation[a]
2,4-DCP				
3.0	0.024	28.88	0.966	13.66
5.0	0.039	17.77	0.996	21.41
7.0	0.089	7.78	0.996	41.26
9.0	0.149	4.65	0.991	60.01
2,4-D				
3.0	0.042	16.50	0.988	21.82
5.0	0.029	23.90	0.987	16.55
7.0	0.013	53.32	0.988	7.62
9.0	0.010	69.31	0.989	5.93

[a]after 6 h.

pH), the degradation efficiency may degrade due to the radical scavenging (Eqs. (9) and (10)). Consequently, the oxidation efficiency in alkaline conditions is lower than that in acidic environment.

$$^{\bullet}OH + S_2O_8^{2-} \rightarrow OH^- + S_2O_8^{\bullet -} \tag{9}$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{10}$$

Such a situation was observed in these studies for the 2,4-D degradation, but also by Huang et al. [31], Ghauch et al. [36], and Fang et al. [41] for oxidation of methyl *tert*-butyl ether, methylene blue, and polychlorinated biphenyls, respectively.

On the other hand, 2,4-DCP is rapidly and efficiently degraded under alkaline conditions than under acidic conditions. At lower pH, rapid transformation of persulfate, according to Eqs. (11) and (12), may increase significantly the concentration of $SO_4^{\bullet -}$. A high sulfate radicals concentration may reduce the oxidation efficiency due to chain termination between $SO_4^{\bullet -}$ (Eq. (13)) [36].

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \tag{11}$$

$$HS_2O_8^- \rightarrow SO_4^{\bullet -} + SO_4^{2-} + H^+ \tag{12}$$

$$2SO_4^{\bullet -} \rightarrow \text{chain termination} \tag{13}$$

Similar results as the ones for 2,4-DCP in this study were obtained by Liang et al. [32] during the oxidation of trichloroethylene. The maximum rate of trichloroethylene degradation occurred at neutral pH, but also the degradation kinetics and the degradation efficiency were significantly higher at pH 9 in comparison to a pH of 4 or 2.

In conclusion, the results showed that the pH influenced on the oxidation of both chloroorganic contaminants and the preferable condition for 2,4-DCP are under alkaline conditions, while for 2,4-D, it is under acidic conditions. Based on the literature, the pH can differently affect organic compounds degradation, and therefore common pH effect cannot be expected.

3.3. Effect of temperature

In order to study the effect of reaction temperature on the 2,4-DCP and 2,4-D degradation, the experiments were performed in the 25–50°C temperature range at the initial 2,4-DCP and/or 2,4-D to persulfate molar ratio 1:200. The initial pH of 2,4-DCP solution was 9.0, and the initial pH of 2,4-D solution was 3.0. Table 2 shows the results of the influence of temperature on persulfate oxidation of both organic contaminants. As can be seen, the degradation efficiency of 2,4-DCP and 2,4-D increases significantly with increasing the temperature from 25 to 50°C. The complete removal of 2,4-DCP and 2,4-D was observed for reactions carried out at 50°C over 2 and 3 h, respectively. The first-order rate constants of 2,4-DCP and 2,4-D oxidation were found to increase with increased temperatures, however, the highest values of k_1 were observed for 2,4-DCP.

The temperature dependency of the kinetic constant was further evaluated using the Arrhenius equation:

$$\ln k_1 = \ln A - \frac{E_A}{R}\left(\frac{1}{T}\right) \tag{14}$$

where A is the Arrhenius constant, E_A is the activation energy (kJ/mol), R is the universal gas constant (8.314 kJ/mol·K), and T the temperature (K). The activation energies were calculated from the slopes of the straight line plots of $\ln k_1$ vs. $1/T$ (Fig. 3).

The correlation coefficients were 0.993 for 2,4-DCP and 0.988 for 2,4-D. The values of E_A were 95.612 and 106.291 kJ/mol for 2,4-DCP and 2,4-D, respectively. The calculated E_A for 2,4-DCP is higher than that of 2,4-D indicating the greater susceptibility of chlorophenol for persulfate oxidation.

3.4. Oxidation by Fe^{2+}-activated persulfate

The experiments were carried out at a constant 2,4-DCP or 2,4-D to persulfate molar ratio 1:10 (initial concentrations of chloroorganic contaminants and persulfate were 0.1 and 1.0 mmol/L, respectively). In

Table 2
Effect of temperature on the kinetic parameters of 2,4-DCP (pH 9.0) and 2,4-D (pH 3.0) degradation (2,4-DCP and/or 2,4-D to persulfate molar ratio 1:200)

Temperature (°C)	k_1 (1/h)	$t_{1/2}$ (h)	R^2	% of degradation[a]
2,4-DCP				
25	0.151	4.59	0.989	60.10
30	0.177	3.912	0.996	65.93
40	0.703	0.99	0.990	99.01[b]
50	1.693	0.41	0.994	93.02[c]
2,4-D				
25	0.040	17.33	0.991	21.52
30	0.071	9.76	0.983	35.36
40	0.391	1.77	0.988	90.43
50	0.982	0.71	0.989	95.87[d]

[a] After 6 h.
[b] After 4 h.
[c] After 2 h.
[d] After 3 h.

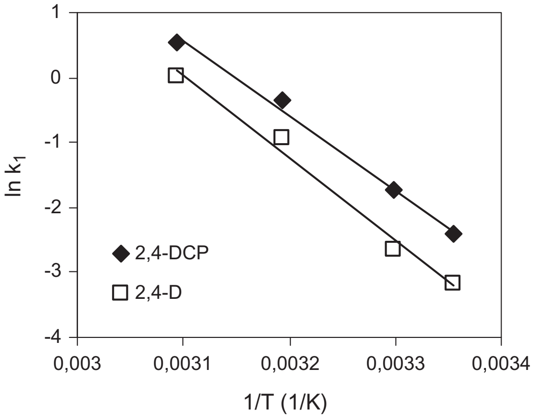

Fig. 3. Arrhenius plots for 2,4-DCP and 2,4-D degradation.

order to avoid the synergistic effect of different factors (e.g. pH, temperature) on the oxidation process, experiments were carried out in deionized water at ambient temperature. To obtain the optimal persulfate to Fe^{2+} ratio, the oxidation of both compounds was investigated under various persulfate to Fe^{2+} molar ratios, including 1:0.1, 1:0.5, 1:1, and 1:2. The required data are summarized in Table 3.

In the absence of ferrous iron, some changes in the 2,4-DCP and 2,4-D concentrations were observed within 6 h. When the persulfate to Fe^{2+} molar ratio was 1:2, about 45.5% of the 2,4-DCP and about 35.9% of 2,4-D were oxidized. The rate of 2,4-DCP and 2,4-D oxidation by persulfate increased when the amount of Fe^{2+} increased, indicating that Fe^{2+} can activate persulfate into sulfate radicals according to Eq. (3). However, the observed differences in the reaction rates, when the persulfate to Fe^{2+} molar ratio is 1:1 and 1:2, are small. A negative impact of excessive iron concentration has been previously described by other authors [34,37]. This is due to the fact that when the ferrous iron concentration is greater than that of persulfate, the excessive ferrous ion can act as a sulfate radicals scavenger, thus, reducing the degradation efficiency (Eq. (15)).

$$\mathrm{Fe^{2+} + SO_4^{\cdot -} \rightarrow Fe^{3+} + SO_4^{2-}} \qquad (15)$$

The results showed that the persulfate could be effectively activated by transition metals. In these studies, the Fe^{2+} ions were used because they have a strong catalytic power to generate highly reactive radicals [29]. Its properties have been known for more than 100 years because the ions have been used to initiate and catalyze the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. Oxidation processes utilizing activation of hydrogen peroxide by Fe^{2+}, classically referred to as Fenton's reagent is known to be very effective in the destruction of many hazardous organic contaminants in water [21,46]. Persulfate activation by ferrous ions is similar to Fenton's reaction, and proved to be effective for removal of lindane [33], polyvinyl alcohol [34], 2,4-dinitrotoluene [35], diuron [37] as well as 2,4-DCP [43] and 2,4-D [45].

The effectiveness of the 2,4-DCP and 2,4-D degradation during simultaneous activation of persulfate by heat and Fe^{2+} has also been investigated. The experiments were carried out at a constant organic compound:persulfate:Fe^{2+} molar ratio of 1:10:20 at 50°C. The results are presented in Fig. 4.

Table 3

Effect of persulfate to Fe^{2+} molar ratio on the kinetic parameters of 2,4-DCP and 2,4-D in water (initial 2,4-DCP and/or 2,4-D concentration 0.1 mmol/L, persulfate concentration 1 mmol/L, temperature 25°C)

Persulfate: Fe^{2+}	k_1 (1/h)	$t_{1/2}$ (h)	R^2	% of degradation [a]
2,4-DCP				
1:0	0.005	138.63	0.992	2.91
1:0.1	0.021	33.01	0.994	11.33
1:0.5	0.040	17.33	0.991	20.63
1:1	0.085	8.15	0.997	40.59
1:2	0.103	6.73	0.987	45.55
2,4-D				
1:0	0.001	693.15	0.994	0.10
1:0.1	0.014	49.51	0.993	7.88
1:0.5	0.028	27.75	0.991	14.67
1:1	0.054	12.84	0.994	28.22
1:2	0.068	10.19	0.990	35.89

[a] After 6 h.

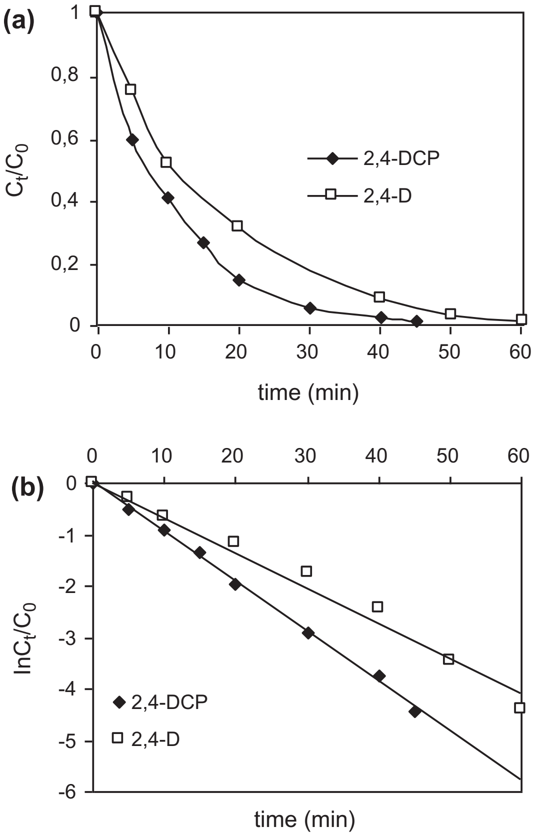

Fig. 4. Degradation of 2,4-DCP and 2,4-D by heat and Fe^{2+}-activated persulfate (a) and first-order plot (b) (2,4-DCP and 2,4-D concentration 0.1 mmol/L, persulfate concentration 1 mmol/L, Fe^{2+} concentration 2 mmol/L, temperature 50°C).

As can be seen, the complete removal of 2,4-DCP and 2,4-D was achieved after about 45 and 60 min. However, the complete degradation of 2,4-DCP and 2,4-D and their intermediates (no peaks on the chromatograms) were observed after approximately 90 and 120 min. The calculated k_1 and $t_{1/2}$ values were 5.852 1/h and 0.118 h for chlorophenol, and 4.271 1/h and 0.162 h for herbicide, respectively. The results demonstrate that synergistic activation of persulfate by heat and Fe^{2+} significantly enhance the oxidation of both contaminants in the persulfate–water system.

4. Conclusions

This study compares the degradation efficiencies of 2,4-DCP and 2,4-D by ammonium persulfate under various activation conditions. The effect of the initial oxidant concentration, pH, temperature, and Fe^{2+} concentrations were studied. The results showed that the initial persulfate concentration had an important effect on the degradation efficiency of both contaminants. The reaction rates increased with an increase in oxidant excess. 2,4-DCP was more rapidly and more efficiently degraded under alkaline conditions, whereas the 2,4-D under acidic conditions. The effect of elevated temperatures on the kinetics of 2,4-DCP and 2,4-D oxidation was examined and the activation energy was estimated. The E_A values calculated for 2,4-DCP and 2,4-D were 95.612 and 106.291 kJ/mol, respectively. The effect of Fe^{2+} concentrations was studied, and persulfate to Fe^{2+} ratio 1:2 was found to be optimal. At 50°C, the addition of Fe^{2+} to the persulfate–water system significantly enhanced the oxidation of both chloroorganic compounds. The complete oxidation of 2,4-DCP and 2,4-D was obtained by heat and Fe^{2+}-activated persulfate in 45 and 60 min, respectively. In all circumstances, the 2,4-DCP was oxidized faster and more efficiently than 2,4-D, which indicates that the herbicide molecule is more stable and less susceptible to degradation by persulfate. Although during the oxidation, different additional peaks on the chromatograms were observed, the concentrations of intermediates were not monitored. The oxidation of chlorophenols and chlorinated phenoxy herbicides has been studied by many authors in various oxidation systems. In general, the formed intermediates were similar and, consequently, pathways for 2,4-DCP and 2,4-D oxidation are well documented [24,25,45].

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