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Diuron abatement using activated persulphate: Effect of pH, Fe(II) and oxidant dosage

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ABSTRACT

The high oxidation efficiencies of the free radicals ($SO_4^{\bullet -}$), in combination with the slow rate of consumption of the oxidant, make this process very effective for the degradation of organic herbicides. Effects of pH, persulphate and Fe(II) concentration on the destruction of diuron by heat-assisted persulphate were examined in batch experiments. All the experiments were performed at 50 °C and an initial diuron concentration of 0.09 mM. The effectiveness of the process was evaluated based on the degradation of diuron and total organic carbon (TOC) removal. Under the reaction conditions, the diuron conversion is enormously influenced by the presence of Fe(II) in solution which rapidly produces the sulphate radical. Fe(II) concentration significantly accelerates diuron degradation at the first stages where the Fe(II) is oxidized to ferric iron. Increasing the persulphate concentration from 1 to 2.1 mM at natural pH accelerated the oxidation rate of diuron, which achieved 60% oxidation in 180 and 90 min, respectively. For the higher persulphate concentration (2.1 mM), complete diuron oxidation was achieved at 0.72 mM Fe(II) concentration in a few minutes. Additionally, diuron degradation by persulphate in bicarbonate-buffer solution was slower, most likely due to the presence of bicarbonate ions (radical scavengers).

1. Introduction

Diuron (CAS number: 330-54-1), N-(3,4-dichlorophenyl)-N,N-dimethyl-urea, is an herbicide belonging to the phenylamide family. It remains as a solid at ambient temperature with a moderate water solubility of 42 mg L^{-1} at 20 °C and a melting point of 158–159 °C. Its vapour pressure and Henry's law constant suggesting that diuron is not volatile from water or soil [1]. Diuron could contaminate the surface water by agricultural runoffs and wastewaters generated from diuron manufacturing plants [2]. It is toxic to the aquatic environment and non-biodegradable. Because of its high persistence, it is a biologically active pollutant that can be found in many environment such as soil, sediments and water [3]. Diuron is a problematic water pollutant which has major impacts on human health and the environment; for example, diuron is absorbed from the gastrointestinal and respiratory systems [1]. The environmental fate of diuron has been the subject of numerous studies [1,4,5]. Diuron has been used worldwide for more than 40 years and its toxicity has been registered in the European Union Water Framework Directive list of priority hazardous substances [6]. Therefore, to prevent the accumulation of this herbicide in the aquatic system, it is important to remove it from wastewater effluent by conventional water and wastewater treatment processes. Fig. 1 shows the chemical diuron structure.

Due to their bio-recalcitrant and toxic properties, wastewaters containing herbicides cannot be directly treated in conventional wastewater treatment plants based on the activity of a microbiological consortium. Among the various treatment technologies, advanced oxidation processes (AOPs) are becoming increasingly popular as an alternative for the treatment of herbicides in soils, groundwater, and industrial wastewater. AOPs are based on the use of highly reactive oxidizing radicals to oxidize organic contaminants. In the last few years, the elimination of diuron from aqueous solutions has been investigated, using photocatalysis [7–9], Fenton and photo-Fenton processes [10–13], electro-Fenton process [14,15], ozonation [16–18]. Among these technologies, sodium persulphate ($Na_2S_2O_8$) is a more recent addition to the list of possible oxidants for organic compounds oxidation. Persulphate could be better for use in soil and groundwater than other AOPs. When persulphate salt dissociates in water, it forms the persulphate anion ($S_2O_8^{2-}$), a strong oxidizing agent ($E^0 = 2.01$ V):

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}, \quad E^0 = 2.01\,\text{V} \qquad (1)$$

Persulphate has drawn increasing attention as an alternative oxidant in the chemical oxidation of contaminants because it has several advantages [19–21]. High aqueous solubility, high stability

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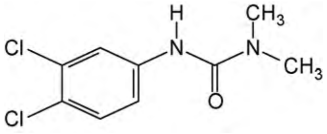

Fig. 1. Diuron chemical structure.

at room temperature, relatively low cost and benign end products make persulphate oxidation a promising choice among the AOPs. Persulphate oxidant has been recently used for the degradation of organic pollutants in wastewaters [22–26]. However, no studies in the literature are offered for diuron abatement using persulphate as oxidant.

The use of persulphate in treatment processes has kinetic limitations as it reacts much more slowly than other oxidants. When the persulphate anion is chemically or thermally activated (Eq. (2)), it produces the sulphate free radical ($SO_4^{\bullet -}$), which is a stronger oxidant ($E^0 = 2.4\,V$) than the persulphate anion (Eq. (3)) [27]. Once the $SO_4^{\bullet -}$ is formed it can destroy oxidizable contaminants. The application of this oxidant to groundwater remediation includes the use of persulphate activated either thermally or chemically to generate the sulphate free radical [28,29]:

$$S_2O_8^{2-} + \text{initiator} \rightarrow SO_4^{\bullet -} + (SO_4^{\bullet -}\ \text{or}\ SO_4^{2-}) \tag{2}$$

$$SO_4^{\bullet -} + e^- \rightarrow SO_4^{2-}, \quad E^0 = 2.4\,V \tag{3}$$

The initiator in the above reaction (Eq. (2)) could be heat or transition metal ions. Among the metal ions, ferrous iron (Fe(II)) is used most often [30,31] (Eq. (4)). Fe(II) is cheap, and readily available. However, if Fe(II) is present in large amounts, Fe(II) would significantly scavenge $SO_4^{\bullet -}$ and inhibit radical oxidation of the contaminants (Eq. (5)). Based on the reaction rate constant between sulphate radicals and Fe(II), quenching of sulphate radicals by Fe(II) can be a major side reaction, especially at higher concentrations of Fe(II). A minimum amount of Fe(II) is required to effectively activate persulphate, while excessive Fe(II) can be detrimental for process degradation efficiency [32,33]:

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet -} \tag{4}$$

$$SO_4^{\bullet -} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}, \quad k = 4.6 \times 10^9\,M^{-1}\,s^{-1}(22\,^\circ C), \quad pH = 3\text{–}5 \tag{5}$$

The sulphate radical is relatively more stable in water than the hydroxyl radical ($HO^\bullet$), and thus may be able to disperse a greater distance in water [34]. The high oxidation efficiencies of the free radicals ($SO_4^{\bullet -}$), in combination with the slow rate of consumption of precursor oxidants (due to their stability), make sulphate radical based processes very effective for the degradation of recalcitrant organic compounds [35–37].

Persulphate activation with Fe(II) can generate the sulphate radical, which may further undergo interconversion to a $HO^\bullet$ depending on pH levels in accordance with Eqs. (6) and (7) [38]. Both $SO_4^{\bullet -}$ ($E^0 = 2.4\,V$) and $HO^\bullet$ ($E^0 = 2.7\,V$) are aggressive oxidants capable of destroying a wide range of organic compounds [39]. Persulphate degradation forms $SO_4^{\bullet -}$ that can undergo radical interconversion to form $HO^\bullet$ under alkaline conditions (Eq. (7)):

$$SO_4^{\bullet -} + H_2O \leftrightarrow HO^\bullet + H^+ + SO_4^{2-} \tag{6}$$

$$SO_4^{\bullet -} + HO^- \rightarrow HO^\bullet + SO_4^{2-} \tag{7}$$

The radicals $SO_4^{\bullet -}/HO^\bullet$ can be present either individually or simultaneously in the persulphate oxidation system [40–42]. The effects of pH on the formation of $SO_4^{\bullet -}/HO^\bullet$ can be demonstrated by varying pH values. $SO_4^{\bullet -}$ is the predominant radical at pH <7; both $SO_4^{\bullet -}$ and $HO^\bullet$ are present at pH 9; $HO^\bullet$ is the predominant radical at a more basic pH (i.e., pH 12) [43].

Under acidic conditions the breakdown of persulphate into sulphate free radicals can be further acid catalyzed as shown in Eqs. (8) and (9). On the other hand, if iron is used as the activator, negligible iron precipitation is produced mainly due to stable acidic pH conditions:

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \tag{8}$$

$$HS_2O_8^- \rightarrow H^+ + SO_4^{\bullet -} + SO_4^{2-} \tag{9}$$

The degradation of diuron by persulphate oxidation has not been studied yet. In this study the thermal and chemical generation of $SO_4^{\bullet -}$ by Fe(II) at 50 °C was studied as a potential alternative oxidant for the abatement of diuron. The effectiveness of the proposed process was evaluated based on the degradation and total organic carbon (TOC) removal efficiencies of diuron and toxicity of intermediates of oxidation. This work was focused on the influence of solution chemistry on the rate and extent of degradation. The influences of oxidant and metal ion concentration and initial adjusted pH on organic degradation by persulphate are presented.

2. Materials and methods

2.1. Reagents

Analytical-reagent grade were used in the experiments. Diuron and sodium persulphate were purchased from Sigma–Aldrich. The acidic pH values of solutions were adjusted with H_2SO_4 from Riedel de Haën whenever required. Sodium bicarbonate from Panreac was used for buffered solutions. Ferrous sulphate heptahydrate obtained from Fluka was used as the catalytic Fe(II) species. Acetonitrile for mobile phase in HPLC was obtained from Riedel de Haën. All of the suspensions and solutions were prepared with Milli-Q water (>18 mΩ cm) purified with a deionizing system.

2.2. Batch oxidation experiments

All experiments were performed in batch mode and were conducted in a reaction vessel with volume of 500 mL at 50 °C. The

Table 1
Operating conditions of diuron oxidation for runs carried out in batch tests. $T = 50\,^\circ C$; $V_L = 500\,mL$.

Run	Contaminant	$C_{Cont.}$ (mM)	C_{PS} (mM)	$C_{Fe(II)}$ (mM)	PS:Fe(II):diuron (molar ratio)	$pH_{initial}$
1	Without contaminant	–	2	0.18	11.1:1:0	4–5
2		–	2	0.72	2.8:1:0	4–5
3		–	2	0.18	11.1:1:0	2–3[a]
4		–	2	0.18	11.1:1:0	7–8[a]
5	Diuron	0.09	1	0.18	11.1:2:1	4–5
6		0.09	2	0.72	22.2:8:1	4–5
7		0.09	2	0.18	22.2:2:1	2–3[a]
8		0.09	2	0.18	22.2:2:1	4–5
9		0.09	2	0.18	22.2:2:1	7–8[a]

[a] The pH of the solution was initially adjusted using $NaHCO_3$ or H_2SO_4.

solution was mixed on a magnetic stirrer and heated with an electric heating. The experiments were also performed in duplicate to assure accurate data acquisition and hence valid interpretation. The total experiments performed are shown in Table 1.

Diuron solution at an initial approximate concentration of 0.09 mM was used. The reaction was initiated by injecting $Na_2S_2O_8$ solution, followed by addition of Fe(II) sulphate ($FeSO_4{\cdot}7H_2O$). A stock solution of sodium persulphate with a concentration of 100 or 200 mM was prepared and a specific aliquot was diluted in the reaction vessel to achieve an initial concentration of 1 or 2 mM. Stock solutions of the metal salt were prepared with concentrations varying from 3.6 to 14.5 mM. Specific aliquots of the stock solutions were added to the vessel in order to achieve a ferrous molar ratio showed in Table 1.

Experiments to investigate the influence of initial pH on the degradation rate of diuron were initially designed at a fixed pH condition. Solutions containing alkalinity species were prepared by adding predetermined amount of sodium bicarbonate to a diuron solution that was buffered for pH (run 9). Another experiment was performed under acidic conditions where the initial pH was adjusted to pH ≈ 2–3 with H_2SO_4 (run 7).

For each reaction samples were collected during the course of reaction to monitor the diuron degradation with time. At each designated time interval the samples were removed from the reaction vessel, chilled to 4 °C in an ice bath for about 5 min to quench the reaction and then used for analysis of different parameters.

Change in pH, oxidation–reduction potential (ORP), TOC and diuron concentration between the beginning and at the end of the experiments were determined. Ecotoxicity and chloride ion formed during the reaction was detected from the final aqueous phase.

In the same experimental conditions previous experiments (runs from 1 to 4 in Table 1) without contaminant were carried out in pure water to study the chemistry of persulphate anion in persulphate activation with ferrous ion and temperature at different initial pH. The pH and ORP values were monitored in these experiments.

2.3. Analytical methods

In order to determine the residual diuron concentration and indicate the presence of its degradation products with time, 20 μL of sample was injected into a high-performance liquid chromatography column. The initial concentration of the substrate was approximately 0.09 mM and its transformation was monitored by HPLC (Agilent, mod. 1100). A Chromolith Performance column (monolithic silica in rod form, RP-18e 100–4.6 mm) was used as the stationary phase. The mobile phase was acetonitrile–water (60:40, v/v) with a flow-rate of 1.00 mL/min for detection and quantification of diuron. The effluent was monitored at 210 nm. Evaluation and quantification were made on a chromatography data system.

The progress of mineralization of diuron was monitored by determination of TOC concentration in the liquid phase by direct injection of the samples into a Shimadzu TOC-V CSH analyzer by oxidative combustion at 680 °C, using an infrared detector. For each set, total carbon (TC) and inorganic carbon (IC) were measured and TOC was calculated by subtracting IC from TC.

Since diuron contains two organic chlorine atoms, formation of Cl^- is expected during the reaction.

Soluble iron concentrations were analyzed using a DR/890 colorimeter with the FerroVer Iron Reagent, supplied by HACH.

Solution pH and redox potential were measured with a combination pH and redox potential electrode (Basic 20-CRISON).

Ecotoxicity was measured by using the Microtox® bioassay. The Microtox bioassay is based on the decrease of light emission by *Photobacterium phosphoreum* resulting from its exposure to a toxicant, using a Microtox® M500 Analyzer (Azur Environmental). The inhibition of the light emitted by the bacteria was measured after 15 min contact time. The EC_{50} is defined as the effective nominal concentration of toxicant ($mg\,L^{-1}$) that reduces the intensity of light emission by 50%. The parameter IC_{50} is defined as the percentage of the initial volume of the sample to the volume of the sample yielding, after the required dilution, a 50% reduction of the light emitted by the micro-organisms. The toxicity units (TUs) of the wastewater are calculated as

$$\mathrm{TU} = \frac{100}{\mathrm{IC}_{50}} \tag{10}$$

If the aqueous sample only contains a compound *i* at a concentration C_i the toxicity units can be predicted by the next relationship:

$$\mathrm{TU}_i = \frac{C_i}{\mathrm{EC}_{50i}} \tag{11}$$

Before measuring the toxicity, the pH values of the samples were re-adjusted to between 6 and 7, in order to prevent the pH effect. All the chemicals used were purchased from Sigma–Aldrich and the micro-organisms were Microtox® Acute Reagent supplied by I.O. Analytical.

3. Results and discussion

3.1. Persulphate–water system

In pure water, the persulphate anion is fairly stable. The rapid change of water chemistry upon the introduction of persulphate activated by iron is reflected by the solution ORP value [21]. In Fig. 2 it is represented the redox potential and the pH value versus the reaction time.

The *y*-axis of Fig. 2a shows the solution redox potential trends after sodium persulphate was added to water at different pH values. After sodium persulphate (2 mM) and Fe(II) (0.18 mM) were added, the redox potential quickly increased in less than 30 s at natural and acidic pH, then raised to 610 and 700 mV respectively in approximately 180 min. The fast increase of redox potential in the presence of persulphate indicates a highly oxidative condition. Meanwhile, with a buffered solution of bicarbonate, redox potential of a sodium persulphate solution was approximately 150 mV. This value indicates a lower oxidative condition for buffered pH conditions. Although persulphate oxidation appears to have the same limitations (alkalinity inhibition) as Fenton's chemistry and ozonation, persulphate is much more stable in the subsurface compared to the other two oxidants.

According to Eq. (4) ferrous activation of persulphate produces both sulphate ion and sulphate radical. Fig. 2b shows the pH value. The pH decrease accords with the redox potential increase. The ORP and pH reach asymptote values by the fast Fe(II) consumption and non regeneration of the active metallic species by reduction of Fe(III). The Fe(II) concentration decreases because it is oxidized to Fe(III) by Eq. (4) and the persulphate chemical activation is stopped. The decrease in pH indicates the formation of protons in the persulphate system. The H^+ production by Eqs. (6) and (12) decreases the pH value:

$$\mathrm{Fe}^{3+} + x\mathrm{H_2O} \rightarrow \mathrm{Fe(OH)}_x{}^{3-x} + x\mathrm{H}^+ \tag{12}$$

Persulphate decomposition is faster at acidic conditions as shown by Eqs. (8) and (9), where the redox potential is higher. Competing reactions with bicarbonates (Eq. (13)) can result in scavenging of sulphate radicals and could possibly limit their oxidation efficiency:

$$\mathrm{SO_4}^{\bullet -} + \mathrm{HCO_3}^{-} \rightarrow \mathrm{SO_4}^{2-} + \mathrm{HCO_3}^{\bullet} \tag{13}$$

Fig. 3 shows the values of redox potential and pH at initial natural pH with two different ferrous concentrations. Both the redox

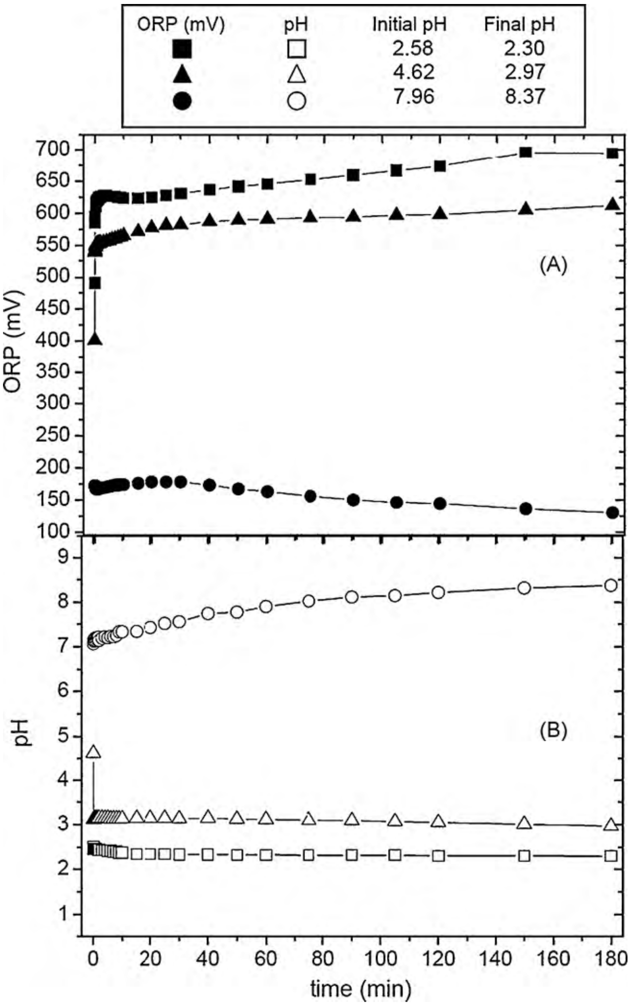

Fig. 2. Water chemistry of persulphate: effect of initial pH. $T = 50\,^{\circ}\mathrm{C}$. $[\mathrm{Fe(II)}]_0 = 0.18$ mM. $[\mathrm{Na_2S_2O_8}]_0 = 2$ mM.

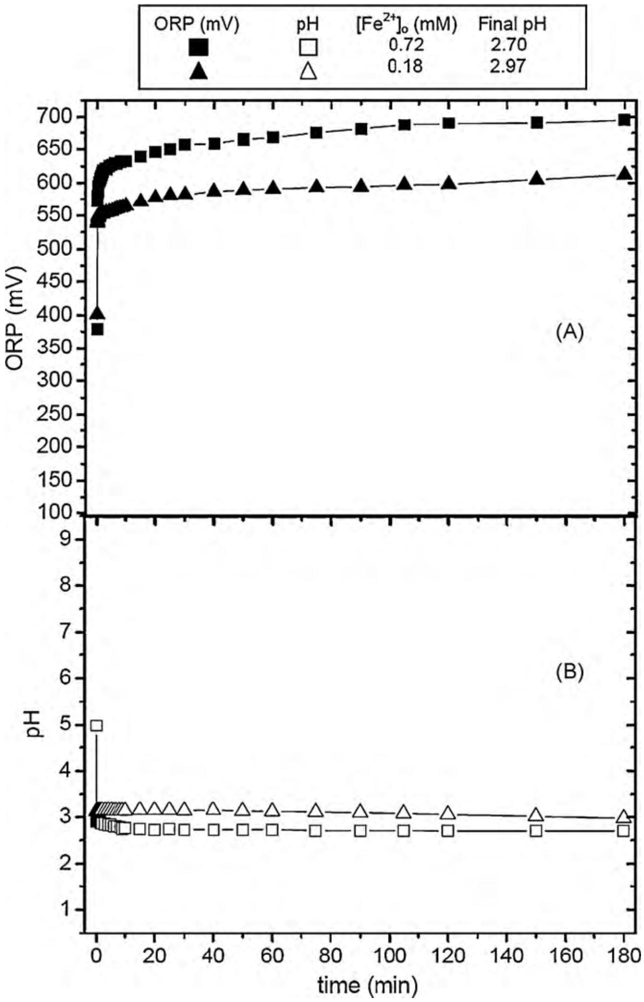

Fig. 3. Water chemistry of persulphate: effect of initial Fe(II) content. $T = 50\,^{\circ}\mathrm{C}$. $\mathrm{pH_{initial}} = 4$–5. $[\mathrm{Na_2S_2O_8}]_0 = 2$ mM.

potential increase and pH decrease, as shown in Fig. 3, suggest quick activation of persulphate by Fe(II). The persulphate decomposition rate was found to increase with the increase in the Fe(II) concentration [33]. The greater redox potential value indicates a higher oxidative condition for organic compound degradation.

3.2. Oxidation of diuron by activated persulphate

3.2.1. Effect of pH on the degradation efficiency

The pH value of the solution is usually an important parameter affecting oxidative degradation of organic contaminants. Therefore, the role of initial pH on the degradation of diuron by activated persulphate was investigated. The results of degradation and mineralization of diuron by persulphate at three pH values (3, 5 and 8 approximately) are shown in Fig. 4. They reveal that the efficiency of contaminant degradation by activated persulphate is dependent on pH value. Diuron degradation (X_{diuron}) was found to decrease with the increase in the initial pH value. As can be seen in Fig. 4 the higher ORP value indicates oxidative conditions, and it accords with higher diuron conversion at acid pH. This result is in agreement with previous studies in literature that employ other contaminants [19,24,44].

As can be seen in Fig. 4, a high redox potential of the sulphate free radical makes it very reactive in destroying organic contaminants. The contaminant degradation in the bicarbonate-buffered solution was lower than in the acidic and natural initial pH solution. Complete diuron removal was reached in few minutes in acidic conditions with a mineralization of 30%, as can be seen in Fig. 4. Although the degradation of diuron at initial natural pH was greater than in buffered pH, the mineralization was lower for both pH conditions. Thus, solutions with strongly acidic conditions are favourable for persulphate oxidation and may further favour the mineralization reactions.

When the decomposition of persulphate is carried out in unbuffered solutions, the pH drops as the reactions proceeds. Due to the pH value, the degradation of diuron was significantly inhibited in the solution buffered by bicarbonate. The reasons for this decrease at alkaline buffered pH could be due to scavenging reaction by $\mathrm{HCO_3}^-$. These results are also in agreement with findings in the literature [45].

After the fast initial diuron oxidation (time $t_i = 1$ min), the linear plots of $-\mathrm{Ln}([\mathrm{diuron}]/[\mathrm{diuron}]_i)$ versus the corrected time $(t - t_i)$, shown in Fig. 5, indicated that the reaction was pseudo-first-order with respect to contaminant with the correlation coefficients (R^2) approximately of 0.993 at both initial pH of 4.62 and 7.96 respectively. The slopes of these linear plots, the observed rate constants (k_{obs}), were 4.51×10^{-3} and $1.26 \times 10^{-3}\ \mathrm{min}^{-1}$. As can be seen in Fig. 5, the k_{obs} lower at basic pH.

In consequence, the rate law for the degradation of diuron by activated persulphate oxidation for each pH value is expressed as

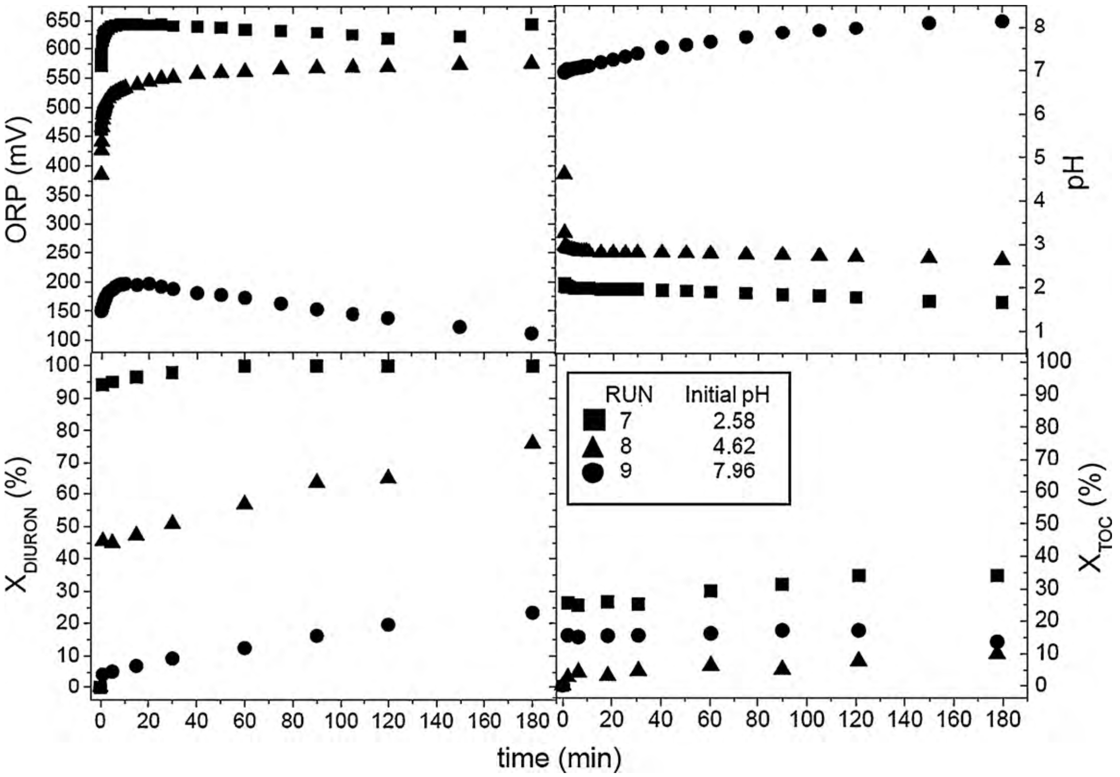

Fig. 4. Effect of initial pH values on degradation and mineralization of diuron. $T = 50\,^{\circ}C$. $[Diuron]_0 = 0.09$ mM. $[Fe(II)]_0 = 0.18$ mM. $[Na_2S_2O_8]_0 = 2$ mM.

Eq. (14):

$$-\frac{d[\text{diuron}]}{dt} = k_{\text{obs}}[\text{diuron}] \Rightarrow -\text{Ln}\left(\frac{[\text{diuron}]}{[\text{diuron}]_i}\right) = k_{\text{obs}} \cdot (t - t_i) \qquad (14)$$

Besides, it can be deduced that the initial increase of diuron conversion observed in Fig. 4 is due to the $SO_4^{\bullet-}$ production by the initial Fe(II) content described in Eq. (4). The ferric ion produced by Eq. (4) should be recovered to Fe(II) by the system organic compounds (Eq. (15)) in order to regenerate Fe(III) to Fe(II):

$$Fe^{3+} + RH \rightarrow R^{\bullet} + Fe^{2+} + H^{+} \quad (RH = \text{diuron}) \qquad (15)$$

However, from results in Fig. 4, it is inferred that this reduction of Fe(III) to Fe(II) occurs at very low rate and the $SO_4^{\bullet-}$ production stops by the absence of Fe(II). It tends to reach an asymptote value in the diuron conversion. This is in accordance with the measurements of Fe(II) concentration in the media; it was found that after 1 min reaction time negligible Fe(II) was detected in the aqueous solution.

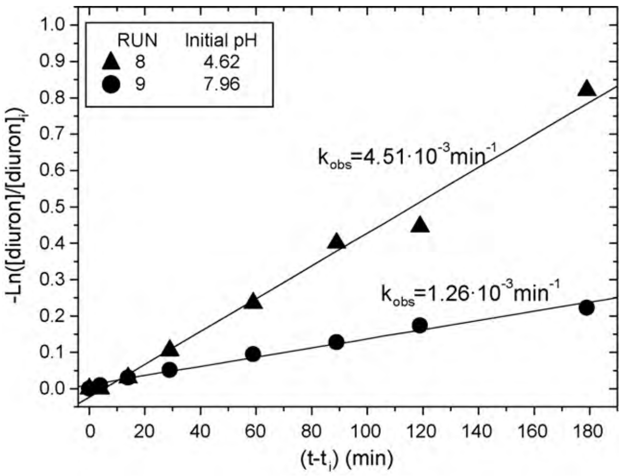

Fig. 5. Diuron degradation rate constant (k_{obs}) at various pHs.

3.2.2. *Effect of persulphate concentration on degradation effectiveness*

Two different molar concentrations of persulphate (1 and 2 mM) activated with Fe(II) (0.18 mM) were employed in the experiments to investigate the influence of oxidant concentration on diuron degradation. The values of ORP, pH, X_{diuron} and X_{TOC} are shown in Fig. 6. The initial increase in diuron conversion was similar for both runs in Fig. 6. This is because the Fe(II) concentration was the same in both runs (5 and 8) and therefore same amounts of sulphate radicals were formed according to Eq. (4). After this initial time ($t_i < 1$ min) the results showed that the degradation rate slightly increased as the initial persulphate concentration increased and no negative effect of high persulphate concentrations was found.

In addition, from Fig. 7 it is evident that after the initial time (<1 min) the diuron oxidation was influenced by oxidant concentration. Without taking into account the initial reaction time (t_i), the logarithm of $[\text{diuron}]/[\text{diuron}]_i$ versus time was plotted for the two levels of persulphate concentrations. The values of the slopes showed that the higher the oxidant concentration, the faster the rate of diuron degradation. The rate constants for this set of experiments are presented in Fig. 7.

After the initial time no Fe(II) is available and the production of $SO_4^{\bullet-}$ radicals is catalysed slowly by the protons, according to Eqs. (8) and (9), and by the thermal activation.

The thermal persulphate activation would act after a rapid consumption of Fe(II) in the system. Persulphate activation with iron requires an activation energy of 14.8 kcal mol^{-1}, which is lower than the value of 33.5 kcal mol^{-1} required for thermal activation [46,47]. The thermal activated persulphate without adding Fe(II) may be a more slow way of degrading contaminants.

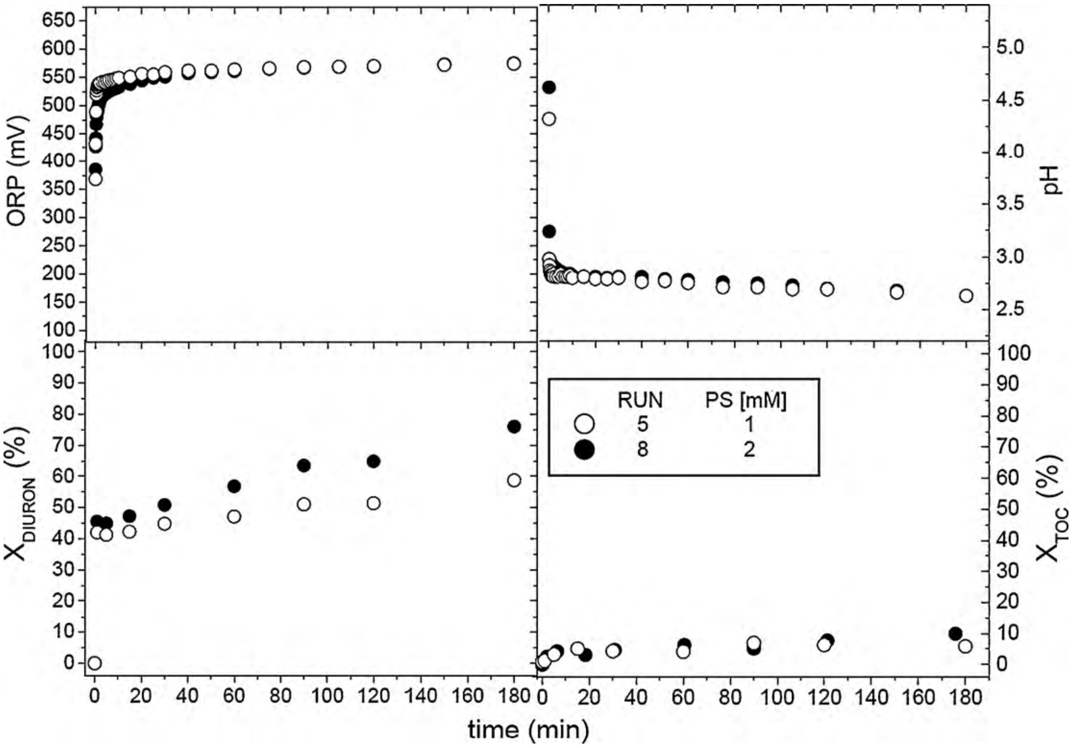

Fig. 6. Effect of initial persulphate concentration on degradation and mineralization of diuron. $T = 50\,^{\circ}\mathrm{C}$. $[\mathrm{Diuron}]_0 = 0.09$ mM. $[\mathrm{Fe(II)}]_0 = 0.18$ mM. $\mathrm{pH}_{\mathrm{initial}} = 4$–5.

3.2.3. *Effect of Fe(II) concentration on the degradation efficiency*

The effect of Fe(II) concentration on diuron and TOC removal efficiencies of Fe(II)–Na_2SO_4 system was evaluated by conducting experiments using two different Fe(II) concentrations (0.18 and 0.72 mM) at fixed oxidant concentration (2 mM). Results are shown in Fig. 8.

The ORP level in runs 6 and 8 was in the range of 300 mV (measured immediately after persulphate injection) and increased to 600 mV (the highest level obtained at 180 min after persulphate injection).

The pH values decreased with time in ferrous-dosed samples, and the magnitude of the pH fall increased with the increase in both the reaction time and Fe(II) concentration. As can be seen in Fig. 8, the pH decrease is greater at 0.72 mM Fe(II) concentration because the sulphate radicals formed according to Eq. (4) is higher and encourages the production of hydrogen protons (Eqs. (6) and (12)).

From results in Fig. 8 it is apparent that increase of solution Fe(II) concentration accelerates the oxidation of diuron by the higher $SO_4^{\bullet-}$ radical concentration produced at the initial stage. A 76% reduction of diuron was recorded with 0.18 mM ferrous ion. Complete removal of diuron was achieved when 0.72 mM Fe(II) was added.

The potential toxicity of intermediates of diuron oxidation by persulphate was determined by Microtox® for theses experiments, runs 6 and 8, as described in Section 2. The toxicity units obtained (≤ 6) were lower than the theoretical value from the initial solution. This value is calculated with Eq. (11). As can be seen in Table 2, this expected value is about $\sum \mathrm{TUs} \approx 6$ having into account the EC_{50} of the diuron ($14\ \mathrm{mg\,L^{-1}}$) and persulphate ($106\ \mathrm{mg\,L^{-1}}$). Therefore, it can be concluded that no toxic intermediates are produced in the degradation of diuron in wastewater by using the persulphate as oxidant (Table 3).

The opposite of that observed in other technologies, such as electro-Fenton and photo-Fenton [14,48], no significant amount

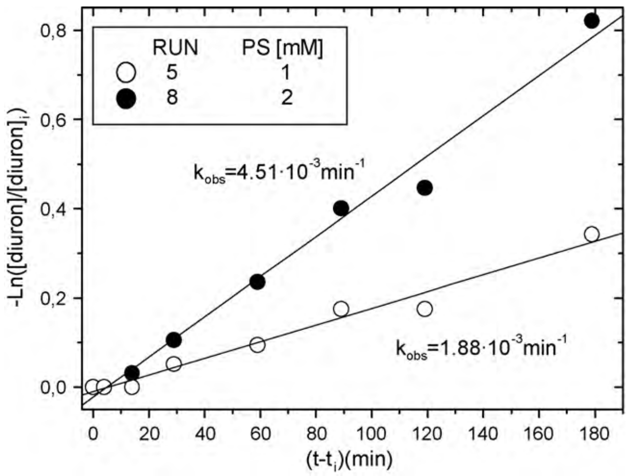

Fig. 7. Pseudo-first-order disappearance of diuron at two initial pH values.

Table 2
Toxicity Units in the initial aqueous solution for the runs 6 and 8 calculated by $TU_i = C_i/EC_{50i}$.

Compound	C_i (mM)	EC_{50i} ($\mathrm{mg\,L^{-1}}$)	TU_i	Initial $\sum TU_i$
Diuron	0.09	14	1.5	6.2
Persulphate-PS	2	106.4	4.7	

Table 3
Toxicity units and chloride concentration in the aqueous sample at 180 min reaction time for runs 6 and 8.

Run	$C_{Fe(II)}$ (mM)	Reaction time (min)	TUs	C_{Cl^-} ($\mathrm{mg\,L^{-1}}$)
6	0.72	180	5.05	5.9
8	0.18	180	6.02	5.6

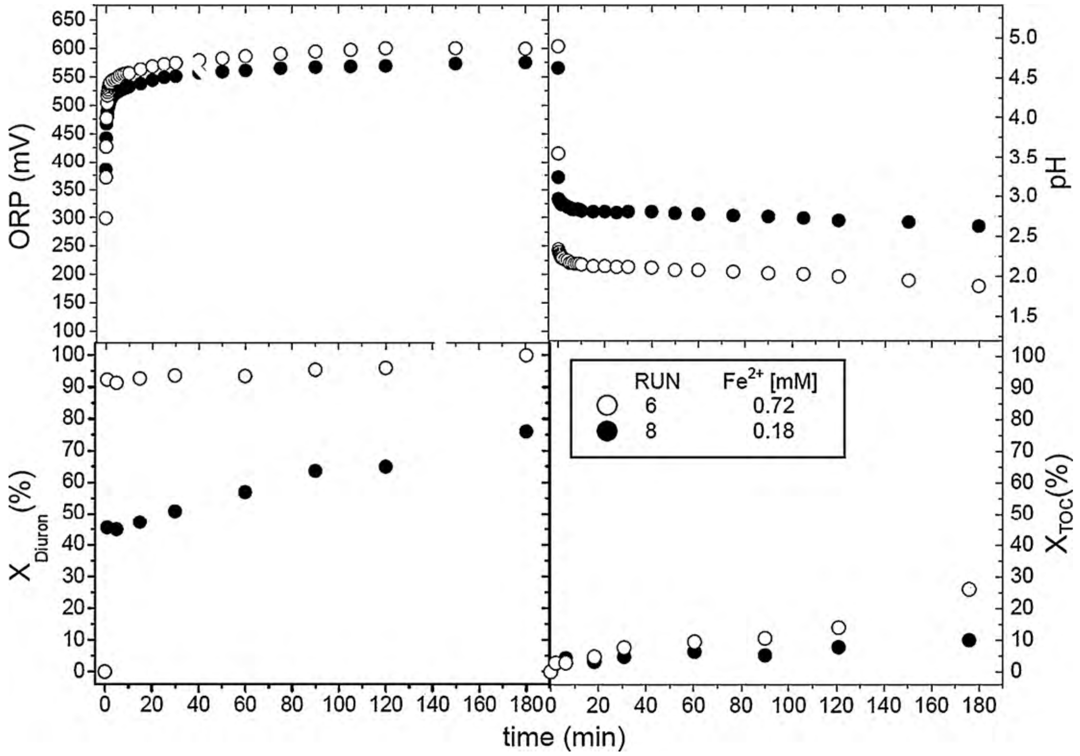

Fig. 8. Effect of ferrous content on degradation and mineralization of diuron. $T = 50\,^{\circ}C$. $[Diuron]_0 = 0.09$ mM. $[Na_2S_2O_8]_0 = 2$ mM. $pH_{initial} = 4–5$.

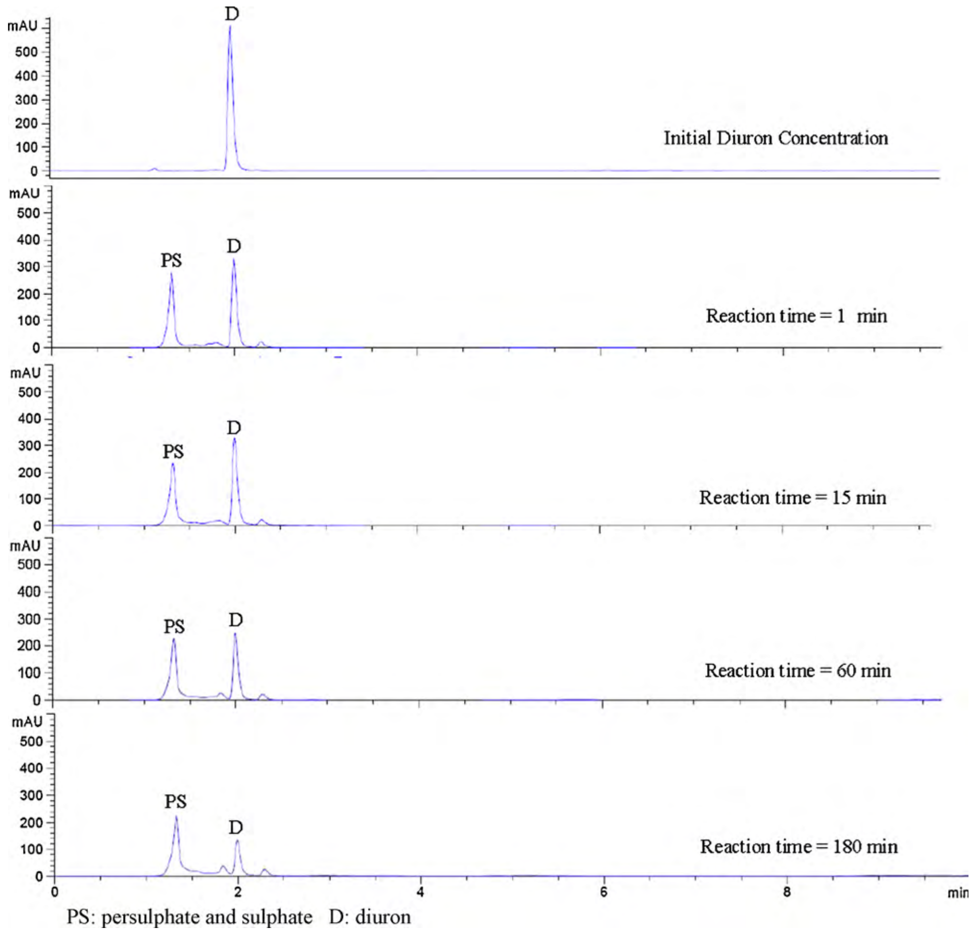

Fig. 9. HPLC chromatograms for the identification of by-products for the run 8. $T = 50\,^{\circ}C$. $[Diuron]_0 = 0.09$ mM. $[Na_2S_2O_8]_0 = 2$ mM. $pH_{initial} = 4–5$. $[Fe(II)]_0 = 0.18$ mM.

of aromatic intermediates are identified along the reaction with persulphate.

As an example, in Fig. 9 are shown some HPLC chromatograms for run 8, at different reaction time. The peaks due to initial oxidation steps, usually chlorinated aromatic compounds, are not very large compared with diuron.

Since the original diuron contains heteroatoms like Cl, formation of Cl^- is expected during the reaction. Taking into account the initial concentration of diuron (0.09 mM) and considering complete mineralization, the maximum stoechiometric concentration of this atom expected in solution is: 0.18 mM or $6.4\,mg_{Cl}\,L^{-1}$. The final Cl^- amount detected is, respectively, 5.9 and $5.6\,mg_{Cl}\,L^{-1}$ for runs 6 and 8. Cl is eliminated from the organic matter, leaving non-halogenated organic intermediates in solution. The detection of the chloride with the disappearance of diuron suggests that no resistant chlorinated oxidation products remain at the end of the experiment.

4. Conclusions

The results of this study serve as a starting point to describe the kinetic behaviour of the persulphate/diuron system at 50 °C. Activated persulphate appears to be an effective oxidizing agent for degradation of diuron. It is postulated that $SO_4^{\bullet-}$ is the active oxidizing agent; therefore, the destruction of diuron in the persulphate system is dependent on the generation of $SO_4^{\bullet-}$. This radical is mainly produced from Fe(II) according to Eq. (4). After a short initial time, Fe(II) is consumed and the sulphate radical is produced slowly from persulphate. Diuron oxidation rates are much slower in absence of Fe(II).

In absence of Fe(II), the results of this study indicate that the degradation rate of diuron by sodium persulphate could be described by a pseudo-first-order kinetic rate equation with the limits of the experimental conditions utilized here. Increasing the Fe(II) or persulphate concentration in the experimental conditions may significantly accelerate diuron degradation. The best results were achieved at acidic conditions (pH <3). The kinetic constant value was found to decrease with the increase in the pH values. Diuron degradation was slower in neutral buffered solutions because the non-target chemical species bicarbonate ions “scavenge” $SO_4^{\bullet-}$ which may otherwise oxidize the target contaminant.

The results obtained in this study are helpful for the treatment of water contaminated with diuron.

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