

Article

Effect of Nitrate and Sulfate Contamination on Degradation of Diuron via Electrochemical Advanced Oxidation in a Microreactor

Worachate Khongthon and Varong Pavarajarn*

Center of Excellence in Particle Technology, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

*E-mail: Varong.p@chula.ac.th (Corresponding author)

Abstract. The degradation of diuron, which is a toxic herbicide that causes a serious environmental problem in many countries, was performed using electrochemical advanced oxidation process (EAOP) in a microreactor. The influence of nitrate and sulfate contamination on the degradation was investigated. The experimental results clearly indicate that both nitrate and sulfate ions retard diuron degradation. Under the applied current of 1 mA, about 91% of diuron in deionized water is degraded within 100 s of residence time, while the degradation achieved is 79% and 76% when nitrate and sulfate ions are presented in the solution at concentration of 50 mM, respectively. Both ions behave as a scavenger for the reactive hydroxyl radical, although other mechanisms might also involve causing this retarding effect. Nitrate ion participates in diuron degradation causing new reaction pathways, while sulfate does not interfere with the diuron degradation pathway. The presence of ion in the solution also shifts the degradation route from one route to another.

Keywords: Diuron, degradation, electrochemical advanced oxidation, microreactor, nitrate, sulfate.

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1. Introduction

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethyl urea] is one of the most common herbicides for weed elimination in Thailand. It is classified as a carcinogenic and genotoxic compound. Regardless of its low solubility, diuron can slowly penetrate through soil and becomes a serious contamination in underground and surface water because of its potent toxicity and great chemical stability [1-3]. Diuron contamination has become a very serious environmental problem in many countries [4-6]. Recently, Directive 2013/39/EU of the European Parliament has considered diuron to be on the first priority substances list [7].

Diuron contaminating in water can be treated by several techniques, such as bio-degradation [8], adsorption [9], and several kinds of advanced oxidation processes (AOPs) which employ highly reactive hydroxyl radicals (OH°) to oxidize the contaminant [10-13]. Electrochemical advanced oxidation process (EAOP) is also an AOP that produces hydroxyl radicals via dissociation of water at an anode, when electrical potential is applied to the electrodes. The dissociation of water is shown in Eq. (1).



Efficiency of the degradation of an organic compound by the EAOP is affected by many parameters including applied potential, electrode materials, solution conductivity and solution pH [14, 15]. Although EAOP is a promising technology for the treatment of organic contaminants in water, EAOP in a conventional scale is usually limited by two main issues, i.e., mass transfer of the compound to the surface of the anode and the requirement of supporting electrolyte to achieve a reasonable cell voltage if the solution does not have adequate conductivity [16, 17]. To overcome the aforementioned limitations, the EAOP is applied in a microreactor, in which the small distance between the electrodes drastically reduces not only the Ohmic resistance, but also the mass transfer resistance [18].

Nevertheless, before applying the EAOP for the degradation of diuron in natural water, effects of anions such as nitrate and sulfate, which are commonly introduced to the water by household and agricultural activities as well as by industrial effluents, should be known. Unfortunately, such effects on diuron degradation are rarely reported. It is therefore the aim of this work to investigate the effects of nitrate and sulfate on the degradation of diuron via the EAOP in a microreactor, both in terms of reaction kinetics and degradation mechanism.

2. Experimental

2.1. Degradation of Diuron in a Microreactor

The microreactor used in this work was a microchannel with the size of 10 mm in width and 21 mm in length. The microchannel was formed using a 250 μm -thick Teflon sheet with a pre-cut opening placed between a graphite anode and a stainless steel cathode. Detail of the reactor assembly can be found elsewhere [14]. In the experiment, 10 ppm aqueous solution of standard diuron (99.5%; Sigma Aldrich) mixed with predetermined amount of either sodium nitrate (97.0% UNIVAR) or sodium sulfate (99.0% UNIVAR) was fed into the microreactor at controlled speed via a syringe pump. The flow rate was adjusted so that a mean residence time in the reactor in the range of 25 s to 100 s was achieved. The system was saturated with the supplied solution for 1 h to ensure adsorption equilibrium of diuron on both electrodes before initiating the degradation by applying direct current (DC) of 1 mA corresponding to a current density of 0.157 mA/cm^2 , across the gap between the electrodes. The solution coming out of the reactor was periodically monitored. The product at steady state was collected and analyzed.

2.2. Chemical Analyses

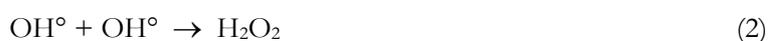
Concentration of diuron was analyzed by a reverse-phase high-performance liquid chromatograph (HPLC, Shimadzu, Class 10VP) equipped with a multiple wavelength UV diode array detector. The column was a C18 column (Luna 5 μ C18(2), Phenomenex). The mobile phase consisting of 70% (v/v) acetonitrile and 30% (v/v) deionized water was fed at the total flow rate of 1.5 ml/min. Concentration of hydrogen peroxide formed from recombination of hydroxyl radicals was also measured using a UV-visible spectrophotometer (Shimadzu, UV-1700) via colorimetric method [19]. It should be noted that the corrosion of the graphite

electrode in this work was so small that it did not interfere with the measurement of hydrogen peroxide by the colorimetric method [14]. Total organic carbon (TOC) was determined using a TOC analyzer (Shimadzu, TOC-VCPH).

3. Results and Discussion

3.1. Degradation of Diuron in Pure Water

Details of degradation of diuron in pure water via EAOP in a microreactor can be found in our previous work [14]. It is found that hydroxyl radicals are formed at the anode via dissociation of water according to Eq. (1) after electrical potential is applied to the electrodes. Although hydroxyl radical cannot be directly measured, its presence is confirmed indirectly from hydrogen peroxide formed via Eq. (2). The concentration of hydrogen peroxide in the product when only pure deionized water is fed to the reactor changes as various parameters, such as applied current, residence time, pH, and conductivity of the solution, are changed. It implies that these parameters directly affect generation of hydroxyl radicals in the system.



When diuron aqueous solution is supplied to the reactor operating under the applied current of 1 mA, degradation of diuron occurs (see solid line in Fig. 1). About 91% of diuron is degraded within 100 s in the reactor whereas the half-life of diuron in nature is over 300 days. The concentration of hydrogen peroxide in the product coming out of the reactor is also found to be lower than when pure water is the feed (0.41 ppm versus 0.67 ppm when the residence time is 100 s). It suggests that parts of hydroxyl radicals generated react with diuron leading to its degradation, while the rest of hydroxyl radicals recombine and form hydrogen peroxide. As the residence time is increased, the extent of diuron degradation increases as it is exposed to reactive hydroxyl radicals for extended period of time.

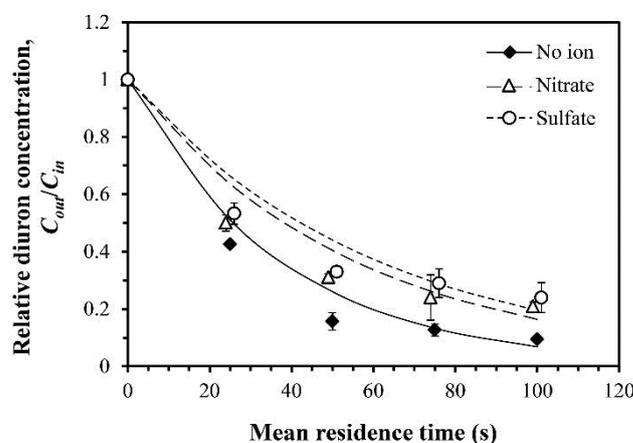


Fig. 1. Degradation of diuron in pure water and in water contaminated with 50 mM nitrate or sulfate ions. The marks show experimental data, while the lines represent value calculated by a pseudo-first-order kinetic model. It should be noted that the plots of the experimental data points are intentionally shifted for clarity of the error bars.

It has also been proved in our previous work that the mass transfer resistance within the microreactor is negligible. In the other words, rate of diuron degradation in this system is controlled by kinetics of the reaction, which was proved by the fact that a simple kinetic model without considering transport phenomena can represent the experimental data as good as a rigorous model [14]. Hence, all data in this work are fitted using a simple pseudo-first-order kinetic model (shown as lines in Fig. 1). The apparent rate constant is found to be $2.69 \times 10^{-2} \text{ s}^{-1}$, which is one to two order of magnitude higher than EAOP in the

conventional scale [20]. The value of R^2 for the fitting of the degradation of diuron without any anion under an applied current of 1 mA is 0.968.

3.2. Effect of Anion Contamination on Extent of Degradation

As shown in Fig. 1, anion contamination, i.e., nitrate and sulfate, retards diuron degradation via the EAOP. At residence time of 100 s, the diuron degradation decreases from 91% in water without ion contamination to 79% and 76% when nitrate and sulfate ions are present in the solution at concentration of 50 mM, respectively. As the concentration of the ion is lowered, the degradation of diuron approaches that in pure water as shown in Fig. 2. It should be noted that the lowest concentration of nitrate (1.3 mM) and that of sulfate (0.5 mM) corresponds to the same solution conductivity of 140 $\mu\text{S}/\text{cm}$. Hence, it is clear that the retarding effect from sulfate ion is more potent than that from nitrate ion. Even at the concentration of 0.5 mM, sulfate ion can still evidently disrupt the degradation of diuron via EAOP.

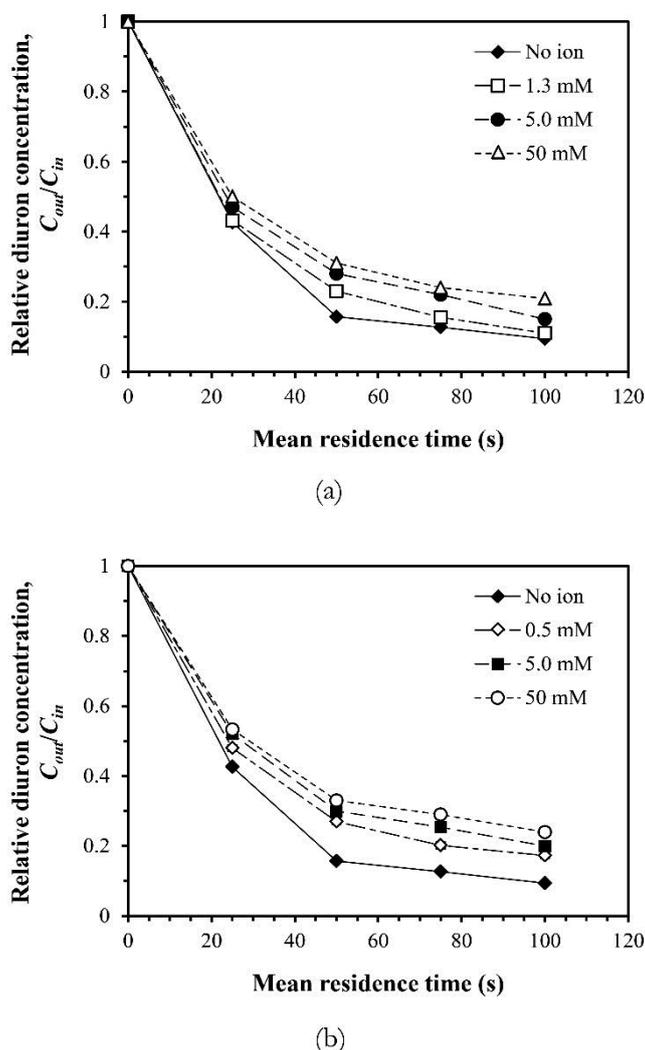


Fig. 2. Degradation of diuron in water contaminated with nitrate (a) and sulfate (b) ions at various concentrations. The EAOP was operated under the applied current of 1 mA for various periods of residence time.

Concentration of hydrogen peroxide detected from experiments using water mixed with nitrate or sulfate ion without diuron is shown in Fig. 3. Significant drop in the concentration of hydrogen peroxide produced via EAOP when ion is present in water suggests that both nitrate and sulfate ions behave as scavenger for hydroxyl radicals. As part of the hydroxyl radicals are neutralized by anions, the effectiveness

of diuron degradation is consequently decreased. The result also indicates that sulfate ion is more effective in scavenging the hydroxyl radicals than nitrate, which agrees with the report in related literature [21]. Nevertheless, it should also be pointed out that the generation of hydroxyl radicals in the sulfate-containing water may not be as high as that in nitrate-containing water because addition of sulfate ion results in a solution with higher conductivity than nitrate ion. For instance, the conductivity of 50 mM sulfate solution is 9000 $\mu\text{S}/\text{cm}$, while that of nitrate solution is only 5000 $\mu\text{S}/\text{cm}$. High solution conductivity tends to lower the formation of hydroxyl radicals, although the effect of the conductivity is less pronounced as the solution conductivity is higher than 500 $\mu\text{S}/\text{cm}$ [14].

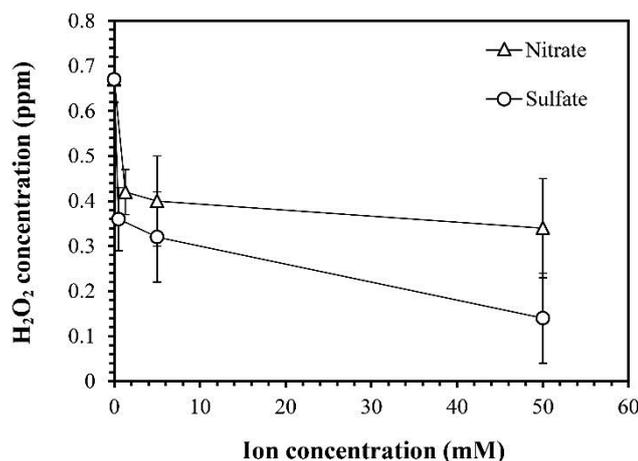


Fig. 3. Concentration of hydrogen peroxide detected in the product stream when pure water mixed with ion at different concentration is supplied to the reactor.

The experimental data in Fig. 2 were also fitted with the simple pseudo-first-order kinetic model as previously did for the degradation in pure water. The calculated apparent rate constants confirm that the rate of diuron degradation is decreased as the concentration of the contaminating ion is increased. The rate constant decreases from $2.69 \times 10^{-2} \text{ s}^{-1}$ for the degradation in ion-free water to 2.43×10^{-2} , 2.06×10^{-2} , and $1.81 \times 10^{-2} \text{ s}^{-1}$ for that in water with nitrate ion at the concentration of 1.3, 5.0, and 50 mM, respectively. For sulfate-containing water, the rate constant is found to be 2.02×10^{-2} , 1.81×10^{-2} , and $1.64 \times 10^{-2} \text{ s}^{-1}$, when the concentration of sulfate ion is 0.5, 5.0 and 50 mM, respectively. In addition, it is found that as the concentration of the contaminating ion is increased, the fitting of the model is worsened. The value of R^2 of the fitting of the degradation in nitrate-contaminated water decreases from 0.968 for pure water to 0.967, 0.952, and 0.930 when the concentration is increased from 1.3 to 50 mM, while that for water added by sulfate ion is 0.945, 0.940, and 0.919, respectively. The results suggest that the ion disrupts the degradation of diuron in more complicated manner than simply taking hydroxyl radicals out from interacting with diuron. Nevertheless, further investigation is needed to clarify the actual mechanism.

For the effect of applied current, it has been known that the extent of diuron degradation is increased as the applied current is increased because of the increased amount of hydroxyl radicals generated [14]. This trend is also observed in ion-contaminated water, together with the retarding effect from nitrate and sulfate ions scavenging the hydroxyl radicals generated (see Figs. 4 and 5). The difference in concentration of hydrogen peroxide generated in ion-free system and that in ion-contaminated water is substantial at high applied current when great amount of hydroxyl radicals are expected to be generated. It implies that the rate of the reaction between hydroxyl radical and either nitrate or sulfate ion depends mainly on concentration of hydroxyl radical since concentration of the ion in the system is in excess when compared with that of hydroxyl radical. In the other words, the scavenging of hydroxyl radical by the ion is not instantaneously fast; otherwise the ions which are present in the system at much higher concentration than diuron should not allow significant diuron degradation.

Another factor that might contribute to the retarding effect by anion at high applied current is the fact that anions such as nitrate and sulfate are attracted to the anode by high applied potential needed for

driving such high applied current. Consequently, a layer of anions is formed near the surface of the anode and may obstruct the diffusion of diuron to interact with hydroxyl radicals at the anode.

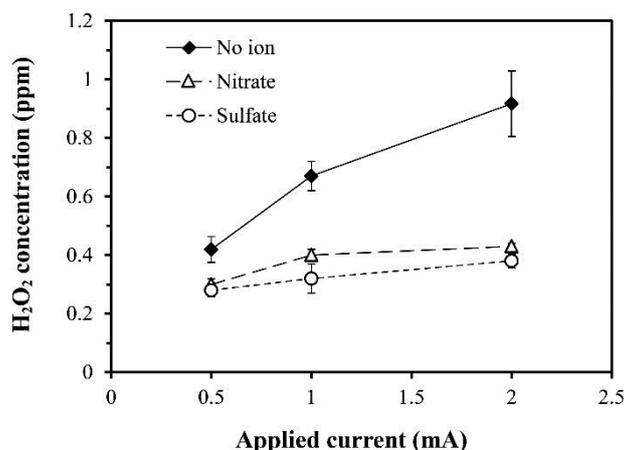


Fig. 4. Effect of nitrate and sulfate ions on concentration of hydrogen peroxide in the product stream when pure water mixed with ion is supplied to the reactor under various values of applied current. The experiment was conducted for 100 s of residence time, while the ion concentration was 5.0 mM.

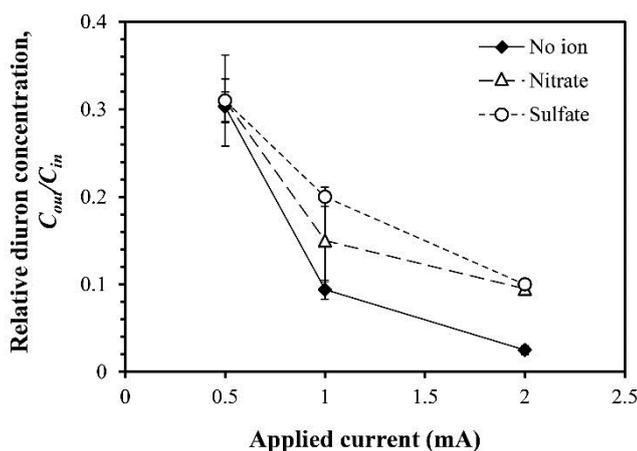
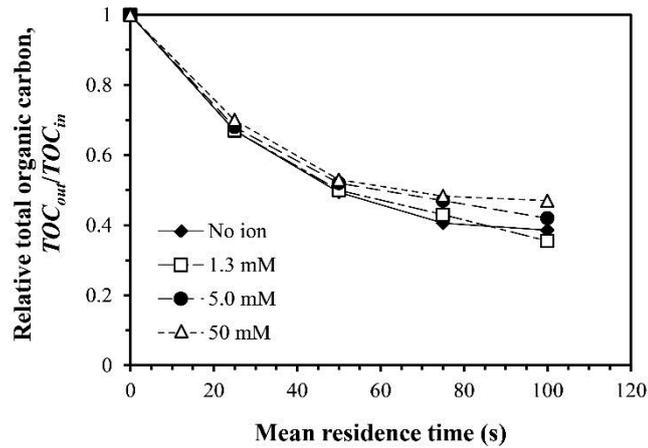


Fig. 5. Effect of nitrate and sulfate ions on degradation of diuron under various values of applied current. The degradation was conducted for 100 s of residence time, while the ion concentration was 5.0 mM.

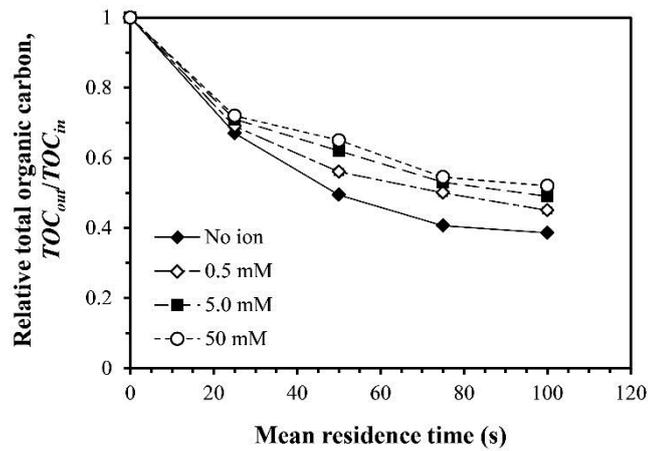
3.3. Effect of Anion Contamination on Degradation Pathway

As diuron is degraded towards its mineralization, the total organic carbon (TOC) of the solution is decreased. However, the results show that the decrease in TOC is not as much as the decrease in the diuron concentration. For the degradation of diuron in pure water under the applied current of 1 mA and residence time of 100 s, diuron is degraded by 91%, but the TOC is decreased only by 61%. This indicates that reaction intermediates are formed.

The results in Fig. 6 suggest that the intermediates are also formed from the degradation in ion-contaminated water. More importantly, the retarding effect from nitrate and sulfate ions on the degradation applies to the degradation of the intermediates as well, since the reduction in TOC in ion-contaminated water is not as much as that in deionized water. Because hydroxyl radical attacks organic compound non-specifically, the reduction of the radicals by scavenging effect from contaminating ions should affect further degradation of the intermediates in the same manner as it affects the degradation of diuron.



(a)



(b)

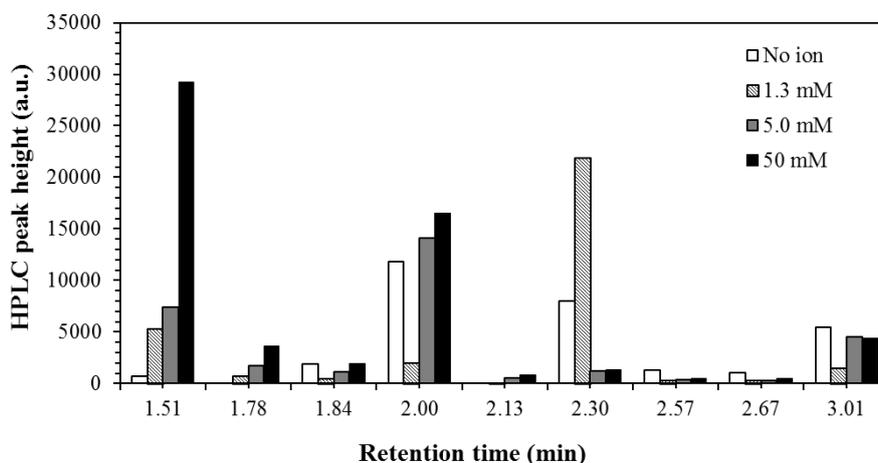
Fig. 6. Reduction of total organic carbon in water contaminated with nitrate (a) and sulfate (b) ions at various concentrations. The EAOP was operated under the applied current of 1 mA for various period of residence time.

According to HPLC analysis, signals from 11 intermediate compounds were detected from the degradation of diuron in pure water (see Table 1). Among these compounds, only three intermediates could be identified using standard reference compounds, namely, 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea (Compound 1, C₁), 3-(3-chlorophenyl)-1,1-dimethylurea (Compound 2, C₂), and 3,4-dichloro-aniline (Compound 3, C₃). For other intermediates, although they were identified using HPLC equipped with a tandem mass spectrometer (LC-MS/MS) [14], the standard compounds are not commercially available. Table 1 also shows intermediates formed from the degradation of diuron in ion-contaminated water.

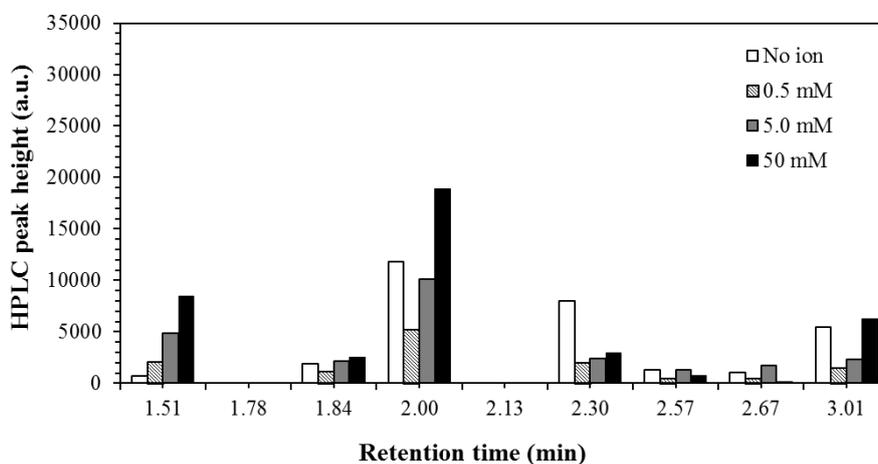
Table 1. Intermediates detected during the degradation of diuron.

Condition	Retention time in HPLC chromatogram (min)												
	1.51	1.78	1.84	2.00	2.13	2.30	2.57	2.67	3.01	3.37	3.57	3.89	4.19
								(C ₂)			(C ₃)	(C ₁)	
no ion	✓		✓	✓		✓	✓	✓	✓	✓	✓	✓	✓
with nitrate ion	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
with sulfate ion	✓		✓	✓		✓	✓	✓	✓	✓	✓	✓	✓

It has been known that diuron degradation via EAOP includes several pathways [14]. Majority of the pathways is not disturbed by either nitrate or sulfate ion. Out of 11 intermediates detected from diuron degradation in pure water, 10 intermediates are also detected when ions are presented during the degradation. The intermediate appearing at the retention time of 3.37 min is the only compound undetectable in ion-contaminated water. Hence, the main structure of the degradation pathway is not altered by ions. For the reaction in sulfate containing water, no other intermediate is detected, which suggests that sulfate ion does not take part in diuron degradation. It only involves in scavenging of hydroxyl radicals. On the other hand, two additional intermediates are detected when the degradation take place with the presence of nitrate ion. These intermediates were then identified by LC-MS/MS to be 1-(4,5-dichloro-2-nitroso-phenyl)-3-methylurea and 3-(4,5-dichloro-2-nitro-phenyl)-1,1-dimethylurea. The fact that these intermediates contain nitrogen atom indicates that nitrate ion participates in the degradation and induces new reaction pathway, in addition to being hydroxyl radical scavenger.



(a)



(b)

Fig. 7. Intermediates profile obtained from the degradation of diuron in water contaminated with nitrate (a) and sulfate (b) at various concentrations. The EAOP was operated under the applied current of 1 mA for 100 s.

Further study was investigated by analyzing the change in concentration of the intermediates with respect to the change in ion concentration. Unfortunately, the actual concentrations of the intermediates were not obtained because of the lack in standard reference compounds. The quantitative analysis was conducted only by analyzing HPLC peak height. Figure 7 shows profile of the intermediates detected from

diuron degradation in water mixed with nitrate and sulfate ion at various concentrations. It should be noted that the signals corresponding to the intermediates appearing at retention time longer than 3.01 min are too low comparing with the rest of the intermediates and they are neglected. It can be seen that concentration of each intermediate strongly depends on concentration of nitrate ion. Hence, although the overall pathway of diuron degradation is mainly unchanged, shifting in the degradation route from one to another occurs as influenced by the ion. The rate of degradation of each intermediate may be affected as well.

4. Conclusion

In the degradation of diuron in an aqueous solution via an electrochemical advanced oxidation process in a microreactor, the presence of anion in the solution affects the degradation. Nitrate and sulfate ions generally retard the degradation because they behave as a scavenger for the reactive hydroxyl radical, although other mechanisms might also involve causing this retarding effect. The effect from sulfate is more potent than that from nitrate ion. The rate of the scavenging is not instantaneously fast, but it is significant enough to cause significant decrease in the apparent rate constant for diuron degradation. Nitrate ion participates in diuron degradation causing new reaction pathways, while sulfate does not interfere with the diuron degradation pathway. Shifting in the degradation route from one route to another is also influenced by the presence of ion in the solution.

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