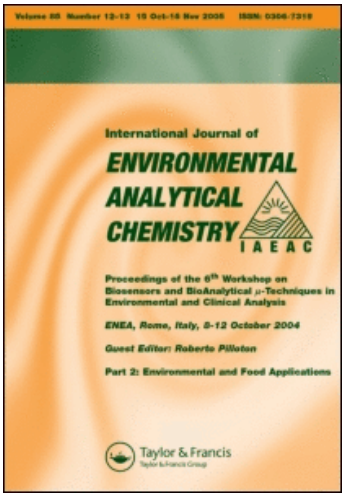

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Aldicarb, a carbamate pesticide, is commonly used in agriculture and can be naturally degraded to metabolites, resulting in their occurrence in drinking water supplies. The disinfection process using different oxidants for the treatment of drinking water provides the opportunity to degrade aldicarb and its metabolites to byproducts that may pose more human health risk than the parent compounds. A comprehensive study of aldicarb and its metabolites involving treatment with free chlorine (FC), monochloramine (MCA), ozone (O_3), chlorine dioxide (ClO_2), hydrogen peroxide, permanganate (MnO_4^-) and UV radiation was performed to identify the degradation products. Free chlorine, high-dosage UV radiation and permanganate exhibited stronger oxidation capacity than the other oxidants studied, with chlorine dioxide showing the weakest oxidation ability among them. Aldicarb sulfoxide was formed as the degradation product of aldicarb by oxidation with free chlorine, MCA, ozone, and hydrogen peroxide. Aldicarb sulfone was identified as an oxidation byproduct of both aldicarb and aldicarb sulfoxide by permanganate. N-chloro-aldicarb sulfone was formed as an oxidation byproduct of aldicarb sulfone by free chlorine. The comprehensive information is very valuable for water treatment facilities and environmental researchers.

Keywords: aldicarb; oxidation byproducts; aldicarb sulfoxide; aldicarb sulfone; HPLC/MS

1. Introduction

Aldicarb [2-methyl-2(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime], an active ingredient in the pesticide TEMIK®, is a soil pesticide used in the agricultural sector worldwide for over 30 years for the control of insects, mites and nematodes [1–4]. The most important usages of this product in the USA are for citrus, cotton, sugar beet, potato, pecan and peanut crops. The commercial product is available as a granular formulation, which is incorporated into the soil at the time of application. After application to the soil, it solubalises and is distributed by groundwater. From the

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groundwater it is absorbed by the roots and translocated throughout the plant, where it acts as a systemic pesticide.

Aldicarb can degrade to aldicarb sulfoxide and aldicarb sulfone in a variety of soil types under both field and laboratory conditions [5–15]. To fully understand the mechanism of degradation in the environment, Richey *et al*. [16] carried out laboratory studies on the degradation of aldicarb in soil using ^{14}C labelled aldicarb in Norfolk sandy loam, Lufkin fine sandy loam, and Lakeland fine sandy loam in a metabolism chamber. The metabolites were determined by using radioactivity assay. Ou *et al*. [13,15] studied the aerobic and anaerobic degradation of aldicarb and aldicarb sulfone in soils and found that aldicarb produced aldicarb sulfoxide, aldicarb sulfone, aldicarb sulfoxide oxime, aldicarb sulfoxide nitrile, aldicarb sulfone oxime, and two other unknowns. Aldicarb sulfone nitrile and aldicarb sulfone acid were detected as the two major degradates of aldicarb sulfone under aerobic and anaerobic soils. The aerobic and anaerobic degradation rates for aldicarb were measured in soil samples collected at different depths. The concentration change of its two toxic oxidation products, aldicarb sulfoxide and aldicarb sulfone, was determined to estimate the first-order rate constants for concurrent oxidation and hydrolysis of aldicarb, aldicarb sulfoxide and aldicarb sulfone, and for the loss of total carbamate residues. Hydrolysis of aldicarb, aldicarb sulfoxide and aldicarb sulfone in Floridan groundwater was observed, and rates decreased in the following order: sulfone > sulfoxide >>aldicarb [17]. In addition, hydrolysis rates of aldicarb, aldicarb sulfoxide and aldicarb sulfone were measured at ppb levels in aqueous solution by using liquid-liquid extraction followed by gas chromatography with flame ionisation detector (FID) and nitrogen-phosphorus detector (NPD) [18,19]. Biotransformation is another reported pathway for degradation of aldicarb. Kazumi *et al*. [20] found that aldicarb biotransformation in sediment was mainly via an oxidation pathway in the presence of O_2; while in the absence of O_2, the biodegradation took place through a hydrolytic pathway. It was also reported [7,14,21] that aldicarb, aldicarb sulfoxide and aldicarb sulfone at the applied dose to soils did not inhibit microbial growth, but rather the microbial component in soil had a significant role in the degradation of these compounds. In fact, some researchers report the capability of soil microorganisms to use carbamate pesticides as a source of carbon and nitrogen for growth [1,13,15]. Kök *et al*. [22] reported the complete removal of aldicarb by using immobilised bacteria as a degradation site/source to decrease the environmental contamination caused by pesticides. Liu *et al*. [23] studied the effect of an anion surfactant on the degradation rate of aldicarb in soil, and found that sodium dodecylbenzenesulfonate (SDBS) could accelerate the degradation of aldicarb and there was a good linear relationship between degradation rate constant and the logarithm of SDBS concentration. Other investigations involving factors affecting chemical and microbial degradation of aldicarb show that temperature is the most important variable affecting the degradation rate of aldicarb and its carbamate metabolites in surface soils [9]. The potential degradation products of aldicarb from previous studies are summarised in Table 1.

In order to quantitatively determine aldicarb and its degradation products, many analytical methods have been developed. In addition to gas chromatography methods [24–27], other methods have been developed, such as RP-HPLC followed by post-column derivatisation and fluorescence detection [28–31], UV detection [32,33] and mass spectrometry [24,27,30,34,35].

As a result of widespread usage, aldicarb and its metabolites have been found in drinking water systems [36–39]. The uses of oxidants in drinking water treatment plants,

Table 1. Aldicarb and its potential immediate degradates in different matrices from previous studies.

Parent Compound	Matrices	Conditions of the degradation study	Degradates
Aldicarb	Soil	Humic acid, anionic surfactant (sodium dodecyl benzene sulfate)	Aldicarb sulfone, aldicarb sulfoxide [5]
Aldicarb	Soil	Humic acid, Autoclave	Aldicarb sulfone, aldicarb sulfoxide [6]
Aldicarb	Soil	Microbial	Aldicarb sulfone, aldicarb sulfoxide [7]
Aldicarb	Soil	Ph, Temperature (hydrolysis)	Aldicarb sulfone, aldicarb sulfoxide [10]
Aldicarb	Soil	Chemical (carbofuran)	Aldicarb sulfone, aldicarb sulfoxide [11]
Aldicarb	Soil	Microorganisms (Bacillus)	Aldicarb sulfone, aldicarb sulfoxide [12]
Aldicarb	Soil	Bacteria; Fungi	Aldicarb sulfone, aldicarb sulfoxide [14]
Aldicarb	Sediments	Anaerobiosis	Aldicarb sulfone, aldicarb sulfoxide [20]
Aldicarb	Packed-bed reactor	Immobilized Methylosinus	Aldicarb sulfone, aldicarb sulfoxide [22]

which are used for disinfection, can interact with aldicarb and its metabolites to produce byproducts which are potentially even more toxic to human beings. Therefore, the oxidative degradations of aldicarb in drinking water by various oxidants must be systematically investigated. Up to date, only two oxidants, ozone and free chlorine, were studied to investigate the degradation byproducts of aldicarb [40,41]. No reports were found in investigating the oxidative degradations of aldicarb and its carbamate metabolites in water treatment system involving treatment with monochloroamine, chlorine dioxide, permanganate, hydrogen peroxide, and UV radiation. In this paper, a detailed study was performed to systematically investigate the oxidation byproducts of aldicarb produced by various oxidation systems using HPLC/MS. The removal of aldicarb, as well as the oxidation reaction features in terms of brief mechanism and relative reaction rate, was determined by using HPLC/UV. This study provides valuable information for understanding the oxidation mechanism of aldicarb and its metabolites with different oxidants in a water treatment system.

2. Experimental

2.1 *Reagents and chemicals*

Aldicarb (99.0%), aldicarb sulfoxide (98%), and aldicarb sulfone (98%) were purchased from ChemService (West Chester, PA, USA). Formic acid (96%, ACS grade), hydrogen peroxide solution (30%) and sodium hypochlorite solution (available chlorine $\geq$4%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Methanol (HPLC grade), acetonitrile (HPLC grade), water (HPLC grade), sodium hydroxide (98.3%), potassium permanganate (certified ACS, 99.5%), and sodium phosphate (dibasic, 99%) were

purchased from Fisher Scientific (Pittsburgh, PA, USA). Sodium phosphate (monobasic, 99%) was purchased from Aldrich (Milwaukee, WI, USA). The pH for the experiments was adjusted with either 1.0 N H_3PO_4 or 1.0 N NaOH.

2.2 *HPLC/ESI/MS and HPLC/UV analyses*

The Hitachi M-8000 3DQ LC/MS^n system with an electrospray ion source (San Jose, CA, USA) was used for the HPLC/MS analyses of aldicarb and its degradation products. A Supelco C18 column (150 × 2.1 mm i.d., 5 μm, Bellefonte, PA, USA) was used for the separation at ambient temperature with a flow rate of 0.25 mL min^{-1}. Solvent A consisted of 0.1% formic acid in water (pH 2.70), and solvent B was acetonitrile. The HPLC separation was performed at an initial 10% B followed by a gradient elution to 40% B at 15 min, then with a drop to 10% B at 15.1 min. A divert valve was placed right before the ionisation source to remove the HPLC fractions containing salts and prevent the contamination of the ionisation source and MS. The ESI parameters were set to the following optimised values: nitrogen sheath gas at 3 kgf cm^{-2}, 4 kV for ESI probe, 30 V for drift plate, 25 V for focus plate, 200°C for desolvator temperature, 180°C for assistant gas heater temperature, 160°C for aperture 1 temperature. Ion trap MS was operated at the following conditions: 500 ms for accumulating time, 0.069V for accumulation voltage, 41.78 amu for low mass cut off, 41.78–400 amu for mass scan range. The UV wavelength for quantification was 200 nm.

2.3 *Methods*

All pH measurements were obtained with an Accumet XL 15 pH meter using an Accumet AccuCap combination pH electrode from Fisher Scientific (Pittsburgh, PA). All oxidation experiments were conducted at a constant temperature (23.5 ± 1°C). Oxidation of aldicarb, aldicarb sulfoxide and aldicarb sulfone was carried out individually in the same way if not specified otherwise, with an initial concentration of 5 mg L^{-1} for each. Quantification was accomplished by HPLC/UV with calibration curve and external standard operation.

2.3.1 *Free chlorine (FC) oxidation system*

The concentration of free chlorine in sodium hypochlorite stock solution was determined with the Hach DPD Method 8221 using AccuVac ampuls obtained from the Hach Company (Loveland, CO, USA). A 50 μL aliquot of aldicarb stock solution (in MeOH, 1.0 mg mL^{-1}) was spiked to 10.0 mL deionised water in a 20 mL amber bottle (reactor). The reaction was initiated by spiking the working solution with 25 uL of sodium hypochlorite stock solution (free chlorine: 4.0 mg mL^{-1}) and the initial concentration of free chlorine in the reaction solution was 10 μg mL^{-1}. The initial concentration of aldicarb was 5.0 mg L^{-1} (26.3 μM). The reactor was put on a shaker table at 150 rpm. Samples were taken after 2 hours and followed by HPLC/MS and HPLC/UV analyses. FC oxidation of aldicarb sulfoxide and aldicarb sulfone were carried out in the same way.

2.3.2 *Ozone (O_3) oxidation system*

Ozone was produced using a Model GLS-1 PCI-WEDECO (Environmental Technologies, West Caldwell, NJ, USA) ozone generator and compressed oxygen. The ozone gas stream

was bubbled from a stone diffuser into deionised water. A Cary 50 Conc UV-Visible Spectrophotometer (Varian Australia PTY LTD, Australia) at 260 nm was then used independently to monitor the decay and concentration of aqueous ozone. The amber glass vial containing 5.0 mL 15 mg L^{-1} aldicarb (78.8 μM) was spiked with 10.0 mL saturated O_3 solution (29.7 mg L^{-1}). The concentration of aldicarb and ozone when reaction was initiated was 5.0 (26.3 μM) and 9.9 mg L^{-1}, respectively. The reaction continued for 4 hours before HPLC/MS and HPLC/UV analyses. The O_3 oxidation of aldicarb sulfoxide and aldicarb sulfone were performed in the same way, with an initial concentrations of 5.0 mg L^{-1} (24.2 μM) and 5.0 mg L^{-1} (22.5 μM), respectively.

2.3.3 *UV radiation system*

A 254 nm low-pressure mercury-vapor lamp (Pen Ray Model 90-0004- 01,254 nm, 1.0 W; UVP Inc., Upland, CA) was used for the UV photo-degradation study. Three amble glass vials (reactors) of 5 mL deionised water, each containing 5.0 mg L^{-1} aldicarb (26.3 μM), were exposed to the UV lamp for 2 seconds (low dosage), 10 seconds (medium dosage), and 60 seconds (high dosage), respectively, by placing the 0.9 cm diameter lamp down the centreline of the vial. The diameter of the reactor was 1.9 cm, and the length of the lamp in the liquid was 2.5 cm. Based on a volume weighted mean radius for the fluid, the fluence was 8.9 mW cm^{-2} for the system. The reaction medium was stirred with a small stirring bar during the UV exposure. The UV oxidation of aldicarb sulfoxide and aldicarb sulfone were performed in the same manner, with the concentration of 5.0 mg L^{-1} (24.2 μM) and 5.0 mg L^{-1} (22.5 μM), respectively.

2.3.4 *Chlorine dioxide (ClO_2) oxidation system*

Gaseous chlorine dioxide was produced using a Bench-Scale ClO_2 Generator (CDG, Bethlehem, PA). The concentration of ClO_2 in the generated saturated ClO_2 solution was determined by a Cary 50 Conc UV-Visible Spectrophotometer (Varian Australia PTY LTD, Australia) at 360 nm. An amber glass vial (reactor) of 10.0 mL deionised water, which contained 5.0 mg L^{-1} aldicarb (26.3 μM), was spiked with 25 μL saturated ClO_2 solution (3.9 g L^{-1}). The initial concentration of ClO_2 was 9.97 mg L^{-1}. Samples were taken after 4 hours of reaction, followed by HPLC/MS and HPLC/UV analyses. ClO_2 oxidation of aldicarb sulfoxide and aldicarb sulfone was carried out individually in the same manner, with the concentration of 5.0 mg L^{-1} (24.2 μM) and 5.0 mg L^{-1} (22.5 μM), respectively.

2.3.5 *Hydrogen peroxide (H_2O_2) oxidation system*

An amber glass vial (reactor) of 10.0 mL deionised water, which contained 5.0 mg L^{-1} aldicarb (26.3 μM), was spiked with 1.0 mL H_2O_2 solution (30%) to initiate a reaction, resulting in an initial H_2O_2 concentration of 27,273 mg L^{-1}. The reaction continued for 4 hours prior to sampling and HPLC/MS and HPLC/UV analyses. H_2O_2 oxidations of aldicarb sulfoxide and aldicarb sulfone were carried out in the same manner, with the concentration of 5.0 mg L^{-1} (24.2 μM) and 5.0 mg L^{-1} (22.5 μM), respectively.

2.3.6 *Monochloroamine (MCA) oxidation system*

MCA stock solutions were prepared from ammonium chloride and sodium hypochlorite at a molar ratio of 1.05:1 at pH 11 [42]. The concentration of a MCA stock solution was

determined by using the total chlorine method (via Hach DPD Method 8167; Loveland, CO, USA) and confirming that no free chlorine concentration remained. An amber glass reactor of 10.0 mL deionised water containing 5.0 mg L^{-1} aldicarb (26.3 μM) was spiked with 50 μL of the MCA stock solution for an initial MCA concentration of 2.0 g L^{-1} (the initial MCA concentration was 10.0 mg L^{-1}). Samples were taken after 4 hours of initiation of reaction for HPLC/MS and HPLC/UV analyses. MCA oxidation of aldicarb sulfoxide and aldicarb sulfone was carried out in the same manner, with the concentration of 5.0 mg L^{-1} (24.2 μM) and 5.0 mg L^{-1} (22.5 μM), respectively.

2.3.7 *Permanganate (MnO_4^-) oxidation system*

A 50 μL aliquot of aldicarb stock solution (1.0 mg mL^{-1} in methanol) was spiked into 10.0 mL deionised water, forming an initial concentration of 5.0 mg L^{-1} (26.3 μM). The reaction was initiated by spiking in 32 μL of potassium permanganate stock solution (1.0 g L^{-1}) (the initial permanganate concentration was 3.2 mg L^{-1}). Samples were taken after 4 hours of initiation of reaction for HPLC/MS and HPLC/UV analyses. Permanganate oxidation of aldicarb sulfoxide and aldicarb sulfone was carried out in the same manner, with the concentration of 5.0 mg L^{-1} (24.2 μM) and 5.0 mg L^{-1} (22.5 μM), respectively.

3. Results and discussion

3.1 *Identification of oxidation byproducts of aldicarb in different oxidation systems*

HPLC/MS was the major technique for identification of oxidation byproduct of aldicarb in different oxidation systems. Using the chromatographic and mass spectrometric conditions described above, the total ion chromatograms (TICs) of aldicarb standard and oxidation byproducts of aldicarb in free chlorine, monochloroamine, ozone, permanganate and hydrogen peroxide systems are shown in Figure 1. As shown in Figure 1, the peak corresponding to aldicarb did not appear for all of the indicated oxidation systems, but

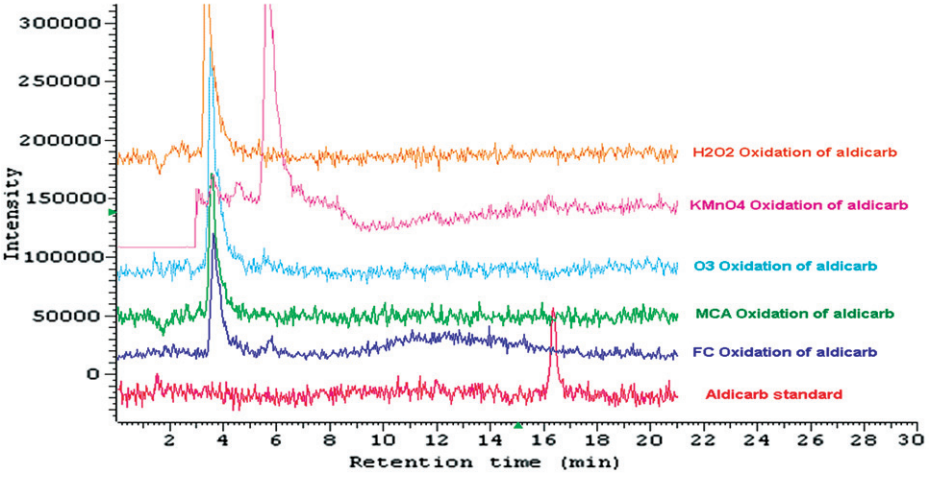

Figure 1. TICs of aldicarb standard and byproducts in various oxidation systems.

two byproduct peaks were observed. The peak that appeared for the permanganate oxidation system had a different retention time from the peak for free chlorine, monochloramine, ozone, and hydrogen peroxide oxidation systems. This clearly indicates that two separate byproducts are formed. Although 70% of the initial aldicarb concentration was removed after using a high-dosage UV radiation, no degradates were detected by current analytical method (chromatogram not shown). No significant removal ($<15\%$) of aldicarb was observed and no degradates were detected for chlorine dioxide as well as medium and low dosages of UV radiation (chromatogram not shown).

To confirm the identity of aldicarb (parent compound), the mass spectra were obtained. The results are shown in Figure 2. The m/z 213 ion is the molecular ion of sodiated aldicarb, while the m/z 116 ion is one of the fragment ions. The m/z 157 and 175 ions have not been interpreted yet. This fragmentation is due to the in-source ionisation mechanism, which is very common to many organic molecules.

To identify the degradation products of aldicarb, standard aldicarb sulfoxide and aldicarb sulfone, the two potential carbamate metabolites of aldicarb found by the previous researchers, were analysed simultaneously by HPLC/MS. The results are shown in Figure 3.

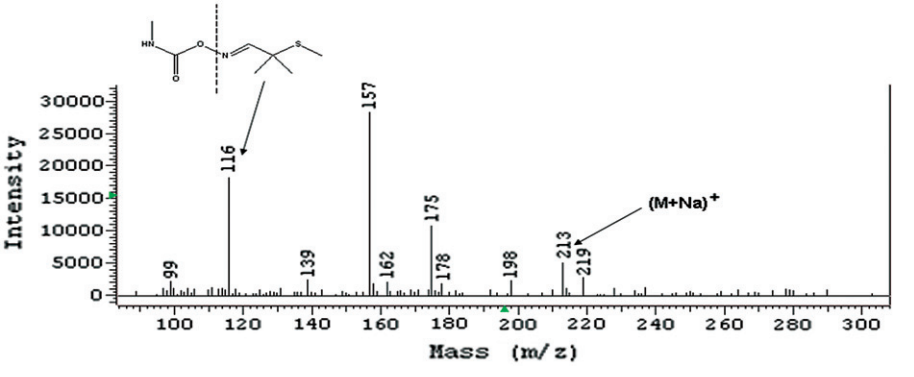

Figure 2. Mass spectrum of aldicarb standard (MW: 190).

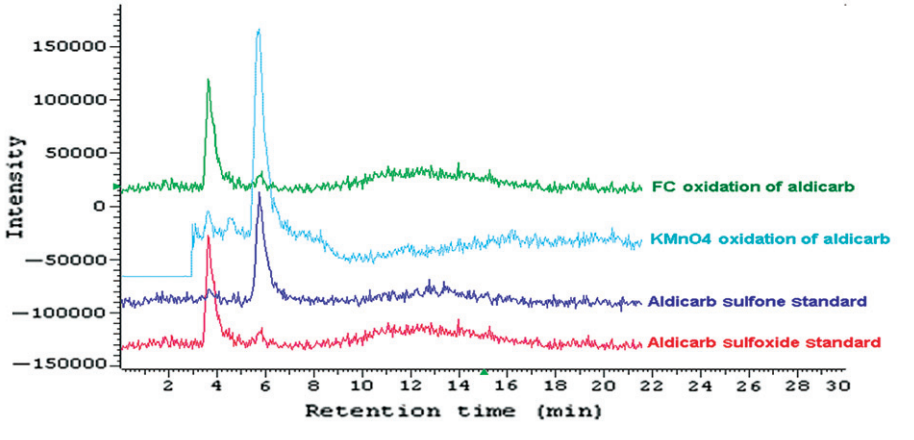

Figure 3. TICs of aldicarb sulfoxide standard, aldicarb sulfone standard, and the representative byproducts of aldicarb in FC and $KMnO_4$ oxidation systems.

The retention time of the standard aldicarb sulfoxide is the same as that of the oxidation byproduct of aldicarb by free chlorine, monochloroamine, ozone and hydrogen peroxide, while the retention time for the standard aldicarb sulfone is the same as that of the permanganate oxidation byproduct of aldicarb.

For further confirmation, the mass spectra of aldicarb sulfoxide and the free chlorine oxidation byproduct of aldicarb, along with the mass spectra of aldicarb sulfone and the permanganate oxidation byproduct of aldicarb, were obtained as shown in Figure 4 and Figure 5.

The mass spectra of aldicarb sulfoxide standard and the oxidation byproduct of aldicarb in free chlorine, monochloroamine, ozone, hydrogen peroxide systems are identical, so only one mass spectrum is presented, as shown in Figure 4. The ion with m/z 206 is the molecular ion, which was rarely observed in ESI mass spectrum because of the in-source ionisation. The ion with m/z 229 is the sodiated molecular ion, while the m/z 132 ion is the in-source fragment ion. Similarly, the mass spectra of aldicarb sulfone standard and the permanganate oxidation byproduct of aldicarb are also identical, so only one mass spectrum is presented as well, as shown in Figure 5. The ion with m/z 222 is the molecular

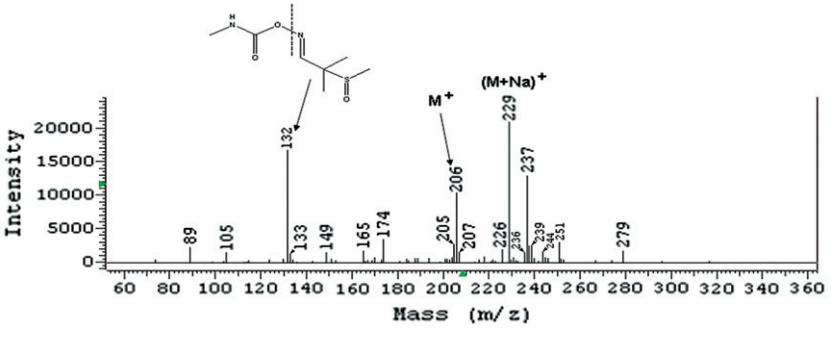

Figure 4. Mass spectra of aldicarb sulfoxide (MW: 206) standard and the oxidation byproduct of aldicarb in FC, MCA, O_3 and H_2O_2 oxidation systems. The spectra are identical for both aldicarb sulfoxide standard and the oxidation byproduct of aldicarb by these four oxidants.

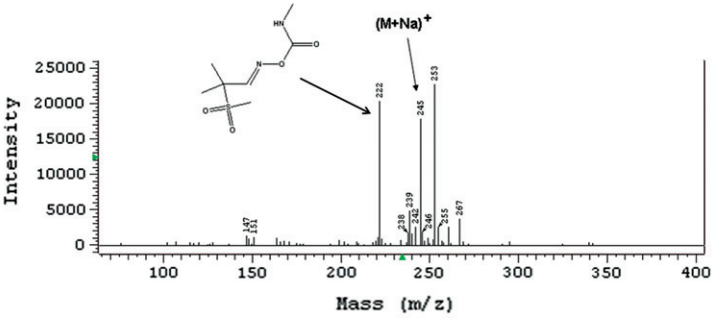

Figure 5. Mass spectra of aldicarb sulfone (MW: 222) standard and the oxidation byproducts of aldicarb in $KMnO_4$ oxidation system. The spectra are identical for both aldicarb sulfoxide standard and the oxidation byproduct of aldicarb by $KMnO_4$.

ion, while the ion with m/z 245 is the sodiated molecular ion. From Figures 4 and 5, it can be concluded that aldicarb will be oxidised to produce aldicarb sulfoxide in free chlorine, monochloroamine, ozone, hydrogen peroxide systems, while aldicarb sulfone will be produced as an oxidation byproduct of aldicarb in permanganate oxidation system.

To investigate the possible further degradations of aldicarb sulfoxide and aldicarb sulfone by these oxidants, these two metabolites were further treated with different oxidants. After aldicarb sulfoxide was treated with all of the oxidants used in this study, it was found that aldicarb sulfoxide can be degradated by permanganate, free chlorine, hydrogen peroxide, and high-dosage UV, but none of the other oxidants. However, only one byproduct was detected following permanganate oxidation. The corresponding total ion chromatograms are shown in Figure 6.

Aldicarb sulfoxide was completely oxidised by permanganate after 5 hours and a new byproduct peak, which showed the same retention time as aldicarb sulfone peak, appeared (as shown in Figure 6). No degradation byproducts were detected in any of the other oxidation systems, although free chlorine, hydrogen peroxide and high-dosage UV radiation resulted in significant percentage removal of aldicarb sulfoxide. Hydrogen peroxide oxidation and UV photodegradation of aldicarb sulfoxide may have different mechanisms from permanganate oxidation and deserve further investigation. The mass spectrum of the permanganate oxidation byproduct of aldicarb sulfoxide was found identical to the one shown in Figure 5, confirming that aldicarb sulfone was the permanganate oxidation byproduct of aldicarb sulfoxide.

Additionally, the comprehensive investigation of oxidation of aldicarb sulfone, another metabolite of aldicarb, was also carried out in various oxidation systems, and the corresponding total ion chromatograms are shown in Figure 7. Aldicarb sulfone was partially oxidised to produce an unknown peak by free chlorine, while other oxidants, except for free chlorine and high-dosage UV radiation which removed 60% and 30% of aldicarb sulfone, respectively, did not show significant removal ($<20\%$) of aldicarb sulfone, and no oxidation byproducts were detected.

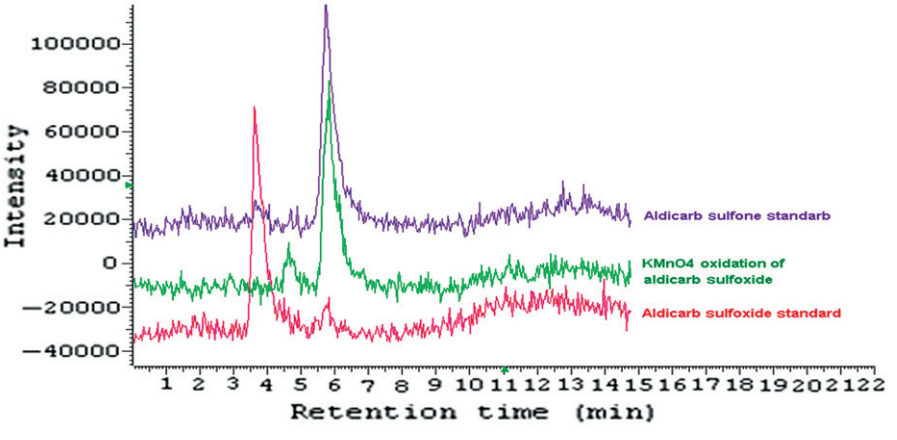

Figure 6. TICs of aldicarb sulfone, aldicarb sulfoxide standards and the oxidation byproduct of aldicarb sulfoxide under $KMnO_4$ oxidation system.

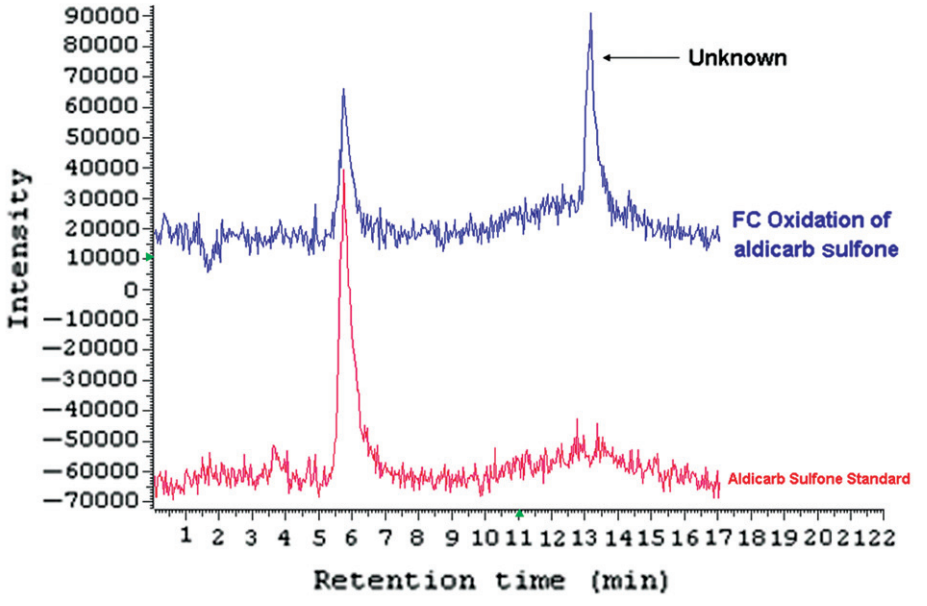

Figure 7. TICs of aldicarb sulfone standard and its oxidation byproduct under FC oxidation system.

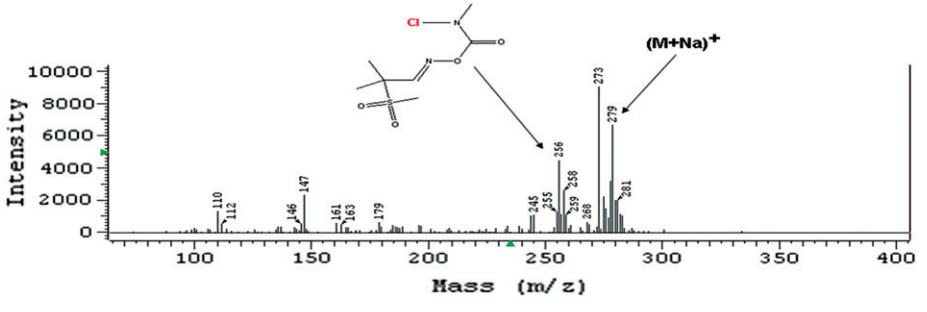

Figure 8. Mass spectrum of the unknown in the oxidation of aldicarb sulfone under FC oxidation system.

The mass spectrum of the unknown is shown in Figure 8. Based on the report in the literature [41] and the mass spectral analysis from this study, it is proposed that the unknown byproduct of aldicarb sulfone oxidised by free chlorine is N-chloro-aldicarb sulfone. The m/z 256 ion is interpreted to be the molecular ion, and the m/z 279 is the sodiated molecular ion. The m/z 273 ion has not been interpreted yet.

Based on the comprehensive investigation of oxidation of aldicarb and its three potential carbamate metabolites (aldicarb sulfoxide, aldicarb sulfone, and N-chloro-aldicarb sulfone) by various oxidants, the oxidative degradation pathways are proposed, as shown in Figure 9. In addition, the oxidation treatment systems used in this study and the potential degradates produced in each oxidation system are summarised in Table 2.

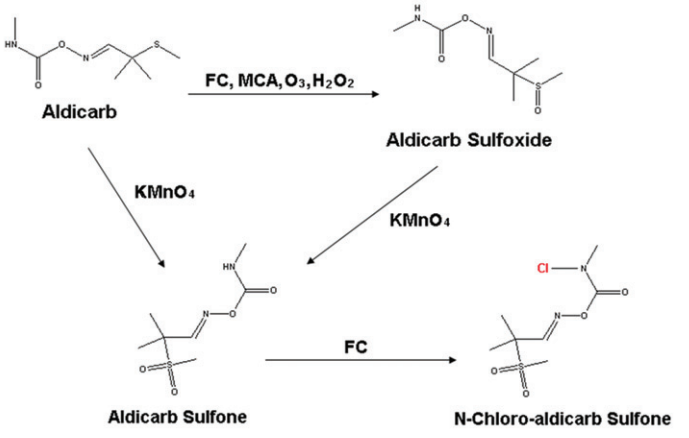

Figure 9. Proposed oxidative degradation pathways of aldicarb.

Table 2. Summarisation of oxidation treatment systems used in this study and the potential degradates.

Compound	Oxidation system	Conditions of the degradation study	Degradates
Aldicarb	Free chlorine (FC)	Initial FC concentration: $10\,\mu g\,mL^{-1}$	Aldicarb sulfoxide
Aldicarb	Ozone (O_3)	saturated O_3 solution ($29.7\,mg\,L^{-1}$)	Aldicarb sulfoxide
Aldicarb	UV radiation	low dosage, medium dosage, high dosage (power density: $8.9\,mW\,cm^{-2}$)	No significant degradation observed at low dosage and medium dosage. No degradates detected at high dosage (~70% removal)
Aldicarb	Chlorine dioxide (ClO_2)	The initial concentration of ClO_2: $9.97\,mg\,L^{-1}$	No degradates detected
Aldicarb	Hydrogen peroxide (H_2O_2)	Initial H_2O_2 concentration: $27{,}273\,mg\,L^{-1}$	Aldicarb sulfoxide
Aldicarb	Monochloroamine (MCA)	Initial MCA concentration: $2000\,mg\,L^{-1}$	Aldicarb sulfoxide
Aldicarb	Permanganate (MnO_4^-)	Initial Permanganate concentration: $5.0\,mg\,L^{-1}$ (26.3 μM)	Aldicarb sulfone
Aldicarb sulfoxide	FC, H_2O_2, UV(high dose)	Same conditions as above	No degradates detected even though significant degradations were observed
Aldicarb sulfoxide	Permanganate (MnO_4^-)	Same conditions as above	Aldicarb sulfone
Aldicarb sulfoxide	MCA, O_3, ClO_2	Same conditions as above	No significant degradation
Aldicarb sulfone	UV radiation	High dosage	~30% removal but no degradates detected
Aldicarb sulfone	Free chlorine (FC)	Same conditions as above	N-chloro-aldicarb sulfone
Aldicarb sulfone	H_2O_2, MCA, O_3, (MnO_4^-), ClO_2	Same conditions as above	No significant degradates observed

3.2 *Quantification of oxidation of aldicarb and its carbamate metabolites in different oxidation systems*

Quantification studies of aldicarb and its metabolites were performed by using HPLC with UV detection, as shown in Figures 10–12. Aldicarb was completely removed by free chlorine, monochloroamine, ozone, permanganate and hydrogen peroxide, and 70% removed by the high-dosage UV radiation (Figure 10), while chlorine dioxide, medium and low dosage UV did not demonstrate measurable removal of aldicarb. Free chlorine, permanganate, hydrogen peroxide and high-dosage UV radiation demonstrated significant removal of aldicarb sulfoxide, but only aldicarb sulfone was detected as the permanganate oxidation byproduct of aldicarb sulfoxide, no other oxidation byproducts were detected (Figure 11).

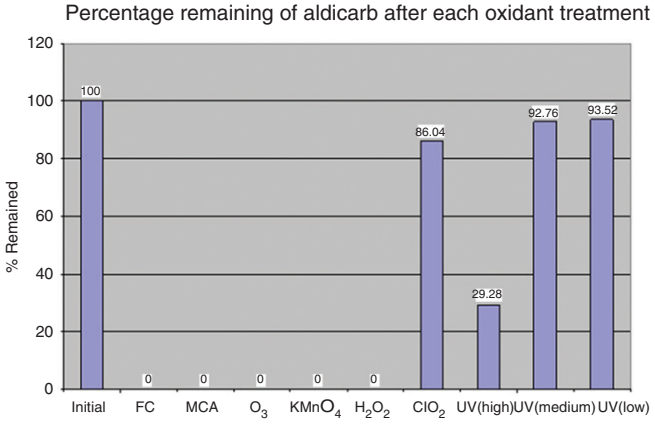

Figure 10. Quantification of aldicarb in terms of percentage remaining in different oxidation systems. The removed aldicarb was transformed into aldicarb sulfoxide, aldicarb sulfone and undetectable degradates. The detailed degradates were shown in Table 2.

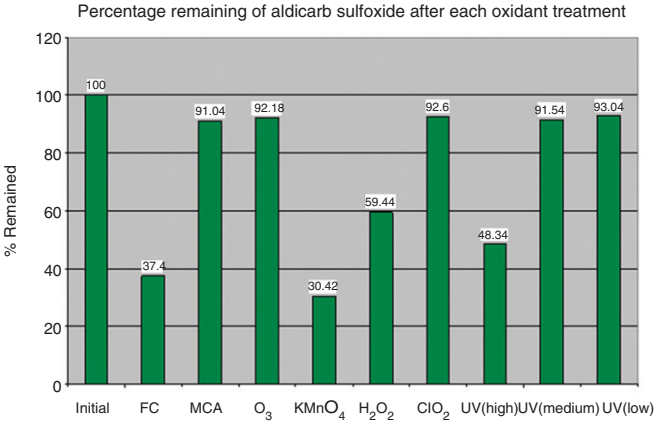

Figure 11. Quantification of aldicarb sulfoxide in terms of percentage remaining in different oxidation systems. The removed aldicarb sulfoxide was transformed into aldicarb sulfone and unknown degradates. The detailed degradates were shown in Table 2.

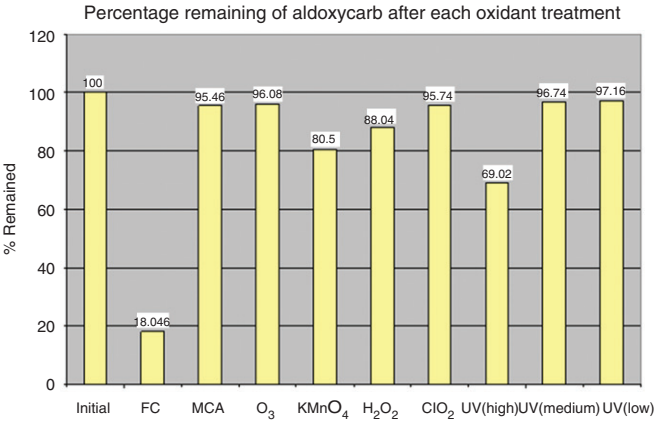

Figure 12. Quantification of aldicarb sulfone in terms of percentage remaining in different oxidation systems. The removed aldicarb sulfone was transformed into N-chloro-aldicarb sulfone and unknown degradates. The detailed degradates were shown in Table 2.

Experiments on oxidation treatment of aldicarb sulfone showed that only free chlorine and high-dosage UV radiation demonstrated significant removal ($>80\%$ for free chlorine and $>30\%$ for high-dosage UV radiation) of aldicarb sulfone, while other oxidants did not show significant removal ($<20\%$) (as shown in Figure 12). Moreover, no oxidation byproducts were detected for the high-dosage UV radiation of aldicarb sulfone. This phenomenon will be further investigated.

4. Conclusions

Systematic study of aldicarb and its metabolites involving treatment with various oxidants demonstrated that aldicarb can be oxidised to produce aldicarb sulfoxide by free chlorine, monochloroamine, ozone and hydrogen peroxide, and can produce aldicarb sulfone when it is oxidised by permanganate. The study concludes that aldicarb is not stable in the presence of these oxidants within certain dosage levels. Aldicarb sulfoxide can also be oxidised to produce aldicarb sulfone by permanganate, while no oxidation byproducts were detected with other oxidants. Aldicarb sulfone can only be oxidised to produce N-chloro-aldicarb sulfone by free chlorine, showing that aldicarb sulfone is more resistant to oxidation than aldicarb sulfoxide. High-dosage UV radiation showed significant removals of aldicarb and its two metabolites, but this dosage is not practical for typical drinking water treatment operations. Based on this systematic study, aldicarb sulfoxide would be the major potential aldicarb degradate existing in drinking water after FC or MCA treatment, which are the two majorly used oxidation treatment systems, if aldicarb was indeed transported into the raw water. The data from this comprehensive study is very valuable for water treatment facilities and environmental researchers. The results will help environmental researchers understanding the oxidation mechanisms of aldicarb and its metabolites with different oxidants in a water treatment system.

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