

Degradation of sulfur mustard in soil by aqueous media

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Abstract

To study the kinetics of sulfur mustard degradation in soil, an efficient analytical method was first established to ensure reliable analyses of mustard. A soil analogue was prepared, and impregnated with sulfur mustard in a manner to obtain an essentially even distribution of mustard content in the matrix. Several aqueous media including water, two basic buffers and a base solution were tested for the study of mustard degradation using the mustard containing soil. In each case, the mustard content in the soil was reduced by more than 70% in 24 hours, and when treated as a pseudo homogenous reaction, the degradation was shown to follow apparent first-order kinetics with a rate constant between 5.0 and $6.0 \times 10^{-2} \text{ hr}^{-1}$, corresponding to a half-life of 11 to 14 hours. Despite the difference in alkalinity among the media, the little variation in the rate constant indicated that the effect of alkalinity on mustard degradation was insignificant.

1. Introduction

Mustard gas, also known as sulfur mustard, or *bis* (2-chloroethyl) sulfide in its purified form, was used in the past wars as a chemical warfare (CW) agent. Although its use has been banned worldwide, and its manufacturing discontinued in most countries, it is still stockpiled in many sites around the world. Over at least the past six decades, areas of Canadian Forces Base and Defense Research and Development Canada (DRDC) at Suffield, Alberta have been contaminated by chemical warfare agents, and the contaminants of primary interest in the highest quantities are mustard and its reaction and hydrolysis products. Efforts were initiated to address actively the known chemically contaminated sites. Due to the extremely hazardous nature of mustard and many related compounds, it has become an urgent task to completely destroy the stockpiles and clean up the contamination. The persistence of mustard gas in the environment, however, has made it more difficult to destroy than other CW agents. Despite a relatively rapid hydrolysis rate upon its dissolution in water, indicated by a short half-life of 4-8 minutes [1], the low solubility in water (only about 900 mg/L) gives rise to its environmental stability. Therefore, mustard buried in the soil, where it cannot vaporize, can remain stable for years [2].

The degradation of mustard gas has been studied extensively in the last two decades in order to establish the mechanisms and develop efficient methods for its destruction. While

the mechanisms mainly involve hydrolysis and oxidation of mustard, the degradation could be achieved via natural [3], thermal [4], chemical [5-9] microbiological [3,10-14] and enzymatic [15] approaches, each with its advantages and disadvantages. Some of these took long to achieve substantial degradation, while others were more effective but required radical conditions or expensive reagents, and most of them were tested only with the agent in the pure form instead of mustard in a natural setting such as soil.

In an attempt to seek a technique that fulfills the criteria of rapid conversion of mustard to the nontoxic compounds, mild conditions, inexpensive reagents and no noxious effluents, in this work a simple method using water and other aqueous media was studied for mustard degradation in soil. The emphasis was on the effect of medium alkalinity on the kinetics of degradation since it plays a significant part in hydrolysis. This study could provide useful information for large scale cleanup of the mustard contaminated sites at Suffield, Alberta.

2. Experimental

2.1. Synthesis of sulfur mustard

A license for the production, use, acquisition or possession of chemicals included in Schedule 1 of the Chemical Weapons Convention was issued by Department of Foreign Affairs of Canada. Mustard (bis-(1-chloroethyl)sulphide) has been prepared by the reaction of 2,2'-thiodiethanol with concentrated hydrochloric acid (HCl) at elevated temperatures (65-75°C) for an hour and then purified by vacuum distillation. The purity of the agent (~99%) was verified by nuclear magnetic resonance (NMR) spectroscopy and gas chromatography-mass spectrometry (GC-MS).

2.2. Preparation of a soil analog

Since there is considerable variability in size fractions of the soils present on the Suffield site, a synthetic analogue was developed to simulate Suffield soil based on an analysis by DRDC, with the composition shown in Table 1. Three kilograms of this soil analog was prepared for the initial work.

2.3. Validation of mustard analysis in soil samples

An efficient procedure for analysis of mustard in soil was established and validated using soil samples spiked with mustard. Each sample was prepared by weighing 0 to 0.30 g soil

analog in a 7-mL vial, to which 15 - 20 mg mustard was added using a Pasteur pipette, and was left overnight in a refrigerator with the cap tightly screwed on the vial. The sample was extracted with 5.0 mL dichloromethane on a wrist action shaker for 3 hours at the maximum stroke length. An aliquot of 50 μ L was taken using a Hamilton syringe and diluted to 10 mL with dichloromethane. The diluted sample was analyzed using a Trace PolarisQ Quadruple GC-MS (Thermo Scientific, Waltham, MA) and the mustard content was calculated using the calibration curve.

2.4. Soil impregnation with mustard for degradation study

An amount of mustard between 0.5 and 1.0 g was dissolved in 20 mL dichloromethane and the solution was added to 20 g soil analogue in a 60-mL wide-mouth sample jar. The jar containing the mixture was left open in a fume hood for 48 hours to evaporate essentially all the solvent. The cap was then screwed tightly on the jar, and it was shaken vigorously to ensure that the content was well mixed and mustard was evenly distributed in the soil. Small samples in triplicates were taken from the jar and extracted with dichloromethane for different time lengths. They were then analysed for mustard following the above procedure.

2.5. Kinetic study of mustard degradation by aqueous media

The soil material thus impregnated with mustard was wetted with water and basic media, respectively. The pH buffers used as media were prepared with capsules from Micro Essential Laboratory, Brooklyn, NY, containing $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ for pH 10.0 and $\text{Na}_2\text{HPO}_4/\text{Na}_3\text{PO}_4$ for pH 12.0 buffer. The slurry was centrifuged at 1,000 rpm for 10 minutes to decant the excess liquid. The wetted soil was then transferred back into a sample jar to allow the hydrolysis of mustard to proceed while the cap was tightly screwed on to prevent moisture and mustard loss through evaporation. Triplicate samples were taken at different time intervals for mustard analyses using the above procedure. The first samples were produced immediately after centrifugation, when it was considered as time zero.

3. Results and discussion

3.1. Extraction and analysis of mustard in soil samples

Due to the limited supply of mustard in this study, chloroethyl ethyl sulfide (half mustard) purchased from Sigma Aldrich Inc. was first used for the validation of the

analytical method. As seen in Table 2, with half mustard only 75 to 90% of the amount spiked was accounted for in most soil samples. This relatively low recovery was experienced by many other researchers in their analyses of soil containing half mustard, and it had long been thought to be a result of the binding of half mustard to soil up until this research. Two soil-free samples (0 g soil in the vial) included in this set of tests as the controls showed similarly low results, indicating that the outcome of half mustard analysis may be due to other causes. One possible explanation could be the vaporization of half mustard during sample preparation, which may have affected the results significantly since only a very small amount of the agent (15-20 mg) was added to the soil. It can be seen that with half mustard, when the soil amount was increased to 0.30 g, the analytical results tended to become even lower than those obtained with smaller amounts of soil. This was possibly because a greater amount of soil would provide a larger surface area, which could facilitate the vaporization of half mustard. Although its vapor pressure at room temperature is unknown, half mustard was observed to evaporate much faster than full mustard at room temperature, indicating a higher vapor pressure of half mustard than full mustard. Therefore, as seen in Table 2, the results of all samples spiked with full mustard were shown to be much higher than those with half mustard, and most of them were close to the full recovery of 100%, confirming the reliability and validity of this analytical method for mustard analyses.

3.2. Preparation of soil containing mustard

Fig 1 shows the analytical results of one batch of soil impregnated with mustard, in which roughly 0.5 g mustard was initially added. It can be seen that increasing extraction time from 1 to 3 hours resulted in a higher mustard content detected in the soil, about 10 mg/g soil, but even this value accounted for only half of the amount of mustard originally added. To ensure that the extraction was essentially complete, the time was further extended to 5 hours with similar results obtained, suggesting that a period of 3 hours was probably sufficient for the extraction of mustard from the soil thus prepared. The unaccountable half was believed to have likely evaporated along with dichloromethane over the 48-hour solvent removal. Unfortunately, this relatively heavy loss up to 50% seemed inevitable in the preparation of a soil material with desirable mustard distribution. The uniformity of mustard distribution in the soil was reflected by the size of standard deviations shown in both figures as the error bars. As the coefficient of variation (CV) was less than 15% in all cases, it was concluded

that mustard distribution was essentially even in the soil prepared in the manner described earlier, which could thus be used to study the kinetics of mustard degradation.

3.3. Kinetics of mustard degradation by aqueous media

Mustard degradation in the soil was tested with various aqueous media to study the effect of alkalinity on the kinetics. It can be seen in Fig. 3 that the mustard content in soil was reduced by over 70% within 24 hours of the reaction in all cases. The effect of all these media including water was phenomenal compared to the natural degradation, for which Medvedeva et al. [3] reported a period as long as 12 months for a similar mustard reduction in various soil samples. Considering the complexity of such a multi-phase system, it was very difficult to study the actual kinetics. The scenario was therefore simplified by treating the process as a single-phase reaction to circumvent complications associated with mass transfer between different phases. Thus, through a logarithmic regression of the mustard data over time, the apparent first order was observed for the kinetics of this pseudo “homogeneous” reaction (Fig. 4). The regression coefficient between 0.97 and 0.99 suggested a reasonably good fit of data into the model in each run. Although both Prasad et al. [8] and Sharma et al. [9] also reported apparent first order kinetics of mustard degradation, they studied the reaction in completely different matrices, and used expensive reagents. The rate constants between 5.0 and $6.0 \times 10^{-2} \text{ hr}^{-1}$ obtained in this study were close to those reported by Prasad et al. [8] in the range from 4.0 to $10.0 \times 10^{-2} \text{ hr}^{-1}$ using activated carbon impregnated with NaOH, CrO_3 and EDA, but higher than most of the data of Sharma et al. [9] ranging from 1.0 to $4.0 \times 10^{-2} \text{ hr}^{-1}$ for Whetlerite carbon impregnated with various salts and acids. GC-MS characterization showed that the main products of mustard degradation in soil were hemimustard and thiodiglycol (TDG), but 1,4-oxathiane and divinyl sulfone detected in the systems of the above researchers were missing in this study. The rise in pH of the medium was expected to accelerate the degradation since the abundance in OH^- would favour the hydrolysis of mustard. The effect of alkalinity was, however, only minor, as shown by only a moderate increase in rate constant of less than 10% (from 5.65 to $6.04 \times 10^{-2} \text{ hr}^{-1}$) over a pH rise of more than 4 units (Table 3). This indicates that despite the simplification to simulate a homogenous reaction, in reality mass transfer may still be the limiting step in mustard degradation in soil. Therefore, when 0.1N NaOH was used as the medium, the rate constant

actually dropped below that of water, possibly as a result of higher viscosity than that of water. It was also speculated that since 0.1N was not high enough for the NaOH solution to be a buffer, its alkalinity may have decreased substantially due to OH⁻ consumption during mustard hydrolysis, thus eventually slowing down the reaction, as indicated by a rate constant lower than those of both pH 10.0 and 12.0 buffers.

4. Conclusion

The analytical method set up in this study was able to analyze mustard in soil samples with high reliability. The soil materials containing mustard prepared by impregnation had an essentially even mustard distribution, thus being ideal for the study of mustard degradation kinetics. An apparent first order model was observed for the kinetics of mustard degradation when the system was treated as a pseudo single phase. The similar rate constants obtained with different media showed that the alkalinity only had limited effect on the reaction, *i.e.*, water was just as effective as any base solutions in mustard degradation. The results also showed that the simple and inexpensive reagents used in this work actually achieved the same results as other studies using costly and complicated methods.

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Table 1
Composition of soil analogue

Material*	Percentage (%)	Supplier
Quartz sand (#00)	55.2	Atlantic Silica
F-20 Feldspar	18.4	The Feldspar Corporation
Bentonite powder	11.0	A local supplier
Redart clay	7.4	Tennessee Clay Company
Limestone	5.0	A local supplier
Black earth powder	3.0	Black Earth Humates Ltd

* Based on the size of particles contained in Suffield soil (sand: 2mm to 50 μm , silt: 50 μm - 2 μm , clay <2 μm)

Table 2

Validation of analytical method of mustard (half and full) in soil

Agent	Soil amount (g)	Solvent/soil ratio	Added amount (mg)	Detected amount (mg)	Recovery (%)
Half mustard	0.30	16.7	15.9	12.1	76.1
Half mustard	0.10	50	16.4	14.0	85.4
Half mustard	0.050	100	16.4	15.0	91.5
Half mustard	0	-	16.8	14.1	88.9
Mustard	0.30	16.7	16.3	16.0	98.2
Mustard	0.10	50	18.8	19.4	103
Mustard	0.050	100	20.3	20.1	99.0
Mustard	0	-	19.8	20.0	101

Table 3

Kinetic parameters of degradation of mustard in soil by aqueous media

Medium	Rate constant ($\times 10^{-2} \text{ hr}^{-1}$)	Half-life (hr)
Water	5.65	12.3
pH 10.0 buffer	5.81	11.9
pH 12.0 buffer	6.04	11.5
0.1 N NaOH	5.04	13.7

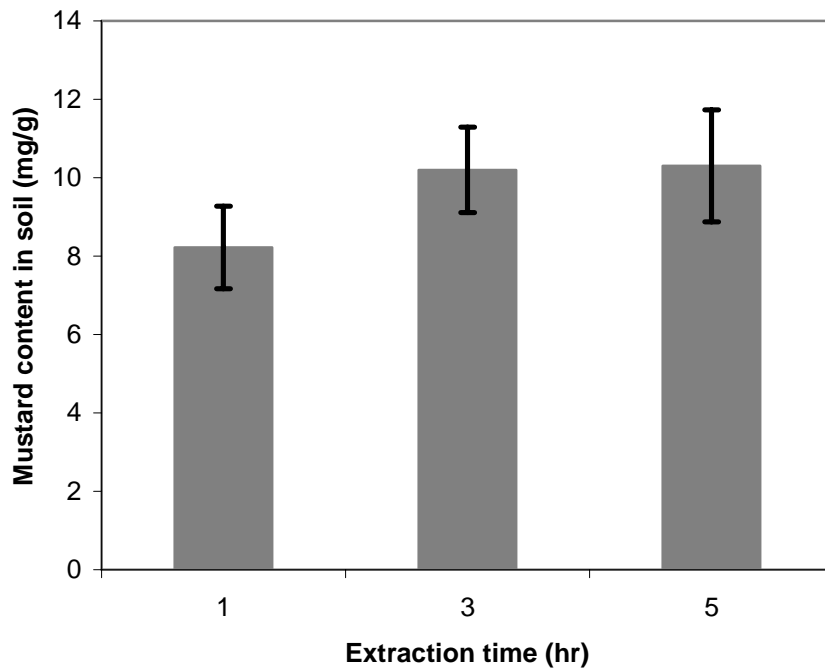


Fig. 1. Mustard content of soil initially with 0.5 g mustard added. Error bars are standard deviations of triplicates.

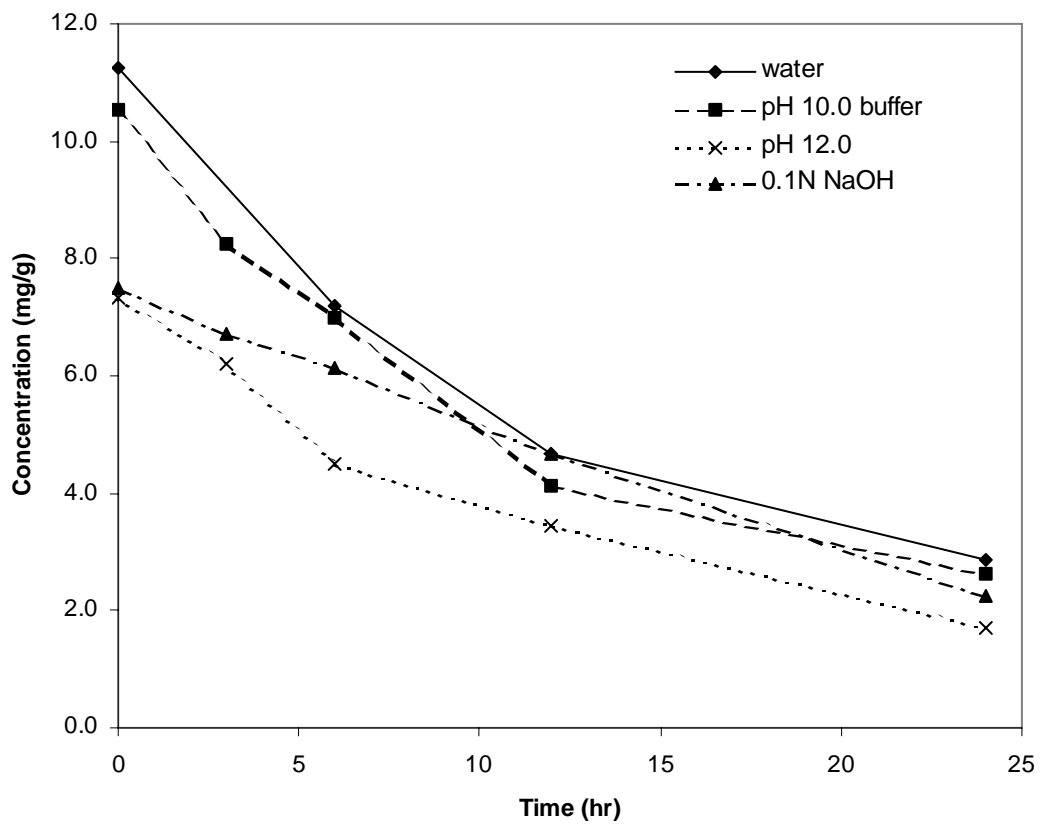


Fig. 2. Mustard degradation in soil by aqueous media. All data points are means of triplicates.

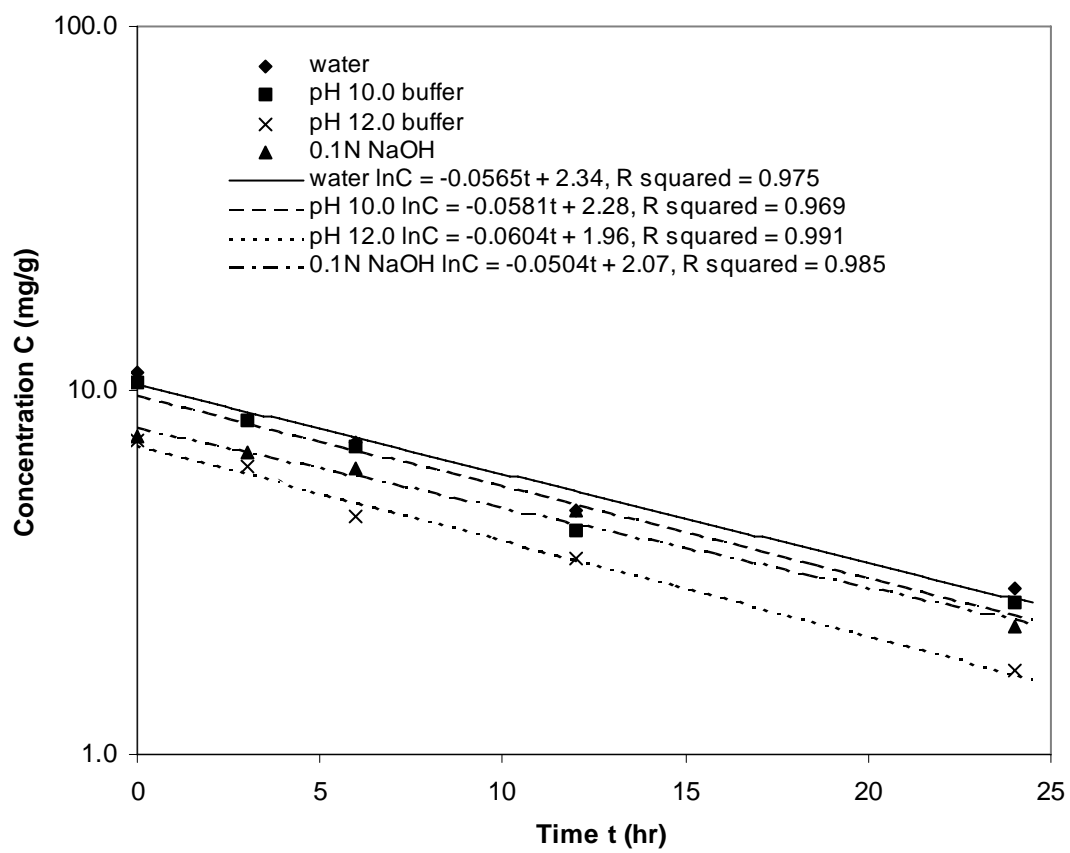


Fig. 3. Logarithmic regression of mustard data over degradation time.