

## Removal of 1, 2-dichloroethane from water using UV/chlorine advanced oxidation process

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### Abstract

One of the major challenges faced by modern urbanized societies is to reclaim their water resources. The present study investigates the removal of 1,2-dichloroethane from deionized water using chlorine alone as well as in a combination with ultraviolet (UV). Results illustrate that, during a reactor run of 1 hour, the concentration of 1,2-dichloroethane decreased from 40 ppb to 4.21 ppb and 3.38 ppb by the application of 50 ppm and 100 ppm Cl<sub>2</sub> respectively. However, in the presence of UV, the same concentration of 1,2-dichloroethane was decreased up to 2.95 ppb and 3.13 ppb for 50 ppm and 100 ppm Cl<sub>2</sub>. Besides, different concentration drops were observed by varying initial concentration of 1,2-dichloroethane. Briefly, without UV, the contaminant concentration was decreased from 60 ppb to 3.87 ppb and 3.54 ppb using 50 ppm and 100 ppm Cl<sub>2</sub> respectively. Similarly, same concentrations of chlorine with the use of UV decreased the concentration of the contaminant from 60 ppb to 4.47 ppb and 3.08 ppb respectively. The study concludes that the combination of UV with Cl<sub>2</sub> resulted into a better degradation of 1,2-dichloroethane compared to the usage of Cl<sub>2</sub> alone suggesting its application for removal of similar compounds from natural water resources.

**Keywords:** Advanced Oxidation Process; Dichloroethane; Water Pollution; UV Photoreactor

### Introduction

Water pollution is a global problem affecting every form of life on the planet earth. It has been observed that the worldwide leading deaths are caused by water pollution and approximately it accounts for the deaths of more than 14,000 people daily (Pink 2006; Larry, 2006). The increasing demands of synthetic products by human beings has resulted into a huge increment in the industrial sector during the past few decades. In fact, industries have become the backbones of the economy of many nations, replacing other sectors such as agriculture. This rapid rise might seem good and beneficial to many but unfortunately it has bulldozed certain important sections of environment to a drastic level. Among these pollutants, chlorinated volatile organic compounds are one class of very harmful and toxic contaminants which have every likelihood to pollute water. These are in immense use in industries nowadays and are readily found in water bodies found near area which have increased number of industrial units there. These materials are used in the plastic industry, pharmaceutical industries and in many other as solvents (Vilve et al., 2010).

Among chlorinated volatile organic compounds, 1, 2-dichloroethane is of serious concern as it has been rendered as a carcinogenic for animal kingdom. It is used largely in the production of vinyl chloride and being volatile it can easily escape into the environment as well. The maximum level of 1,2-dichloroethane that can be accommodated in ground water is just 5 ppb. According to another report the quantity of 1,2-dichloroethane should be less than 100 ppb in in land and sea water (Vilve et al., 2010; Chan et al., 2012). In order to rectify the problem of 1,2-dichloroethane in water, various methods have been exploited including advanced oxidation processes (AOPs). The advanced oxidation process makes use of strong hydroxyl radicals to degrade chemical compounds into smaller and biodegradable materials. Although many other processes have been in use for the treatment of water regarding different contaminants, yet the advanced oxidation process is found to be very effective (Vilve et al., 2010). Wide range of photochemical and non-photochemical methods have been used to generate the hydroxyl ions such as

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ozonation, ozone coupling hydrogen peroxide, Fenton oxidation,  $O_3/UV$ ,  $H_2O_2/UV$ ,  $O_3/H_2O_2/UV$  and  $UV/Cl_2$  (Smirnov et al., 1989). Although many other processes have been in use for the treatment of water regarding different contaminants, yet the advanced oxidation process is found to be very effective (Vilve et al., 2010).

The current study involves removal of 1,2-dichloroethane in bench scale reactor using chlorine alone as well in combination with UV. Specifically, the study is designed to investigate the removal of 40 ppb, 50 ppb and 60 ppb of 1,2-dichloroethane from deionized water using chlorine and  $UV/Cl_2$  at concentration of 50 ppm and 100 ppm of aqueous chlorine. Moreover, the study assess the effect of residence time in the reactor on the advanced oxidation process for 1,2-dichloroethane.

## Materials and Methods

### UV Photoreactor

The UV photoreactor was used for the advanced oxidation process. It is a bench-scale unit from NORMAG Co. Hessenstraße, Hofheim, Germany. The low pressure UV lamp of 15W, manufactured by Heraeus Holding GmbH, Germany, was used which has the ability to emit light 254 nm with an intensity of  $6.5 \times 10^{-3} \text{ W/cm}^2$ . The lamp produces a spectrum mainly at 254 nm and it can be described practically as monochromatic. During the runs in the photoreactor, the temperature and pressure were kept at ambient levels while the motor speed was kept at 20%.

### Concentration Analysis: Gas Chromatography – Mass Spectrometer (GC-MS)

The GC-MS (Thermo Scientific single quadrupole) equipped with TriPlus for headspace injection was used to detect the concentrations of 1,2-dichloroethane in the water samples before and after treatment in the photo reactor. The capillary column of 60 m length with 0.32 mm internal diameter Rtx-502.2 (Restek Corp., USA) was used for the separation analysis. The carrier gas was helium with the flow rate of 1.7 ml/min at split of 1:10. The column temperature was programmed at 50 °C for 1-minute ramp to 225 °C at 20°C/min, while on hold for 1 minute. One milliliter of the water sample for each experiment was immediately transferred to the head space of standard vials (Thermo Scientific); which were subsequently placed in the autosampler sequence for the analysis. The spectrometer was operated in the selected ion mode. Before the use of the GC-MS, a calibration curve for 1,2-dichloroethane was generated for a range of determination of 1 ppb to 100 ppb. The output of GC-MS was processed in a Thermo Scientific™ Xcalibur software and the analyses were carried out in triplicates for all the samples. Chemical analyses were done on the GC-MS apparatus with the conditions mentioned above. Samples from the reactor were withdrawn in clean glass vials. Each vial contained a sample of 2 ml to be tested on the GC-MS.

### Experimental Procedure

The experimental layout constituted of five different parameters being varied. Each parameter was studied for the advanced oxidation process and results were generated. The variations were as per

the concentrations of aqueous chlorine and 1,2-dichloroethane; two concentrations of the contaminant were spiked in deionized water separately which were subsequently treated with two different levels of aqueous chlorine one by one. Moreover, the presence of UV was available only once in each set. Different sets pertaining to the experimental work are as follows:

(1) In the first set of experiments, 40 ppb of 1,2-dichloroethane was spiked in deionized water and it was treated with 50 ppm chlorine with and without the use of UV each for a reaction run of 1 hour. (2) In the second set of experiments, 40 ppb of 1,2-dichloroethane was spiked in deionized water and it was treated with 100 ppm chlorine with and without the use of UV each for a reaction run of 1 hour. (3) In the third set of experiments, 50 ppb of 1,2-dichloroethane was spiked in deionized water and it was treated with 50 ppm chlorine with and without the use of UV each for a reaction run of 1 hour. (4) In the fourth set of experiments, 50 ppb of 1,2-dichloroethane was spiked in deionized water and it was treated with 100 ppm chlorine with and without the use of UV each for a reaction run of 1 hour. (5) In the fifth set of experiments, 60 ppb of 1,2-dichloroethane was spiked in deionized water and it was treated with 50 ppm chlorine with and without the use of UV each for a reaction run of 1 hour. (6) In the sixth set of experiments, 60 ppb of 1,2-dichloroethane was spiked in deionized water and it was treated with 100 ppm chlorine with and without the use of UV each for a reaction run of 1 hour.

### Preparation of Stocks

The contaminant 1,2-dichloroethane was obtained from AnalaR Normapur® with purity 99.8%. The dilution method was used to prepare the stock solution of 1,2-dichloroethane of 1 ppm concentration. This stock was used as a source of 1,2-dichloroethane for spiking into the deionized water. Each concentration was pipetted using the following relation, i.e.,  $C_1V_1 = C_2V_2$ ; where  $C_1$  = concentration of 1, 2-dichloroethane in the stock,  $C_2$  = concentration of 1, 2-dichloroethane required to be prepared,  $V_1$  = volume of 1, 2-dichloroethane required from the stock, and  $V_2$  = volume of 1, 2-dichloroethane to be prepared. The same formula for dilution mentioned above was used to determine the different concentrations of aqueous chlorine. A commercial chemical was used for cleaning purposes, i.e., CLOROX. The initial concentration of hypochlorite in CLOROX was calculated to be 37500 ppm. Consequently, this was the value used as the initial concentration  $C_1$ . Deionized water was spiked with 1,2-dichloroethane and the aqueous chlorine according to the concentrations mentioned above. In each set of experiments, deionized water allowed to run through the photo reactor for 15 minutes for the purpose of cleaning as well.

Two equipment were used to conduct the research. The photoreactor was used to run the used to run the oxidation reactions and carry out the removal of 1,2-dichloroethane, whereas the gas chromatography mass spectrometer was used to detect the concentration levels of 1,2-dichloroethane before and after the treatment.

### Advanced Oxidation Process

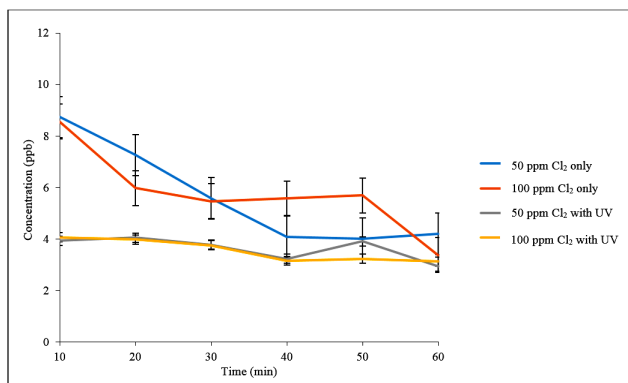
The stocks of both 1,2-dichloroethane and aqueous chlorine were used to spike deionized water. Before this, a 15 minute run was given to the photoreactor with deionized water only for cleaning

purposes. It was then replaced with fresh deionized water and first-ly, it was spiked with 1,2- dichloroethane. The photo reactor pump motor was allowed to run for 10 minutes in order to maximize the mixing of the contaminant. The contaminated water was then spiked with the desired concentration of aqueous chlorine and the reactor was allowed to run for 1 hour. During this, samples were withdrawn at regular intervals of 10 minutes to study the effect of residence time on the treatment process. Similar method was adopted for each set of experiments mentioned above and for each run. The UV lamp was kept on and off depending on the requirement of the samples.

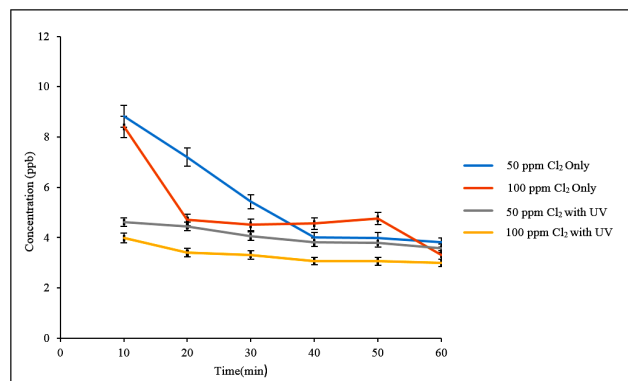
## Results and Discussion

The concentrations of each sample of 1,2-dichloroethane at 40, 50, and 60 ppb of 1,2-dichloroethane concentration spiked in deionized water is presented in Figure 1-3. Each treatment is investigated in the presence or absence of UV during the treatment process. It is clear from the results that there has been a sharp decrease in concentration of 1, 2-dichloroethane from the initial value especially during the first 10 minutes of the run. This trend can be seen for both concentrations of 1,2-dichloroethane. Such a level of treatment is found for other materials like BTEX (Benzene, Toluene, Ethylbenzene, and Xylene), using the same procedure but different materials for oxidation namely a combination of UV and  $H_2O_2$  (Sichel et al., 2011). As the curves move along after the 10 minutes' interval in each run, it can be seen that the concentration almost becomes constant. In contrast to this, the curves of the 50 ppm  $Cl_2$  in both Figures 2 and 3 represents a different sort of trend especially the one for the 60 ppb contaminant concentration which is most likely due to cross contamination. A close look at these results shows that the use of 100 ppm concentration of the aqueous chlorine has a marked effect on the removal of 1,2-dichloroethane be it used with UV or without UV. This comparison is solely based on the presence of just two different concentrations of chlorine in this case, the other being the 50 ppm. However, even the 50 ppm concentration results are acceptable in this regard because the maximum contaminant level for 1,2-dichloroethane is 5 ppb or less than 10 ppb (Chan et al., 2012).

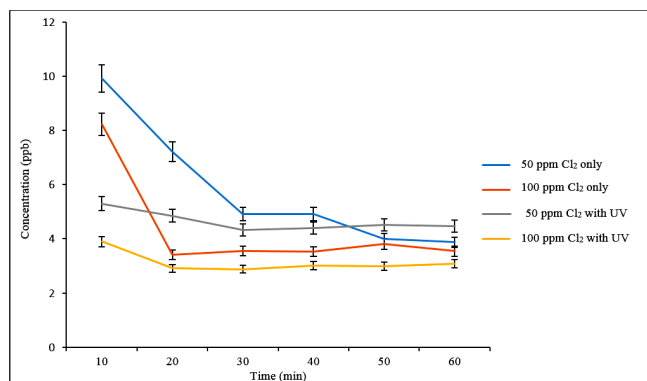
The use of UV enhances the removal of 1, 2-dichloroethane. This can be seen by the trends, showing  $Cl_2 + UV$  for both, the 50 ppm and 100 ppm concentrations of chlorine. The UV photons are in-



**Figure 1:** Trends of change in concentration of contaminated water spiked with 40 ppb of contaminant



**Figure 2:** Trends of change in concentration of contaminated water spiked with 50 ppb of contaminant



**Figure 3:** Trends of change in concentration of contaminated water spiked with 60 ppb of contaminant

involved in the generation of OH radicals which can be considered worthwhile for the treatment process (Jin et al., 2011). It is seen that the overall minimum values of concentration fall further below for the UV assisted experimental results. That is the comparison between, the more significant removals using 100 ppm of aqueous chlorine with and without UV for both concentrations of the contaminant. It is evident that for the first 10 minutes for which the maximum treatment has taken place, system has achieved a lower value of concentration when UV is used as compared when it is not. The raw data is provided as supplementary Tables 1-3.

## Conclusions

In light of the entire research work performed, all the results obtained and their comparison and discussion, it is concluded that although other substances are in use for advanced oxidation process, yet chlorine has all the potential to become a powerful source of OH radicals to oxidize in the AOP. Moreover, the use of UV has a very crucial role and a significant effect on the removal of 1,2-dichloroethane using chlorine. Using other different concentrations of aqueous chlorine can give some more insight into this research and these avenues must be searched for. The range of contaminant concentration spiked in water can also be varied and worked on. For this particular research work, the range was a bit below required for study. It is recommended that the lower limit should be defined more close to the maximum contaminant level (MCL) of 1,2-dichloroethane and the number of concentrations

should also be increased. Another important constraint that can be varied is the intensity of the UV lamp. The use of ground water for the similar procedure would be of much higher significance and interest.

#### **Compliance with ethical standards**

#### **Conflict of Interest**

The authors declare that they have no conflict of interests.

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## Appendix

### 40 ppb concentration of 1,2-dichloroethane

Time (min)	Chlorine without UV		Chlorine with UV	
	50 ppm (chlorine)	100 ppm (chlorine)	50 ppm (chlorine)	100 ppm (chlorine)
	Concentration of 1,2 dichloroethane after treatment (ppb)	Concentration of 1,2 dichloroethane after treatment (ppb)	Concentration of 1,2 dichloroethane after treatment (ppb)	Concentration of 1,2 dichloroethane after treatment (ppb)
10	8.74	8.564	3.933	4.073
20	7.265	5.983	4.058	3.989
30	5.581	5.475	3.784	3.763
40	4.081	5.586	3.236	3.159
50	4.012	5.7	3.913	3.235
60	4.206	3.381	2.948	3.127

Supplementary Table 1: Mean concentration levels of 1,2-dichloroethane in samples of 40 ppb contaminant spiked deionized water

### 50 ppb concentration of 1,2-dichloroethane

Time (min)	Chlorine without UV		Chlorine with UV	
	50 ppm (chlorine)	100 ppm (chlorine)	50 ppm (chlorine)	100 ppm (chlorine)
	Concentration of 1,2 dichloroethane after treatment	Concentration of 1,2 dichloroethane after treatment	Concentration of 1,2 dichloroethane after treatment	Concentration of 1,2 dichloroethane after treatment (ppb)
10	8.821	8.41	4.616	3.984
20	7.213	4.704	4.454	3.404
30	5.432	4.514	4.055	3.321
40	4.001	4.556	3.814	3.071
50	3.998	4.755	3.798	3.061
60	3.809	3.321	3.576	2.998

Supplementary Table 2: Mean concentration levels of 1,2-dichloroethane in samples of 50 ppb contaminant spiked deionized water

### 50 ppb concentration of 1,2-dichloroethane

Time (min)	Chlorine without UV		Chlorine with UV	
	50 ppm (chlorine)	100 ppm (chlorine)	50 ppm (chlorine)	100 ppm (chlorine)
	Concentration of 1,2 dichloroethane after treatment (ppb)	Concentration of 1,2 dichloroethane after treatment (ppb)	Concentration of 1,2 dichloroethane after treatment (ppb)	Concentration of 1,2 dichloroethane after treatment (ppb)
10	9.915	8.215	5.3	3.896
20	7.218	3.41	4.851	2.911
30	4.925	3.551	4.327	2.881
40	4.923	3.526	4.392	3.007
50	3.99	3.81	4.51	2.991
60	3.871	3.54	4.475	3.085

Supplementary Table 3: Mean concentration levels of 1,2-dichloroethane in samples of 60 ppb contaminant spiked deionized water