Removal of Dichloromethane from Groundwater Using Photo-Degradation

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Contents

Introduction

- Broad application of dichloromethane makes its presence in the environment inevitable
- Its property as an excellent solvent of a wide number of organic compounds makes it a highly utilized chemical especially in paint industries in some part of the world till date
- It is included in the EU Water Framework Directive (2006/60EC) as a priority contaminant.
- Its MCL and MCLG in drinking water are 0.005mg/L and 0 respectively.

Introduction

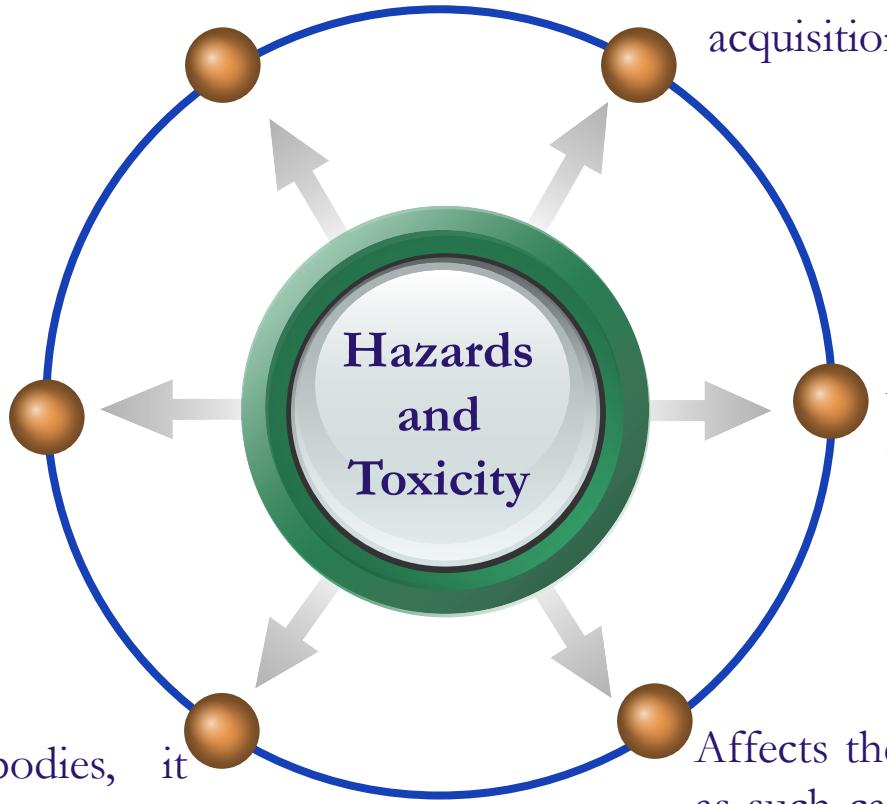
Properties of Dichloromethane

- Dichloromethane exists as colorless, sweet scented, volatile chlorinated hydrocarbon at room temperature
- It is miscible with many organic solvents such as alcohol, ether and carbon tetrachloride and adhesives.
- It dissolves conveniently plastics, paints, and varnishes

Introduction

Increases the level of spontaneous abortion

Increases the risk of cancer acquisition and



It can cause arrhythmia and heart attacks

Affects the central nervous system

Dissolved in water bodies, it inhibits the growth and reproduction of aquatic organisms

Affects the liver and kidney and as such cause pulmonary edema and renal dysfunctions

Introduction

Mode of release into environment

A. Manufacturing stage and use of end products

B. Component of waste water

C. Accidental spills and leaching from landfills

D. Septic tank degreasers

Introduction

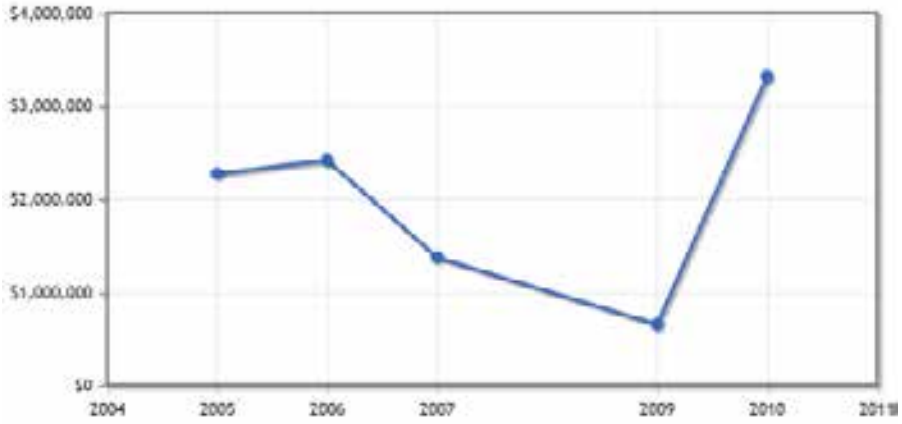
- Adsorption
- Biological treatment
- Pervaporation
- Persulfate oxidation
- Chemical reduction

Mode of treatment

Introduction

Importance of study

- World production of dichloromethane in 1991 was estimated as 437,000 tonnes (OECD, 1994)
- While in 2004, about 600,000 tonnes of dichloromethane was consumed globally (Jiade & Jianmeng, 2006).
- Saudi Arabia is the 26th largest importer of DCM (UNCTSTD, 2010)



Year	Trade Value	Weight (kg)	Quantity
2005	$2,271,352	2,671,825	2,671,825
2006	$2,414,817	2,718,704	2,718,704
2007	$1,369,291	1,874,870	1,874,870
2009	$649,922	240,000	240,000
2010	$3,312,537	3,544,000	3,544,000

Figure 1: Saudi Arabia Yearly Imports in US Dollars - Dichloromethane (methylene chloride) (UNCTSD, 2010)

Introduction

Why groundwater?

- While the half-life of DCM in other water media may range from few hours to several weeks, in groundwater it can exist for years.
- This is due to its inability to evaporate
- Characterized by low water resources, groundwater is one of Saudi Arabia's major water sources
- The potential of DCM being present in water bodies has increased due to a rise in the use of DCM in industries and institutions.

Literature Review

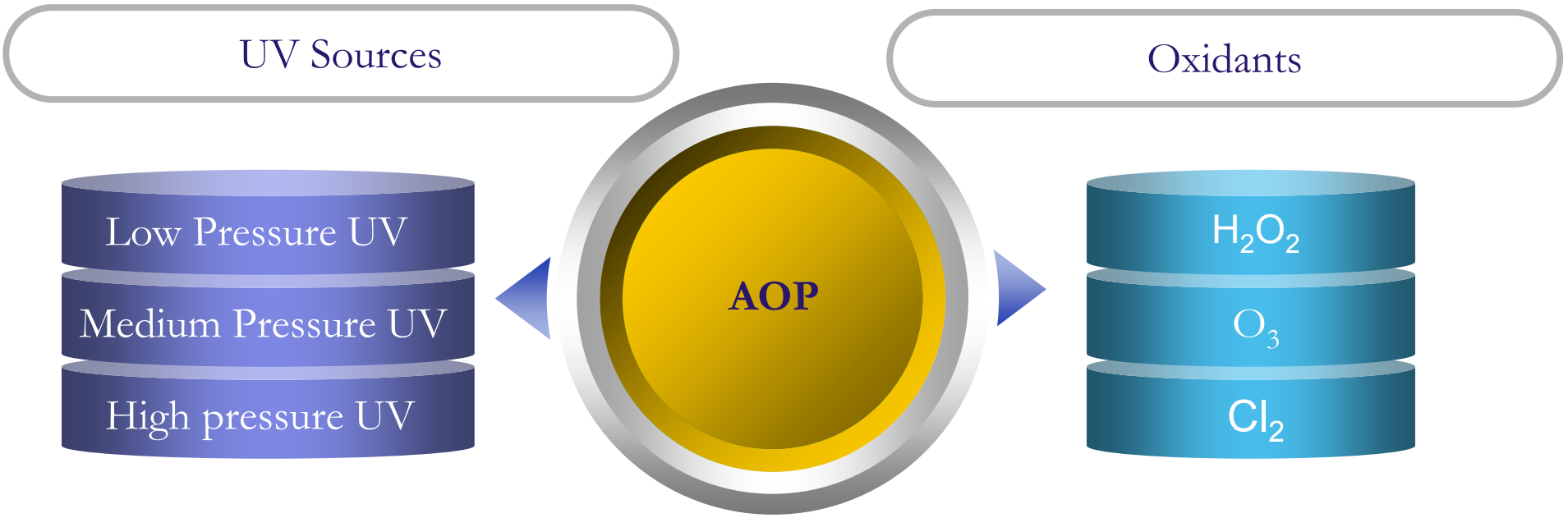
Advanced Oxidation Processes

- The AOPs is a promising technology that can be used for the removal of organic pollutants in water by breaking them down into carbon dioxide and water.

- This technology is based on generating highly reactive radicals such as the hydroxyl radicals (OH*) through the combined effect of ultraviolet light (UV) and an oxidant such as hydrogen peroxide (H_2O_2) and ozone (O_3)

- The efficiency of the AOP is generally maximized by the use of an appropriate catalyst and/or ultraviolet light

Literature Review



Literature Review

- Different technologies have been studied for the removal of dichloromethane both in groundwater and waste water
- The commonly used methods include adsorption, aeration, air stripping, biological remediation and chemical oxidation (Shestakova & Sillanpää, 2013)
- A brief review of some of the techniques used so far include;

Biological Treatment	Wu *et al.*, (2009)	Effective and relatively cheap but limited to very low concentration of contaminants
Chemical reduction and heterogeneous catalysis	Ahuja *et al.*, (2013)	Efficient but expensive

Literature Review

- The use of advanced oxidation in the removal of other organic chloride from different water samples has been previously studied.
- While the results obtained have been promising, they have each showed different level of efficiency

Photo-Fenton AOP	Malato *et al.*, 2004	Requires careful selection of operating conditions and leads to formation of other toxic substances
H_2O_2/UV Advanced Oxidation Process	Stepnowski *et al.*, (2002)	Research focused on waste water

Research gap and Objectives of study

- My literature search does not reveal any work on removal of DCM in Saudi Arabia's groundwater using AOP

- The objectives of this research is:

✓ To demonstrate the removal of DCM in De-ionized water and local ground water using Advanced Oxidation Technique

✓ To evaluate the efficiency of AOT at varying conditions of UV, ground water and de-ionized water

Methodology

- Water samples:

- De-ionized water from Millipore Q water systems
- Ground-water samples collected from the Reverse Osmosis Plant, King Fahd University of Petroleum and Minerals campus, Dhahran, Saudi Arabia.

- Reagents and Materials:

- Highly pure dichloromethane (99.9 %, analytical-grade) with CAS NO: 75-09-02
- Hydrogen peroxide (35% purity) obtained from sigma Aldrich chemicals, Steinheim Germany and stored within 0-4^{o}C
- 500ml capacity NORMAG photo-reactor with low pressure and medium pressure UV lamps of 15W and 150W intensity respectively

Methodology

❖ Reagents and Materials:

- Equipped with a UV lamp holder
- A slot to introduce oxidant
- An in-built stirrer to stir the mixture effectively

Methodology

Methodology

- Experimental Procedure

Both the de-ionized water samples and the groundwater samples were spiked with approximately the same stock solution of dichloromethane (initial concentration = 100 ppb) in the photo-reactor

- Treatment condition was varied as follows:
  - Use of different UV lights (low and medium pressure).
  - Use of different hydrogen peroxide concentrations (50 ppm and 100ppm).
  - Combined UV and different concentration of Hydrogen peroxide

- Samples were collected at time intervals; 0, 15, 30, 60 (minutes)

Methodology

- Analytical Determination
- Groundwater samples were analyzed for the presence of anions using Ion chromatography
- Treated water samples were analyzed for dichloromethane using the GC/MS set at conditions: flow rate 1.7ml/min, split 1:10 with helium as career gas. The temperature was programmed for 50^{o}C for 1min ramp to 225^{o}C at 20^{o}C/min and hold for 1min
- The temperature of the photo-reactor was maintained at 20^{o}C throughout the procedure.

Results and Discussion

- Result of chemical properties analysis

Ions	Chloride	Bicarbonate	Nitrate	Sulfate
Concentrations (mg/L)	1420	200.8	16.3	750

Results and Discussion

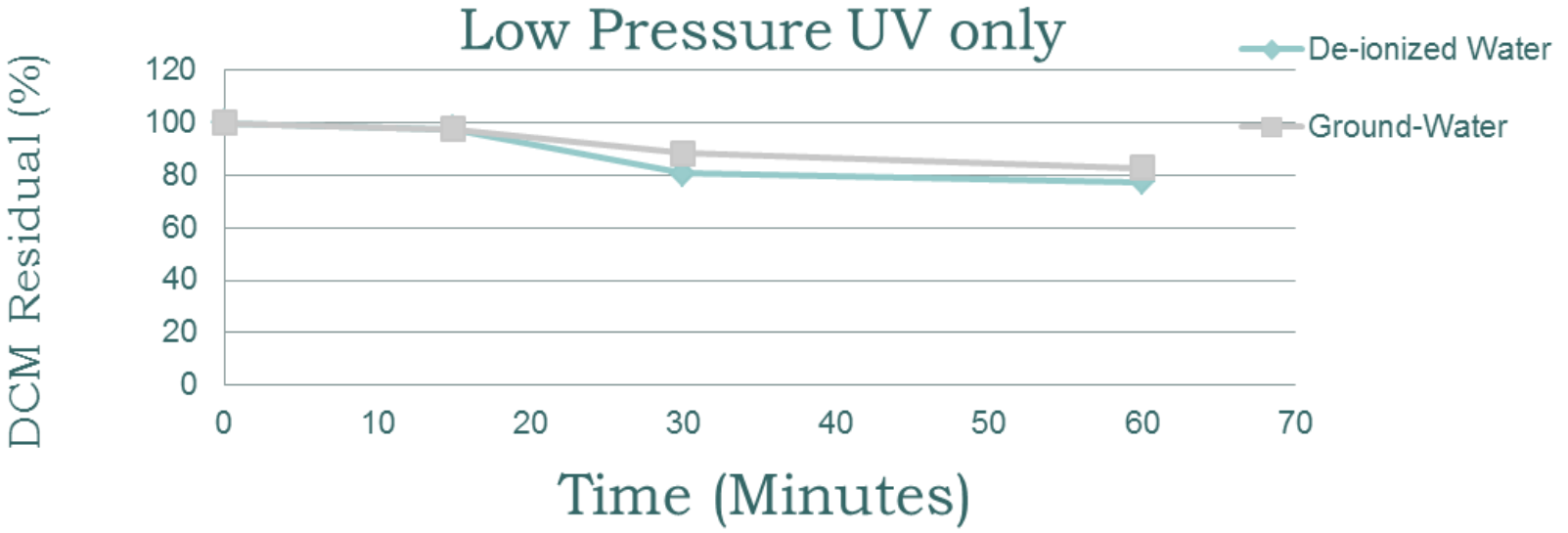


Figure showing percentage of mercury removal using LP UV H_2O_2 in ground and de-ionized water

Results and Discussion

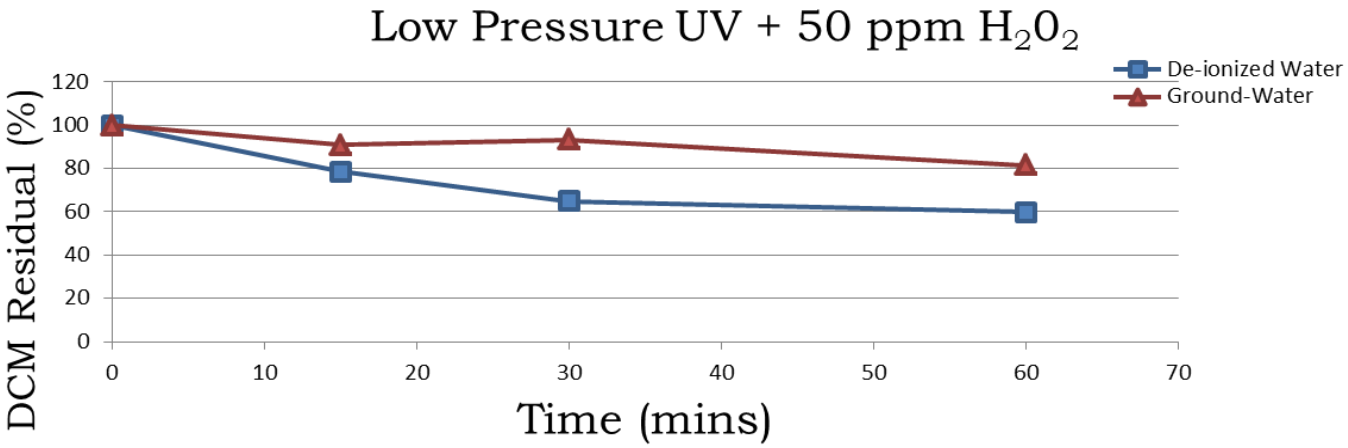


Figure showing percentage of mercury removal using LP UV + 50 ppm H_2O_2 in ground and de-ionized water

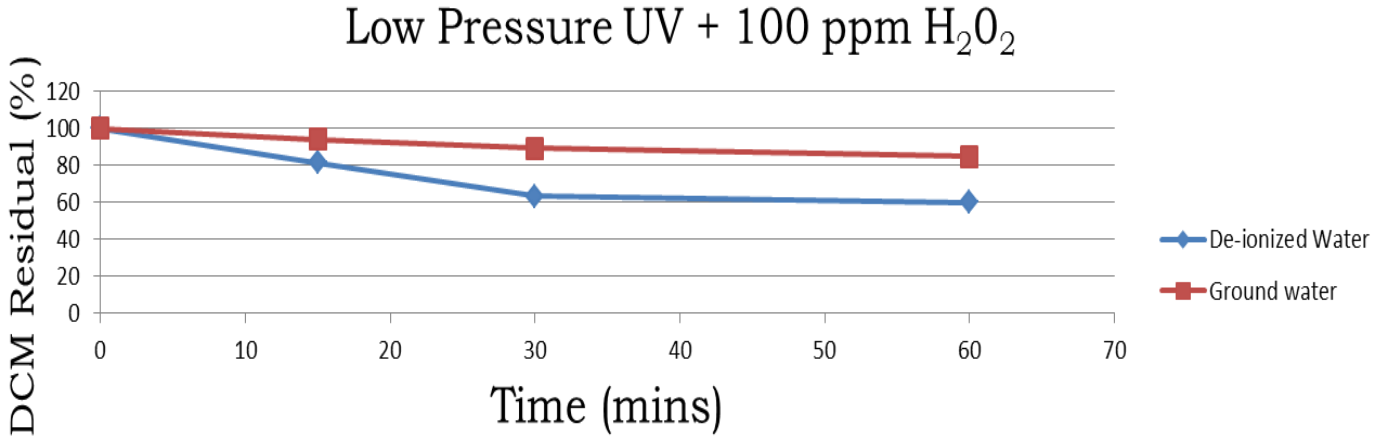


Figure showing percentage of mercury removal using LP UV + 100 ppm H_2O_2 in ground and de-ionized water

Results and Discussion

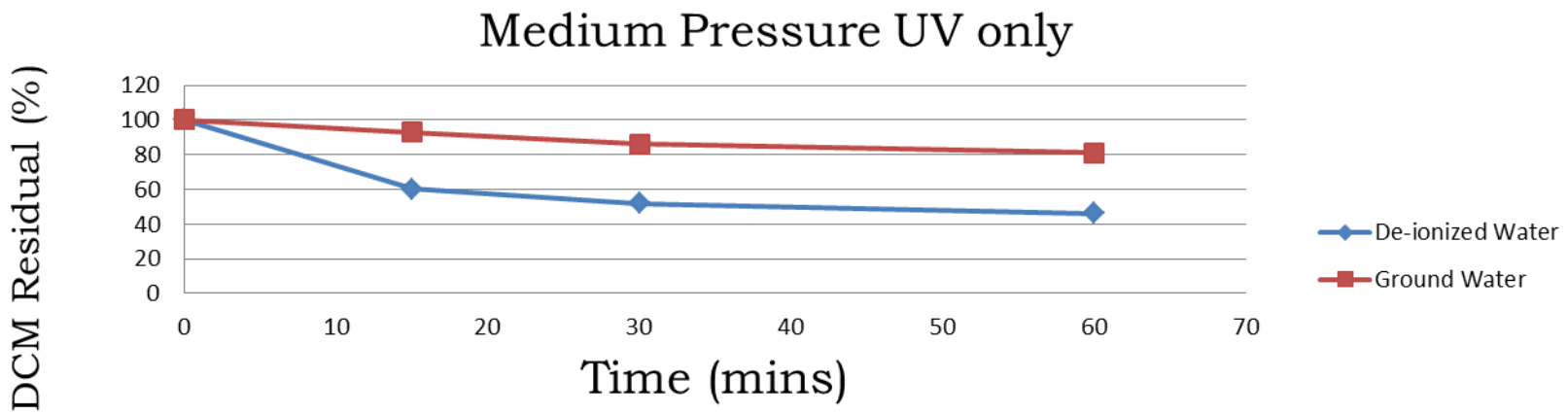


Figure showing percentage of mercury removal using MP UV only in ground and de-ionized water

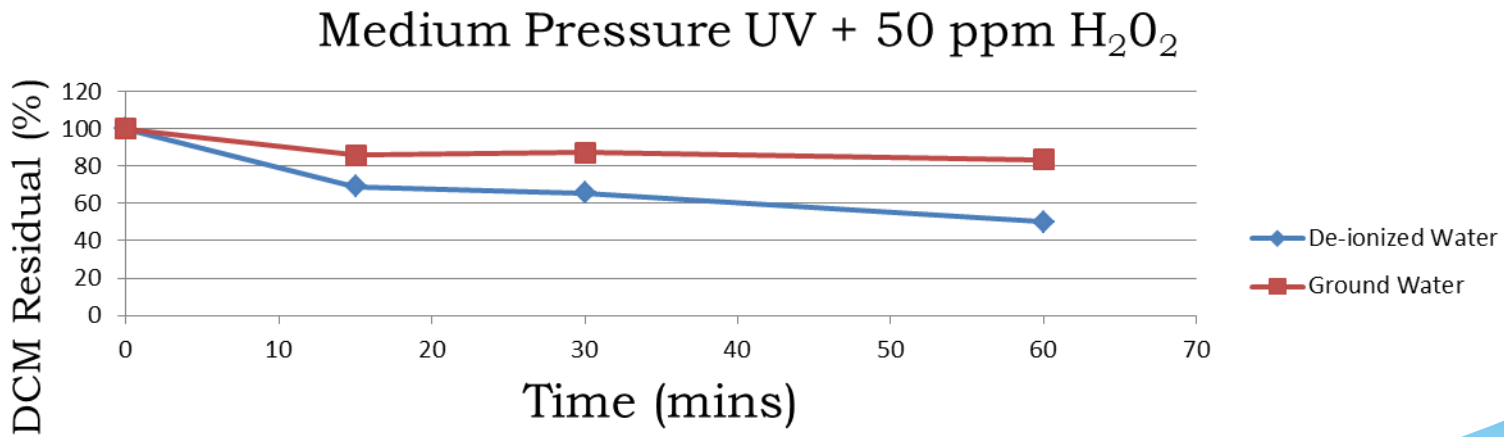


Figure showing percentage of mercury removal using MP UV + 50 ppm H_2O_2 in ground and de-ionized water

Results and Discussion

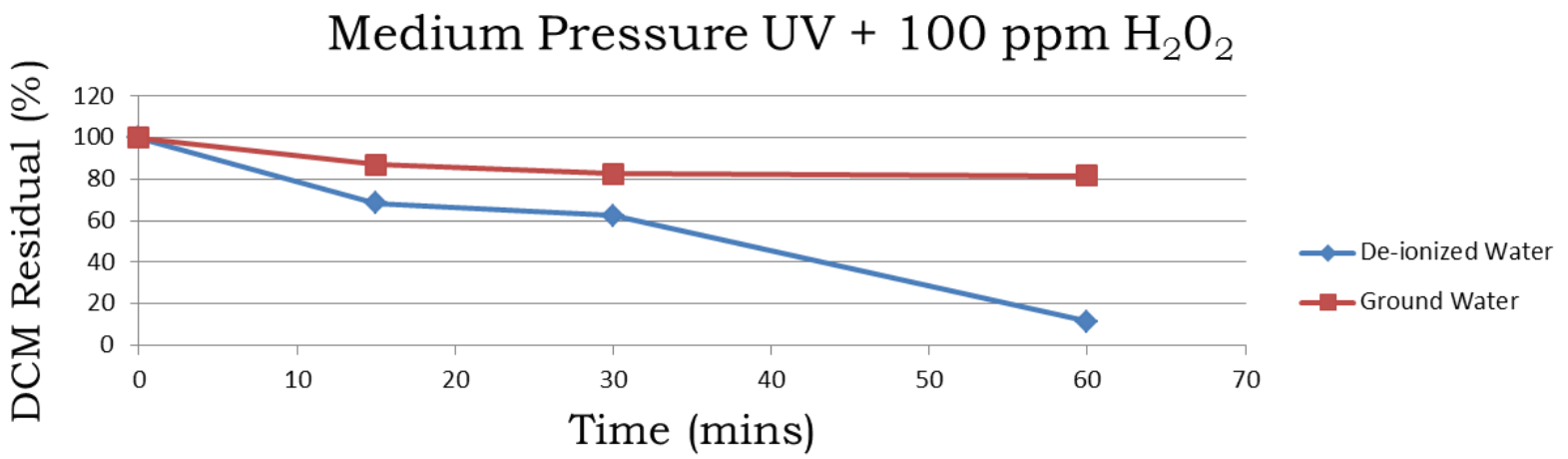


Figure showing percentage of mercury removal using MP UV + 100 ppm H_2O_2 in ground and de-ionized water

Conclusion

- The treatment process demonstrated low degradation more in groundwater samples compared to the de-ionized water samples
- This confirms the high stability and persistence of dichloromethane in water irrespective of the type of water in which it is dissolved
- Although the degradation rate increased more with time for de-ionized compared to the local ground water, the highest efficiency was obtained using medium pressure dichloromethane in combination with 100ppm

Conclusion

- The low removal efficiency in groundwater may be attributed to the presence of anions in these samples
- These anions may serve as radical scavengers, affecting the hydrogen radicals formed during the reaction.
- Anions are known to have more reactivity towards hydroxyl radical and as such may react with the radicals before the contaminant

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Thank You !