DEGRADATION AND REMOVAL OF TRIHALOMETHANES FROM DRINKING WATER

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

Degradation and Removal of Trihalomethane from Drinking Water

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A major problem that exists within the field of water treatment is that chemicals must be added to the influent in order to disinfect the water. The most common disinfectant used is chlorine, which has the tendency to react with organic matter in water to form certain disinfection-by-products (DBPs). These include trihalomethanes (THMs), which are suspected carcinogens found in trace amounts in drinking water. The US Environmental Protection Agency has announced a limit of 0.08 mg/L for the THMs. Previous research has shown that zinc oxide (ZnO) is able to effectively degrade other contaminants, and that UV light can aid in the degradation of certain contaminants by the creation of hydroxyl radicals. This experiment's aim is to test the effectiveness of ZnO to remove THMs as anew method to eliminate these compounds from drinking water.

ACKNOWLEDGEMENTS

NOMENCLATURE

DBP   Disinfection By Product

ZnO   Zinc Oxide

THM   Trihalomethanes

HAA5   Haloacetic Acids

GC/MS   Gas Chromatography Mass Spectrometry

NDMA   N-Nitrosodimethylamine

$CHBrCl_2$ Bromodichloromethane

$CHBr_3$ Bromoform

$CHCl_3$ Chloroform

$CHBr_2Cl$ Dibromochoromethane

CHAPTER I

INTRODUCTION

A problem with water treatment prior to desalination

Due to the pervasive droughts in the Western United States, there is currently a huge need in our country for large-scale seawater desalination and water treatment to provide clean water for human consumption and agricultural use. When desalinating water, it is important to use chemical disinfectants to make sure the water is safe for use. However, a big problem lies in that some of the chemicals used for disinfection, particularly chlorine, form disinfection by-products when they react with organic matter, which can form harmful compounds that are strictly monitored by many regulation agencies (Kim et al. 2015).

Disinfection by-products and why they matter

Most research that has currently been done in regard to water treatment has been focused on surface water, wastewater, and power plants, but very little is known about these DBPs and how they form when treating seawater. The most common types of DBPs are trihalomethanes (THMs), which are known carcinogens that form from the reaction of chlorine or bromine with organic matter. Other DBPs are haloacetic acids (HAA5), 1,4-dioxane, and chlorite. The rate at which these DBP form when in contact with chlorine is strongly dependent on the dosage of chlorine and the contact time. Seawater treatment can be especially challenging because it contains high levels of iodine and bromine, which can lead to the formation of particularly toxic DBPs (Kim et al. 2015).

CHAPTER II

METHODS

Theoretical experimental background

This experiment tests the effectiveness of using photo catalytic processes to degrade harmful THMs in a water-based solution. The way this is done is by using an energy source and a semi-conducting metal to transfer energy to create free radicals within the solution. In this experiment, the ZnO acts at the semi-conductor and the UV light is the power input. The UV light will provide energy input into the ZnO by exciting its electrons, which will then transfer this energy into an aqueous solution. As the water receives this energy influx, the OH will be converted to OH^- as a free radical is released in the solution when they receive the energy from the UV light via the ZnO. These free radicals will then carry energy into the present organic compound, in this case the THMs, and break their bonds. This ultimately leads to the degradation of the THMs, and leaves free chloride and bromide ions in the solutions.

Experimental design and procedure

The methodology that will be followed for this experiment will center around testing a mixture of 4 different DBPs after being introduced to commercial ZnO and UV light over different time steps. The mixture consists of $CHBrCl_2$, $CHBr_3$, $CHCl_3$, and $CHBr_2Cl$. The first solution that is to be prepared will use an 1 g/L concentration of ZnO and 75 uL of the DBP mixture in order to determine the overall effectiveness of the treatment. Tap water will be used in preparing the solution rather than DI water in order to replicate realistic experimental conditions. After the DBPs are exposed to the solution containing the ZnO, the sample will be placed in a dark, sealed

cabinet with direct exposure to UV light. The solution will then be evaluated using time steps of 12, 24, and 48 hours using an IC machine. At each time interval, the samples will be taken out and stored in a freezer until all samples are ready to be tested by the IC together. This will allow the exact percentage of de-chlorination to be known that will occur in proportion to the original amount to measure the effectiveness of the degradation of these DBPs. There will be 12 total samples run with this THM mixture. This will allow for one control sample at 0, 12, 24, and 48 hours that will have no exposure to ZnO at all, but will still be exposed to the UV light. This will allow testing to see if it is the ZnO or UV light that is responsible for the majority of the degradation. The other samples will be run in duplicate in order to verify their results.

After testing the THM mixture, the same experiment will be run with just $CHCl_3$ in order to determine the effectiveness of the de-chlorination alone. The same 1 g/l concentration of ZnO with water will be prepared, and 75 uL of the DBP will be added. The samples will be run in duplicates and tested every 12, 24, and 48 hours. After being tested, the samples are to be run with the IC machine to determine the percent level of de-chlorination.

CHAPTER III

RESULTS

A test experiment was conducted by initially creating a 1 g/L stock solution of ZnO in DI water, and then creating a 5 mL solution of both the ZnO concentrate and 75 uL of the DBP mixture. A control 5 mL solution was also created and frozen at time 0. The other solution was exposed directly to UV light for 5 days, then evaluated using a chloride probe. The ultimate de-chlorination of the solution was marked at 30.61%, demonstrating the ability of ZnO to degrade DBPs.

An extended test was conducted using 11 total samples containing 5 mL of the 1g/L ZnO solution and the 75 uL of THMs. The experiment consisted of duplicate samples to be tested at 0, 12, 24, and 48 hours, and a control sample for 0, 12, and 24 hours. The results from the IC machine confirmed the initial test experiment by demonstrating increased de-chlorination for each increasing time step. The results demonstrated an average of 14.53%, 21.68%, and 28.36% de-chlorination over the three time step intervals. A chart demonstrating the de-chlorination against time for the samples are shown in **Figure-1.** The control samples without the ZnO showed no de-chlorination. A more comprehensive breakdown of the experimental design and results are shown in **Table-1** and **Table-2** in the Appendix.

The same experiment was repeated with chloroform alone, with 12 total samples to be run, and 8 containing 5 mL of the ZnO solution and 75 uL of chloroform. Duplicate samples containing the chloroform and the ZnO were tested at 0, 12, 24, and 48 hours of UV exposure, and 4 control samples were created without ZnO to be tested over the same time interval. The results from the

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IC machine indicated a high level of de-chlorination, giving an average percentage between both the duplicates of 78.32%, 89.28%, and 86.25% over the course of the 3 time step intervals. **Figure-2** demonstrates the de-chlorination over time for the chloroform sample. The samples without the ZnO showed no de-chlorination at all. Further detailed design and results are shown in **Table-3** and **Table-4** in the Appendix.
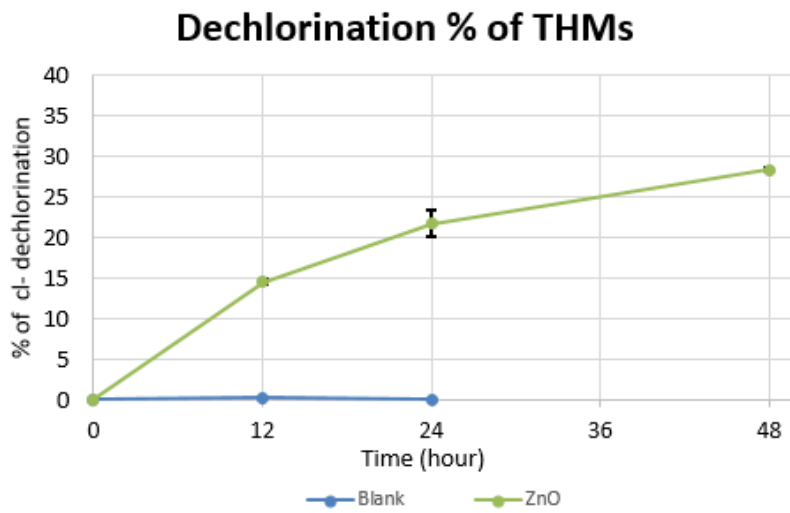

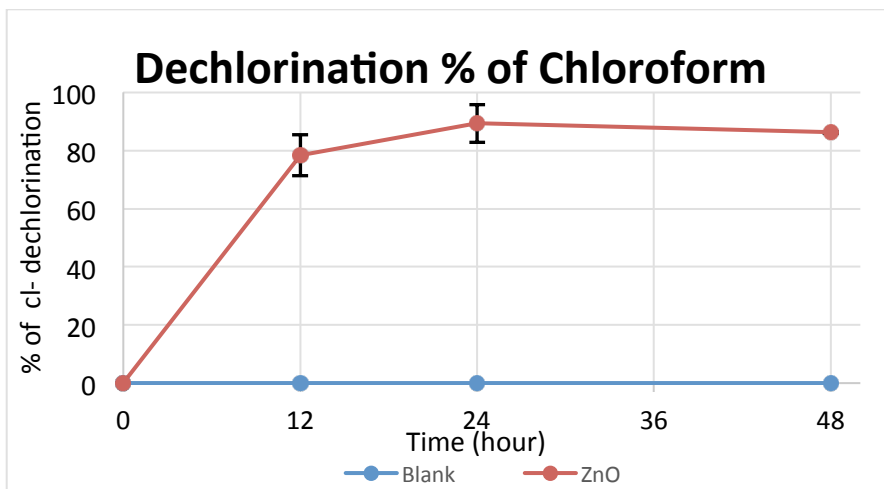**Figure-1 % De-chlorination of THM mixture samples vs. time**

Figure-2 % De-chlorination of chloroform samples vs. time

CHAPTER IV

CONCLUSION

ZnO, as a photocatalyst, appears to be a promising method to degrade harmful THMs and shows potential to be a useful step towards their treatment and ultimate removal from drinking water. The THM mixture showed a lower rate of overall de-chlorination, which could be because of heterogeneous bond types and geometries between the 4 different compounds, or because of the presence of bromine in 2 of the compounds affected the efficiency of the free radical's ability to release a free chlorine ion. There did appear to be a relationship of increasing de-chlorination over the increasing time steps. The chloroform samples tested demonstrated a much higher percentage of de-chlorination, but did not show any correlation between time and degradation. The control samples that had no ZnO showed no level of de-chlorination whatsoever, demonstrating the importance of the presence of a semi-conductor to transfer the energy from the UV light to the solution.

More research will have to be done in order to optimize the amount of ZnO and sensitivity analysis must be performed to determine the best way to utilize exposure to UV light in de-chlorinating THMs. Further research could also be done to determine why the process seems to work much faster and more effectively in the chloroform sample than the mixture. However, the process does exhibit the ability of the ZnO and UV light to break down these harmful compounds, which is an exciting prospect as more research and development are performed to best improve their effectiveness.

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	Dechlorination %			
	0	12	24	48
Blank	0	0.21	0.00	
ZnO	0	14.77	20.53	28.16
ZnO_2	0	14.28	22.83	28.56
ZnO_A	0	14.53	21.68	28.36
ZnO_STD	0	0.35	1.63	0.28

Table-1 THM mixture de-chlorination results

	Preparation Exp Samples					Preparation IC samples	IC results concentration (ppb)			
Samples	Liq Vol (ml)	Vol of stock solution to be	Final Concentration (mg/L)	theoretical Cl-released (mM)	theoretical Cl-released, ug/L (ppb)	Liq Vol (ml)	0	12h	24h	48h
Blank	5	75	3	0.1310	4651	1	52.1	61.7	45.5	
ZnO	5	75	3	0.1310	4651	1	306.3	993.2	1260.9	1616.1
ZnO_2	5	75	3	0.1310	4651	1	306.3	970.5	1367.83	1634.3

Table-2 Experimental setup for THM mixture trial

	Dechlorination %			
	0	12	24	48
Blank	0.00	0.00	0.00	0.00
ZnO	0.00	83.33	93.86	85.99
ZnO_2	0.00	73.31	84.71	86.51
ZnO_A	0.00	78.32	89.28	86.25
ZnO_STD	0.00	7.09	6.47	0.37

Table-3 Chloroform de-chlorination results

	Preparation Exp Samples					Preparation IC samples	IC results concentration (ppb)			
Samples	Liq Vol (ml)	Vol of stock solution to be added (ul)	Final Concentration (mg/L)	theoretical Cl- released (mM)	theoretical Cl- released, ug/L (ppb)	Liq Vol (ml)	0	12h	24h	48h
Blank	5	75	3	0.0750	2663	1	0	0	0	0
ZnO	5	75	3	0.0750	2663	1	0	2218.7	2499.1	2289.5
ZnO_2	5	75	3	0.0750	2663	1	0	1951.9	2255.3	2303.4

Table-4 Experimental setup for chloroform degradation test