

## ALTERNATIVE TECHNIQUES TO INCREASE THE DECHLORINATION KINETICS OF ORGANIC CHLORAMINES

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### ABSTRACT

Organic chloramines are a potential source of aquatic toxicity. Destruction of organic chloramines by dechlorination with sulfur dioxide is possible. However, the reaction proceeds slowly. The goal of this study was to investigate reaction enhancements to accelerate the dechlorination of organic chloramines. The dechlorination enhancements investigated were 1. Aeration mixing, 2. Chemical addition, and 3. Radiation activation. Aeration mixing was done with an air diffuser. Chemical addition included an additional dechlorinating agent, sodium sulfide. Short-wave ultraviolet radiation applied to the reaction was the third alternative. Dechlorination rates were tracked using MICROTOX analysis. The results of this laboratory bench-scale investigation indicate that each of the enhancement alternatives did accelerate the dechlorination kinetics of organic chloramines.

### KEYWORDS

Dechlorination, organic chloramines, aeration, short-wave UV, sodium sulfide, MICROTOX.

### Introduction

Chlorination of wastewater treatment plant effluent can produce chlorination by-products when the effluent contains precursors that will react with chlorine. Chlorination of wastewaters containing organic nitrogen compounds such as glycine will produce organic chloramines. A method is needed to destroy the organic chloramines once they are formed.

Organic chloramines can have complex chemical structures. The destruction of organic chloramines using sulfur dioxide is an oxidation-reduction type reaction. The mechanism for oxidation-reduction type reactions requires the exchange of electrons during molecular collisions between reactants. Chemical kinetics literature has terminology for the inefficient exchange of electrons and uses the term "steric factor" to define the problem. The steric factor causes an increase in the activation energy needed for the successful exchange of electrons to complete the reaction (Moore, W.J., 1962).

Chlorinated/dechlorinated wastewater effluents have significant levels of aquatic toxicity. Application of dechlorinating agents reduces effluent toxicity at a slow rate; therefore, the potential for exceedance of regulatory limits remains a considerable issue (Helz and Nweke, 1995). An investigation of the dechlorination kinetics of organic chloramines prepared from the chlorination of model compounds with amino acid and peptide type structure provides important results. It was determined that the half-life of the reaction between specific organic peptide

chloramines and sodium sulfite is on the order of hours. Also, organic chloramines are not detectable using standard analytical methods for analysis of total residual chlorine (Stanbro and Lenkevich, 1982). Organic chloramines have low germicidal potential for disinfection of wastewater effluents (White, G.C., 1986).

The purpose of this laboratory investigation was to increase the dechlorination rate of organic chloramines such as glycine. The reaction enhancement alternatives were: 1. Aeration-mixing, 2. An additional dechlorinating chemical, sodium sulfide, and 3. Short-wave UV radiation.

## Methodology

This investigation was a laboratory bench-scale study. A 500 ml conical flask was used as a reaction chamber. Saturated chlorine water was the chlorinating agent. Saturated sulfur dioxide water was the dechlorinating agent. The MICROTOX Model 500 analyzer was used to measure toxicity. Total residual chlorine analysis was done using amperometric titration (Fisher & Porter Model 17T2000). A cylindrical aquarium air stone, 1-inch length was used for aeration. An Ultra-violet Products unit, Chromato-Vue, was used for UV radiation. Glycine solution test samples were used for this study. Glycine solution samples containing ammonia-N were made up using chlorine-free tap water.

The three dechlorination enhancement alternatives were individually tested using the same test sequence. Sample A was the control sample; Sample B was the experimental sample; Sample C was an auxiliary control sample. Glycine solution samples were chlorinated at the same applied dose of 4.5 mg/l. The resulting TRC was 4.0 mg/l. The chlorination contact time for all test samples was 15 minutes. Sample A test samples were dechlorinated using 1.2 SO<sub>2</sub>:1 part TRC. Sample B test samples were dechlorinated with 1.2 parts SO<sub>2</sub>:1 part TRC plus a reaction enhancement. Sample C test samples were dechlorinated with 3.0 parts SO<sub>2</sub>:1 part TRC.

The dechlorination kinetics were tracked using the MICROTOX test. Aliquots of test samples were taken from the reactor at time = 0, 20, 40 minutes and analyzed. Each aliquot of test sample was measured for toxicity. Results were obtained as EC<sub>50</sub> values at 5, 10, and 15 minutes of incubation. Effective concentration (EC<sub>50</sub>) is the % concentration of a test sample that causes a defined response, which is a 50% loss of light emission. A lower EC<sub>50</sub> value indicates higher toxicity.

## Results

### Test Series 1 - Aeration mixing.

For test series 1, glycine solution was tested using aeration mixing as the dechlorination enhancement.

Samples 1-A, 1-B and 1-C make up the first glycine solution test group. After 15 minutes of contact, this solution was divided into portions. Portion #1 was dechlorinated at the 1.2 SO<sub>2</sub>: 1.0 TRC and was immediately subdivided into 1-A and 1-B. Sample 1-A was mechanically stirred. Sample 1-B was mixed by aeration. Portion #2 of the chlorinated glycine solution was used to make up sample 1-C which was dechlorinated at a level of 3.0 SO<sub>2</sub>: 1.0 TRC and was

mechanically stirred. Table 1 contains the results. Samples 1-A and 1-C had a decrease in toxicity during the 40-minute time interval. Sample 1-B, the aerated sample, had a significant decrease in toxicity.

**Table 1 – Aeration**

	<b>MICROTOX EC50</b>		
<b>Time 0</b>			
5 min.	12.36		12.37
10 min.	7.80		7.76
15 min.	5.81		5.99
	<b>1 - A</b>	<b>1 - B</b>	<b>1 - C</b>
<b>Time 20</b>			
5 min.	16.01	23.34	17.07
10 min.	10.16	14.16	11.77
15 min.	7.92	11.29	8.99
<b>Time 40</b>			
5 min.	22.00	61.54	21.36
10 min.	12.31	35.14	14.02
15 min.	10.43	26.04	11.29

An experiment was also carried out to determine if aeration mixing caused any loss of reactants as a result of volatilization. Test samples were prepared from glycine solution. After chlorination, the sample was dechlorinated using 1.2 parts SO<sub>2</sub>:1 part TRC. The sample was immediately divided into two portions. Sample A was mixed by aeration and Sample B was mechanically stirred. Chemical analysis of both samples after 40 minutes of contact time determined that there was no loss of ammonia-N or organic N or COD from either the mechanically stirred or the aeration mixed sample.

### **Test Series 2 - Chemical addition.**

The second part of this investigation studied the improvement in dechlorination rate using sodium sulfide in combination with sulfur dioxide. The combination of 1.2 part SO<sub>2</sub>: 0.5 part Na<sub>2</sub>S: 1.0 part TRC was determined from preliminary tests to be the most effective dose.

The set of the glycine solution samples, 2-A, 2-B and 2-C was chlorinated and after 15 minutes was divided into three portions. The chlorinated glycine solution samples were dechlorinated as follows: 2-A - 1.2 parts SO<sub>2</sub>: 1 part TRC, 2-B - 1.2 parts SO<sub>2</sub>: 0.5 part Na<sub>2</sub>S: 1 part TRC and 2-C - 3.0 parts SO<sub>2</sub>: 1 part TRC. Test results are shown in Table 2.

**Table 2 – Chemical Addition**

	<b>MICROTOX EC50</b>		
<b>Time 0</b>			
5 min.	10.32	14.21	9.60
10 min.	6.27	7.99	5.45
15 min.	4.54	5.52	4.34
	<b>2 - A</b>	<b>2 - B</b>	<b>2 - C</b>
<b>Time 20</b>			
5 min.	18.88	>100	20.55
10 min.	11.04	>100	12.72
15 min.	8.57	>100	9.97
<b>Time 40</b>			
5 min.	26.59	>100	32.56
10 min.	15.80	>100	20.32
15 min.	11.32	>100	15.64

Sample 2-A and 2-C had high levels of toxicity after 40 minutes. Sample 2-B containing 1.2 SO<sub>2</sub> and 0.5 Na<sub>2</sub>S, show an EC<sub>50</sub> > 100 after just 20 minutes of reaction time; that is, toxicity was reduced significantly.

### **Test Series 3 - Radiation activation.**

The following test procedure was used for Test Series 3. The glycine solution was chlorinated and after 15 minutes of contact was divided into portions. Portion #1 samples were dechlorinated at a level of 1.2 parts SO<sub>2</sub>: 1 part TRC. Immediately, these samples were subdivided. Sample 3-A was mechanically stirred for 40 minutes; sample 3-B was exposed to short-wave UV radiation while being mechanically stirred. Portion #2 samples were dechlorinated at a level of 3 parts SO<sub>2</sub>: 1 part TRC and also mechanically stirred.

**Table 3 – Radiation Activation**

	<b>MICROTOX EC50</b>		
<b>Time 0</b>			
5 min.	11.63		10.30
10 min.	7.00		6.98
15 min.	5.31		5.57
	<b>1 - A</b>	<b>1 - B</b>	<b>1 - C</b>
<b>Time 20</b>			
5 min.	18.21	>100	15.48
10 min.	11.24	62.40	10.78
15 min.	8.41	48.21	8.08
<b>Time 40</b>			
5 min.	22.00	>100	20.30
10 min.	13.31	>100	14.52
15 min.	10.43	>100	11.70

Table 3 contains test series 3 results. Test results for Sample 3-B, which received UV exposure, had the most significant change in toxicity; that is no detectable toxicity was found in the 40-minute test sample. Results for samples 3-A and 3-C had detectable toxicity after 40 minutes.

## Conclusions

The following are the conclusions of this investigation:

1. Aeration mixing significantly increased the dechlorination rate of organic chloramines.
2. Chemical addition of 0.5 part sodium sulfide to 1.2 parts sulfur dioxide produced increased dechlorination kinetics.
3. Radiation activation using short-wave UV radiation increased the dechlorination kinetics.

## References

Helz, G. R.; Nweke, A. C. (1995) Incompleteness of Wastewater Dechlorination. *Environ. Sci. Technol.*, **29** (4), 1018.

Moore, W. J. (1962) Physical Chemistry, Third Edition, Prentice-Hall, Inc. Englewood Cliffs, N.J.

Stanbro, W. D.; Lenkevich, M. J. (1982) Slowly Dechlorinated Organic Chloramines. *Science*, **215** (215), 967.

White, G. C., (1986) Handbook of Chlorination, Second Edition, Van Nostrand Reinhold, New York.