The formation of N-Nitrosodimethylamine in wastewater and its dependence on the conditions of the surrounding system

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USC Viterbi School of Engineering

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Introduction

The disinfection of wastewater is a vitally important step in the process of producing potable drinking water that is safe for human consumption. The addition of free chlorine to wastewater often spurs reactions with secondary amines such as dimethylamine (DMA) to produce toxic disinfectant by-products (DBPs). For example, different species of chloramine react with precursors in the wastewater to form potent carcinogens such as n-nitrosodimethylamine (NDMA). NDMA is a toxic DBP that is known to cause cancer in humans. In our models, we will look at the concentration of certain compounds as a function of time in order to identify conditions with the highest NDMA yields. Additionally, we will be modelling different pH levels and the ratio of free chlorine to ammonia to determine a favorable set of conditions that support the lowest NDMA yields.[1]

Impact of Prof McCurry's Research

Professor McCurry's lab is devoted to finding ways to decrease the production of toxic disinfection byproducts found within wastewater. He and his students work to find efficient ways to provide potable reuse water that will one day be safe for human consumption. They study different methods of water disinfection and analyze the results in order to limit the amount of dangerous carcinogens produced during the process. As clean water is becoming more and more difficult to find, Professor McCurry's research offers an alternative method for producing potable water.

MATLAB Code

```
clear
clc
t = 0:0.0000001:0.00001;
[t,y]=ode45(@my_ode,t,[2;1;0;0;0;0]);
plot(t,y(:,4),'-x');
grid
```

```
dC(1) = -k1*C(1)*C(2)+ k2*C(3)- k3*C(1)*C(3) + k4*C(4) + 
dC(2) = -k1*C(1)*C(2) + k2*C(3) + k5*2*C(3) - k6*C(4)*C(2
dC(3) = k1*C(1)*C(2)- k2*C(3)- k3*C(1)*C(3) + k4*C(4) - 2
dC(4) = k3*C(1)*C(3) - k4*C(4) + k5*2*C(3) - k6*C(4)*C(2)
dC(5) = ((k7*C(4))/10^(-7)) - k8*C(4)*C(5) - k9*C(3)*C(5);
```

Figure 1: Screenshot of the MATLAB code used to model the mechanism. The top image shows the command used to plot the graph. The bottom image includes some of the rate laws written based off the reaction scheme proposed by Professor Daniel McCurry.

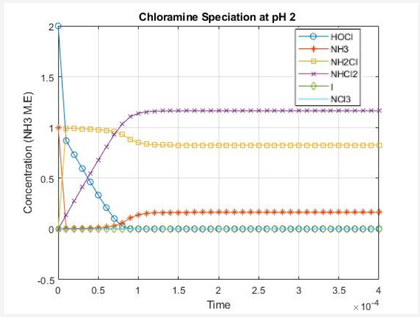
Skills Learned

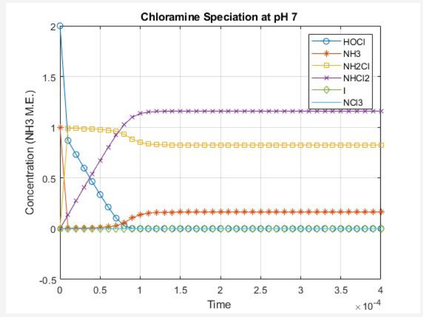
- MATLAB
- Lab safety
- Analysis of results
- At home chlorine testing
- Use of scholarly literature

References

[1] Huang, M. Huang, S. McCurry, D. (2018). Re-Examining the Role of Dichloramine in High-Yield N-Nitrosodimethylamine Formation from N,N-Dimethyl-α-arylamines, 2018.

Results





- At a low pH, the formation of dichloramine is slightly higher than at a neutral or basic pH.
- The concentration of monochloramine and dichloramine is much lower at a high pH.
- Dichloramine is known to react with precursors to produce NDMA in high yields.

Figure 2: Chloramine speciation at different pH levels. The graph at the top left is modelled at pH 2, the graph in the top right is at pH 7, and the bottom graph is at pH 11.

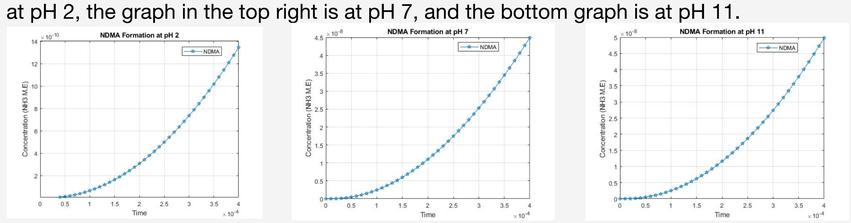


Figure 3: These graphs depict the isolated formation of NDMA at pH 2 (left), pH 7 (middle), and pH 11 (right).

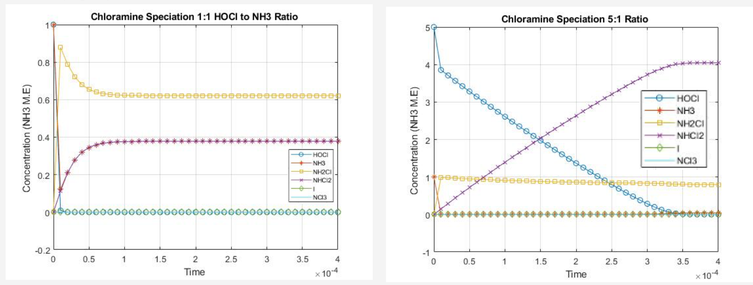


Figure 4: Chloramine speciation at pH 7 with different free chlorine to ammonia concentration ratios. Left: 1:1, right: 5:1. The concentrations are in molar equivalent to ammonia.

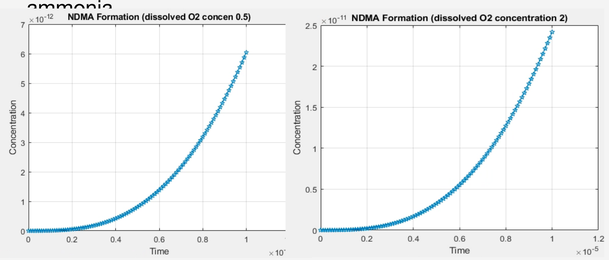


Figure 5: These graphs model the formation of NDMA at pH 7 based on the concentration of dissolved oxygen in the wastewater. The graph on the left had a starting concentration of oxygen at 0.5. The graph on the right had a starting concentration of 2.

Testing the Chlorine Levels of my Tap Water

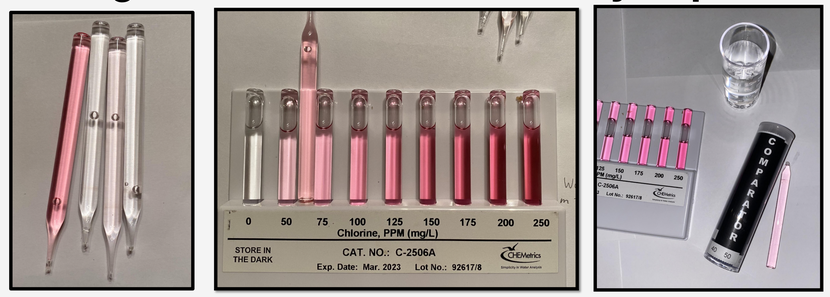


Figure 6: Using the CHEMets Chlorine Test Kit, I tested my tap water, distilled water, Brita filtered water, and Arrowhead bottled water for their chlorine concentrations. Those four samples are shown in respective order in the far-left image.

- Chlorine levels were highest in tap water. The filtered water contained less than 5 mg/L of chlorine
- In both the bottled water and distilled water, the indicator did not change color, meaning that they contained negligible concentrations of chlorine.

Conclusion

The data I collected suggests that NDMA formation is lowest at an acidic pH while dichloramine formation is lowest at a basic pH. NDMA formation was highest at pH 11 which contradicts the graphs in Figure 2. Dichloramine formation at pH 11 is lowest, which would usually be a sign that NDMA formation would also be low (due to the nature of the overall reaction mechanism). This discrepancy can most likely be attributed to another factor within the system that is causing NDMA formation to increase at a high pH. When the ratio of free chlorine to ammonia is high (i.e. a lot of initial HOCl), there is a higher yield of dichloramine. Additionally, the graphs in Figure 5 suggest that this is an oxidizing process since higher levels of dissolved oxygen yield more NDMA.

Relation to my Coursework

- I took Honors Chemistry last year and will be continuing my studies by taking AP Chemistry next year. Thanks to SHINE, my understanding of reaction kinetics has improved, and I am excited to search for real world applications of the topics I study in class. SHINE has also prepared me for high level analysis and the ability to be accepting of the unknown.
- Prior to completing SHINE, I had very little coding experience. Due to Covid-19, our lab was forced to use MATLAB to model the wastewater systems rather than collecting data. This shift proved to be rewarding, as I was introduced to an unfamiliar field of engineering and was challenged to acclimate to a completely new environment while also learning more about programming.

Acknowledgements

I want to say thank you to my professor, Dr. Daniel McCurry and my mentor, Lily Shi who helped me understand their research and answered all my questions. Also, a huge thank you to the whole SHINE 2020 cohort, Dr. Mills, Cathalina, and all the center mentors who guided me through this process.