Chlorine Radical Applications to Wastewater Treatment

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INTRODUCTION:

Advanced Oxidation Processes (**AOPs**) are a series of chemical filtration steps used in waste water treatment facilities. AOPs operate by using the photolysis of hydrogen peroxide or bleach to create hydroxyl radicals according to the following chemistry: **H_2O_2 + hv → •OH** and **HOCl + hv → •OH**, respectively. After the hydroxyl radical has been generated, an oxidation reaction occurs between the radical and contaminants to eliminate it within the waste water.

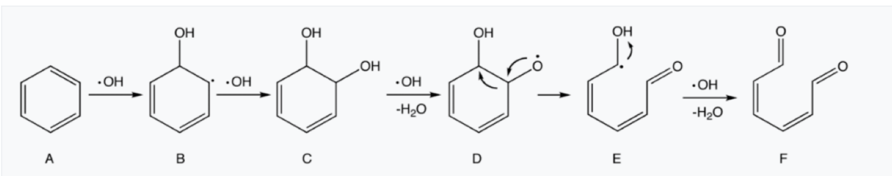


Figure 1. proposed AOP reaction mechanism involving benzene and hydroxyl radical

However, within the AOP another chemical species known as chloramines (**NHxCly**) are also present. Chloramines are added from previous filtration steps necessary to prevent biofouling. The chloramines present in the system will also photolyze and yield **chlorine radicals** according to the following chemistry: **NHxCly + hv → •Cl**. The chlorine radical can further react with a chlorine anion to produce a chlorine dimer radical: **•Cl + Cl- → Cl_2^-•** The AOP does not consider reactions involving chlorine radicals and waste water contaminants. Previous research has indicated that chlorine radicals are responsible for most of the chemistry taking place. **Hydroxyl radicals are only 0.0002% effective in their implementation.** Despite this, there is a lack of research behind the chemistry of chlorine radicals in the AOP. This study aims to quantify the chlorine, **•Cl**, chemistry taking place so that the AOP process is better understood and made more efficient.

METHODS:

- The photolysis of **$[Co^{2+}(NH_3)_5Cl]^{2+}$** is used to generate **•Cl** according to the following chemistry: **$[Co^{2+}(NH_3)_5Cl]^{2+}$+ hv → Co3+(NH3)5 + •Cl**

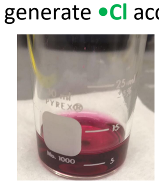
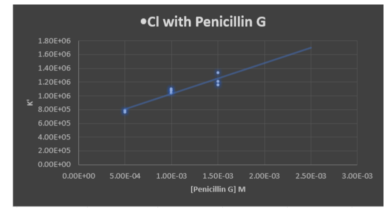
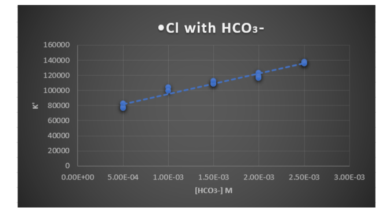


Figure 2. $[Co^{2+}(NH_3)_5Cl]^{2+}$ in solution

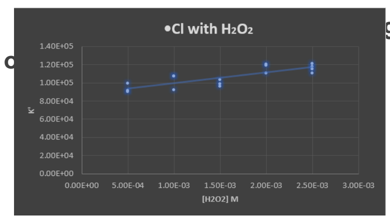
- The laser flash photolysis systems use short pulses (6 ns) of high-energy photons (wavelength = 308, 266 or 248 nm) to photolyze the aqueous solutions. Samples are prepared in fixed-volume cuvettes, and UV-Vis transient spectroscopy used to monitor the Cl radical absorbance directly.
- The solutions are kept slightly acidic pH (pH 4-6), and directly monitored using transient absorption spectroscopy.
- The absolute kinetic data of reactions between **•Cl** and waste water contaminants are compared to previous literature reported values, and to the analogous rate constants obtained for hydroxyl radical and the dichloride radical anion (**Cl_2^-•**)reactions.

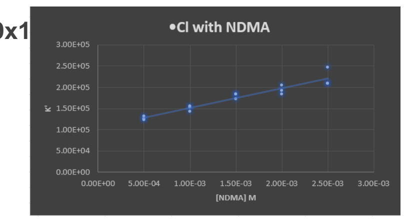
RESULTS:





•Cl reacted with the antibiotic Penicillin G, bicarbonate. hydrogen peroxide, and the known carcinogenic chemical NDMA. These chemicals would exist under waste conditions in AOP treatment systems.





The pseudo-first order K’ constant is plotted against the concentration of the previous chemicals to calculate the 2nd order rate constant, which is the true speed of the speed of the reaction.

CONCLUSION:

According to trends established in previous literature, it is highly likely that **•Cl** reacted with the chemicals in this experiment. This is likely the case as **•Cl** is unstable, and has a higher rate constant than hydroxyl and dichloride radical anion.

FUTURE WORK:

More rate constants of reactions involving **•Cl** are needed. Antibiotics, amino acids, and carcinogenic compounds that would be present in waste water will be tested to obtain kinetic data. Additionally, the rate constants obtained from these reactions will need to analyzed and compared to previous literature.

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ACKNOWLEDGEMENTS:

This research was supported by the National Institute of General Medical Sciences of the National Institutes of Health under Award Numbers; UL1GM118979; TL4GM118980; RL5GM118978. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health.

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