Disinfection of Drinking Water

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Importance of Disinfection of drinking Water

- Pathogens: bacteria, viruses and protozoa that can cause diseases

- Natural Organic Matter (NOM): materials from plants and animals, not harmful by themselves but react with disinfectants!
- Micropollutants: persistent pharmaceuticals, pesticides and industrial chemicals that present long-term health risks
- Clean water is essential for human health.
- Natural sources are minimal [1].
- Disinfection of dirty water is critical for safe consumption .

Drinking water disinfection

- Residual Chlorine Levels: Chlorine is added to water to inactivate microbial contaminants and prevent regrowth. However, as chlorine travels through the distribution system, it reacts with various substances, leading to a decrease in residual chlorine levels. If these levels fall below the recommended safety limits, there is an increased risk of microbial reactivation and regrowth, which can compromise water quality.
- Formation of Disinfection By-Products (DBPs): Chlorine reacts with natural organic matter (NOM) present in the water, leading to the formation of DBPs, which can be harmful to human health. High chlorine dosages can exacerbate this issue, resulting in elevated levels of DBPs in the water supply. Therefore, managing chlorine levels is crucial to minimize DBP formation while ensuring adequate disinfection.

UV Irradiation for Disinfection

- Ultraviolet (UV) light is a physical disinfection method that uses short-wavelength light to inactivate microorganisms [2, 3].
- Enhances disinfection by damaging microorganism DNA.
- Reduces DBP formation and degrades micropollutants.
- Effective against bacteria, viruses, and protozoa, including chlorine-resistant organisms
- Limitations: Ineffective against UV-resistant pathogens [3].

Experimental Insights

- Enhanced bacterial inactivation with combined UV and chlorine treatment.
- Complexity introduced by UV-induced chlorine decay in disinfection models.

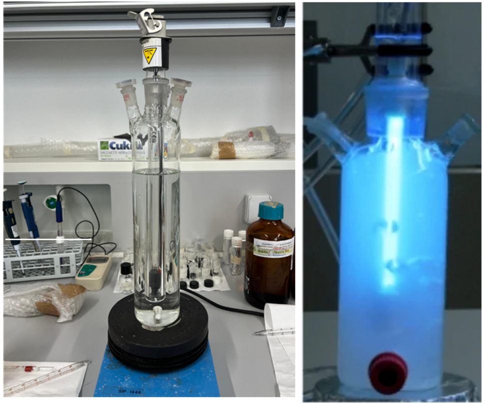

Figure: Lab scale photoreactor

Objectives

- Disinfection Efficiency: Evaluating the effectiveness of combined UV-Chlorine disinfection.
- Chlorine Consumption Pathways: Understanding the interactions between chlorine and NOM.
- Model Validation: Testing the proposed mathematical model against experimental data

Bacteria-Chlorine Model

- The initial model of Chick-Watson.

$$\frac{dB}{dt} = kC_0B,$$

where B is the bacteria poulation, C_0 is the initial chlorine population and k is an overall a rate constant.

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where B is the bacteria poulation, C_0 is the initial chlorine population and k is overall a rate constant.

- **The proposed model**: Setting the chlorine and bacteria populations are represented as ratios of the current population with the initial value, i.e. $C = C^*/C_0, B = B^*/B_0$.

$$\frac{dC}{dt} = -k_1BC,$$

Bacteria-Chlorine Model

- The initial model of Chick-Watson.

$$\frac{dB}{dt} = kC_0 B, \quad (1)$$

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- The proposed model: the chlorine and bacteria populations are represented as ratios of the current population with the initial value, i.e. $C = C^*/C_0, B = B^*/B_0$.

$$\frac{dC}{dt} = -k_1 BC,$$
$$\frac{dB}{dt} = -k_5 BC.$$

where $k_5 > k_1$. Subject to $C = B = 1$ at $t = 0$. No space dependence = Well-mixed

Bacteria-Chlorine Model

- The initial model of Chick-Watson.

$$\frac{dB}{dt} = kC_0 B, \tag{2}$$

where B is the bacteria poulation, C_0 is the initial chlorine population and k is overall a rate constant.

- The proposed model: the chlorine and bacteria populations are represented as ratios of the current population with the initial value, i.e. $C = C^*/C_0, B = B^*/B_0$.

$$\frac{dC}{dt} = -k_1 BC, \tag{3}$$

$$\frac{dB}{dt} = -k_5 BC. \tag{4}$$

where $k_5 > k_1$. Subject to $C = B = 1$ at $t = 0$. No space dependence = Well-mixed

Conts...

- The analytic solution of the proposed model is

$$C = 1 + K(B-1), \quad B = \frac{1}{(1+1/\omega^2)e^{K_1\omega^2 t} - 1/\omega^2}, \tag{5}$$

- where $\omega^2 = \frac{K_5}{K_1} - 1$ and $K = \frac{K_1}{K_5}$ is ratio of reaction constants.

E.Coli - Chlorine Against Data

Non-linear least squares data fitting

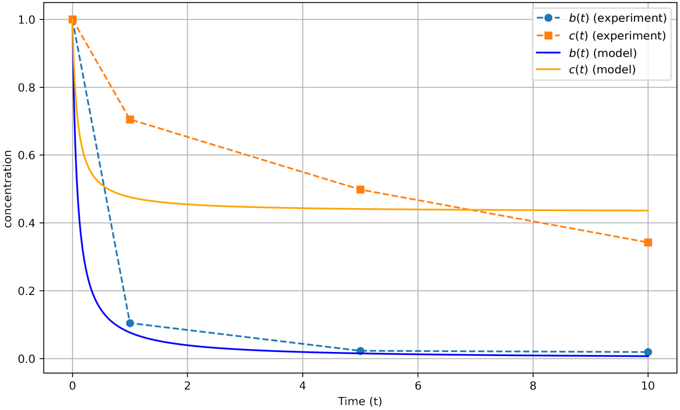

Figure: k = 0.5677, $k_c = 11.7865$, $\omega^2 = 0.00362$, $k_b = 20.7618$

Pseudomonas Aeruginosa-Chlorine Against Data

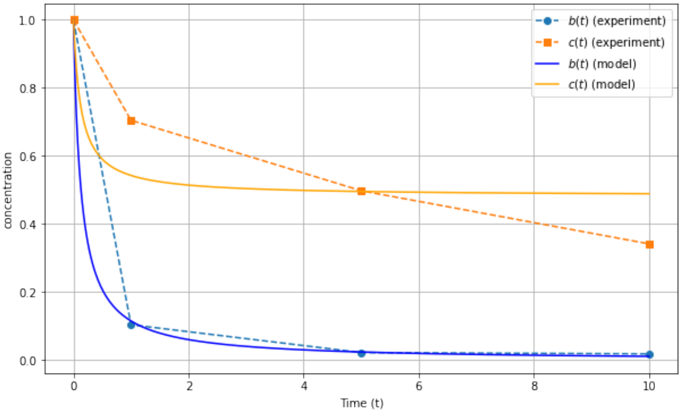

Figure: $k = 0.5167,\ k_c = 7.5409,\ \omega^2 = 0.0032,\ k_b = 14.5932$

UV-Bacteria

UV-Bacteria model

$$\frac{dB}{dt} = -k_7 B$$

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UV-Bacteria model

$$\frac{dB}{dt} = -k_7 B, \quad \text{thus} \quad B(t) = e^{-k_7 t}. \tag{6}$$

UV-Chlorine Reactions

UV light provides energy to break chemical bonds in HOCl and OCl^-, forming reactive radical species, which can further react:

$$\mathrm{HOCl} + \mathrm{UV} \rightarrow \mathrm{HO} \cdot + \mathrm{Cl} \cdot$$
$$\mathrm{OCl}^- + \mathrm{UV} \rightarrow \mathrm{ClO} \cdot + e^-$$

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Radicals *(Super-Chlorine)* react to form other radicals *(more Super-Chlorine)*:

$$\mathrm{HOCl} + \mathrm{HO}\cdot \rightarrow \mathrm{ClO}\cdot + \mathrm{H_2O}$$
$$\ldots$$
$$\mathrm{Cl}\cdot + \mathrm{Cl}^- \rightleftharpoons \mathrm{Cl_2}\cdot^-$$

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$$HOCl + UV \rightarrow HO\cdot + Cl\cdot$$
$$OCl^- + UV \rightarrow ClO\cdot + e^-$$

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...

Recombination of radicals to form Chlorine:

$$2\,Cl\cdot \rightarrow Cl_2$$
$$2\,HOCl\cdot \rightarrow 2\,HOCl$$

UV-Chlorine model(No bacteria)

- Setting S as population of Super-Chlorine

$$\frac{dC}{dt} =$$
$$\frac{dS}{dt} =$$

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$$\frac{dC}{dt} = -K_2 C$$
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UV-Chlorine model(No bacteria)

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$$\frac{dC}{dt} = -K_2 C - K_3 CS$$
$$\frac{dS}{dt} = K_2 C + K_3 CS$$

UV-Chlorine model(No bacteria)

- Setting S as population of Super-Chlorine

$$\frac{dC}{dt} = -K_2 C - K_3 CS + K_4 S$$
$$\frac{dS}{dt} = K_2 C + K_3 CS - K_4 S$$

UV-Chlorine model (No bacteria)

- Setting S as population of Super-Chlorine

$$\frac{dC}{dt} = -K_2C - K_3CS + K_4S$$
$$\frac{dS}{dt} = K_2C + K_3CS - K_4S$$

Subject to: $S(0) = 0, \quad \text{and} \quad C(0) = 1.$ The solution is

$$\ln\frac{(C - C_1)(1 - C_2)}{(C - C_2)(1 - C_1)} = -K_2(C_1 - C_2)t$$

UV-Chlorine model (No bacteria)

- Setting S as population of Super-Chlorine

$$\frac{dC}{dt} = -K_2 C - K_3 CS + K_4 S \tag{11}$$
$$\frac{dS}{dt} = K_2 C + K_3 CS - K_4 S \tag{12}$$

- Subject to: $S(0) = 0, \quad \text{and} \quad C(0) = 1.$ The implicit solution is

$$\ln \frac{(C - C_1)(1 - C_2)}{(C - C_2)(1 - C_1)} = -K_2(C_1 - C_2)t \tag{13}$$

where $C_1 > C_2 > 0 = \frac{\alpha \pm \sqrt{\alpha^2 - 4K_3K_4}}{2K_3}$ and $\alpha = K_2 + K_3 + K_4$.

Conts..

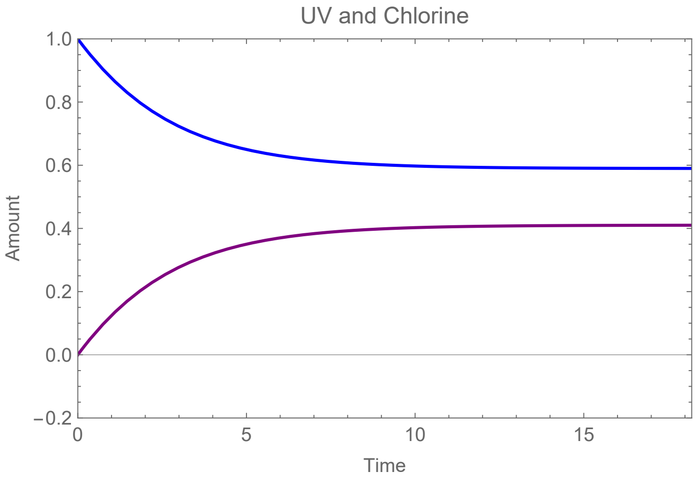

Figure: Numerical solution of UV-Chlorine when $k_2 = 0.15$, $k_3 = 0.2$, and $k_4 = 0.32$.

UV-Chlorine and Bacteria Model

- The Overall Model

$$\frac{dC}{dt} = -K_1 BC$$
$$\frac{dB}{dt} = -K_5 BC$$

UV-Chlorine and Bacteria Model

- The Model

$$\frac{dC}{dt} = -K_1 BC - K_2 C - K_3 CS + K_4 S,$$
$$\frac{dB}{dt} = -K_5 BC$$
$$\frac{dS}{dt} = K_2 C \qquad + K_3 SC - K_4 S.$$

UV-Chlorine and Bacteria Model

- The Model

$$\frac{dC}{dt} = -K_1 BC - K_2 C - K_3 CS + K_4 S,$$
$$\frac{dB}{dt} = -K_5 BC - K_6 BS - K_7 B,$$
$$\frac{dS}{dt} = K_2 C - K_8 BS + K_3 SC - K_4 S.$$

UV-Chlorine and Bacteria Model

- The Model

$$\frac{dC}{dt} = -K_1 BC - K_2 C - K_3 CS + K_4 S, \quad (14)$$

$$\frac{dB}{dt} = -K_5 BC - K_6 BS - K_7 B, \quad (15)$$

$$\frac{dS}{dt} = K_2 C - K_8 BS + K_3 SC - K_4 S. \quad (16)$$

- Where $K_i, i = 1, 2, ..., 8$ are the overall rate constants.
- Subject to:

$$S(0) = 0, \quad \text{and} \quad C(0) = B(0) = 1.$$

UV-Chlorine and Bacteria Model solution

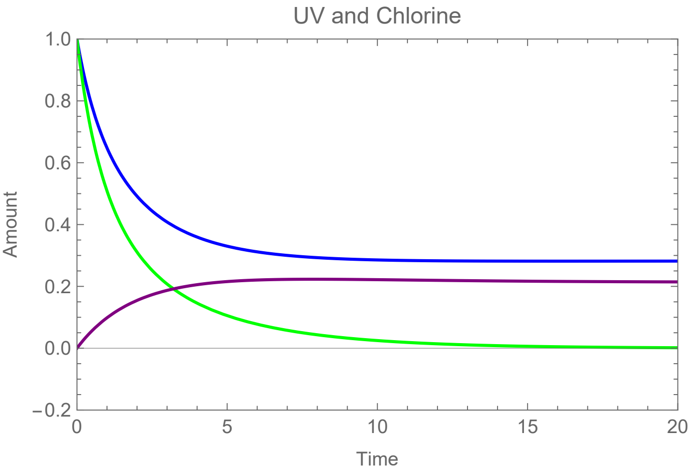

Figure: $k_1 = 0.44$, $k_2 = 0.131$, $k_3 = 0.187$, $k_4 = 0.226$, $k_5 = 0.8$, $k_6 = 0.089$, $k_7 = 0.028$, $k_8 = 0.031$

UV-Chlorine , Bacteria and Organic Matter Model

- Assuming we start off with clean water *(no dirt but there is still bacteria)*

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$$M(t) = 1 - B(t) \quad , \quad M(0) = 0$$

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- The model

$$\frac{dC}{dt} = -K_1 BC - K_2 C - K_3 CS + K_4 S$$
$$\frac{dB}{dt} = -K_5 BC - K_6 BS - K_7 B,$$
$$\frac{dS}{dt} = K_2 C - K_8 BS + K_3 SC - K_4 S$$

$$S(0) = 0 \quad \text{and} \quad C(0) = B(0) = 1$$

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- Assuming we start off with clean water *(no dirt but there is still bacteria)*
- The dead bacteria become part of the organic matter $M(t)$ which then also reacts with the chlorine and the super-chlorine

$$M(t) = 1 - B(t) \quad , \quad M(0) = 0$$

- The model becomes,

$$\frac{dC}{dt} = -K_1 BC - K_2 C - K_3 CS + K_4 S - K_9 MC,$$
$$\frac{dB}{dt} = -K_5 BC - K_6 BS - K_7 B,$$
$$\frac{dS}{dt} = K_2 C - K_8 BS + K_3 SC - K_4 S - K_{10} MS.$$

$$S(0) = 0 \quad \text{and} \quad C(0) = B(0) = 1$$

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- Assuming we start off with clean water *(no dirt but there is still bacteria)*
- The dead bacteria become part of the organic matter $M(t)$ which then also reacts with the chlorine and the super-chlorine

$$M(t) = 1 - B(t) \quad , \quad M(0) = 0$$

- The model becomes,

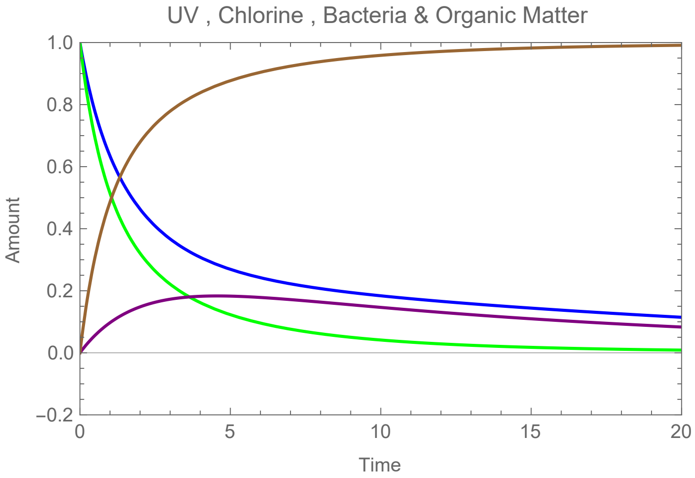
$$\frac{dC}{dt} = -K_1BC - K_2C - K_3CS + K_4S - K_9(1-B)C, \tag{23}$$

$$\frac{dB}{dt} = -K_5BC - K_6BS - K_7B, \tag{24}$$

$$\frac{dS}{dt} = K_2C - K_8BS + K_3SC - K_4S - K_{10}(1-B)S. \tag{25}$$

$$S(0) = 0 \quad \text{and} \quad C(0) = B(0) = 1$$

Solution with Organic Matter



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Perturbation approximation for small t

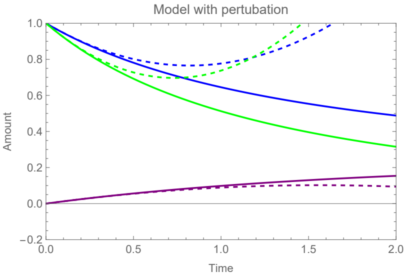
Use to estimate K's from early data points

- Applying the perturbation approximation by setting $t = \epsilon\tau$ and then $B = 1 + \epsilon f_1 + \epsilon^2 f_2$, $C = 1 + \epsilon g_1 + \epsilon^2 g_2$, $S = \epsilon r_1 + \epsilon^2 r_2$.
- Thus,

$$
\begin{aligned}
B &= 1 - \alpha_1 t + \frac{\alpha_2}{2} t^2, \\
C &= 1 - \beta_1 t + \frac{\beta_2}{2} t^2, \\
S &= \gamma_1 t + \frac{\gamma_2}{2} t^2,
\end{aligned}
\tag{26}
$$

Perturbation approximation for small t

where
$$\alpha_1 = K_5 + K_7, \quad \alpha_2 = K_5(K_1 + K_2 + K_5 + K_7) - K_6K_2 + K_7(K_5 + K_7),$$
$$\beta_1 = K_1 + K_2,$$
$$\beta_2 = (K_1(K_1 + K_2 + K_5 + K_7) + K_2(K_1 + K_2) - K_3K_2 + K_4K_2),$$
$$\gamma_1 = K_2, \quad \gamma_2 = -K_2(K_1 + K_2) - K_8K_2 + K_3K_2 - K_4K_2.$$



Leading order gives simple expressions for K's => early data important

Conclusion

- A series of models was proposed to capture the dynamics of disinfection in drinking water using chlorine, UV and their combination (c.f. previous models).
- Lots of K's - reduced models permit simpler calculation of K values
- Tested against limited data sets => reasonable agreement
- But ... don't have enough data to find all K's - sets have 4 data points (for 8 unknowns).

  Guessing K's we can do anything! Need to determine fixed K for a given effect

Conclusion

Future work:

- Need more experimental data = more experiments, **experiments with isolated effects**, e.g. UV+Cl
- Models appear surprisingly new - test against existing models. Explain issues/ inconsistencies with current models (e.g. contact time)
- Use in pipes - travelling wave implies simple extension
- **If K values known we can easily determine improved strategies**

Provide a foundation for optimizing disinfection processes, with potential applications in improving water treatment systems

Conclusion

References I

[1] Javier Gámiz et al. "Automated chlorine dosage in a simulated drinking water treatment plant: A real case study". In: *Applied Sciences* 10.11 (2020), p. 4035.

[2] Naoyuki Kishimoto. "State of the art of UV/chlorine advanced oxidation processes: Their mechanism, byproducts formation, process variation, and applications". In: *Journal of Water and Environment Technology* 17.5 (2019), pp. 302–335.

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