Chapter 3- PAA Disinfection Kinetics

1 Overview of current knowledge on the PAA mechanisms of microbial inactivation

This chapter provides an overview of the current state of knowledge about how PAA works. First, the most current research on mechanisms of action of PAA toward bacteria and viruses is explained, and the kinetics of those reactions is described. Next, a review of combined disinfection using PAA and UV is presented which includes an explanation of the PAA photochemistry, a discussion about the possible synergies between the two technologies, a proposed modeling technique to quantify combined disinfection, and finally an economic analysis to determine when combined disinfection is cost effective. Next, the kinetics of PAA decomposition and pathogen inactivation in wastewater is explained, and modeling techniques are described to quantify and predict inactivation. Following this is a detailed discussion about how commonly occurring water quality constituents in wastewater effect PAA decomposition and inactivation kinetics. Lastly, PAA dosing control strategies are explained and compared.

1.1 Mechanisms of PAA Microbial Inactivation

Among the compounds present in a PAA equilibrium quaternary mixture (i.e. acetic acid (CH_3COOH), hydrogen peroxide (H_2O_2), PAA (CH_3COOOH), and water (H_2O)), PAA itself had been shown to have the greatest antimicrobial properties compared to hydrogen peroxide and acetic acid (Wagner et al., 2002; Kitis et al., 2004). The mode of microbial inactivation of peracetic acid (PAA) for disinfecting wastewater, has received increasing attention over the past two decades. Different mechanisms based on different types and species or organisms have been advanced in the literature.

In investigating the mode of action of PAA, it is important to understand the speciation of PAA as a function of pH. PAA dissociates to peracetate anion (CH_3COOO^-) which has a pK_a of 8.2. At pH less than 8, the undissociated acid (CH_3COOOH) is the primary molecule and it

1   has greater antimicrobial activity than the dissociated peracetate anion which is prevalent at pH

2   greater than 8. (Liberti and Notarnicola, 1999; Koivunen and Heinonen–Tanski, 2005). The high

3   biocidal efficacy of PAA at pH less than 8 may be explained by the higher redox potential of

4   PAA at lower pH (i.e. E^0=1.748 volts versus the standard hydrogen electrode (SGE)at pH=0, and

5   E^0=1.005 volts versus the SHE at pH=14) (Zhang et al., 2018, Dunkin et al, 2018).

6   In addition to the previously discussed PAA species, the disinfection (e.g. inactivation of

7   microbes) and oxidation (e.g. degradation of micropollutants) properties of PAA in wastewater

8   treatment can also be attributed to the formation of reactive oxygen species (ROS) such as

9   hydroxyl radical (HO·), superoxide anion ($O_2^{\cdot-}$), hydroperoxyl radical ($HO_2^{\cdot}$), and peracyl

10   radicals (CH3COO·). These reactive species may contribute to the inactivation of bacterial cells

11   (Block, 1999). The formation of the aforementioned ROS during PAA disinfection may occur

12   through multiple reactions (Equations 3.1-3.7). The reaction described in Equation 3.1 represents

13   the formation of the acyloxy and hydroxyl radicals via homolysis of PAA. This reaction may be

14   initiated by activation of PAA by a transition metal catalyst or through UV radiation (Rokhina et

15   al., 2010; Luukkonen and Pehkonen, 2017).

16   Equation 3-1. CH3COOOH → CH3COO· + HO·

17   Equation 3-2. CH3COOOH + HO· → CH3CO· + O2 + H2O

18   Equation 3-3. CH3COOOH + HO· → CH3COOO· + H2O

19   Equation 3-4. CH3COO· → ·CH3 + CO2

20   Equation 3-5. 2CH3COO· → 2·CH3 + 2CO + O2

21   Equation 3-6. ·CH3 + O2 → CH3OO·

22   Equation 3-7. CH3COO· + HO· → CH3COOOH

23   Disinfection by PAA occurs according to reactions with against the bacterial wall, the

24   cytoplasmic membrane, or the metabolisms of the cell (Figure 3.1). These include (i) disruption

25   of cell wall and chemiosmotic function, (ii) disruption of biochemical process and intracellular

solute levels, (iii) enzyme, protein, and metabolic oxidation, and (iv) reduction of catalase
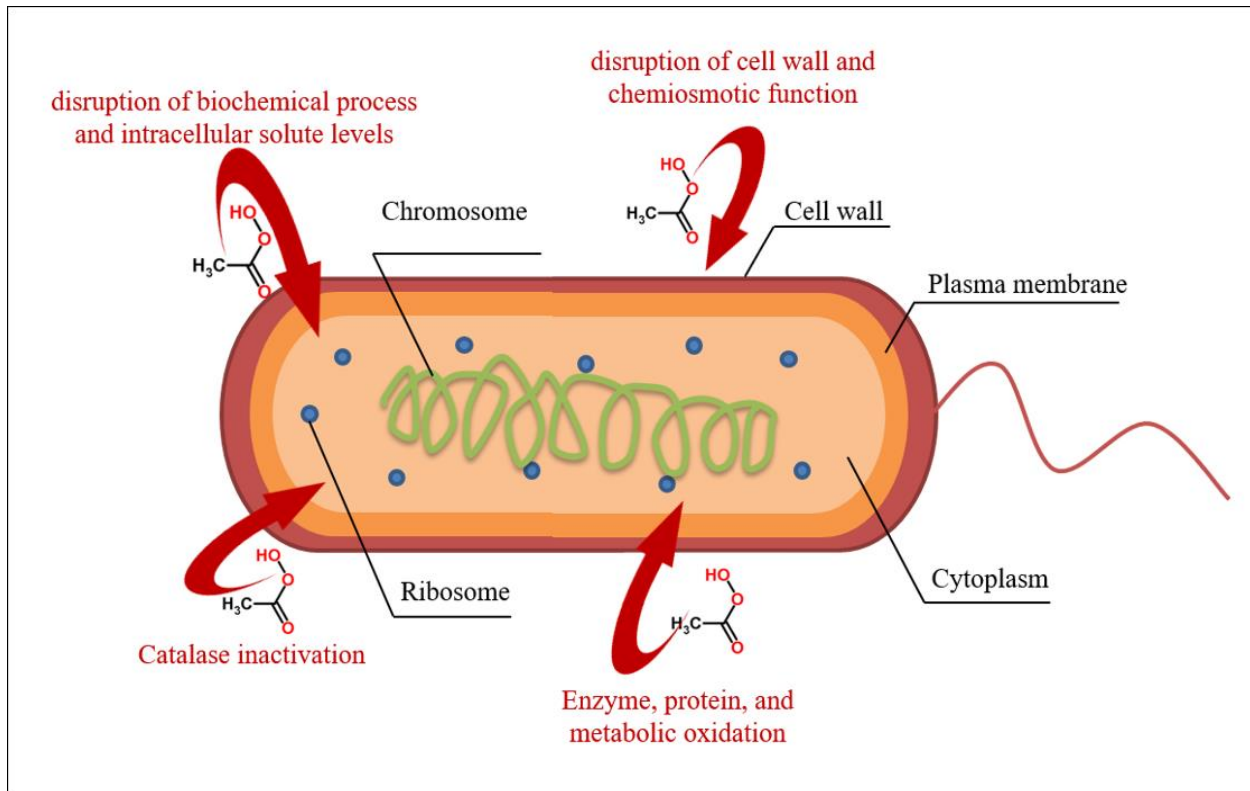
activity

Figure 3-1: Illustration of disruption of cellular targets by PAA

The disruption of the cell wall and chemiosmotic function occurs through reactions of

PAA with sulphydryl (-SH) groups, the disulfide (-S-S) bonds, and to double bonds within

enzymes, proteins and other metabolites contained in the cell membrane wall. Thus, the chemi-

osmotic function of the lipoprotein cytoplasmic membrane is interrupted, and the cell wall

permeability is increased (Baldry and Fraser, 1988; Lefevre et al. 1992; Liberti & Notarnicola,

1999). PAA may also penetrate intracellular and oxidize essential enzymes (e.g. the peroxidase),

causing the weakening of biochemical routes, and the disruption of the intracellular solute levels

(Fraser et al., 1984). The ovicidal properties of PAA are probably related to its protein

denaturation action, exemplified by its use as a sporocide (Block, 1991). The nucleotide bases of

1   DNA molecules may also be affected by PAA, disrupting cell replication. As opposed to the

2   oxidizing action of hydrogen peroxide, which is inhibited through the reduction of free hydroxyl

3   radicals by catalase enzymes found in all living organisms, PAA exerts damage though inner

4   diffusion (Block, 1991).

5   Despite the progress in investigating the modes of action of PAA in microbial

6   inactivation, they are not thoroughly understood. PAA inactivation in municipal wastewater is

7   complex because it results from combined pathways and simultaneous routes and modes of

8   action. Moreover, organic and inorganic constituents in municipal wastewater may promote or

9   inhibit various reactions Thus, future research is necessary to further elucidate the process and

10   role played by multiple species potentially involved in the inactivation of bacteria, viruses and

11   protozoa by PAA.

12   **1.1 Disinfection using a combination of UV and PAA**

13   In the last 20 years, numerous studies have been performed investigating potential

14   synergies between UV and PAA disinfection processes. A number of researchers have reported

15   on the benefits of combining of UV and PAA to enhance the disinfection of municipal

16   wastewater (Rajala-Mustonen et al., 1997; Lubello et al., 2002; Caretti and Lubello, 2003;

17   Koivunen et al., 2005; Budde and Vineyard, 2010; Gonzalez et al., 2012; Block and Tran, 2015).

18   However, the exact mechanism for this enhancement is not clear, and there is no general

19   consensus on how the combination of UV and PAA can result in an enhanced disinfection

20   process. It is generally reported that the addition of PAA before UV irradiation increases

21   inactivation by the result of an advanced oxidation process (AOP), resulting from the photolysis

22   of the O–O bond in the PAA molecule, generating a hydroxyl radical ($\cdot$OH) (Lubello et al.,

23   2002; Caretti and Lubello, 2003). While investigating the combination of UV and PAA, Lubello

24   et al. (2002) found a PAA concentration between 2 and 8 mg/L or a UV fluence of 120 to 300

1   mJ/cm2 were unable to reach the target disinfection levels; however, when a PAA concentration

2   of 2 mg/L was applied immediately before a UV fluence of 192 mJ/cm2, over 4 logs inactivation

3   of total coliforms was achieved. However, Gonzalez et al. (2012) reported that when peracetic

4   acid and ultraviolet irradiation were combined, at UV doses of 13 mJ/cm2 more relevant to

5   wastewater disinfection, there was no synergistic benefit observed of adding PAA before or after

6   UV irradiation. This highlights the ambiguity in the current understanding of the synergistic

7   effects of UV and PAA treatments.

8   If synergies do occur between UV and PAA disinfection, a few mechanisms can be

9   hypothesized. Where PAA precedes UV, it has been proposed that PAA can destabilize or

10   disrupt particle associated bacteria, thereby eliminating shielding mechanisms and enhancing

11   performance of downstream UV disinfection. Another hypothesis, which will be critically

12   discussed later in this section, is equilibrium PAA solutions can be photolyzed when exposed to

13   UV irradiation resulting in the formation of radical species that can enhance disinfection

14   performance. In summary, while some studies have purported a synergy between UV and PAA,

15   resulting in enhanced disinfection performance, more researchers have merely observed an

16   additive effect.

17   Even without disinfection synergies, there may be other advantages to combined

18   disinfection. The combined use of UV and PAA may lead to an integrated, green disinfection

19   solution that allows optimization of both capital and operating costs while minimizing

20   environmental impacts. UV systems offer the benefit of a chemical free solution, typically with

21   the lowest overall lifecycle cost. Recently, Murray et al. (2016) reported on the use of UV and

22   PAA disinfectants, and their combinations, for a very challenging secondary effluent. Murray et

23   al. (2016) performed 20-year NPV calculation for various combinations of UV and PAA

1   required to achieve a disinfection target of 126 cfu / 100 mL in a low quality, highly colored

2   secondary effluent. The study found that while UV alone always offered the lowest 20-year net

3   present value (NPV), there is still a benefit to combined disinfection if a utility had a capital

4   budget constraint. It was observed that a combined approach could meet disinfection targets

5   while offering a resilient and cost-effective approach that balanced capital and operating costs.

6   Thus, irrespective of whether or not there are mechanistic pathways that give way for a

7   synergistic UV and PAA disinfection process, there are clear operational and financial synergies.

8   **1.2.1   Photochemistry of PAA photolysis**

9   Equilibrium solutions of PAA contain a combination of PAA, H_2O_2, acetic acid, and

10   water. Of these four chemicals, under some conditions PAA and H_2O_2 can be photolyzed during

11   253.7 nm UV irradiation of wastewater, leading to the generation of radical species including

12   hydroxyl radicals and carbon centered radicals.

13   The first law of photochemistry states that in order for a photochemical reaction to occur,

14   a molecule must first absorb a photon (Bolton and Cotton, 2008). Beer's law relates the

15   attenuation of light to the properties of a material and states that the concentration of a chemical

16   is directly proportional the absorbance of a solution (Patnaik et al, 2018).

17   The photochemical parameter used to quantify the ability of a chemical to absorb light at

18   a specific wavelength is the molar extinction coefficient (ε, L/mol/cm). At the typical pH of

19   wastewater (pH 7-8), the molar extinction coefficient of H_2O_2 at 254 nm is 19.6 L/mol/cm

20   (Buxton et al. 1988). Under the same pH range, the molar extinction coefficient of PAA at 254

21   nm has been reported as 10.0 L/mol/cm (Cai et al. 2017). Given these molar extinction

22   coefficients and the typical equilibrium PAA solutions used in wastewater disinfection, Table 1.1

23   lists the absorbance by PAA and H_2O_2 in concentrated commercial solutions typically used in

1   wastewater disinfection. It is observed that for a 15% PAA solution, H_2O_2 will absorb more

2   photons than PAA but for 22% PAA, where the H_2O_2 concentration is relatively low, PAA is the

3   greater absorber. It should be noted that the relative concentrations of PAA and H_2O_2 will be

4   different when added to the wastewater due to different instantaneous reactions with the water

5   matrix as well as residual decays.

6   Table 3-1: Absorbance at 254 nm of H2O2 and PAA in PAA formulations typically used in
7   wastewater disinfection.

	Molar Concentration (mol/L)		Molar Extinction Coefficient (L/mol/cm)		Absorption Coefficient (cm^{-1})	
	PAA	H_2O_2	PAA	H_2O_2	PAA	H_2O_2
12% PAA, 20% H_2O_2	1.58	5.88	10.0	19.6	15.8	115.3
15% PAA, 23% H_2O_2	1.97	6.76	10.0	19.6	19.7	132.6
22% PAA, 5% H_2O_2	2.89	1.47	10.0	19.6	28.9	28.8

8

9   After a photon is absorbed, a photochemical reaction may occur. The measure of how

10 many photochemical products are formed per number of photons absorbed is known as the

11 quantum yield. Cai et al. (2017) reported the quantum yield at 254 nm of PAA as 1.2

12 mol/Einstein at neutral pH. It was argued that since this value is over twice the quantum yield at

13 254 nm of H_2O_2 (0.5 mol/Einstein), photolysis of PAA may generate more hydroxyl radicals

14 than photolysis of H_2O_2. However, it should be noted that as per the chemical reaction

15 expression, each mole of H_2O_2 can yield two moles of hydroxyl radical, and so, the apparent

16 quantum yield of H_2O_2 photolysis is 1.0. In contrast, each mole of PAA can only yield one mole

17 of hydroxyl radical. Therefore, from quantum yield, and efficiency, perspective PAA and H_2O_2

18 are similar in terms of their potential to generate hydroxyl radicals under exposure to 254 nm UV

19 irradiation.

1   It should be noted that although radicals can form from the photolysis of equilibrium

2   PAA solutions, this is a direct function of the oxidant concentration as well as the UV dose

3   applied. Moreover, since radical species are highly reactive and non-selective, not all generated

4   radicals react with the target species. Rather, the large majority of radicals generated are

5   "scavenged" by background organic and inorganic material in a wastewater matrix (Satinder,

6   2014). Using a simple photochemical model and assuming a steady-state hydroxyl radical

7   concentration, one can understand just how relevant the radical driven disinfection process is.

8   Therefore, given the low potential for radical generation, due to relatively low UV doses

9   and PAA concentrations applied in wastewater disinfection, and high potential for radical

10   scavenging, due to the high concentration of organics and inorganics in wastewater, it is

11   impractical to consider that UV plus PAA can be considered as a process for generating radical

12   species for disinfection at doses commonly applied at wastewater treatment plants. That said, a

13   combined UV and PAA disinfection process does have potential complementary benefits as well

14   as operational and cost synergies.

15   **1.2.2   Complementary inactivation kinetics**

16   The selection of order and sizing of a UV and PAA disinfection processes is dependent

17   on the disinfection kinetics of each disinfectant alone as well as potential synergies. For example,

18   an experimental methodology to determine order of disinfection and required doses may include

19   consideration of : (1) the dose response curve of each individual disinfectant, (2) the correlation

20   of microbial log inactivation to relevant treatment constraint (e.g., cost, time required, energy

21   demand, footprint, etc.), (3) an algorithm to determine the sequence and amount of disinfectant

22   dose where the disinfectant with the fastest kinetics (i.e., greatest slope) is always selected in

23   order to minimize the treatment constraint, (4) dose response curves generated for the

24   combinations of UV and peracid disinfectants; with each disinfectant applied sequentially, in

1 vice-versa order, and simultaneously. If synergies are observed for a particular sequence, this

2 sequence is selected.

3 Basically, by knowing the kinetics of each disinfectant alone, using the concept of multi-

4 target disinfection (i.e., the ability of two or more disinfectant to inactivate the same bacterial

5 population via two or more mechanisms or mode of actions), one can determine the most cost

6 effective sequence of the two disinfectants, and the relative amount that minimizes overall

7 treatment constraint (e.g. cost, footprint, energy demand, or time).

8 Below are reported several examples illustrating the application of this method to

9 maximize disinfection efficiency using UV and PAA. In the first scenario (Figure 3.2a), given

10 the slope of the fast and slow regimes of the UV and PAA kinetics, the best combination is PAA

11 first (to give the amount of kill noted on the left as PAA dose) and UV after (to give the amount

12 of kill noted on the left as UV dose). In the second scenario (Figure 3.2b), given the slope of the

13 fast and slow regimes of the UV and PAA kinetics, the best combination is UV first (to give the

14 amount of kill noted on the left as UV dose) and PAA after (to give the amount of kill noted on

15 the left as PAA dose). In the third scenario (Figure 3.2c), given the slope of the fast and slow

16 regimes of the UV and PAA kinetics, the best combination is PAA first (to give the amount of

17 kill noted on the left as PAA dose 1) followed by UV after (to give the amount of kill noted on

18 the left as UV dose), followed by PAA dose after (to give the amount of kill noted on the left as

19 PAA dose 2). In the last scenario (Figure 3.2d), different populations of microorganisms display

20 different resistances to UV and PAA disinfection. Neither disinfectant alone can reach the

21 treatment goal in a feasible manner. Here the best combination is to apply UV disinfection until

22 tailing occurs, thereby only leaving behind UV resistant microorganisms. Then PAA is applied

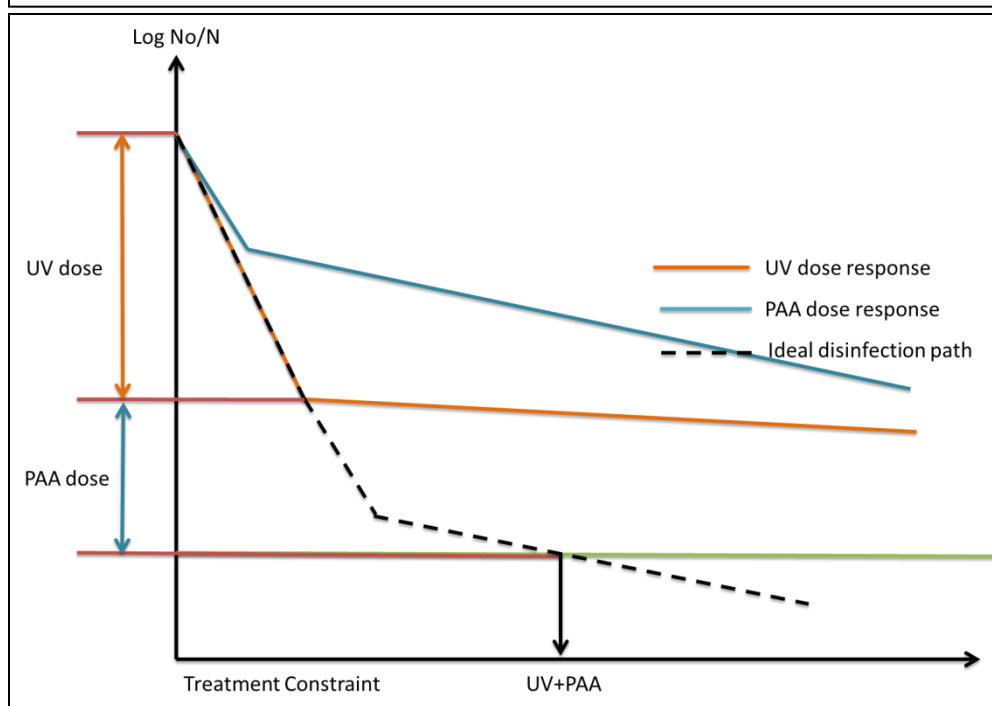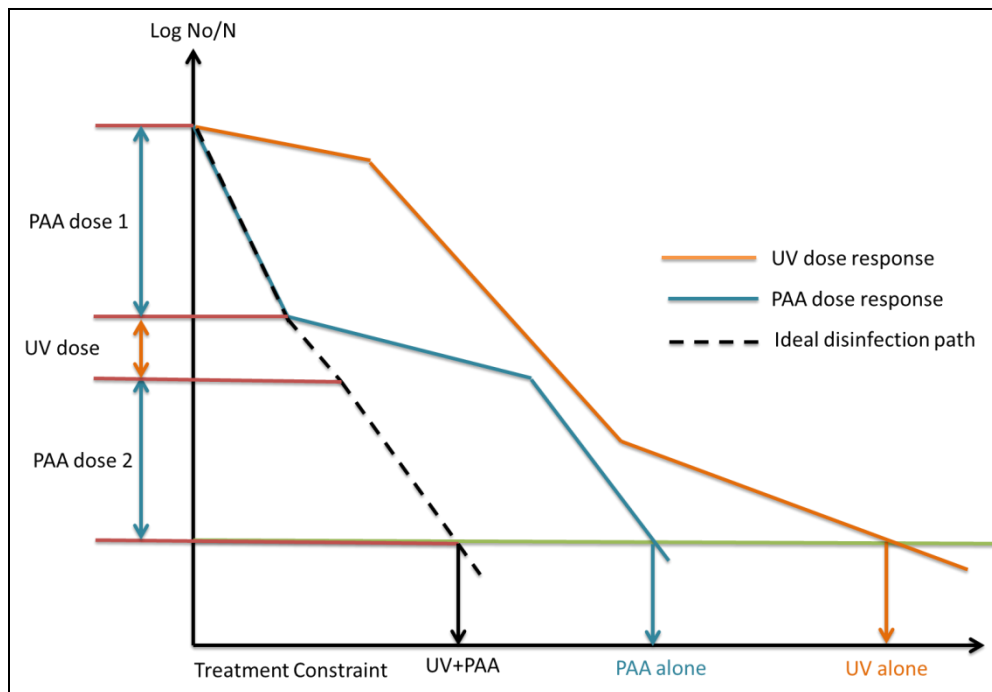23 to inactivate the remaining microorganisms that are susceptible to PAA.

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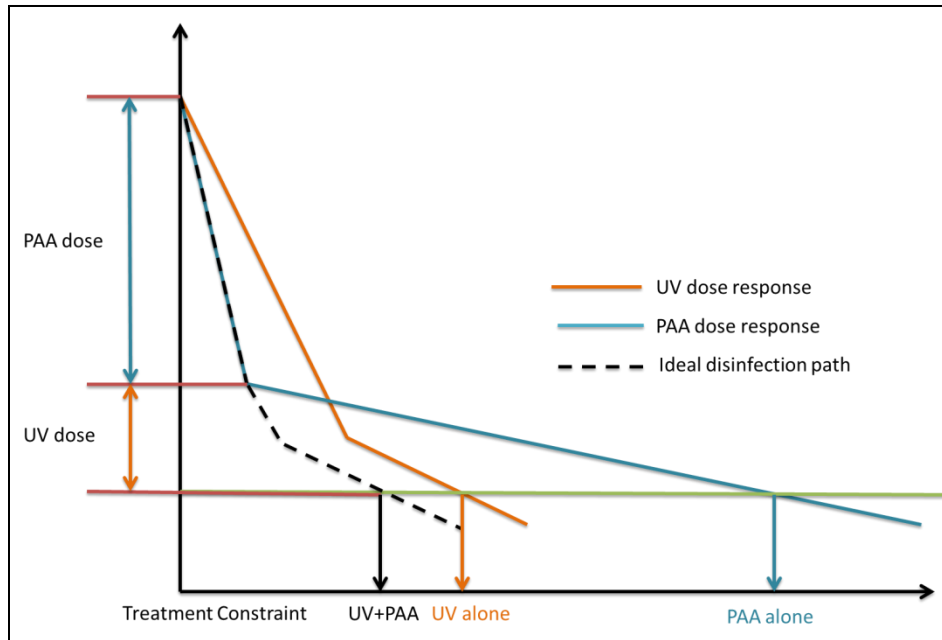
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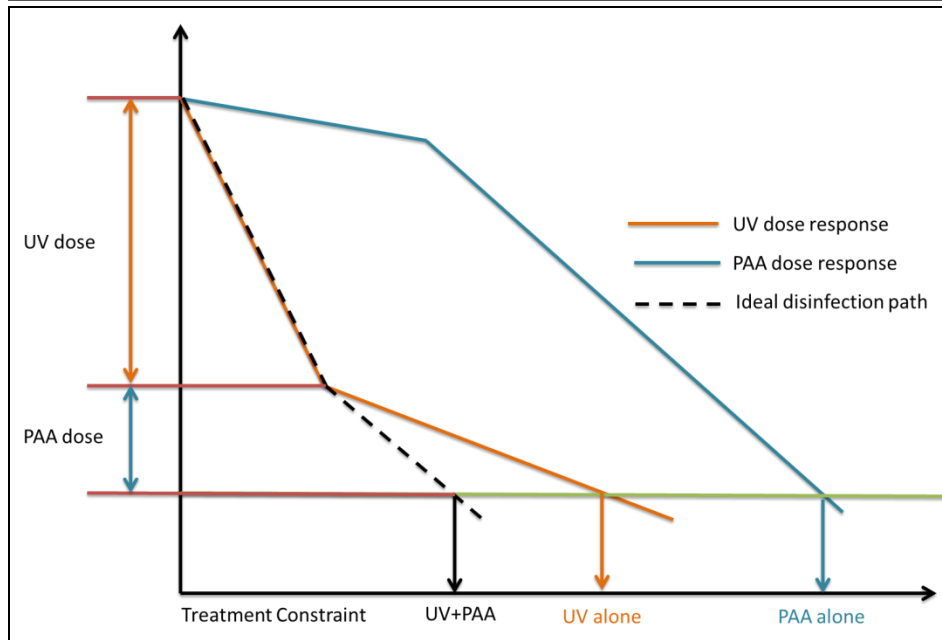
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Figure 3- 2: Four scenarios for sizing and selection of a combined UV and peracid disinfection
process.

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1.2.3 Modelling dual disinfection inactivation kinetics

Murray et al. (2016) conducted UV+PAA tests where UV fluences of 10, 15, and 20 mJ/cm^2 were applied prior to PAA which was applied at CTs ranging from 5-25 mg·min/L. Figure 3.3 presents the concentration of culturable *E. coli* as a function of PAA CT at various UV fluences applied prior to PAA treatment. The data showed a clear, consistent, and logical trend in that (i) for the initial UV treatment, increasing UV fluences treatment resulted in reduced concentration of viable *E. coli* and (ii) for the secondary PAA treatment, increasing PAA CTs resulted in either reduced or constant concentration of viable *E. coli*.

The authors went on to develop a pseudo-mechanistic model where populations of microbes were separated and modelled based on their susceptibility to a single disinfectant (UV or PAA) with each population having its own inactivation kinetics. For the cases where two disinfectants were applied (UV and PAA), the microbes were modelled as four populations: (A0) easy to inactivate by UV and PAA, (B0) easy to inactivate by UV, hard to inactivate by PAA, (C0) hard to inactivate by UV, easy to inactivate by PAA, and (D0) hard to inactivate by UV, hard to inactivate by PAA. Figure 3.3 provides a conceptual illustration of this mechanistic approach.
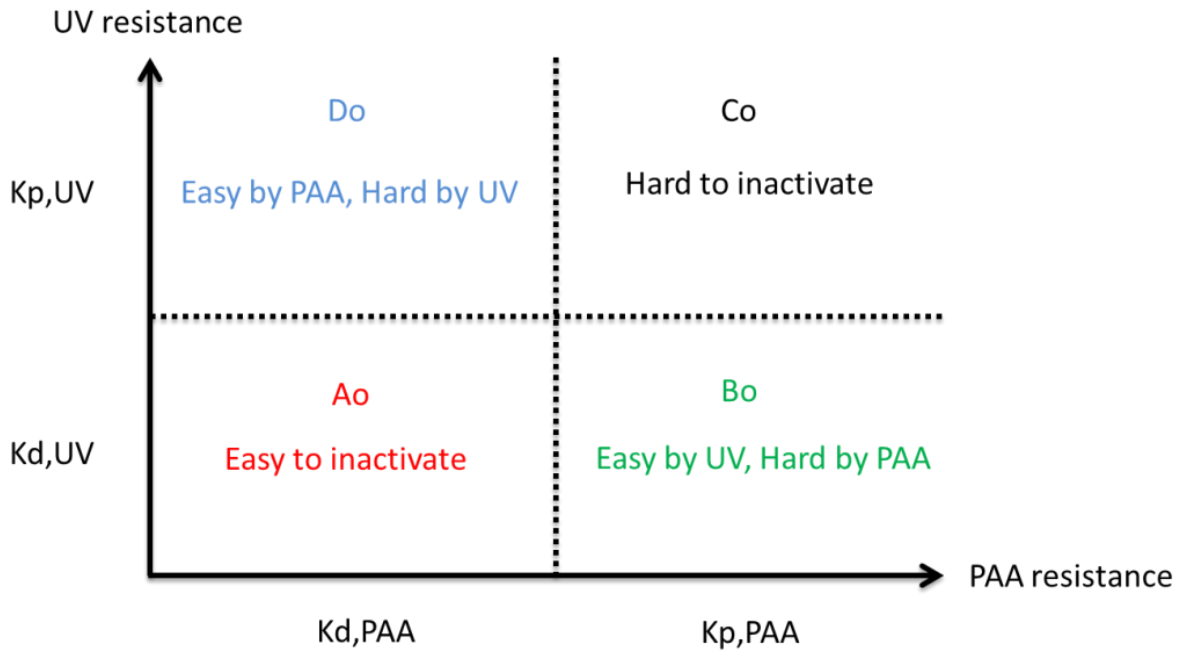
UV resistance

Do
Easy by PAA, Hard by UV

Co
Hard to inactivate

Kp,UV

Ao
Easy to inactivate

Bo
Easy by UV, Hard by PAA

Kd,UV

PAA resistance

Kd,PAA

Kp,PAA

1

2   Figure 3-3: Four population mechanistic approach to model a dual disinfectant system consisting
3   of UV and PAA disinfectants. (Source – Murray et al., 2016)

4

5   Formulas for this system are given in Figure 3.4 and the following Equation 3.1 was used

6   to quantify the concentration of culturable organisms after disinfection.

7          $N_{total,viable} = A2_{viable} + B2_{viable} + C2_{viable} + D2_{viable}$ [Equation 3.8]

8   where,

9          $N_{total,viable}$ is the total concentration of viable *E. coli*; MPN / 100 mL

10         $A2_{viable}$ is the concentration of viable organisms from population A0 remaining after UV

11   and PAA treatment

12         $B2_{viable}$ is the concentration of viable organisms from population B0 remaining after UV

13   and PAA treatment

14         $C2_{viable}$ is the concentration of viable organisms from population C0 remaining after UV

15   and PAA treatment

1    $D2_{viable}$ is the concentration of viable organisms from population D0 remaining after UV

2   and PAA treatment

	Kd,UV				Kd,UV	
Ao (viable)	→	A1 (viable)		A1 (viable)	→	A2 (viable)
Ao (viable)	Kd,PAA →	A1 (viable)		A1 (viable)	Kd,PAA →	A2 (viable)
Bo (viable)	Kd,UV →	B1 (viable)		B1 (viable)	Kd,UV →	B2 (viable)
Bo (viable)	Kp,PAA →	B1 (viable)	+	B1 (viable)	Kp,PAA →	B2 (viable)
Co (viable)	Kp,UV →	C1 (viable)		C1 (viable)	Kp,UV →	C2 (viable)
Co (viable)	Kp,PAA →	C1 (viable)		C1 (viable)	Kp,PAA →	C2 (viable)
Do (viable)	Kp,UV →	D1 (viable)		D1 (viable)	Kp,UV →	D2 (viable)
Do (viable)	Kd,PAA →	D1 (viable)		D1 (viable)	Kd,PAA →	D2 (viable)

STEP 1   STEP 2

3

4   Figure 3-4: Formulas representing inactivation products and respective first order rate constants
5   for the proposed four population system with dual disinfectants. (Source – Murray et al., 2016)

6   The four population, dual disinfectant model was fitted to the UV only, PAA only, and

7   UV+PAA experimental data in order to estimate the model parameters A0, B0, C0, D0, kd,UV,

8   kd,PAA, kp,UV, and kp,PAA. The resulting model is shown with observed results for UV only

9   and PAA only (Figure 3.5) and for UV→PAA (Figure 3.6).
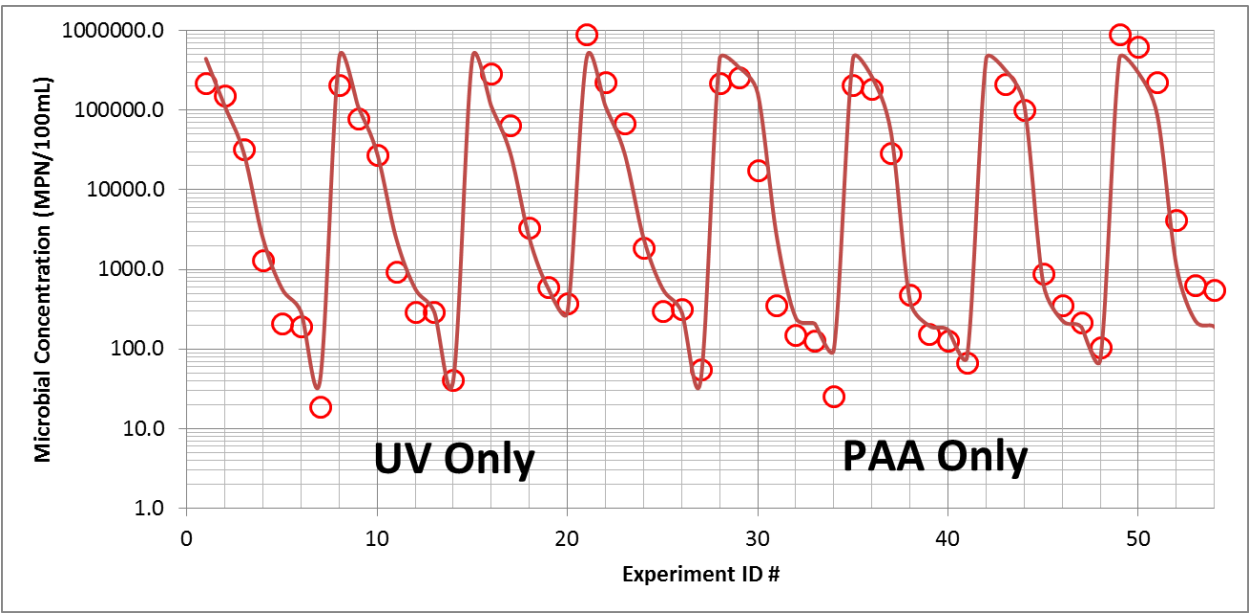
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3 Figure 3-5: Experimental results from inactivation using UV or PAA alone (circles) and
4 predicted values using the four population, dual disinfectant model. (Source – Murray et al.,
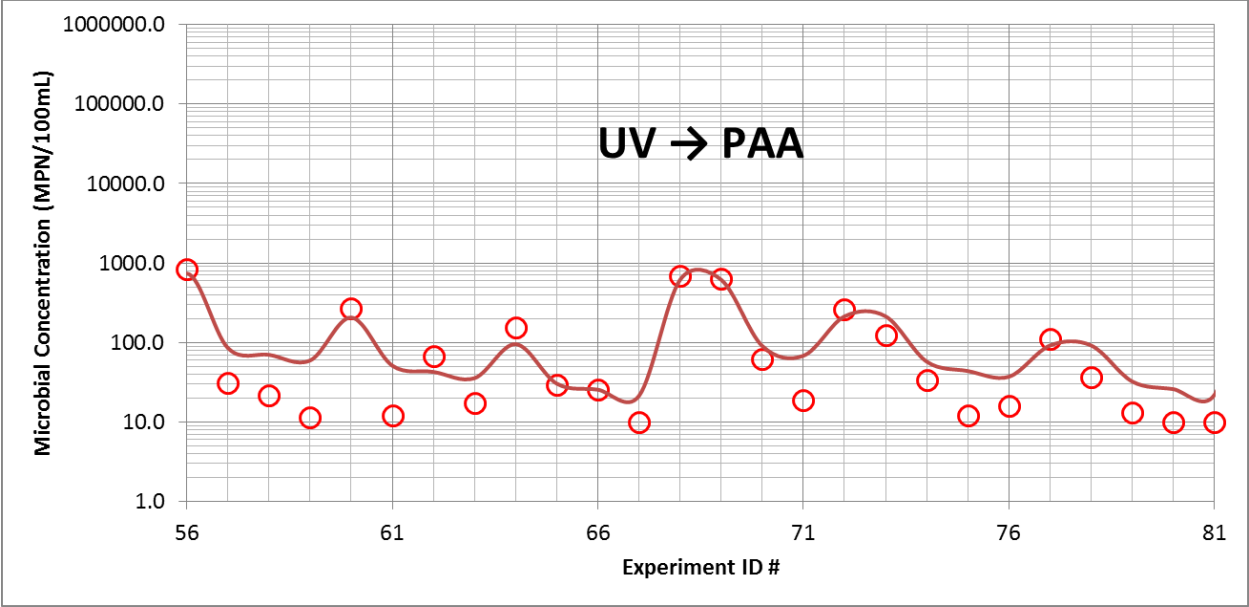5 2016)

6

7 Figure 3-6: Experimental results from inactivation using UV→PAA (circles) and predicted
8 values using the four population, dual disinfectant model. (Source – Murray et al., 2016)

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Figure 3.7 illustrates the comparison between actual results and model predicted concentrations

of culturable E. coli. In general, the four populations, dual disinfectant model was able to

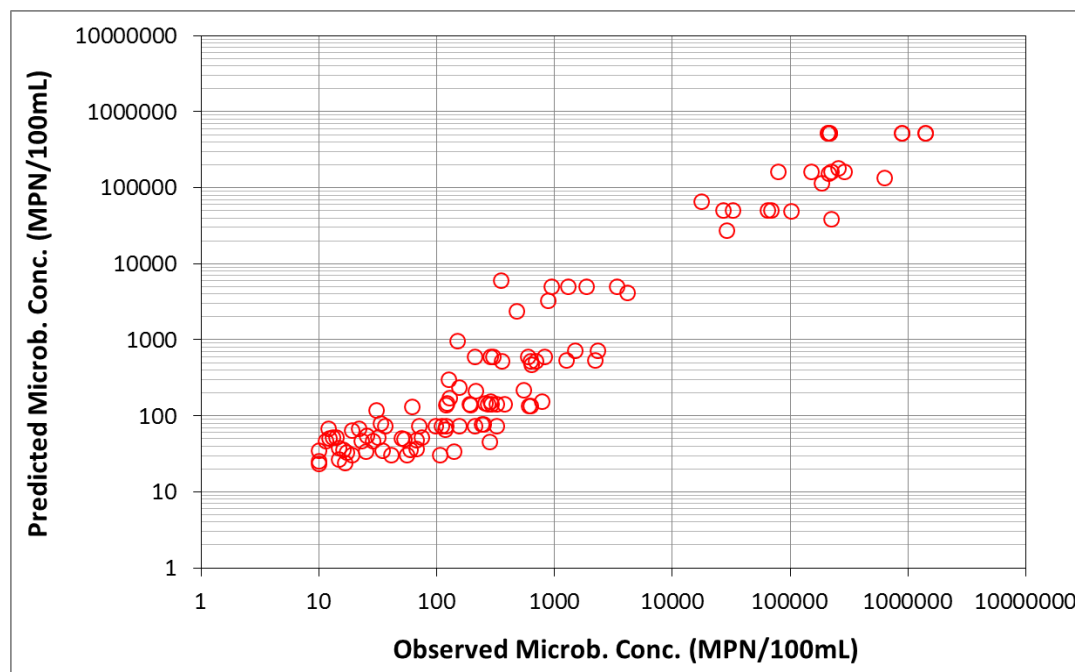reasonably predict the effect of UV only, PAA only, and UV+PAA disinfection of E. coli.

5

Figure 3-7: Comparison of the observed concentrations of viable E. coli after disinfection (UV,
PAA, and UV+PAA) and the four population, dual disinfectant model predicted concentration of
viable E. coli. (Source – Murray et al., 2016)

1.2.4   Operational and economic benefits of UV plus PAA disinfection

Murray et al. (2016) used the aforementioned model to determine the combination of UV

fluences and PAA CT that would achieve a disinfection target of 63 MPN / 100 mL. Figure 3.8

illustrates the model predicted combinations of disinfectants that would be required to meet the

disinfection target. This plot shows that as the delivered UV fluence is decreased, PAA can be

brought online to supplement UV and still meet the disinfection target. Potential situations where

the delivered UV fluence could drop, and PAA could be brought online, include (1) storm events

leading to flows above the design capacity, (2) a drop in UVT as a result of an industrial

1   discharge, and/or (3) secondary clarifier upset conditions leading to an excess escape of

2   suspended solids. The trendline in Figure 3.8 shows the predicted PAA CT for varying pre-UV

3   doses. This correlation could be used to evaluate the economics, including operating and capital

4   costs, associated with various UV and PAA combinations.

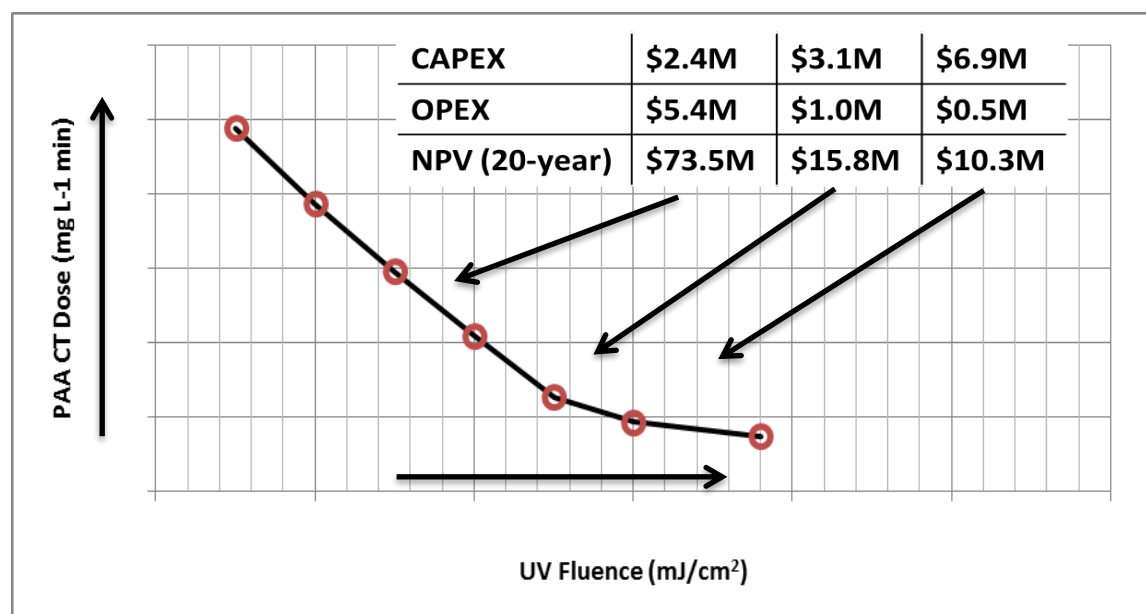|			
CAPEX	$2.4M	$3.1M	$6.9M
OPEX	$5.4M	$1.0M	$0.5M
NPV (20-year)	$73.5M	$15.8M	$10.3M

6   Figure 3-8: Model predicted combinations of PAA dose and UV fluence required to achieve a E.
7   coli disinfection target of 63 MPN / 100 mL when applying the sequential UV→PAA treatment
8   process.

9   **2 PAA decomposition mechanisms and kinetics**

10   **2.1 Hydrolysis, auto-decomposition, reaction with non-target species**

11   PAA is more stable under a variety of conditions as compared to sodium hypochlorite.

12   When kept below 55°F, spontaneous decomposition is negligible, but if the solution comes into

13   contact with metals or organics, decomposition reactions will occur (Jurkiewicz, 2012, Zhao

14   2008). If rapid decomposition occurs as a result of these reactions, the result is highly exothermic

15   Vianelloa, 2018), so procedures should be followed to prevent contact with organics or metals

16   and safety precautions should be taken to prepare for these types of reactions.
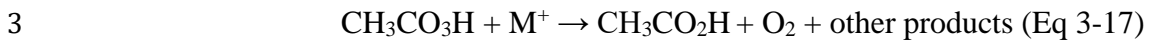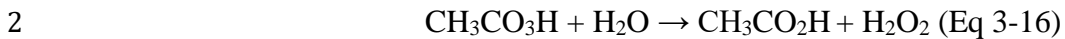
1   At room temperature, Greenspan et al (1956) found that a 40% solution of peracetic acid

2   decayed by 1-2% per month. Another investigator observed that 1% solutions of PAA lost their

3   entire microbial inactivation efficacy in 6 days. (Kunigk, 2001). PeroxyChem, a major PAA

4   manufacturer and supplier, reports that their 15% solution is formulated to maintain equilibrium

5   for one year when stored at temperatures below 29°C. The rate of the decay (day $^{-1}$) is related to

6   temperature by the Arrhenius equation (Equation 3-9), where A is the pre-exponential factor, E is

7   the activation energy, R is the universal gas constant, and T is temperature in °K. Table 3-2

8   shows the approximate shelf life of a 15% peracetic acid solution at three temperatures

9   (PeroxyChem, 2014).

10   $k = Ae^{\frac{-E}{RT}}$ (Equation 3-14)

11   Table 3-2: Approximate Shelf Life of 15% Peracetic Acid

Temperature	Approximate Shelf Life
30°C	1 year
37.8°C	4 months
37.8°C	1 month

12

13   When dosed in typical municipal wastewater, PAA is generally consumed in three

14   competing reactions (Eq 3-15, 3-16, and 3-17). Spontaneous decomposition occurs when PAA

15   degrades into acetic acid and oxygen. In the hydrolysis reaction, it reacts with water to form

16   acetic acid and hydrogen peroxide. Hydrogen peroxide quickly decomposes into water and

17   oxygen. At the same time, PAA reacts with any transition metals that are present to form acetic

18   acid, oxygen, and other byproducts (PeroxyChem, 2015).

$$2CH_3CO_3H \rightarrow 2CH_3CO_2H + O_2 \text{ (Eq 3-15)}$$

$$CH_3CO_3H + H_2O \rightarrow CH_3CO_2H + H_2O_2 \text{ (Eq 3-16)}$$

$$CH_3CO_3H + M^+ \rightarrow CH_3CO_2H + O_2 + \text{other products (Eq 3-17)}$$

Numerous studies have shown that the decomposition of PAA occurs in two distinct and independent phases and can be modeled by a modified first order kinetic equation (Eq 3-10) (Dell'Erba, 2004). The first phase is an instantaneous reduction that occurs as soon as the PAA contacts the wastewater. This phase of decomposition is controlled mainly by water quality and is usually associated with oxidation of organic matter (Domínguez et al, 2018). Recent bench scale studies designed to quantify PAA demand and decay by Domínguez et al, concluded that initial PAA demand was primarily a result of the reaction of disinfectant with organic material, and that this type of consumption occurred within the first five minutes after initially dosing the PAA. Bench studies concluded that casein and peptone, in particular, were the predominant cause of most of the initial demand because of hemolytic fission of PAA, generating peroxyl and hydroxyl radicals that are highly reactive with proteins (Domínguez et al, 2018). Initial demand may also be related to particles and microorganisms (Antonelli et al, 2013; Falsanisi et al, 2006).

The second phase of decomposition characterized by a first order decay coefficient and is associated with hydrolysis and transition metal-catalyzed decomposition (Dell'Erba 2004). Exponential decay has been shown to be associated with inorganics such as reduced iron and orthophosphate (Dominguez, 2018). Iron consumes PAA directly by catalysis, while orthophosphate acts as chelating compound towards iron, reducing the effect of iron (Dominguez et al, 2018; Liu et al, 2014) Lui et al reports that decay occurs more rapidly in waters with high salinity, such as seawater.

1   The magnitude of both the instantaneous demand (D), and the first order decay

2   coefficient, k, is dependent on initial dose, PAA formulation (%PAA), pH, salinity, hardness

3   (Luukkonen et al, 2016). When PAA is added to demand-less water, the concentration decreases

4   25-30% in one hour, at a rate consistent with first order kinetics. Generally, PAA demand varies

5   more than decay over various water qualities (Dell'Erba, 2004); however, Falsanisi et al (2006)

6   observed a ten times greater decay rate in primary effluent versus secondary effluent.

7   **2.2 The instantaneous demand equation**

8   PAA residual concentrations can be predicted by determining fitting parameters k and D

9   in the standard decomposition equation (Equation 1) (Haas and Finch, 2001; Antonelli, 2013)

10   from an experimental data set, where C is the PAA concentration at time t, C_0 is the initial PAA

11   dose, D is the instantaneous demand, and k is the decay coefficient. This is performed using an

12   iterative solver and minimizing the sum square difference between the measured and calculated

13   residual. Typical modeled decay curves are shown in Figure 1.

14   Equation (3-10): $C = (C_0 - D) * e^{-kt}$

15   The goodness of fit will be affected by changes in water quality. In data sets in which

16   there are large variations in water quality, it may be necessary to determine more than one set of

17   fitting parameters by separating the data set into subsections that relate to specific water quality

18   conditions, such as changes inorganic loading. Another option is to model one or both of the

19   fitting parameters as a function of water quality variables such as TSS, color, or COD. Table 1

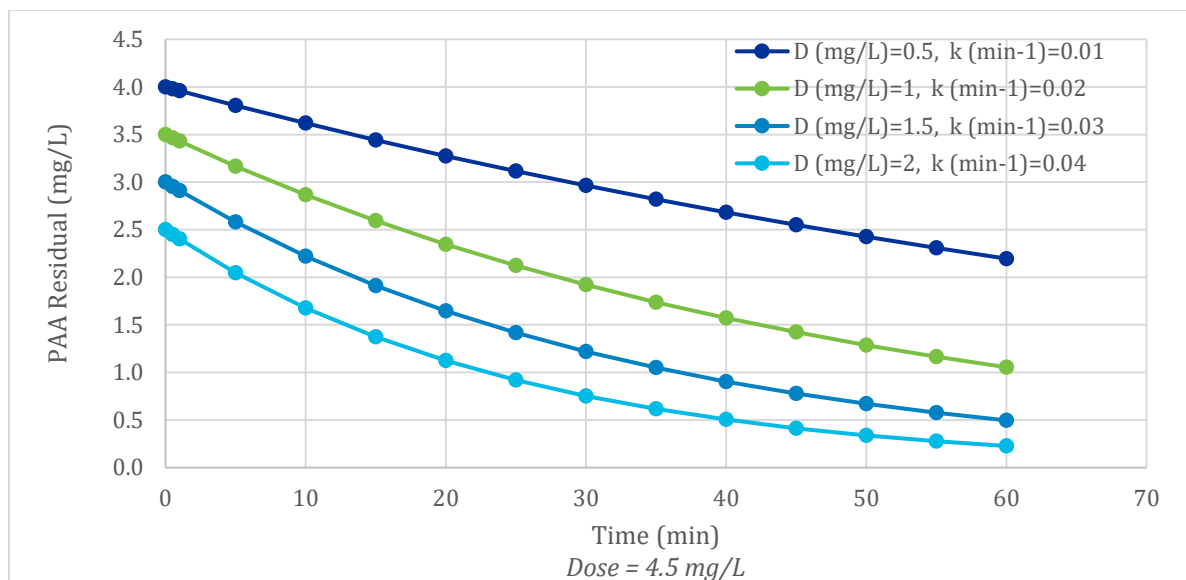20   shows typical demand and decay values for PAA in wastewater.

1

2   Figure 3-9: Typical PAA Decay Curves

3   Table 3-3: Typical Demand Decay Rates in Wastewater

Parameter	Typical values
D (demand) mg/L	0.5-3.0
K (decay) min-1	0.01 – 0.06

4

5   The efficacy of PAA for the inactivation of microorganisms is most often considered in

6   terms of a CT concept, which is based on both time of exposure and residual concentration.

7   When calculating the PAA CT, it is important to use the integral method instead of simply

8   multiplying the residual by the exposure time to account for the exponential decay of peracetic

9   acid. PAA can be visualized as the area under the decay curve, and it is calculated by integrating

10   the decay equation from time zero, to time t. The analytical solution to the decay equation is

11   shown in Equation (3-11) where C_0 is the initial PAA dose, D is the instantaneous demand, and k

12   is the decay constant. If conventional methods are used to determine the PAA CT, a significant

13   amount of error will occur (Rossi et al, 2007). Figure 3-2 compares the calculated PAA CT using

21

1   the integral method to calculations based on dose or residual multiplied by time (Santoro, et al,

2   2015).

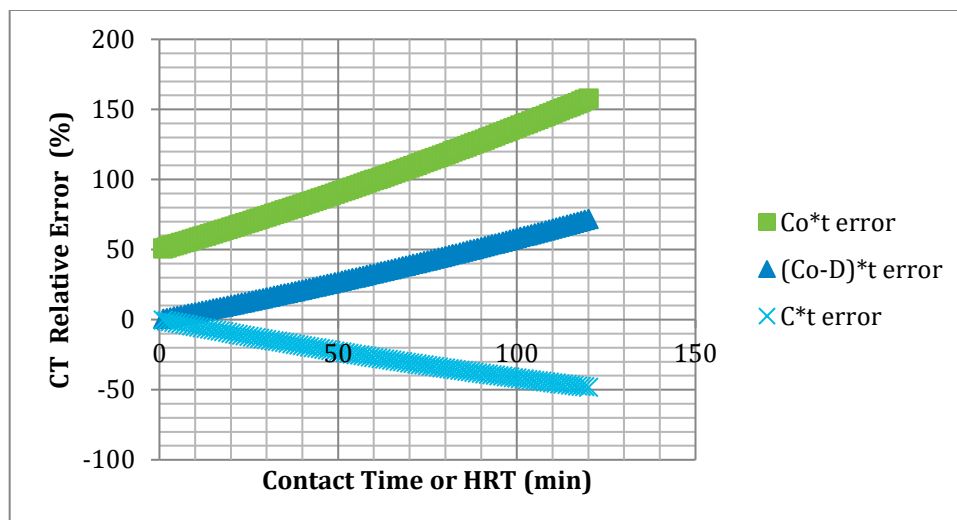3   Equation (3-11) $PAA\ CT = \frac{(C_0 - D)}{k} * (1 - e^{-kt})$
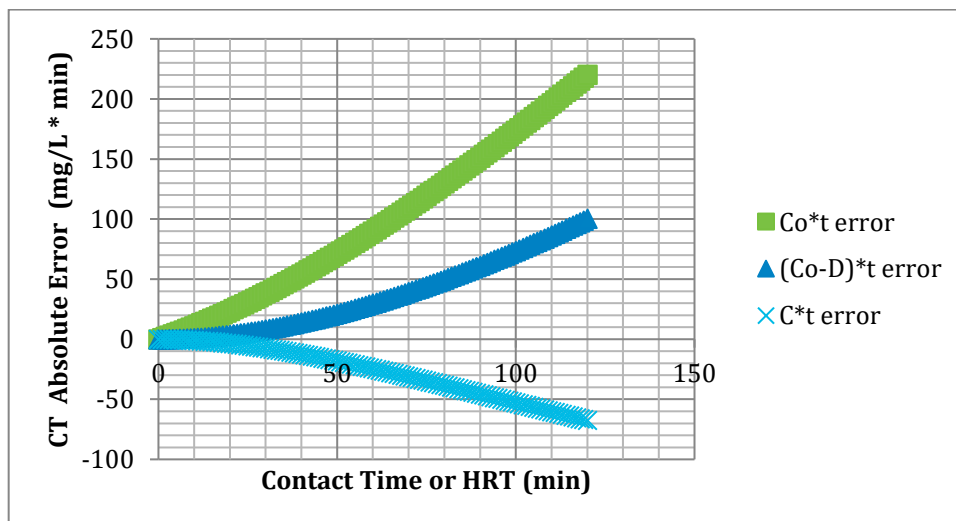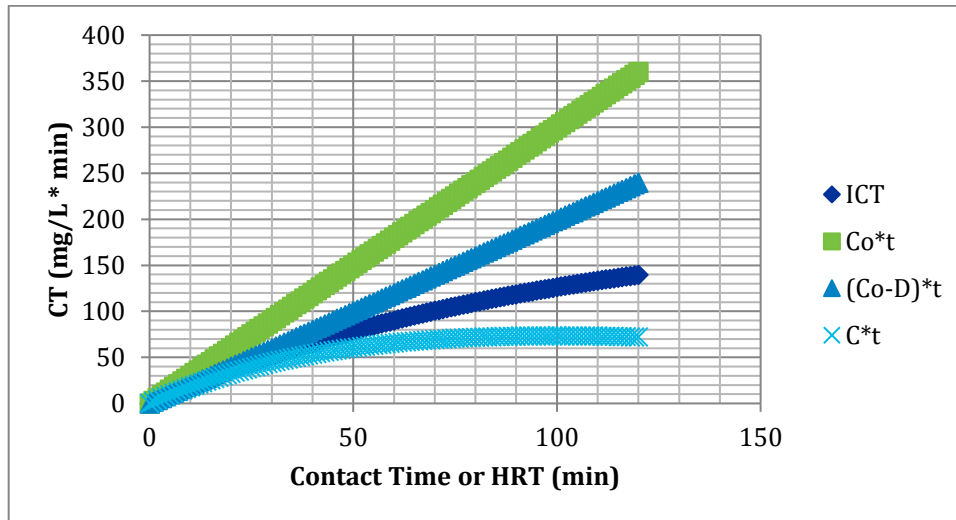
Figure 3-10: Error Associated with Using Typical CT Calculation Methods

1 **3 PAA microbial inactivation kinetics**

2   PAA disinfection efficacy is similar to that of hypochlorite for typical bacterial indicator

3 organisms such as total and fecal coliform bacteria and *Escherichia. coli (E. coli).* Limited

4 studies have been performed to measure PAA disinfection efficacy towards viruses and phages,

5 but a recent study compared the disinfection efficacy of PAA to that of monochloramine towards

6 MS2 and norovirus and found it to be comparable. However, to achieve 1-log removal of MS2,

7 more than 1000 mg/L*min was required (Dunkin, et al, 2017). This is much higher than what is

8 required for typical bacterial targets, as shown in Table 3-4.

9   Although UV irradiation is generally considered a more effective disinfection technology

10 than PAA, UV irradiation is more susceptible to changes in water quality and they usually have

11 less flexibility in dosing capabilities than PAA systems. PAA also has similar disinfection

12 efficacy to chlorine dioxide, but the latter is usually more expensive to use because it needs to be

13 generated, *in situ*. A significant advantage of PAA over chlorine is that it does not generate

14 regulated disinfection byproducts (Luukkonen 2016). A literature review of peracetic acid

1 disinfection efficacy for several common organisms for different wastewater matrices is shown

2 in Table 3-3 (Luukkonen, 2017).

Organism	Dose	Contact Time	Log Inactivation	Wastewater Matrix	Reference
EC	1.5	60	--	TE	Luukkonen et al, 2015
EC	2–25	6–54	--	TE	Azzellino et al, 2011
EC	2–25	6–54	--	TE	Mezzanotte et al, 2007
EC	2	55	--	SE	Rossi et al, 2007
EC	1–8	30	--	SE	Santoro et al, 2007
TC	2–25	6–54	--	TE	Azzellino et al, 2011
TC	2–25	6–54	--	TE	Mezzanotte et al, 2007
FC	1–8	30	--	SE	Santoro et al, 2007
FC	1–2	55	--	SE	Rossi et al, 2007
FC	5–15	55	--	SE	Rossi et al, 2007
E	1.5	60	--	TE	Luukkonen et al, 2015
EC	5-10	35-50	4	SE	Antonelli et al, 2013
EC	4	10	2	SE	Santoro et al, 2007
FC	4.3	45	2	SE	Santoro et al, 2007

3 SE=secondary effluent, TE=tertiary effluent, EC=E. coli, FC=fecal coliform, TC=total coliform,
4 E=Enterococcus

5 Table 3-4: Review of PAA Disinfection Efficacy

6 Several mechanisms have been proposed to explain the mechanism of bacterial

7 inactivation by PAA, although there is not yet a definitive explanation. The disinfectant's mode

8 of action may be similar to other peroxides and oxidizing agents (Block, 1991).   One study

9 suggests that the it is related to the oxidation of sulfhydryl (-SH) and sulfur (S-S) bonds in

10 enzymes by "active oxygen" (Lefevre et al, 1992). Another proposed mechanism is the rupture

11 of cell walls (Baldry and French, 1989). PAA may also oxidize enzymes that affect the vital

12 biochemical pathways of microorganisms as well as transport directly across cell membranes

13 (Fraser, 1984). In addition, hydroxyl radicals generated during the decomposition process may

1   directly participate in the inactivation of microorganisms (Bianchini et al, 2002; Lubello et al,

2   2002).

3   Disinfection efficacy is affected by wastewater characteristics, although some of these

4   dependencies are more related to the effect on PAA decomposition rates which are discussed

5   earlier in this section. These include suspended solids and organic matter which affect initial

6   demand, transition metals which increase the decay rate, and salinity which abates radicals.

7   Temperature affects the kinetics of both decomposition and inactivation. It increases the rate of

8   decomposition, which decreases effective concentration (and CT) more quickly, but the reaction

9   rate with microorganism also increases, increasing disinfection efficacy. Disinfection efficacy is

10   greater at lower pH because the non-dissociated form of PAA is more active. Above, pH 9, there

11   is marked decreases in disinfection efficacy (Luukkonen et al, 2014).

12   Inactivation models relate the PAA concentration and contact time to the log inactivation

13   of target microorganisms. Most validated inactivation models are related to the integral of the

14   generalized inactivation rate (Equation 3-12) where

15   $$\frac{dN}{dt} = -k'C^n m N^x t^{m-1} \text{ (Equation 3-12)}$$

16   Where:

17   K', n, m, x = model parameters (n, m, and x are exponents [dimensionless]; k' takes the SI units
18   depending on the values of the n, m, and x exponents, to give the left term of eq 2 in CFU/100
19   mL per minute).

20   N = microbial density (CFU/100 mL).
21   C = disinfectant concentration (mg/L).
22   t = contact time (minutes).

23   Limiting the fitting parameters of this equation lead to the Chick, Chick-Watson, Hom,

24   Power Law, and Hom Power Law inactivation models. Limits on these parameters that lead to

1   these models are shown in Table 3-4 (Santoro, et al, 2007). These models can be used to

2   determine the required time or active concentration required to achieve a given amount of log

3   inactivation under specific water quality conditions. However, PAA decomposition kinetics must

4   be applied to determine the *PAA dose* required to achieve a given active concentration at a given

5   time. It should be noted, however, that the models discussed are simply a mathematical way to

6   fit microbial inactivation data and are specific to a particular set of conditions. As such, there is

7   no mechanistic basis for the inactivation observed.

8   Table 3-4: Inactivation Model Comparison

Model parameters	Chick	Chick-Watson	Hom	Power law	Hom PL
k'	$k' \neq 0$	$k' \neq 0$	$k' \neq 0$	$k' \neq 0$	$k' \neq 0$
n	0	$n \neq 0$	$n \neq 0$	$n \neq 0$	$n \neq 0$
m	1	1	$m \neq 1$	1	$m \neq 1$
x	1	1	1	$x \neq 1$	$x \neq 1$
dN/dt	$-k'N$	$-k'C^nN$	$-k'C^nmNt^{m-1}$	$-k'C^nN^x$	$-k'C^nmN^xt^{m-1}$

9

10   Rossi et al (2007) compared the fit of several disinfection models including the Selleck

11   model (1978), the Chick-Watson model (1908), the Hom's model (1972), and the S-model

12   (1998) to experimental data from full scale wastewater treatment plants. Neither the Selleck

13   model nor the Chick-Watson model fit the data, but the S-model and the Hom's model fit the

14   data within acceptable limits. The S-model fit the data better for PAA doses less than 5 mg/L

15   whereas the modified Hom's model fitted the data better for PAA doses greater than 5 mg/L.

16   Data from the study described above indicated that bacterial inactivation was more

17   sensitive to residual concentration than contact time, although the latter became more important

1   at lower PAA doses. In this study, microbes damaged by PAA were unable to repair and regrow

2   up to 5 hours after the PAA residual was quenched, suggesting that the damage to

3   microorganisms is permanent and eventually results in cell death.

4   When PAA is used in secondary effluent, the pseudo-mechanistic double exponential

5   model (Equation 3-13) is especially useful in describing inactivation kinetics (Santoro et al,

6   2015). In this model, log inactivation is related directly to integral CT. The bacterial populations

7   are split into two distinct subpopulations, each linked to a separate decay coefficient. One

8   subpopulation (which can be considered non-particle associated, i.e, free floating) has a fast

9   inactivation rate, and the other targeted subpopulation (which can be considered particle-

10   associated) has a slower inactivation rate which is limited by diffusion. A correlation analysis

11   performed on the parameters in the double exponential model and the decomposition model

12   showed that Np was directly correlated with kinetic parameters k and D. This indicates that

13   poorer wastewater quality results in a greater population of particle associated bacteria, a greater

14   instantaneous demand, and faster decomposition kinetics. The opposite is true as wastewater

15   quality improves. For filtered wastewaters (or other situations) in which the microorganism

16   population is more homogenous, this model can be simplified to describe the relationship

17   between log inactivation and CT using a single inactivation decay coefficient.

18   $$N_t = N_0(1 - \beta)e^{-k_d CT_{PAA}m} + N_0(\beta)e^{-k_p CT_{PAA}} \quad \text{(Equation 3-13)}$$

19   Where:

20   N_t = the microbial concentration at time, t
21   N_0 = the microbial concentration at time, 0.
22   β = the percent of the microbial subpopulation that is particle associated
23   k_p = the decay coefficient associated with the particle associated subpopulation
24   k_d = the decay coefficient associated with the free-floating subpopulation
25   CT_{PAA}= the integral CT
26   m=coefficient to describe "shouldering" effect

27

1

2 None of these models are definitively mechanistic, and the application of inactivation models to

3 experimental data is essentially a curve fitting exercise, so it is acceptable to use whichever

4 model fits the data best to determine the required PAA dose for a specific application and water

5 quality. However, determining the instantaneous demand and the decay coefficient is essential

6 for correct dosing. In addition, when collecting data, it is important to gather enough information

7 to generate a robust model that is valid over the entire range of operational conditions.

8 **4 Water quality impacts on PAA**

9 The decomposition rate of PAA as well as its disinfection efficacy are strongly affected by

10 water quality. Some influencing factors are pH and water matrix composition, including the

11 presence of transition metals, organic matter, suspended solids, and water hardness (Domínguez

12 Henao et al., 2018a, 2018b; Falsanisi et al., 2006; Howarth and Harvey, 2010; Lazarova et al.,

13 1998; Liu et al., 2014; Pedersen et al., 2009; Sanchez-Ruiz et al., 1995; Yuan et al., 1997a,

14 1997b). In the following paragraphs, the main water characteristics impacting PAA disinfection

15 of wastewater are discussed in detail.

16 **4.1 pH**

17 Various authors have reported the effect of pH on PAA decomposition rate and

18 disinfection efficacy (Kitis, 2004; Luukkonen et al., 2014; Luukkonen and Pehkonen, 2016;

19 Yuan et al., 1997a, 1997b). As detailed in Chapter 2, since the pK_a of PAA is 8.2, at pH higher

20 than this value the equilibrium moves towards its dissociated form (CH_3COOO^-), affecting both

21 PAA decay rate and bacterial inactivation performance. In a pH range of 5.5-8.2 PAA decay is

22 mainly due to spontaneous decomposition, while at values between 8.2 to 9.0, PAA decay is

23 mainly driven by spontaneous decomposition and hydrolysis (Yuan et al., 1997a). However,

24 PAA decomposition rate is approximately stable in a range of pH between 6.5 and 8.2 (Pedersen

et al., 2013), that is the typical pH interval of wastewater. The influence of pH on PAA

decomposition is discussed in detail in Chapter 2. In addition, pH also affects PAA efficacy in

terms of microbial inactivation, being more effective under acidic conditions and decreasing at

pH values above 9 (Kitis, 2004; Luukkonen et al., 2014). Again, this might be related to PAA

dissociation at alkaline pH values, since the non-dissociated form is thought to be a more active

disinfectant than the dissociated form (Yuan et al., 1997b).

4.2 Inorganic compounds

The presence of some inorganic compounds in water can promote PAA decomposition

depending on the nature of these molecules and consequently, it can determine a reduction in

disinfection efficacy. Various authors have addressed efforts to elucidate the role of different

inorganic compounds, according to their typology, such as transition metals, phosphate, nitrogen

compounds, hardness and salinity. The following paragraphs describe their role on PAA

decomposition and disinfection efficacy.

4.2.1 Transition metals

Various studies (Kitis, 2004; Luukkonen et al., 2014; Luukkonen and Pehkonen, 2016;

Pedersen et al., 2013; Wagner et al., 2002; Yuan et al., 1997a, 1997b; Zhao et al., 2008) have

documented the effect of the presence of transition metals in water on PAA decomposition.

According to the study on the decomposition kinetics of PAA carried out by Yuan et al. (1997a,

1997b), particularly reduced metal ions, such as iron (Fe^{2+}), manganese (Mn^{2+}), copper (Cu^{2+})

and cobalt (Co^{2+}), catalyze PAA decomposition via complex redox reactions. These reactions

were further assessed in other works (Popov et al., 2005; Rothbart et al., 2012), reporting that a

number of different oxidation states of metal ions are involved. Moreover, it has been observed

that chelating agents, such as diethylenetriaminepentaacetic acid (DTPA) and

diethylenetriaminepentamethylenephosphonic acid (DTMPA) counteract the catalytic effect of

1   these reduced metal ions.

2   In agreement with these findings, Domínguez Henao et al. (2018b) observed that the

3   concentration of Fe^{2+} has a significant effect on PAA decomposition under the investigated

4   operating conditions (0.1-5 mg/L of Fe^{2+}). This effect can be counteracted by the presence of

5   phosphates that can indeed, act as chelating agents towards transition metals in water inhibiting

6   their catalyzing action on PAA decomposition (Aklil et al., 2004; Domínguez Henao et al.,

7   2018b; Elouear et al., 2008; Irani and Morgenthaler, 1963; Klueh and Robinson, 1988; Larson,

8   1957; Varner et al., 1996).

9   Despite their catalytic action on PAA decomposition, the presence of transition metals,

10 such as copper (Cu^{2+}) and silver (Ag^+), can also enhance the formation of radicals, improving

11 PAA efficiency in terms of microbial inactivation. A synergy between Ag^+ and PAA in the

12 removal of *V. cholerae, Salmonella* sp*., Shigella, P. aeruginosa*, helminth eggs, and fecal

13 coliforms was observed by Orta de Velásquez et al. (2017). Similar synergistic effects were

14 reported by Luna-Pabello et al. (2009) for systems combining Ag^+/PAA and Ag^+/Cu^{2+}/PAA for

15 the removal of helminth eggs. The authors highlighted that one major advantage of the addition

16 of Cu^{2+} and/or Ag^+ ions is a decrease in the required contact time (Luna-Pabello et al., 2009;

17 Luukkonen and Pehkonen, 2016; Orta de Velásquez et al., 2017). However, the addition of metal

18 ions can cause secondary contamination, impairing water quality. Furthermore, the economic

19 feasibility of the use of Cu^{2+} and Ag^+ should be evaluated (Luukkonen and Pehkonen, 2016).

20 **4.2.2 Phosphates**

21 An interesting feature of phosphates, besides their role as chelating agents towards

22 transition metals in solution, is their potential capacity to inhibit inactivation as observed by

23 Mattle et al. (2011) on bacteriophage MS2. In detail, the authors reported that high phosphate

24 concentrations (400 mM, about 746 mg/L) reduce the inactivation extent by a factor of 5.1

compared to lower phosphate concentrations (15 mM, about 28 mg/L). The protective effect of

phosphate was attributed to its capacity to quench free radicals (Booth and Lester, 1995; Mattle

et al., 2011).

4.2.3 Nitrogen compounds

Despite the ubiquitous presence of inorganic nitrogen-containing compounds in different types

of water, such as biologically treated effluents, little work has addressed their effect on PAA

disinfection. Domínguez Henao et al. (2018b) investigated the role of ammonia nitrogen (NH^{4+}),

nitrate (NO^{3-}), nitrite (NO^{2-}) on PAA decay. A minor effect of these compounds on PAA

oxidative demand was observed; however, this effect was not statistically significant under the

investigated operating conditions (0.5-25 mg/L as N for NH^{4+} and NO^{3-} and 0.1-1 mg/L as N for

NO^{2-}).

4.2.4 Hardness and salinity

A faster decomposition of PAA in water with high salinity (ionic strength) has been

suggested in a number of studies (Soares Cavallini et al., 2013; European Centre for

Ecotoxicology and Toxicology of Chemicals, 2001; Luukkonen et al., 2014). The effect of

salinity and water hardness on PAA decomposition was investigated in detail by Liu et al. (2014)

using NaCl and sea salt to reach concentrations of 1% (10 g/L) and 3% (30 g/L) in distilled

water. The authors found that salinity has a relevant effect on PAA and interestingly, sea salt led

to higher PAA degradation rates than pure NaCl. Indeed, the main components of sea salt used

were NaCl and KCl, which represent around 85 % w/w of its composition, while the remaining

15% w/w is composed of SO_4^{2-}, Mg^{2+} and Ca^{2+}. This suggests that the ionic composition also

plays a relevant role on PAA decomposition. The authors attribute this effect to Mg^{2+}/Ca^{2+} and

Na^+/K^+ ratios, since higher Mg^{2+}/Ca^{2+}ratios (85% in standard dilution water) lead to slower

1   kinetics, while higher Na^+/K^+ ratios (85% in sea salt) resulted in faster reactions. Regarding

2   water hardness, the same authors found that water hardness (46-460 mg/L Ca^{2+} and Mg^{2+}) had

3   only a slight impact on PAA decomposition. No other research work on PAA mentions hardness

4   as one of the main parameters driving its decomposition in water.

5   **4.3 Organic matter**

6   Several authors (Domínguez Henao et al., 2018b; Gehr and Cochrane, 2002; Koivunen and

7   Heinonen-Tanski, 2005; Liu et al., 2014; Pedersen et al., 2013) have highlighted that the

8   presence of high loads of organic matter in water leads to an important PAA consumption. For

9   instance, municipal wastewater after primary treatment characterized by high COD

10   concentrations (124-240 mg/L), total suspended solids (TSS) (16-45 mg/L) and turbidity (16-31

11   NTU) determines an important PAA oxidative demand (Gehr and Cochrane, 2002). Moreover

12   PAA residuals are typically very low or absent after the disinfection of primary effluents with

13   high COD, TSS and turbidity levels (Koivunen and Heinonen-Tanski, 2005), while they are

14   typically present after the disinfection of secondary and tertiary effluents. Pedersen et al. (2013)

15   studied the effect of different levels of organic matter content as COD concentration (up to 70.8

16   mg/L of COD) on PAA decomposition. A significant and positive correlation between COD

17   concentration and PAA oxidative demand was observed. The effect of organics on PAA

18   oxidative demand was also observed adopting dissolved organic carbon (DOC) as indicator of

19   organic matter. In agreement with previously cited works, Liu et al. (2014) observed increasing

20   trend of PAA oxidative demand at increasing DOC concentration in a range between 8 and 24

21   mg/L, using a synthetic media prepared from commercial humic acids.

22   Organic matter is a heterogeneous and complex mixture; thus, most of research work

23   adopted macro-parameters as indicators of organic content, such as COD and DOC. However,

24   different organic macromolecules, namely carbohydrates, lipids and proteins are expected to

32

1 exert different effects on PAA oxidative demand due to their different nature and composition.

2 Domínguez Henao et al. (2018b) studied the effect of the different groups of organic

3 macromolecules on PAA consumption, evaluating them by their contribution as COD (10-35

4 mg/L). Macromolecules displayed different effects on PAA oxidative demand, being proteins the

5 only macromolecules that had a significant consumption of PAA, whereas the carbohydrates and

6 lipids had a minor effect, evidencing that not all the COD represents a PAA consumption. Thus,

7 the authors hypothesized that PAA has a specific oxidative action on proteins, which can entail

8 PAA consumption. Indeed, previous works have also addressed the specific oxidative capacity of

9 PAA towards amino acids. For instance, Kerkaert et al. (2011) observed a rapid oxidation of

10 cysteine, tryptophan, and methionine present in dairy proteins. In agreement with this findings,

11 Finnegan et al. (2010) observed that PAA specifically oxidizes amino acids in the cell wall of

12 microorganisms, degrading for instance bovine serum albumin and enzymes.

13 **4.4 Suspended solids and particulate matter**

14   Suspended solids and particulate matter in wastewater have a heterogeneous composition,

15 which varies with the characteristics of the effluent, depending mainly on the source (domestic,

16 industrial, agricultural, stormwater); thus, a detailed characterization of their composition is very

17 challenging (Domínguez Henao et al., 2018a). However, regardless the relevant differences in

18 composition, several works highlighted the detrimental effect of TSS on decomposition and

19 disinfection efficacy of PAA (Chhetri et al., 2014; 2016; Domínguez Henao et al., 2018a;

20 Falsanisi et al., 2008; Koivunen and Heinonen-Tanski, 2005; Lazarova et al., 1998; Lefevre et

21 al., 1992; McFadden et al., 2017; Sánchez-Ruiz et al., 1995; Stampi et al., 2001). In addition, a

22 relevant feature of TSS regarding PAA disinfection is related to their structure. As particles, TSS

23 are not smooth and rigid but rather irregular sponge-like matrixes with pores in which bacteria

24 can be shielded (Dietrich et al., 2003). Accordingly, TSS can impact PAA disinfection via two

1 mechanisms, namely determining a PAA oxidative demand (and associated reduction of PAA

2 actual disinfecting dose) and acting as protective shields for bacteria against the disinfectant

3 (Domínguez Henao et al., 2018a).

4   The detrimental effect of TSS on PAA decomposition has been discussed in various works

5 on PAA disinfection, including Chhetri et al. (2016, 2014), Falsanisi et al. (2008), Koivunen and

6 Heinonen-Tanski (2005), Lazarova et al. (1998), Lefevre et al. (1992), McFadden et al. (2017),

7 Sánchez-Ruiz et al. (1995), and Stampi et al. (2001) and Domínguez Henao et al. (2018a). Water

8 matrixes with a high content of TSS, such as combined sewer overflows (CSOs) and primary

9 effluents, require higher PAA concentrations for disinfection than secondary and tertiary

10 effluents (Chhetri et al., 2016; Gehr and Cochrane, 2002; Koivunen and Heinonen-Tanski, 2005;

11 Luukkonen et al., 2014). Moreover, it has been observed that the pretreatment of CSOs and the

12 removal of suspended solids decrease the required disinfectant dose (Chhetri et al., 2016). The

13 effect of different concentrations of TSS (5, 40, 80, 120 and 160 mg/L) on PAA decay was

14 studied by Domínguez Henao et al. (2018a), evaluating as well the effect of the soluble matter

15 associated to the TSS. Increasing TSS concentrations lead to higher PAA decomposition rates,

16 which grow significantly above 40 mg/L of TSS. In addition, the effect of TSS on PAA

17 decomposition was much more relevant than the effect of the associated soluble fraction, and the

18 two components were found to be independent and additive.

19   Although the presence of TSS and particulate matter results in high decomposition rates of

20 PAA, the most relevant effect of TSS on PAA disinfection is often related to the inactivation of

21 bacteria. Indeed, it has been largely documented that TSS impair water disinfection with

22 chemical (chlorine-based compounds, ozone, PAA) or physical methods (UV radiation)

23 (Tchobanoglous et al., 2014). Due to their morphology, suspended solids and particulate matter

24 can afford protection to microorganisms within their pores (Chhetri et al., 2016), allowing them

to resist even high disinfectant dosages (Dietrich et al., 2007; Falsanisi et al., 2008). The effect of the particle size of the solids on this aspect has gained increasing attention over the last decade. Previous works addressed to elucidate this aspect (Falsanisi et al., 2008; McFadden et al., 2017) reported that TSS with a particle size between 10 to 100-120 µm have a minor effect on PAA disinfection, affording a protection to microorganisms of 0.6 logs, while particles larger than 120 can afford around 1.3 logs of protection. In addition, since bacteria tend to aggregate in natural environments as protection mechanism against extreme conditions, particulate matter can act as a condensation nucleus for bacteria aggregation, resulting in the survival of the microorganisms located in the core of the aggregate (Bohrerova and Linden, 2006; Mir et al., 1997; Turolla et al., 2017). This result in the survival of the microorganisms located in the core of the aggregate (Domínguez Henao et al., 2018a). Thus, either embedded or aggregated, microorganisms associated to TSS, have increased resistance to inactivation by different disinfectants, including PAA, compared to free-swimming microorganisms (Bohrerova and Linden, 2006; Dietrich et al., 2007; LeChevallier et al., 1984; Winward et al., 2008).

Lefevre et al. (1992) reported that high TSS concentrations ranging between 10 and 50 mg/L had no significant effect on the disinfection performance of PAA, while TSS concentrations over 100 mg/L reduce the extent of inactivation by 1 log in secondary effluents. Other authors (Lazarova et al., 1998; Stampi et al., 2001) observed that the effect on PAA disinfection performance is moderate and constant for TSS concentrations between 10 and 40 mg/L.

5 DOSE CONTROL FOR DISINFECTION OF WASTEWATER

5.1 Disinfection Control Strategies

1   The main aspects of ensuring effective disinfection are via the integration of a) microbial

2   inactivation/disinfection by-products formation kinetics, b) disinfectant demand (D) and decay

3   (k), and c) reactor (chemical contact basin, CCB) hydraulics into an integrated disinfection

4   design framework (IDDF) (Bellamy et al., 1998). As discussed in previous sections,

5   understanding of the water quality and treatment requirements in terms of ICT dose (i.e. the area

6   under the PAA decay curve (Santoro et al., 2015)) is important for the development of advanced

7   control strategies to maintain constant disinfection performance. Under-dosing a disinfectant will

8   result in poor disinfection performance. Conversely, over-dosing results in increased operational

9   cost due to increased consumption of chemical disinfectant. Moreover, if the disinfecting agent is

10   applied in excess, the formation of undesired disinfection by-products is enhanced, and the

11   treated water may adversely affect the environment and public health (Richardson et al., 2002).

12   Thus, it is important to develop control strategies able to maintain constant ICT dose (ICT-dose

13   pacing) hence constant disinfection performance.

14   The most commonly used chemical disinfection control strategies target a constant

15   concentration of the chemical disinfectant using feed-forward flow-pacing control (Kobylinski et

16   al., 2006). The flow-pacing control strategy ignores both contact time and decay (k), hence it

17   does not maintain a constant ICT dose. As a result, the disinfection performance varies with

18   water quantity and quality. Figure 1 shows an illustration of the effect of water quantity (flow or

19   contact time) and quality (k) on two control strategies, i.e. flow pacing and ICT-dose pacing.

20   Flow-pacing control maintains a constant inlet disinfectant concentration (C1) at varied flow

21   (Figure 1a). However, the higher the flow the shorter the contact time, hence maintaining a

22   constant C1 results in varied ICT dose, i.e. dose decreased with a decrease in contact time

23   (Figures 1a and 1b). The k of the disinfectant is ignored by flow-pacing control; hence, the ICT

24   dose varies with water quality changes (Figures 1c and 1d). In the case of ICT-dose pacing, C1

1   varies with varied flow to maintain a constant ICT dose (Figures 1a and 1b). Importantly, ICT-

2   dose control strategy considers water quality variation by increasing/decreasing C1 at

3   increased/decreased k, hence a constant ICT dose is achieved (Figures 1c and 1d). The

4   instantaneous disinfectant demand, D, of a chemical disinfectant may also vary significantly

5   during a day, and this will affect the dose when flow-pacing is applied, i.e. the higher the D the

6   lower the dose.

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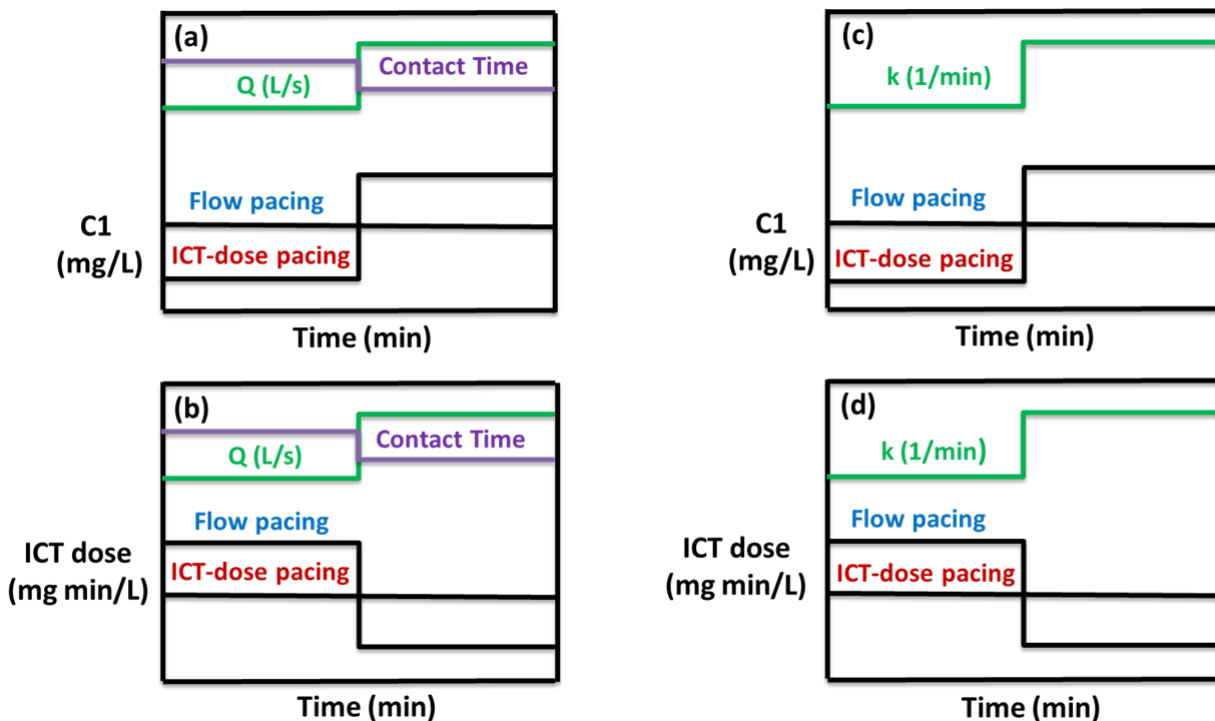11   Figure 3-11: Illustration of effects of flow on (a) disinfectant inlet concentration (C1) and (b)
12   ICT dose, and disinfectant decay (k) on (c) C1 and (d) ICT dose, for flow-pacing and ICT-dose
13   pacing control strategies.

14   In wastewater disinfection, the issue of advanced ICT-dose control is the most obvious as

15   the quantity and quality of the water can vary significantly over time due to several factors such

1   as diurnal fluctuations in human activity, industrial discharges, and wet-weather events. Under

2   such circumstances, conventional control methodologies such as flow-pacing would be

3   inadequate as they are unable to respond appropriately to maintain constant disinfection during

4   these events. A flow-pacing strategy, that aims to consider varying water quality, using chemical

5   oxygen demand and color measurements of the inlet wastewater to feed-forward control the

6   concentration of PAA has been proposed (Block et al., 2015). However, the aforementioned

7   control strategy still targets a constant inlet PAA concentration. Recently, an innovative ICT-

8   dose pacing control strategy has been developed and compared to flow-pacing control under

9   similar conditions (Sarathy et al., 2017). Experimental results of the recently developed ICT-

10   dose strategy are presented below in this section.

11

12   **5.2 Demonstration of Advanced Dose Control Strategy for PAA Disinfection**

13   The demonstration of the two control strategies was carried out in a 3-m^3 CCB consisting

14   of four passes. The CCB was located in a wastewater treatment plant enabling the use of real-

15   time secondary effluent wastewater as the influent of the CCB. A controller programmed with

16   conventional flow-pacing logic as well as the innovative ICT-dose pacing logic was used to

17   control the PAA dosing pump. PAA was dosed upstream of the pilot-scale serpentine CCB, and

18   PAA probes were installed at the inlet and outlet of the CCB to incorporate wastewater quality

19   changes (i.e. D and k) into the ICT-dose pacing control strategy. The flow of secondary effluent

20   wastewater has been adjusted accordingly to simulate relevant wastewater flow variation during

21   a day. Inlet and outlet viable fecal coliforms (FC) were measured to monitor disinfection

22   performance.

23   Initially, a flow-pacing experiment was carried out. The flow ranged from 1.0 L/s (over-

24   night) to 3.5 L/s (morning and evening peak flows) corresponding to hydraulic retention times

1   (HRTs) from 14 to 51 minutes. The ICT dose varies during the day, resulting in high ICT dose at

2   low flow (i.e. longer contact time, higher k), and low ICT dose at high flows (i.e. shorter contact

3   time, lower k) (Figure 2). This variation in ICT dose is confirmed through the observation that

4   concentration of viable FC at the outlet is not consistent. That is, the FC counts increased with

5   increasing flow since the ICT dose was inadequate. The reduction in the ICT dose is an

6   immediate indication of a potential disinfection permit violation (Figure 2). The varied ICT dose,

7   hence varied disinfection performnance during flow-pacing operation was expected due to the

8   fact that the water quality (D and k) and flow (contact time) are ignored. To ensure disinfection

9   compliance at all times by flow-pacing control, the inlet PAA concentration setpoint has to be set

10   as high as needed to ensure sufficient ICT dose is provided at peak flow/poorest water quality.

11   However, this will result in over-dosing of PAA at all lower flows/better water qualities,

12   increasing the operational cost of the process and the potential of disinfection by-products
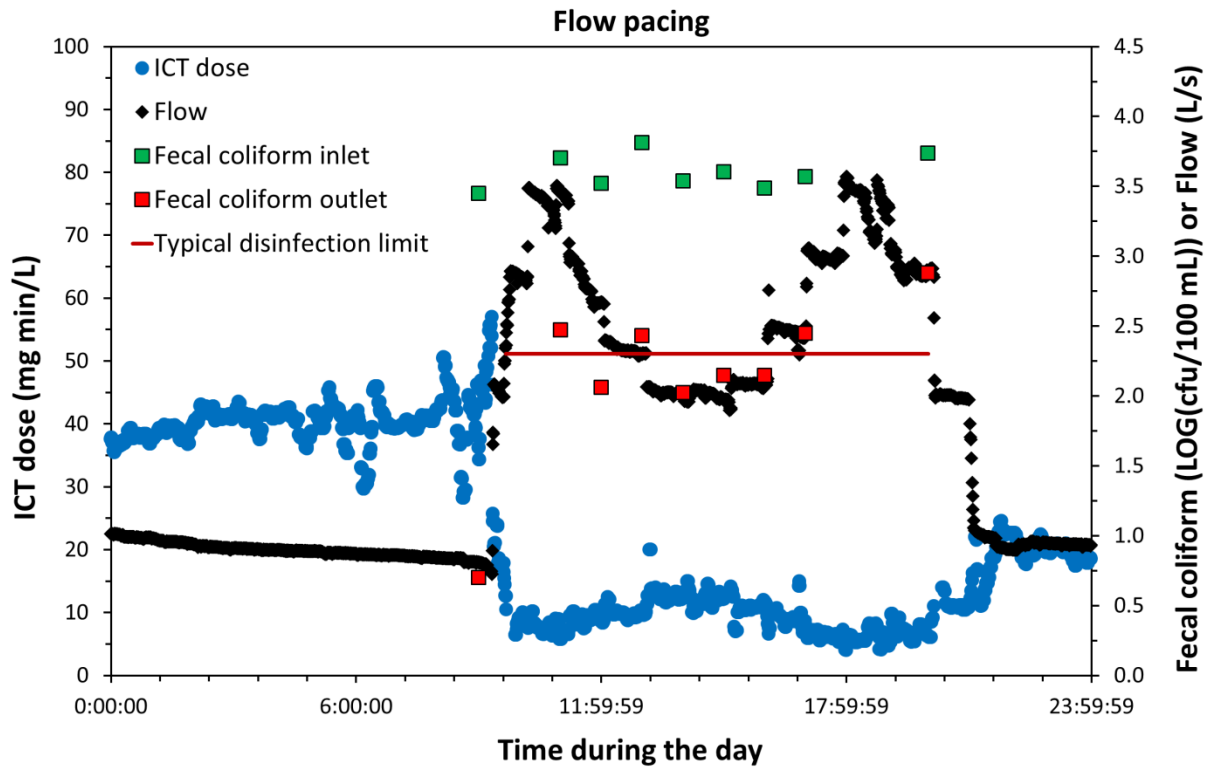
13   formation.

14

Figure 3-12: Performance of flow-pacing control strategy in pilot-scale test.

In contrast, ICT-dose pacing was able to achieve a constant ICT dose (16 mg·min/L defined by batch experiments) through the numerous flow changes, thereby ensuring consistent disinfection performance (Figure 3). Results show clearly that the disinfection performance is driven by the ICT dose, i.e. constant disinfection performance is achieved by constant ICT dose. The small fluctuation of the outlet counts of FC is due to the variation of the FC counts at the inlet (Figure 3).
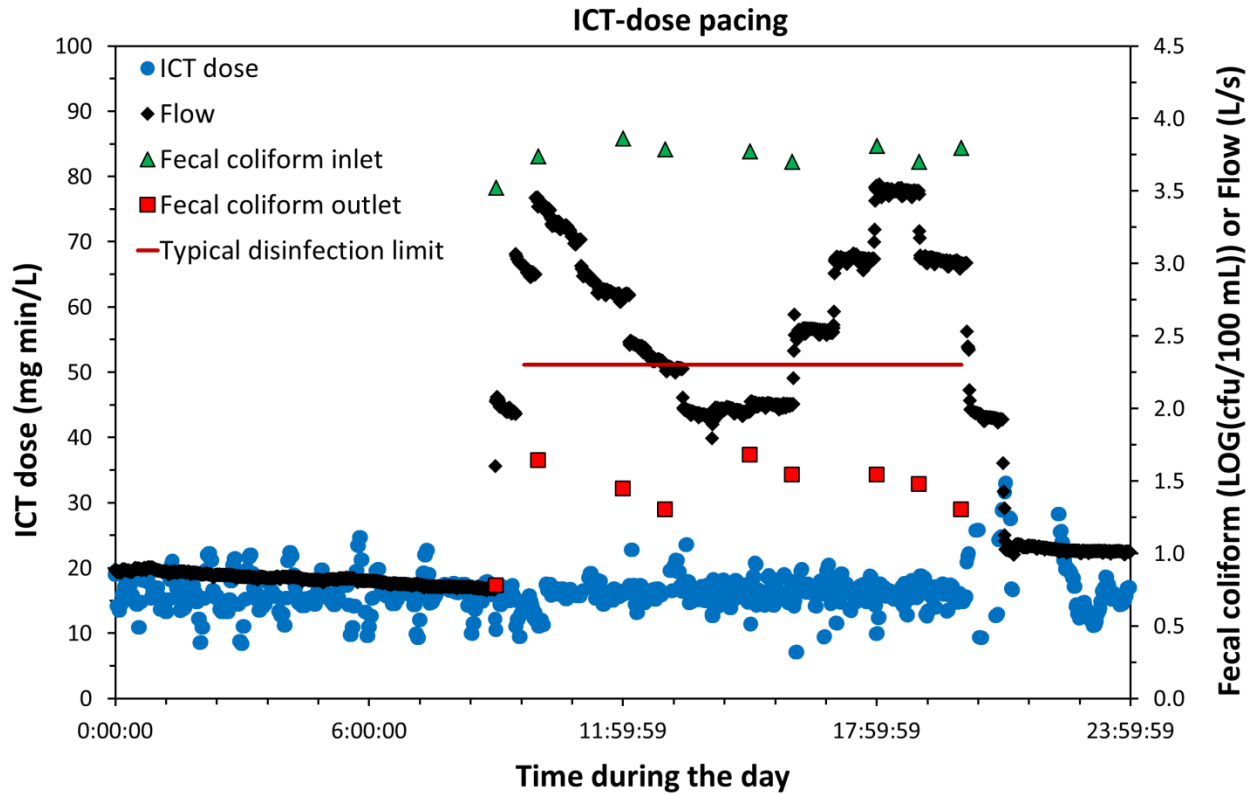
Figure 3-13: Performance of ICT-dose pacing control strategy in pilot-scale test.

More pilot-scale tests were carried out under flow-pacing operation. The collected data were processed to calculate the amount of PAA needed to treat 1000 m^3 of secondary effluent wastewater. Results showed that flow-pacing operation required twice the amount of PAA than ICT-dose pacing, in order to maintain a minimum ICT dose of 16 mg·min/L and ensure consistently meeting disinfection limits.
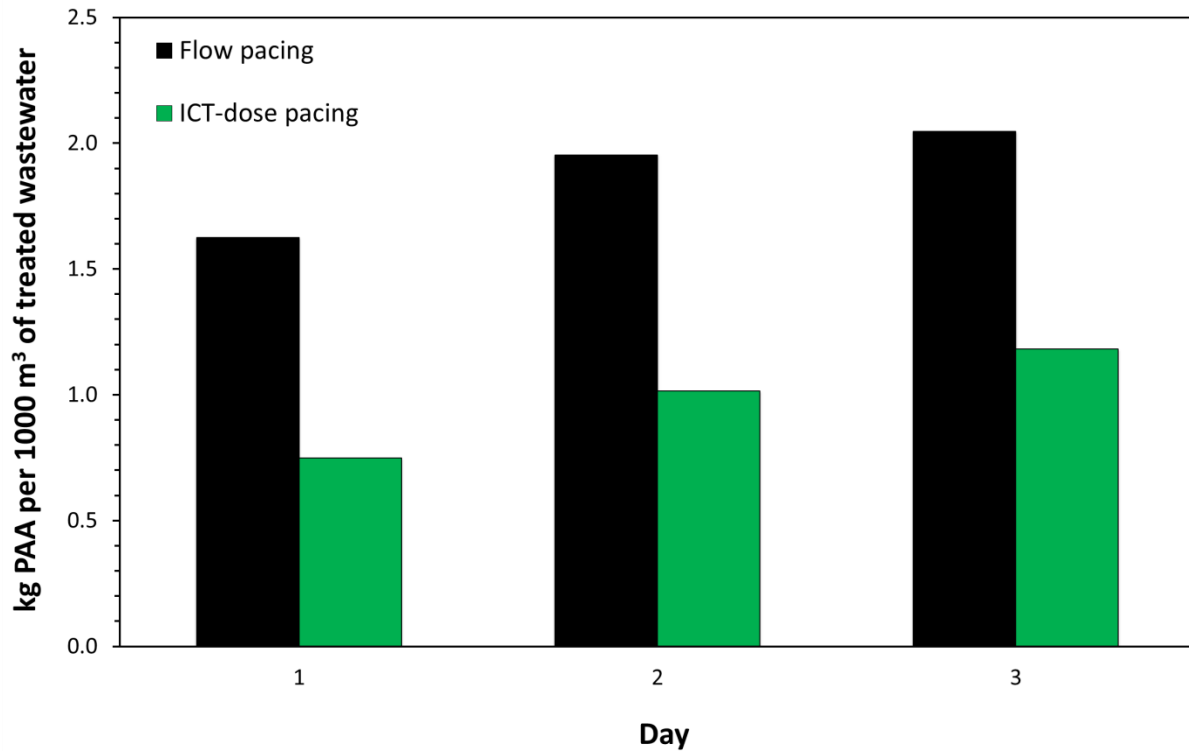
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Figure 3-14: Amount of PAA required per 1000 m3 of treated secondary effluent wastewater for each day of pilot-scale tests.

5.3 Dose Control Strategy for Combine UV and PAA Disinfection Process

Since the PAA disinfection performance is a function of ICT dose, a relation between the log reduction of specific microbes and ICT dose can be established, using any ICT-dose-based microbial inactivation kinetic model, e.g. double-exponential model. This relation allows one to predict the concentration of the microbes at the outlet of the disinfection reactor, at a particular ICT dose applied, given the initial concentration of microbes, i.e. concentration of microbes at the inlet of the reactor. It is well known that ultraviolet (UV) disinfection is also designed and controlled by dose, in this case the UV dose (mJ/cm^2) (Bolton and Linden, 2003). Hence, models can be applied to predict UV disinfection performance of specific microbes at a given UV dose. The fact that both UV and PAA disinfection processes depend on dose is important for the combination of the two technologies.

42

The combination of UV and PAA disinfection processes in series has been investigated and it was previous discussed in Chapter 3, Section 1. However, a dual-disinfection control strategy is also required for the efficient application of a combine UV and PAA disinfection process. Since dose is the key parameter to control both disinfection processes, an advanced dose control strategy would be able to control the UV dose as well as the ICT dose. This would enable the selection of disinfectant specific dose setpoints to achieve optimal disinfection pathways considering the nature of the microbes, i.e. their relative resistance to UV and PAA disinfection. Moreover, an intelligent control would transfer disinfection credits from one disinfection process to the other.

Overall, PAA disinfection performance is governed by ICT dose. In other words, a constant ICT dose ensures constant disinfection performance by PAA. UV dose is the key parameter to control UV disinfection too. This enables the use of dual-disinfection network. An intelligent dual disinfectant control algorithm could apply the most efficient disinfection setpoints considering the resistance of specific microbes, water quality, flow, UV lamp output, sleeve fouling, and chemical concentration.

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