



# Effect of suspended solids on peracetic acid decay and bacterial inactivation kinetics: Experimental assessment and definition of predictive models

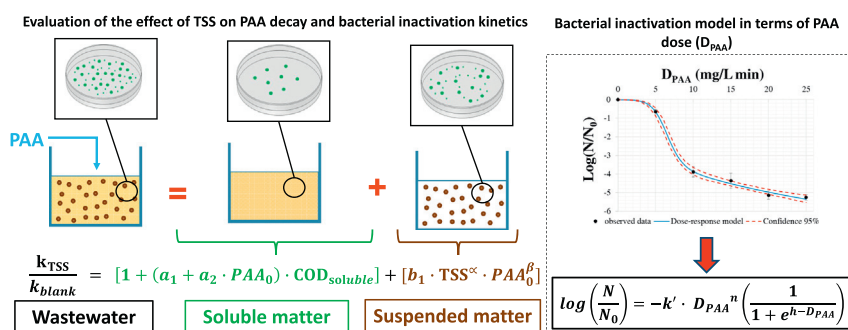
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## HIGHLIGHTS

- TSS concentrations higher than usual values of secondary effluents affect PAA decay.
- The effect of soluble matter associated to TSS is less relevant for PAA decay.
- Exposure dose is a reliable parameter to describe PAA disinfection performance.
- The presence of TSS decreases PAA disinfection efficiency.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The work addresses the effect of total suspended solids (TSS) on disinfection by peracetic acid (PAA) concerning both PAA decay and bacterial inactivation kinetics. The effect of TSS on PAA decay was evaluated at five TSS concentrations (5, 40, 80, 120 and 160 mg/L), obtained from stock TSS solutions prepared from activated sludge samples. The influence of the soluble matter associated to the suspended solids on PAA decay was evaluated separately, using the same stock TSS solution after the removal of solids by filtration. The contributions of suspended and soluble fractions were found to be independent, and a predictive model formed by two additive sub-models was proposed to describe the overall PAA decay kinetics. Moreover, an uncertainty analysis was performed by a series of Monte Carlo simulations to propagate the uncertainties associated to the coefficients of the model. Then, the disinfectant dose (mg/L min) was highlighted as the main parameter determining disinfection efficiency on a pure culture of *E. coli* and an inactivation kinetic model was developed based on the response of *E. coli* to various PAA doses. Finally, the effect of TSS (40 and 160 mg/L) on the inactivation of free-swimming *E. coli* was investigated at two PAA doses (5 and 20 mg/L min). TSS reduced inactivation extent an average of 0.4 logs at 5 mg/L min and 1.5 logs at 20 mg/L min. It was hypothesized that this might be due to the formation of bacteria aggregates as defense mechanism against disinfection, enhanced by the presence of solids.

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## 1. Introduction

Disinfection is a key process in wastewater treatment and it plays a fundamental role in public health protection. Peracetic acid (PAA) gained momentum over the last decades as disinfectant for wastewater

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## Nomenclature

PAA	peracetic acid
CSO	combined sewer overflow
WWTP	wastewater treatment plant
TSS	total suspended solids (mg/L)
PAB	particle associated bacteria
<i>E. coli</i>	<i>Escherichia coli</i>
$D_{PAA}$	peracetic acid dose (mg/L min)
MBBR	moving bed biofilm reactor
CAS	conventional activated sludge
BOD	biological oxygen demand (mg/L)
COD	chemical oxygen demand (mg/L)
$N_{tot}$	total nitrogen (mg/L)
$PO_4^{3-}$	phosphate (mg/L)
CFU	colony forming units
$N_0$	initial number of bacteria before disinfection (CFU/mL)
$N$	number of bacteria after disinfection (CFU/mL)
ABS	absorbance
y, z	coefficients of the standard curve for PAA measurement
PAA0	initial PAA concentration (mg/L)
PAA <sub>t</sub>	PAA concentration at time t (mg/L)
OD	oxidative demand (mg <sub>PAA</sub> /L)
t	contact time (min)
k	decay rate constant (min <sup>-1</sup> )
$k_{blank}$	blank decay rate constant (min <sup>-1</sup> )
$k_{sol}$	decay rate constant ascribable to the soluble matter (min <sup>-1</sup> )
$k_{TSS}$	decay rate constant ascribable to the suspended and soluble matter (min <sup>-1</sup> )
$k^*$	decay rate constant ascribable to the suspended matter (min <sup>-1</sup> )
$a_1, a_2, b_1, \alpha, \beta$	coefficients of the non-linear regression
$k'$	bacterial inactivation rate constant
n, m, x	parameters of the generalized inactivation rate (GIR) model
C	disinfectant concentration in the GIR model (mg/L)
h	parameter of the <i>E. coli</i> inactivation model

due to its powerful antimicrobial activity (Kitis, 2004; Luukkonen et al., 2014) combined with a limited formation of disinfection by-products (Dell'Erba et al., 2007; Liberti and Notarnicola, 1999), even in case of poor quality of the water matrix, as for combined sewer overflows (CSOs) disinfection (US EPA, 1999). However, PAA decays rapidly in aqueous solutions (Yuan et al., 1997). Previous studies suggested that the water matrix composition, particularly organic and suspended matter content, has a significant influence on PAA decay, as readily oxidable compounds immediately consume the disinfectant (Falsanisi et al., 2006; Koivunen and Heinonen-Tanski, 2005; Lazarova et al., 1998; Liu et al., 2014; Pedersen et al., 2013). Therefore, guarantying a sufficient amount of disinfectant to reach bacterial inactivation targets, while avoiding high residuals at effluent discharge, is a key objective in the design and operation of effective disinfection systems.

Suspended solids in wastewater treatment plants (WWTPs) include a wide and heterogeneous group of particles whose characteristics and composition are determined by a combination of factors, including the characteristics of the influent wastewater, which mainly depend on the source (domestic, industrial, agricultural, storm) and on the type of the sewer (combined or separated), and the treatment processes occurring in the WWTP. A key element when dealing with suspended solids is the particle structure, that is not smooth and rigid but rather an irregular sponge-like matrix characterized by pores of different sizes in which bacteria can be shielded (Dietrich et al., 2003).

Suspended solids affect PAA disinfection mainly by two mechanisms: (i) consumption of PAA entailing a reduction of the available concentration for disinfection and, thus, a lower PAA exposure dose for bacteria inactivation, and (ii) shielding of bacteria against the action of the disinfectant.

As for PAA decay, previous works investigated the contribution of soluble organic content in terms of macro-parameters such as chemical oxygen demand (COD) and biological oxygen demand (BOD), while the effect of suspended matter has been scarcely studied, although it has been observed in different works (Chhetri et al., 2016, 2014; Falsanisi et al., 2008; Koivunen and Heinonen-Tanski, 2005; Lazarova et al., 1998; Lefevre et al., 1992; McFadden et al., 2017; Sánchez-Ruiz et al., 1995; Stampi et al., 2001). Several authors have indicated that primary effluents and CSOs require higher PAA concentrations for disinfection than secondary and tertiary effluents (Chhetri et al., 2016; Gehr and Cochrane, 2002; Koivunen and Heinonen-Tanski, 2005; Luukkonen et al., 2014). Furthermore, Chhetri et al. (2016) observed that a pre-treatment of CSO for the removal of suspended solids decreases the required disinfectant dosage.

Regarding the protective shielding afforded to bacteria, suspended solids play a major role. Microbial aggregates and microorganisms attached to or embedded into particles demonstrated increased resistance to inactivation by different disinfectants compared to non-attached, free-swimming microorganisms (Bohrerova and Linden, 2006; Dietrich et al., 2007; LeChevallier et al., 1984; Winward et al., 2008). However, it should be considered that approximately 99% of the overall bacterial population in wastewater is free-swimming (i.e., bacteria size < 10 µm) and only approximately 1% or less consists of particle associated bacteria (PAB) (Falsanisi et al., 2008; Qualls et al., 1985, 1983). As for the particle size of suspended solids, Falsanisi et al. (2008) observed that it has a paramount importance during PAA disinfection, as the protection afforded by TSS was 0.6 and 1.3 logs for solids between 10 and 120 µm and >120 µm, respectively, whereas McFadden et al. (2017) observed that solid size in the range between 10 and 100 µm had a minor effect on PAA disinfection. A decrease in disinfection efficiency of PAA with increasing TSS concentrations has been observed in previous works (Kitis, 2004; McFadden et al., 2017); however, limited research has been conducted to elucidate this aspect. Stampi et al. (2001) reported that the detrimental impact on PAA disinfection performance is moderate and constant for TSS concentrations between 10 and 40 mg/L, while Lefevre et al. (1992) found that PAA presents an excellent disinfection performance even up to 100 mg/L.

When dealing with PAA disinfection, another key aspect is related to the actual dose (mg/L min) as the main parameter determining disinfection efficiency, whose estimation must depend on the changing concentration of disinfectant at which bacteria are exposed over contact time (Santoro et al., 2015). Usually the design and operation of disinfection processes with chlorine-based compounds, for simplicity, is based on the estimation of the exposure dose calculated as the product of initial disinfectant concentration and contact time. Consequently, the most widely used inactivation models are based on this concept and therefore on these two parameters. However, this approach neglects the disinfectant decay, thus it is not a reliable predictor for PAA disinfection performance. On the contrary, PAA decay should be considered in the calculation of the actual PAA dose ( $D_{PAA}$ ), considering the disinfectant active concentration at any contact time (Haas and Joffe, 1994; Turolla et al., 2017).

The present study aims at elucidating the effect of suspended solids on PAA decay and *E. coli* inactivation performance. PAA decay was assessed in the presence of five different TSS concentrations (5, 40, 80, 120 and 160 mg/L), representing secondary effluents of good (well settled) and medium (not well-settled) quality, and CSOs. In detail, stock TSS solutions were prepared from activated sludge samples to obtain test solutions at different TSS concentrations. In addition, the effect on PAA decay of the soluble matter in solution with suspended solids was also evaluated, after removing the solids by filtration at 0.45 µm. A

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