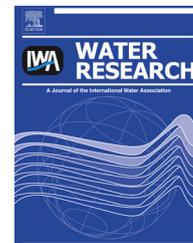




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# Enhancing disinfection by advanced oxidation under UV irradiation in polyphosphate-containing wastewater flocs

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## ARTICLE INFO

### Article history:

Received 5 November 2013

Received in revised form

3 January 2014

Accepted 6 January 2014

Available online 5 February 2014

### Keywords:

Wastewater

Ultraviolet disinfection

Advanced oxidation

Polyphosphate

Phosphate accumulating organisms

Modeling

## ABSTRACT

In this paper, the role of naturally occurring polyphosphate in enhancing the ultraviolet disinfection of wastewater flocs is examined. It was found that polyphosphate, which accumulates naturally within the wastewater flocs in the enhanced biological phosphorus removal process, is capable of producing hydroxyl radicals under UV irradiation and hence causing the photoreactive disinfection of microorganisms embedded within flocs. This phenomenon is likely responsible for the improved UV disinfection of the biological nutrient removal (BNR) effluent compared to that of conventional activated sludge effluent by as much as 1 log. A mathematical model is developed that combines the chemical disinfection by hydroxyl radical formation within flocs, together with the direct inactivation of microorganisms by UV irradiation. The proposed model is able to quantitatively explain the observed improvement in the UV disinfection of the BNR effluents. This study shows that the chemical composition of wastewater flocs could have a significant positive impact on their UV disinfection by inducing the production of oxidative species.

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## 1. Introduction

Ultraviolet disinfection is a well established technology for disinfecting secondary wastewater effluents. UV light, specifically around the germicidal wavelengths (200–300 nm), inactivates microorganisms by penetrating through the cell wall and altering the microorganism's DNA (Jagger, 1967; Pfeifer et al., 2005; Piluso and Moffatt-Smith, 2006). This is widely believed to be the main mechanism for the UV disinfection of wastewater effluents.

It has been reported that UV light can also cause disinfection through the production of highly oxidative species such

as hydroxyl radicals in the presence of certain photocatalysts and photoactive species. The formation of hydroxyl radicals could cause the oxidation of cell wall and cause cell death (Matsunaga et al., 1985; Maness et al., 1999). In particular Cho et al. (2004) measured the release of  $\bullet\text{OH}$  in the UV/TiO<sub>2</sub> process and reported a linear correlation between the concentration of hydroxyl radicals and the inactivation rate of free *E. coli*. They found that the CT value of  $\bullet\text{OH}$  for 2 log inactivation of *E. coli* was  $0.8 \times 10^{-5}$  mg.min/L. Their results showed that  $\bullet\text{OH}$  was approximately 3–4 orders of magnitude more effective for *E. coli* inactivation compared to common disinfectants such as chlorine and ozone.

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Nomenclature	
DRC	Dose Response Curve
BNR	Biological nutrient removal
BNR-UCT	Biological nutrient removal – modified University of Cape Town
CAS	Conventional activated sludge
EPS	Extracellular polymeric substances
PAO	Phosphorus accumulating organisms
MLSS	Mixed liquor suspended solids (g/L)
VSS	Volatile suspended solids (g/L)
COD	Chemical oxygen demand (mg/L)
SVI	Sludge volume index (mL/g)
TEM	Transmission electron microscopy
RO	Reverse Osmosis
CFU	Colony forming units
TEM	Transmission electron microscopy
EDX	Energy dispersive X-ray
$k''$	production rate constant of $\bullet\text{OH}$ in the presence of polyphosphate and UV light ( $\text{mg}\cdot\text{cm}^2/\text{L}\cdot\text{mW}$ )
$k'$	Inactivation rate constant of free <i>E. coli</i> with $\bullet\text{OH}$ ( $\text{L}/\text{mg}\cdot\text{min}$ )
MB	Methylene blue
$I$	Average UV intensity at the surface of a floc ( $\text{mW}/\text{cm}^2$ )
$k_{\text{MB}, \bullet\text{OH}}$	Reaction rate constant of methylene blue and the hydroxyl radical ( $\text{L}/\text{mol}\cdot\text{s}$ )
$R$	Floc radius ( $\mu\text{m}$ )
$\delta$	The distance of the point of interest from the surface of the floc ( $\mu\text{m}$ )
$D_{\text{eff}}(\delta)$	The effective UV dose delivered in the distance of $\delta$ from the floc's surface ( $\text{mJ}/\text{cm}^2$ )
$k_{\text{UV}}$	Inactivation rate constant of free <i>E. coli</i> with UV light ( $\text{cm}^2/\text{mJ}$ )
$k_{\bullet\text{OH}}$	Inactivation rate constant of free <i>E. coli</i> with $\bullet\text{OH}$ , combined with the production of $\bullet\text{OH}$ ( $\text{L}/\text{mg}\cdot\text{min}$ )
$N_0(R, \delta)$	Initial concentration of viable flocs ( $\text{CFU}/100\text{ mL}$ )
$N(R, \delta)$	Final concentration of viable flocs ( $\text{CFU}/100\text{ mL}$ )
$k_{\text{effUV}}(\delta)$	Effective UV inactivation constant at the distance $\delta$ from the surface of the floc inwards ( $\text{cm}^2/\text{mJ}$ )
$k_{\text{eff}\bullet\text{OH}}(\delta)$	Effective $\bullet\text{OH}$ inactivation constant at the distance $\delta$ from the surface of the floc inwards ( $\text{L}/\text{mg}\cdot\text{min}$ )
$A$	UV absorbance of EPS ( $\text{cm}^{-1}$ )
$f(R, \delta)$	Probability density function of $R$ and $\delta$
$V$	Total floc volume ( $\mu\text{m}^3$ )
$\delta_s$	Shell thickness in the core–shell model used for the CAS flocs ( $\mu\text{m}$ )

Over the past two decades, many wastewater treatment plants have been constructed for the purpose of biological nutrient removal (BNR) (Trivedi, 2009). In a BNR process, anaerobic and/or anoxic zones are incorporated with aerobic zones for biological removal of nitrogen and/or phosphorus in addition to carbonaceous nutrients. However, the shift between aerobic, anoxic and anaerobic conditions is known to cause sludge bulking and affects the particle size, sludge settling time, and effluent turbidity (Eikelboom et al., 1998; Yun et al., 2000; Martins et al., 2004; Vaiopoulou et al., 2007). It has been reported that when alternating aerobic/anaerobic conditions, the number of small particles increased during the anaerobic period and higher turbidities were observed (Wilén and Balmér, 1999), and that anaerobic flocs were smaller than aerobic ones (Moon et al., 2004). Meanwhile, Martins et al. (2004) concluded that the presence of microaerophilic zones in the anoxic stages of BNR systems led to worsening sludge-settling characteristics. In a recent study, we reported that wastewater flocs generated in a BNR system are more readily disinfected under UV irradiation (Azimi et al., 2013). However, the exact mechanism for such an improvement is not well understood.

In BNR processes with enhanced biological phosphorus removal, phosphorus accumulating organisms (PAOs) remove phosphorus from wastewater and store it in the form of polyphosphates. In the aerobic zone of an enhanced biological phosphorus removal process, polyhydroxyalkanoates; that are synthesized by the PAOs in the anaerobic zones, are oxidized by the PAOs. During this process the energy reserves from oxidation are stored through phosphate uptake and polymerization (WEF & ASCE, 2006; Hirota et al., 2010). The total phosphorus content of sludge generated in this process can reach up to 10–15% (Stowa, 2002). Hirota et al. (2010)

heated sludge collected from an enhanced biological phosphorus removal process to extract the polyphosphates, and applied polyacrylamide gel electrophoresis to determine the chain length of the released polyphosphate. They concluded that the main compounds stored by the PAOs are polyP compounds with a chain length of 100–200  $P_i$  residues and trimetaphosphate.

Here it is hypothesized that the phosphorus compounds that accumulate in the flocs during the biological phosphorus removal process, were responsible for the improved UV disinfection of the modified BNR-UCT (University of Cape Town) wastewaters by inducing photooxidation under UV irradiation. Accordingly, the main objective of this study was to explore the role of polyphosphate storage in the UV disinfection of PAO-containing wastewater flocs.

## 2. Materials and methods

### 2.1. Samples

The samples used for this study were collected from two continuous pilot scale reactors (effective volume of 350 L), treating real municipal wastewater, at the National Water Research Institute (NWRI), Environment Canada, Burlington, Canada. Both reactors were equipped with identical secondary clarifiers and had recycling sludge streams. One of the reactors was a conventional fully aerated activated sludge system, and the other was a BNR-UCT, which contained anaerobic, anoxic and aerobic zones for simultaneous nitrogen and phosphorus removal. Details of the influent COD, total nitrogen and phosphorus in addition to the operating

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