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Conversion Of Soluble Recalcitrant Phosphorus to Recoverable Orthophosphate Form Using UV/H_2O_2

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Abstract

Soluble non-reactive phosphorus (sNRP), such as inorganic polyphosphates and organic P, is not effectively removed by conventional physicochemical processes. This can impede water resource reclamation facilities' ability to meet stringent total P regulations. This study investigated a UV/H_2O_2 advanced oxidation process (AOP) for converting sNRP to the more readily removable/recoverable soluble reactive P (sRP), or orthophosphate, form. Synthetic water spiked with four sNRP compounds (beta-glycerol phosphate, phytic acid, triphosphate, and hexa-meta phosphate) at varying H_2O_2 concentration, UV fluence, pH, and temperature was initially tested. These compounds represent simple, complex, organic, and inorganic forms of sNRP potentially found in wastewater. The efficiency of sNRP to sRP conversion depended on whether the sNRP compound was organic or inorganic and the complexity of its chemical structure. Using 1 mM H_2O_2 and 0.43 J/cm^2 (pH 7.5, 22 °C), conversion of the simple organic beta-glycerol phosphate to sRP was 38.1 ± 2.9%, which significantly exceeded the conversion of the other sNRP compounds. Although conversion was achieved, the electrical energy per order (E_{EO}) was very high at $5.2 \times 10^3 \pm 5.2 \times 10^2$ kWh/m^3. Actual municipal wastewater secondary effluent, with sNRP accounting for 15% of total P, was also treated using UV/H_2O_2. No wastewater sNRP to sRP conversion was observed, ostensibly due to interference from wastewater constituents. Wastewater utilities that have difficulty meeting stringent P levels might be able to target simple organic sNRP compounds, though alternative processes beyond UV/H_2O_2 need to be explored to overcome interference from wastewater constituents and target more complex organic and inorganic sNRP compounds.

Keywords

Advanced oxidation, Hydroxyl radicals, Organic phosphorus, Ultraviolet, Hydrogen peroxide, Polyphosphates

Abbreviations

AEP Aminoethylphosphonate
AOP Advanced oxidation process
ATP Adenosine triphosphate
BGP Beta-glycerol phosphate
DF Divergence factor
DOC Dissolved organic carbon
EEO Electrical energy per order
HMP Hexa-meta phosphate
NOM Natural organic matter
NRP Non-reactive phosphorus
OP Organic phosphorus
P Phosphorus
PA Phytic acid
PCBA Para-chlorobenzoic acid
PF Petri factor
pNRP Particulate non-reactive phosphorus
pP Particulate phosphorus
pRP Particulate reactive phosphorus
RF Reflection factor
RP Reactive phosphorus
sNRP Soluble non-reactive phosphorus
sP Soluble phosphorus
sRP Soluble reactive phosphorus
TEP Tri-ethyl phosphate
TP Total phosphorus

TrP Tri-phosphate
UV Ultraviolet
WF Water factor
WRRF Water resource reclamation facility

1. Introduction

As increasingly stringent P discharge regulations are implemented to limit eutrophication in receiving surface waters, there is increased emphasis on improving current phosphorus (P) removal processes in water resource reclamation facilities (WRRFs) (Macintosh et al., 2018; Mayer et al., 2016; Venkiteshwaran et al., 2018). Beyond meeting P discharge regulations, P recovery for reuse as a valuable commodity in the fertilizer industry promotes a circular P economy. However, wastewater P speciation affects P removal in terms of the ability to achieve lower total phosphorus (TP) regulatory limits, as well as the potential for subsequent P recovery (Venkiteshwaran et al., 2018).

Sub-fractions of TP include soluble P (sP), which passes through a 0.45 µm filter, and particulate P (pP), the fraction retained by the filter. Reactive P (RP), also known as orthophosphate, is the fraction that is readily available for chemical reactions via coulombic attraction to cations (APHA, 2012; McKelvie, 2005). Alternately, non-reactive P (NRP), also known as condensed or acid hydrolysable P, includes inorganic polyphosphates (i.e., metaphosphates and di-, tri-, and tetra-polyphosphates) and organic P (OP) constituents (APHA, 2012). Sources of polyphosphate range from naturally occurring compounds to anthropogenic sources such as polyphosphate fertilizers (USEPA, 2010; Yuan et al., 2012). Natural OP in wastewater can come from animals, plants, or microbial cellular materials including phospholipids, nucleotides, and nucleic acids (Murphy, 2007). Synthetic OP may enter water or wastewater following the use of organophosphorus-based pesticides (e.g., malathion) or herbicides (e.g., glyphosate) (Sud and Kaur, 2012; Theriot and Grunden, 2011).

Conventional physicochemical P removal techniques, including coagulation, flocculation, precipitation, ion exchange, micro- or ultra-filtration, and adsorption, are effective in removing RP, and particulate NRP (pNRP) fractions (Neethling et al., 2010), but sNRP is recalcitrant to removal and recovery using typical wastewater treatment processes (Qin et al., 2015; Venkiteshwaran et al., 2018). As the sNRP fraction is not effectively removed using current technologies, it can pass unaffected through the treatment train, leading to difficulties in meeting effluent TP standards. Gu et al. (2011) observed >93% removal of soluble RP (sRP), pRP, and pNRP; however, <40% sNRP was removed in a full-scale enhanced biological phosphorus removal (EBPR) plant. If sNRP cannot be effectively removed, it contributes disproportionately to TP discharges and it cannot be recovered for beneficial reuse as part of an integrated approach to resource recovery.

Venkiteshwaran et al. (2018) reviewed potential physical, chemical, and biological treatment processes that have been successfully applied and/or have potential for NRP to RP conversion. Advanced oxidation processes (AOPs) featuring the oxidative power of hydroxyl radicals (HO•, E° = 2.80 V) may offer one approach and can facilitate P removal and recovery efforts through conversion of sNRP to sRP. A number of AOPs have been developed for wastewater treatment applications. Some of the AOPs used in research or application include photochemical degradation processes (UV/O_3, UV/H_2O_2, X-ray/H_2O_2), photocatalysis (TiO_2/UV, photo-Fenton), sonolysis (ultrasonication/H_2O_2), chemical oxidation (O_3/H_2O_2, H_2O_2/Fe^{2+}), and electrochemical processes (Poyatos et al., 2010; Wang and Xu, 2012). Several studies have reported the use of AOPs to degrade sNRP in the form of organophosphorus pesticides (Badawy et al., 2006; Daneshvar et al., 2004; Farooq et al., 2003; Trebše and Arčon, 2003). Degradation of 50–70% of the organophosphorus compounds profenofos, diazinon, and fenitrothion was achieved using AOPs such as UV/H_2O_2, Fenton, and photo-Fenton (Badawy et al., 2006). These studies focused on removal of the original organophosphorus compound but did not assess the extent of organophosphorus compound conversion to sRP.

We identified only two previous studies evaluating sNRP conversion using AOPs. Gray et al. (2020) reported conversion of two organic sNRP compounds (adenosine triphosphate [ATP] and aminoethylphosphonate [AEP]) as well as wastewater sNRP using TiO_2/UV. However, a substantial portion of their overall sNRP removal (93% for ATP, 38% for AEP, and 40%–50% for wastewater) was via sNRP adsorption to the TiO_2 particles. On the other hand, Sindelar et al. (2016) achieved approximately 40–95% conversion of the sNRP tri-ethyl phosphate (TEP) to sRP using UV/H_2O_2 (1.47–2.94 mM H_2O_2 and 2.4–28.5 J/cm^2) and 50%–67% conversion of naturally occurring sNRP in water from the Everglades (2.94 mM H_2O_2 and 21.8–26.1 J/cm^2).

Based on these early successes using AOPs to degrade recalcitrant sNRP compounds, the objective of this study was to evaluate the effectiveness of UV/H_2O_2 in converting a range of sNRP species to sRP, and to quantify energy efficiency for this application. Four model compounds were chosen as representative sNRP compounds in municipal wastewaters in order to explore the influence of varying sNRP structure on AOP-based conversion. Their conversion to sRP was tested at varying H_2O_2 dose, UV fluence, pH, and temperature. Additionally, the relative abundance of each P fraction in real wastewater samples was quantified, and the efficacy of wastewater sNRP conversion using UV/H_2O_2 was investigated.

2. Materials and methods

2.1. Model sNRP compounds and wastewater samples

This study used four model compounds to represent a range of sNRP chemical structures that may be found in wastewater: hexa-meta phosphate (HMP), tri-phosphate (TrP), beta-glycerol phosphate (BGP), and phytic acid (PA) (Sigma-Aldrich, St. Louis, MO, USA). HMP and TrP are inorganic phosphates and BGP and PA are organic phosphates. TrP and BGP have a simple linear structure, whereas HMP and PA have more complex cyclic structures, as shown in Fig. 1.

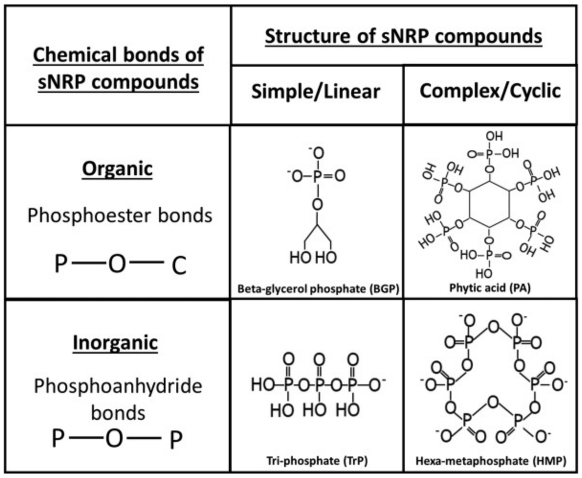

Fig. 1. Structure of the sNRP compounds.

Phosphorus fractions were quantified in secondary treated municipal wastewater samples obtained from the South Shore Water Reclamation Facility in Oak Creek, WI, USA. The conversion of sNRP to sRP in both the synthetic and wastewater samples was evaluated using UV/H_2O_2 tested at varying H_2O_2 dose, UV fluence, pH, and temperature.

2.2. UV irradiation system

A bench-scale UV collimated beam apparatus was used, as described by Ryu et al. (2008) (Figure S1). It featured a 46-cm, 15-W, low-pressure, mercury arc bulb (Model G15T8, USHIO, Cypress, CA), which produced monochromatic light at a peak wavelength of 254 nm. The collimating tube was 61 cm in length with a diameter of 5.2 cm, providing a length-to-diameter ratio of approximately 12 (Kuo et al., 2003). This design standardized the irradiation by forming nearly parallel rays of light within the collimating column. The sample platform was adjusted to maintain a 1-cm separation between the end of the collimating column and the water surface. The light intensity at the sample surface was measured using an IL1700 research radiometer with sensor SED005W and narrowband filter NS254 (International Light, Newburyport, MA, USA). The average intensity was calculated using Equation (1) (Bolton and Linden, 2003):

(1)

$$I_{AVG} = I_0 \times RF \times PF \times WF \times DF$$

where I_{AVG} = average intensity (W/cm^2), I_0 = uncorrected peak intensity measured using the radiometer (W/cm^2), RF = reflection factor, PF = Petri factor, WF = water factor, and DF = divergence factor.

Following a 20-min warm-up period for the UV lamp, the uncorrected peak intensity, I_0, was measured as ≈ 1.4×10^{-4} W/cm^2. The correction factors were determined as described by Bolton and Linden (2003) as RF = 0.975, PF = 0.92, WF ≈ 1, and DF = 0.99 for the system used in this study. Accounting for the correction factors, the average intensity (I_{AVG}) was approximately 1.2×10^{-4} W/cm^2. The UV fluence for each experiment was then calculated using Equation (2):

(2)

$$\text{UV fluence (J/cm}^2) = I_{AVG} \times t$$

where t is the time of exposure in seconds.

2.3. Conversion of sNRP compounds to sRP in Milli-Q water using UV/H_2O_2 as a function of H_2O_2 dose, UV fluence, pH, and temperature

In separate tests, the four sNRP compounds were dissolved in 14 mL Milli-Q water to a final concentration of 1 mg-P/L in 52-mm inner diameter quartz petri dishes (Fisher Scientific, Waltham, MA, USA). Separate experiments were conducted in which the four sNRP compounds were exposed to varying H_2O_2 dose, UV fluence, initial pH, and temperature, as shown in Table 1.

Table 1. UV/H_2O_2 experimental conditions.

Water Matrix	**Experimental Conditions**	**Temperature (°C)**	**Initial pH**	**H_2O_2 Conc. (mM) [mg/L]**	**UV Fluence (J/cm^2)**
Milli-Q water spiked separately with 1 mg-P/L BGP, PA, TrP, or HMP[a]	Varying H_2O_2 Conc.	22	7.5	1 [34]	0.43
				6 [204]	
				12 [408]	
				18 [612]	
				24 [816]	
	Varying UV Fluence	22	7.5	1 [34]	0.43
					1.3

					2.1
	Varying pH	22	3	1 [34]	0.43
			5.5		
			7.5		
			9		
			11		
	Varying Temperature	14	7.5	1 [34]	0.43
		22			
		37			
Secondary wastewater	Wastewater	22	7.5	1 [34]	0.43
Secondary wastewater spiked with 1 mg-P/L BGP	Wastewater Spiked with BGP				

[a] BGP: Beta-glycerol phosphate; PA: Phytic acid; TrP: Tri-phosphate, and HMP: Hexa-metaphosphate.

The desired H_2O_2 concentration was achieved by adding varying volumes of 30% H_2O_2 solution (Sigma-Aldrich, St. Louis, MO, USA). Variable UV fluence was achieved by varying the UV exposure time. The initial water pH was adjusted by adding 1 M HCl or NaOH. For temperature variation, the UV irradiation system was placed in a 49 ft^3 refrigerator (Cole-Parmer, Vernon Hills, IL, USA) or a heated room to achieve 14 °C and 37 °C, respectively. The Milli-Q water was also pre-cooled and pre-heated to match these temperatures prior to the experiments.

In all experimental conditions, parallel tests were operated as controls, including no treatment, UV only (same fluence), and H_2O_2 only (same H_2O_2 dose) for comparison against the UV/H_2O_2 tests. For all controls, the four sNRP compounds were dissolved in Milli-Q water at a concentration of 1 mg/L as TP and allowed to stir for the same exposure time. All experiments were performed in triplicate.

After the desired exposure time, MnO_2 (Sigma-Aldrich, St. Louis, MO, USA) was added in excess to all samples to quench residual oxidants. The solution was then filtered using 0.45 µm PTFE syringe filters (Agela Technologies, Wilmington, DE, USA) to remove excess MnO_2 prior to P analysis. All sNRP to sRP conversion results were normalized to the relative control tests.

2.4. Conversion of sNRP in real wastewater using UV/H_2O_2

The conversion of sNRP to sRP in real wastewater was conducted as described previously except using municipal secondary wastewater effluent. Raw secondary wastewater was treated with the UV/H_2O_2 AOP, as shown in Table 1. In another set of experiments, raw secondary wastewater was spiked with 1 mg-P/L BGP (compound with highest conversion in Milli-Q water) and treated with UV/H_2O_2 to ascertain the effects of wastewater constituents on conversion.

2.5. Energy consumption of UV/H_2O_2

Electrical energy per order (E_{EO}) is a tool for comparing the efficiency of first-order degradation using AOPs (Bolton and Stefan, 2002). It is defined as the electrical energy necessary to reduce a contaminant by one order of magnitude in one cubic meter of water (Equation (3)).

(3)

$$E_{EO} = (P \times t)/(V \times \log (C_i/C_f))$$

where E_{EO} is the electrical energy per order (kWh/m^3), P is the lamp power (kW), t is time (hours), V is volume irradiated (m^3), and C_i and C_f are the initial and final sNRP concentrations (mg-P/L).

2.6. Analytical methods and statistical analysis

P fractions, including sRP, RP, sP, and TP were analyzed per Standard Methods using the ascorbic acid method (APHA 2012). For sRP and sP analysis, the samples were filtered using a 0.45 µm pore size filter (Bonna-Agela Technologies Inc., Tianjin, China). Other P fractions were derived from these measures, including:

- Particulate RP (pRP = RP - sRP)
- Soluble NRP (sNRP = sP - sRP)
- Particulate NRP (pNRP = TP – RP – sNRP)

The absorbance in the ascorbic acid methods was measured using a UV–visible spectrophotometer (GENESYS™ 10, ThermoFisher Scientific Inc., Waltham, MA USA) with a 1-cm light path and a minimum detection limit (MDL) of 0.006 mg-P/L, as determined using USEPA (2016) methods.

The pH was measured using a micro pH probe (Orion™ 9810BN, ThermoFisher Scientific Inc.). Dissolved organic carbon (DOC) was measured in filtered (0.45 µm pore size filter) samples using a total organic carbon analyzer (Shimadzu Vcsn, Shimadzu, Kyoto, Japan). Total alkalinity in secondary wastewater samples was measured using a Hach (Loveland, CO, USA) model AL-AP alkalinity test kit.

Generation of HO• was quantified in accordance with Barazesh et al. (2016). Briefly, para-chlorobenzoic acid (PCBA) was added to Milli-Q water and treated with UV/H_2O_2 (1 mM H_2O_2, 0.43 J/cm^2, pH 7.5, and 22 °C). The residual PCBA concentration was measured by LC-MS (LCMS-2000, Shimadzu, Kyoto, Japan) and the kinetic rate constant for PCBA degradation ($k_{PCBA\ \bullet OH} = 5 \times 10^9\ M^{-1}\ s^{-1}$) was used to quantify the HO• concentration.

Statistical differences in sNRP conversion at different conditions were determined using one-way ANOVA with Tukey post hoc analysis using GraphPad Prism 6 (GraphPad Software, Inc., La Jolla, CA, USA). All statistics were performed at a significance level $\alpha = 0.05$.

3. Results and discussion

3.1. Conversion of sNRP compounds to sRP in Milli-Q water as a function of H_2O_2 dose, UV fluence, pH, temperature, and type of sNRP compound

3.1.1. Influence of H_2O_2 and UV dose

Conversion of sNRP to sRP as a function of increasing H_2O_2 concentration at a constant UV fluence of 0.43 J/cm^2 is shown in Fig. 2A. The simple, organic sNRP compound BGP demonstrated the highest conversion at all H_2O_2 concentrations tested, followed by the complex organic PA. At the lowest H_2O_2 concentration of 1 mM, the extent of BGP conversion was 38.1 ± 2.9%, which improved significantly ($p = 0.003$, $n = 3$) at a concentration of 18 mM H_2O_2. Over the course of this treatment, solution pH dropped a maximum of 0.6 pH units from an initial value of 7.5. PA conversion increased gradually as H_2O_2 increased from 1 mM to 12 mM, with the maximum conversion observed at the highest H_2O_2 concentration of 24 mM. The conversion observed for the organics BGP and PA using UV/H_2O_2 was statistically higher ($p < 0.05$) than the controls exposed to UV only and H_2O_2 only at all H_2O_2 concentrations tested (Table S2A). In contrast, the inorganics TrP and HMP showed ≤2% conversion at the lowest H_2O_2 concentration of 1 mM. The conversion of TrP and HMP increased gradually with increasing H_2O_2 concentration. However, the conversion observed with UV/H_2O_2 was not statistically greater than the conversion observed with samples exposed to H_2O_2 only ($p > 0.05$), indicating that UV addition did not improve inorganic sNRP conversion to sRP (Table S2A).

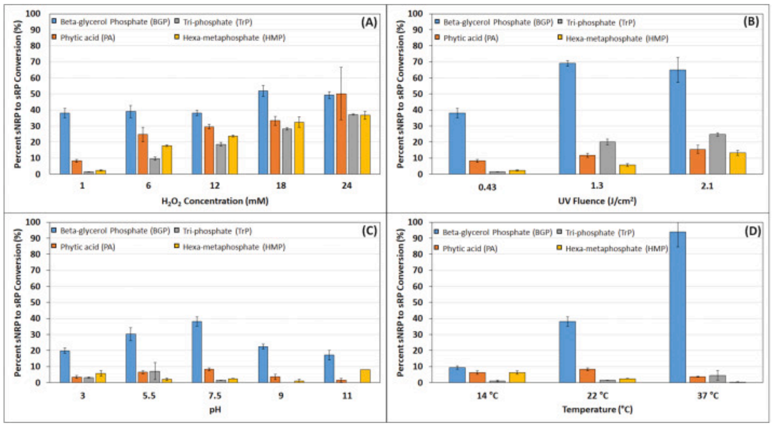

Fig. 2. Summary of percent sNRP to sRP conversion for four sNRP compounds -- BGP, PA, TrP, and HMP -- using UV/H_2O_2 treatment at different experimental conditions. (A) Effect of H_2O_2 concentration at a constant UV fluence = 0.43 J/cm^2, pH = 7, and temperature = 22 °C. (B) Effect of UV fluence at constant H_2O_2 dose = 1 mM or 34 mg/L, pH = 7, and temperature = 22 °C. (C) Effect of pH at constant H_2O_2 dose = 1 mM or 34 mg/L, UV fluence = 0.43 J/cm^2, and temperature = 22 °C. (D) Effect of temperature at constant H_2O_2 dose = 1 mM or 34 mg/L, UV fluence = 0.43 J/cm^2, and pH = 7. All data were normalized to the control, which was not exposed to UV or H_2O_2. Error bars represent standard deviation of triplicate experiments.

Conversion of sNRP to sRP as a function of UV fluence at a constant H_2O_2 concentration of 1 mM is shown in Fig. 2B. The simple-structured organic BGP demonstrated the highest conversion to sRP at all UV fluences tested. The conversion of BGP increased significantly ($p = 1.71 \times 10^{-3}$) as UV fluence increased from 0.43 J/cm^2 to 1.3 J/cm^2 and was statistically higher ($p < 0.05$) than the controls exposed to UV only and H_2O_2 only (Table S2B). No further increase in conversion was observed for BGP when the UV fluence increased to 2.1 J/cm^2. The final pH decreased by 0.2 and 0.5 units at 0.43 J/cm^2 and 1.3 J/cm^2, respectively, with no further decrease at 2.1 J/cm^2. PA conversion increased at a UV fluence of 2.1 J/cm^2 but was not statistically greater than the conversion observed with samples exposed to H_2O_2 only ($p > 0.05$). Conversion of the simple inorganic TrP increased significantly ($p = 1 \times 10^{-3}$, $n = 3$) as the UV fluence increased from 0.43 J/cm^2 to 1.3 J/cm^2 and was statistically higher ($p < 0.05$) than the controls exposed to UV only and H_2O_2 only. No further increase in TrP conversion was observed when the UV fluence increased to 2.1 J/cm^2 (Fig. 2B). HMP conversion increased from a UV fluence of 0.43 J/cm^2 to 1.3 J/cm^2 and 2.1 J/cm^2, and was statistically higher ($p < 0.05$) than the controls exposed to UV only and H_2O_2 only (Table S2B).

Although the extent of conversion varied among the four sNRP compounds, in general increasing H_2O_2 concentration and UV fluence improved conversion of all four sNRP compounds to sRP (Fig. 2A and B). The rate of H_2O_2 photolysis depends directly on the incident power and initial H_2O_2 concentration. Thus, higher UV fluence and H_2O_2 concentration typically increase the rate of HO• generation, which increases oxidation of organics such as organophosphorus compounds (Collivignarelli et al., 2017; Gantner et al., 2011; Monge, 2011; Nollet and De Gelder, 2014; Patton, 2013; Rubio-Clemente et al., 2017; Wu and Linden, 2010). However, excess H_2O_2 dose can also reduce the rate of pollutant destruction either due to HO• reacting with itself to form H_2O_2 or due to reactions between HO• and excess H_2O_2 forming less reactive hydroperoxyl radicals (HO_2•) and its subsequent decomposition to H_2O and O_2 (Gultekin and Ince, 2004; Monge, 2011; Muruganandham, 2004; Shemer and Linden, 2006; Sudarjanto et al., 2005; Wu and Linden, 2008). Reduced organic pollutant destruction due to quenching of HO• activity has been reported at H_2O_2 concentrations ranging from 0.73 mM to 25 mM (Gultekin and Ince, 2004; Muruganandham, 2004; Shemer and Linden, 2006). In this study, no further conversion of BGP and minimal increase (<10%) in conversion of PA, TrP, and HMP sNRP compounds was observed beyond 18 mM H_2O_2, ostensibly due to quenching of HO• (Fig. 2A).

Similarly, the impact of UV fluence is also dependent on the H_2O_2 concentration in the solution and quenching of HO• (Aleboyeh et al., 2005; Muruganandham, 2004; Rubio-Clemente et al., 2017; Shemer and Linden, 2006; Stefan, 2017; Sudarjanto et al., 2005; Wu and Linden, 2008, 2010). BGP and TrP showed no further improvement in conversion beyond a UV fluence of 1.3 J/cm^2 (Fig. 2B). Conversion of the more complex sNRP compounds showed little to no improvement with increasing UV fluence (no improvement for PA and <10% improvement for HMP beyond 1.3 J/cm^2) (Fig. 2B).

3.1.2. Influence of pH and temperature

The organic BGP and PA sNRP compounds showed greatest influence on P conversion due to pH (Fig. 2C). The highest conversion for BGP and PA was at pH 7.5, and conversion gradually decreased as the initial pH increased to pH 11 or decreased to pH 3. The pH had no influence on conversion of the inorganics TrP and HMP, which remained at <5% across all pH conditions. The pH plays an important role in the degradation of organic pollutants using UV/H_2O_2 as it can affect speciation of both oxidants and the organic targets. Previous studies have reported similar trends, with low observed degradation at high/low pH and high degradation at neutral pH during UV/H_2O_2 degradation of organic pollutants in textile wastewaters (Galindo and Kalt, 1999; Gultekin and Ince, 2004; Muruganandham, 2004; Shu et al., 1994; Sudarjanto et al., 2005). Low or high pH can make pollutants more susceptible to UV/H_2O_2 degradation by inducing acid/alkaline hydrolysis or deprotonation of the organic molecule (Aleboyeh et al., 2005; Muruganandham and Swaminathan, 2004; Shemer and Linden, 2006; Sudarjanto et al., 2005). On the other hand, high and low pH conditions can reduce HO• activity due to increased scavenging or H_2O_2 decomposition to H_2O and O_2 (Galindo and Kalt, 1999; Gultekin and Ince, 2004; Shemer and Linden, 2006). There are insufficient reports on the effect of pH on the degradation of inorganic compounds using UV/H_2O_2 to make an informed inference from the results observed in this study.

Temperature had a significant effect on the conversion of BGP (Fig. 2D). Increasing temperature during UV/H_2O_2 treatment has been shown to positively affect organic pollutant degradation by increasing HO• generation and activity, and increasing the susceptibility of organic pollutants to UV/H_2O_2 degradation via thermal hydrolysis (Galindo and Kalt, 1999; Sapach and Viraraghavan, 1997; Stefan, 2017; Sudarjanto et al., 2005). However, temperature had no effect on conversion of the organic PA and inorganics TrP and HMP. Together with the differences in sNRP compound conversion observed at varying H_2O_2 dose, UV fluence, and pH, these temperature results indicate that the type of sNRP compound heavily influences the efficacy of the UV/H_2O_2 process in converting sNRP to sRP.

3.1.3. Influence of type of sNRP compound

The process of oxidative degradation by HO• takes place through one or more combined mechanisms of hydrogen abstraction, electrophilic addition, and electron transfer reactions, which have only been described for compounds containing organic (C–H) bonds (Legrini et al., 1993). Organic sNRP compounds like BGP and PA demonstrated higher conversion to sRP. These organics contain C–H bonds, which are susceptible to hydrogen abstraction, and phosphoester (P–O–C) bonds, which may be more susceptible to subsequent cleavage (free energy = −15 kJ/mol) as compared to the inorganic sNRP compounds. The inorganic compounds (TrP and HMP) contain phosphoanhydride (P–O–P) bonds (free energy = −30 kJ/mol) and no organic bonds to provide a site for HO•-induced hydrogen abstraction (Fitchett et al., 1988; Legrini et al., 1993; Samuni and Neta, 1973).

In addition to the type of bonds (organic or inorganic), the significant difference in sNRP to sRP conversion between the linear BGP and cyclic PA sNRP compounds indicates that the complexity of the chemical structure may also have a major influence. Samuni and Neta (1973) investigated the reaction mechanism of HO• with various phosphate esters, including BGP and PA, in irradiated aqueous solutions, and found that the initial reaction step is hydrogen abstraction, which takes place at all available C–H positions. In the case of BGP, the most likely mechanism involves the abstraction of a terminal hydrogen and the formation of an initial β-phospho radical, which undergoes rapid elimination of phosphate (Fig. 3). Also expected are low yields of the α-phospho radical ($HOCH_2\dot{C}(OPO_3^{2-})CH_2OH$). The reaction between HO• and PA produced α-phospho radicals; however, subsequent elimination of the phosphate group was not observed by Samuni and Neta (1973). Previous studies have shown that the rate of degradation of molecules with phosphoester bonds strongly depends on factors such size or length of the organic molecule, its structure (linear versus ringed or branched), and the presence of radical scavenging groups in the molecule (Manassero et al., 2010). As the type of sNRP compounds in real wastewaters can vary, the efficacy of UV/H_2O_2 for converting sNRP to sRP will also vary significantly and must be separately evaluated for wastewaters with different sNRP compositions.

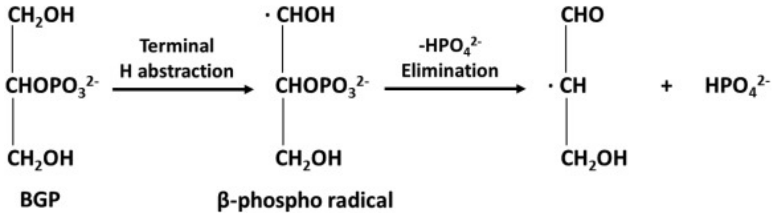

Fig. 3. Proposed reaction mechanism of HO• reacting with beta-glycerol phosphate (BGP). Adapted from Samuni and Neta (1973).

3.2. Conversion of sNRP to sRP in secondary wastewater using UV/H_2O_2

Secondary clarifier effluent samples were analyzed for TP concentrations (0.71 ± 0.07 mg/L) and P fractions (Fig. 4). The dominant P fraction was sRP at 67 ± 0.5%, with sNRP contributing the second highest P fraction at 15 ± 0.7% of the TP concentration. This agrees with earlier studies that reported sNRP fractions can constitute a substantial fraction of the TP in secondary treated wastewaters (Gu et al., 2011).

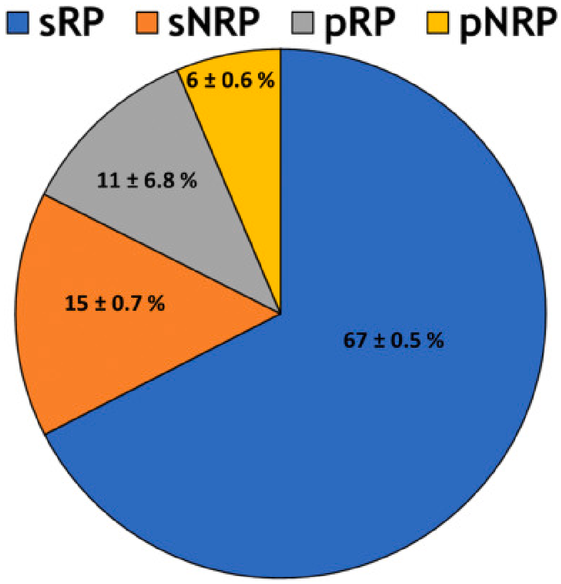

Fig. 4. Secondary effluent wastewater P fractions: soluble reactive P (sRP), soluble non-reactive P (sNRP), particulate reactive P (pRP), and particulate non-reactive P (pNRP). The secondary wastewater effluent was obtained from the South Shore Water Reclamation Facility located in Oak Creek, WI, USA. The TP concentration in the secondary wastewater effluent was 0.71 ± 0.07 mg/L.

Fig. 5 illustrates sRP and sNRP concentrations in UV/H_2O_2 treated (1 mM H_2O_2, 0.43 J/cm^2, pH 7) and untreated secondary wastewater samples. Secondary wastewater samples treated with UV/H_2O_2 had a statistically higher sRP concentration at 0.39 ± 0.01 mg/L, compared to the control wastewater samples at 0.35 ± 0.01 mg/L which were not exposed to UV or H_2O_2 (Fig. 5A; p = 0.04, n = 3). However, there was no decrease in the sNRP concentration between the control and UV/H_2O_2 wastewater samples (p = 0.5, n = 3). The increase in sRP could have come from the oxidation of pP (pRP or pNRP) fractions in the secondary wastewater samples. The pP fractions were not measured in this experiment as all samples were filtered through 0.45 µm membranes to remove the MnO_2 quencher after UV/H_2O_2 treatment. Lack of observed decrease in sNRP after UV/H_2O_2 treatment could ostensibly be due to the presence of recalcitrant sNRP compounds in the secondary wastewater or the HO• scavenging influence of other wastewater constituents.

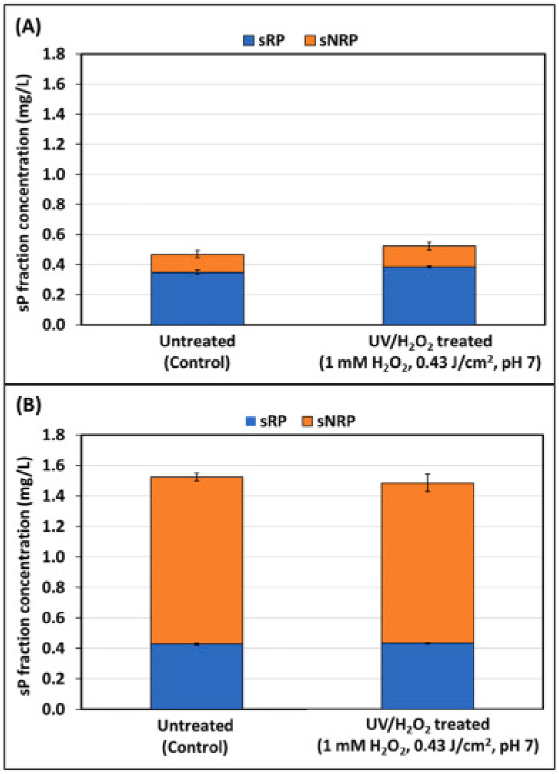

Fig. 5. sP (sRP + sNRP) concentrations in UV/H_2O_2 treated (1 mM or 34 mg/L H_2O_2, 0.43 J/cm^2, and pH 7) and untreated secondary wastewater samples. (A) secondary wastewater samples. (B) secondary wastewaters spiked with BGP at 1 mg-P/L. Error bars represent standard deviation of triplicate experiments. No significant conversion of sNRP to sRP fractions was observed from UV/H_2O_2 treatment in BGP spiked or un-spiked secondary wastewater samples.

To better isolate the influence of the wastewater constituents, the samples were spiked with 1 mg-P/L of BGP (compound that demonstrated the highest conversion in synthetic water tests). Up to 38.1 ± 2.9% of BGP was converted to sRP in Milli-Q water under similar UV/H_2O_2 treatment conditions (1 mM H_2O_2, 0.43 J/cm^2, pH 7.5) (Fig. 2). However, no significant decrease in sNRP (p = 0.39, n = 3) or increase in sRP (p = 0.47, n = 3) concentration was observed in BGP-spiked secondary wastewater samples after UV/H_2O_2 treatment (Fig. 5B). The rate of PCBA degradation showed that the UV/H_2O_2 process generated 1.51×10^{-13} M HO•, which is within the typical steady-state range of 10^{-14} to 10^{-9} M (Crittenden et al., 2012). Together, these results indicate that wastewater constituents scavenged the oxidants, thereby yielding negligible conversion of sNRP to sRP (Autin et al., 2013; Bazri et al., 2012; Grant and Hofmann, 2016; Miklos et al., 2018; Molnar et al., 2015; Rosenfeldt and Linden, 2007; Souza et al., 2014).

The main non-selective HO• scavengers in most wastewaters include natural organic matter (NOM) such as DOC, nitrite, bicarbonate, and carbonate ions. In this study, the DOC concentration in the BGP-spiked secondary wastewater was 11.5 ± 2 mg/L, which is 10 times higher than in the BGP-spiked Milli-Q sample.

Additionally, the total alkalinity in the secondary wastewater was 160 mg/L as $CaCO_3$. Autin et al. (2013) observed an inhibition in the rate constant from 24% to 86% as the molar ratio of NOM to metaldehyde increased from 10:1 to 10,000:1. Souza et al. (2014) reported that organic compounds in secondary wastewater effluent were responsible for 85% of the total HO• radical scavenging and for the 12-fold reduction of the atrazine removal rate. Grant and Hofmann (2016) stated that organic matter in secondary municipal clarifier and membrane effluents contributed >70% of HO• scavenging, except when nitrite exceeded 0.3 mg NO_2–N/L. Bicarbonate and carbonate alkalinity can also contribute to HO• scavenging; however, its inhibition of UV/H_2O_2 efficacy is less compared to other AOPs (Autin et al., 2013).

Overcoming the presence of HO• scavenging constituents, especially NOM, will require higher UV/H_2O_2 doses for converting sNRP to sRP in most wastewaters, which will not be feasible due to high chemical and energy costs. Preliminary treatment to remove these constituents prior to AOP treatment offers a more palatable alternative. For example, membrane filtration systems have been used in wastewater treatment to reduce DOC to an average of 0.7 mg/L (Peltier et al., 2002).

3.3. Energy consumption using UV/H_2O_2 for sNRP conversion

Energy efficiency was calculated as electrical energy per order or E_{EO} (based on first order kinetics, Figure S2). Due to its higher conversion, BGP had the lowest E_{EO} values compared to PA, TrP, and HMP at all conditions tested (Table S1). The lowest calculated E_{EO} value for BGP was observed at 1 mM H_2O_2, 0.43 J/cm^2, pH 7.5, and 37 °C; however, the energy required for heating the water to 37 °C was not taken into consideration. At room temperature, the second lowest E_{EO} value of $5.2 \times 10^3 \pm 5.2 \times 10^2$ kWh/m^3 for BGP was observed at UV/H_2O_2 conditions of 1 mM H_2O_2, 0.43 J/cm^2, pH 7.5, and 22 °C. The E_{EO} value for BGP conversion was much higher than those previously reported for degrading various organic contaminants using UV/H_2O_2, which ranged from 0.006 to 886 kWh/m^3, with a median value of 0.76 kWh/m^3 (Miklos et al., 2018).

One study by Sindelar et al. (2016) investigated the conversion of the organophosphorus compound TEP to sRP using UV/H_2O_2. They reported approximately 40% TEP to sRP conversion in synthetic surface water with a calculated E_{EO} value of 22.2 kWh/m^3 using 1.47 mM H_2O_2 and 2.4 J/cm^2 at room temperature and neutral pH (Sindelar et al., 2016). In comparison, under similar conditions in Milli-Q water (1 mM H_2O_2, 2.1 J/cm^2, pH 7.5, and 22 °C), BGP demonstrated 65 ± 7.8% conversion to sRP with a 500-fold greater E_{EO} (Table S1). Although E_{EO} is useful for comparing the treatment efficiency of AOPs, direct comparison of E_{EO} values from different studies could be misleading as E_{EO} values are strongly influenced by factors such as water quality, lamp type, compound reactivity, and process capacity (lab/bench or full-scale) (Abbate et al., 2018; Bolton and Stefan, 2002; Miklos et al., 2018).

To facilitate a more direct comparison against Sindelar et al. (2016), an additional experiment was conducted comparing TEP and BGP conversions in the bench-scale UV collimated beam apparatus from this study, using the same synthetic surface water matrix and UV/H_2O_2 conditions (1.47 mM H_2O_2, 2.4 J/cm^2, pH 7, 22 °C) as described by Sindelar et al. (2016) (Figure S3). BGP demonstrated 65.7 ± 8.4% conversion to sRP, which is close to the 65 ± 7.8% conversion observed in the Milli-Q water experiments (1 mM H_2O_2, 2.1 J/cm^2, pH 7.5, and 22 °C) (Figure S3). However, TEP only showed 5.1 ± 7.3% conversion to sRP, which was much lower than the 40% conversion reported by Sindelar et al. (2016). Since type of compound and water quality were same, and the UV lamp (15 W vs 8 W low pressure lamp) closely resembled the Sindelar et al. (2016) study, differences in experimental apparatus seem to be the root of the difference. Specifically, the distance from the lamp to the surface of the water can affect the order of magnitude removal for the same exposure time (Abbate et al., 2018; Bolton and Stefan, 2002; Miklos et al., 2018). The bench-scale UV collimated beam apparatus in this study maintained a 1-cm separation between the end of the collimating column and the water surface (62 cm total from the lamp), whereas Sindelar et al. (2016) used a 163 mL reactor with a quartz sleeve to submerge the UV lamp. Based on this, the apparatus used by Sindelar et al. (2016) may result in a higher conversion of the four sNRP compounds to sRP and lower E_{EO} values than observed in this study; however, this hypothesis would need to be experimentally validated.

4. Conclusions

Recalcitrant sNRP is not effectively and consistently removed in WRRF treatment processes, meaning it can be a main culprit in TP violations. In this study, UV/H_2O_2 was investigated for converting four sNRP compounds to the more readily removable/recoverable sRP form at varying H_2O_2 concentration, UV fluence, pH, and temperature. The efficiency of sNRP to sRP conversion was generally higher at higher UV/H_2O_2 doses, higher temperatures, and at neutral pH. Conversion was also highly dependent on the type and the complexity of the sNRP compounds, with the organic sNRP compounds like BGP and PA demonstrating higher conversion to sRP compared to the inorganic sNRP compounds TrP and HMP. The simple structured, organic BGP showed the highest susceptibility to conversion using UV/H_2O_2 in most conditions tested. Up to 38.1 ± 2.9% of BGP was converted to sRP using 1 mM H_2O_2, 0.43 J/cm^2, pH 7.5, and 22 °C. Although BGP conversion was achieved, the E_{EO} value was 2–3 orders of magnitude higher than values reported in previous studies of UV/H_2O_2 degradation of organic pesticides. No conversion of sNRP to sRP was observed in real secondary wastewater, likely due to interference from natural wastewater constituents, which can play a major role in reducing the efficacy UV/H_2O_2 treatment. WRRFs interested in converting sNRP to sRP to improve TP removal will have better results if the sNRP fraction consists of simple organic P compounds. However, other technologies besides UV/H_2O_2 should be investigated to overcome the interference from natural wastewater constituents, improve energy efficiency, and increase conversion of other complex sNRP fractions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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