Water Research X 11 (2021) 100097

Contents lists available at ScienceDirect

Water Research X

journal homepage: www.elsevier.com/locate/wroa

Control of sulfides and coliphage MS2 using hydrogen peroxide and UV disinfection for non-potable reuse of pilot-scale anaerobic membrane bioreactor effluent

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ARTICLE INFO

Article history:
Received 3 December 2020
Revised 3 March 2021
Accepted 5 March 2021
Available online 10 March 2021

Keywords:
Anaerobic membrane bioreactors
Non-potable reuse
Sulfide
Hydrogen peroxide
UV treatment
Bacteriophage MS2

ABSTRACT

Anaerobic membrane bioreactors reduce the energy cost of wastewater treatment and meet filtration requirements for non-potable reuse. However, sulfides (H_2S/HS^-) formed during anaerobic treatment exert a high chlorine demand and inhibit UV disinfection by photon shielding at 254 nm. This study evaluated the feasibility of hydrogen peroxide (H_2O_2) for sulfide oxidation, UV disinfection for inactivation of MS2 bacteriophage, and chlorine to provide a residual for distribution. H_2O_2 treatment at pH $\geq$ 8 favored sulfide oxidation to sulfate in 30 min at a 4:1 H_2O_2:sulfide stoichiometry. Compared to a 6:1 H_2O_2:sulfide molar ratio, treatment of anaerobic effluent with 0.5 mM sulfides with a 4:1 H_2O_2:sulfide molar ratio would increase the applied UV fluence needed for 5-log MS2 inactivation from 180 mJ cm^{-2} to 225 mJ cm^{-2}. However, the lower H_2O_2 dose reduced the dose of chlorine needed to quench residual H_2O_2 and provide a residual for distribution. Treatment at the 4:1 H_2O_2:sulfide molar ratio was favored, because the cost savings in H_2O_2 and chlorine reagents outweighed the energy savings associated with UV treatment. However, H_2O_2/UV/chlorine treatment of anaerobic effluent was cost-competitive with conventional treatment of aerobic effluent for non-potable reuse only for < 285 µM sulfides.

Introduction

Increasing energy costs have led water treatment utilities to consider replacing aging infrastructure with energy-efficient technologies (Haffner and Gennady, 2011; Grigg, 2003; Longo et al., 2016). Aeration during aerobic secondary biological wastewater treatment accounts for nearly half (~0.3 kWh/m^3) of the total energy costs at full-scale conventional wastewater treatment plants in the United States (Owen, 1982). Anaerobic secondary treatment can lower the net energy costs of wastewater treatment by ~0.45 kWh/m^3 by foregoing aeration and generating methane that can be harvested for energy (McCarty et al., 2011). However, until this decade, anaerobic treatment of municipal wastewater was considered impractical. Anaerobic bacteria are less efficient than aerobic bacteria at metabolizing organics, such that anaerobic reactors would require large area footprints or long hydraulic retention times (HRTs) to meet discharge goals (McCarty et al., 2011). Anaerobic membrane bioreactors developed over the past decade have overcome this challenge. An example is the Staged Anaerobic Fluidized Membrane Bioreactor (SAF-MBR), which integrates granular activated carbon (GAC) and ultrafiltration membranes to increase microbial density and solids retention time to overcome anaerobic microbe inefficiency (Bae et al., 2014; Yoo et al., 2014). At temperatures as low as 8 °C, a pilot-scale SAF-MBR was able to treat primary effluent to discharge quality at HRTs < 8 h and area footprints typical of aerobic secondary treatment (Shin et al., 2014).

Further, water scarcity has encouraged wastewater utilities to pursue non-potable reuse for applications that do not involve human consumption, such as irrigation (Okun, 2000; Lazarova and Bahri, 2004). California's Title 22 Code of Regulations exemplifies standards for unrestricted non-potable applications. Key elements of Title 22 include use of an "oxidized" wastewater (e.g., treated by an aerobic biological process), filtration targeting < 0.2 nephelometric turbidity units (NTU), disinfection to achieve < 2.2 most probable number (MPN)/100 mL 7-day median total coliform con-

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https://doi.org/10.1016/j.wroa.2021.100097

centrations, and maintenance of a chlorine or chloramine residual for distribution (CADPH, 2014). Non-potable reuse systems in the United States typically employ chloramines for disinfection (Furst et al., 2018). For systems treating oxidized, filtered wastewaters, Title 22 requires that processes provide a CT (product of total chlorine residual and contact time) value of 450 mg-min/L with a contact time of at least 90 min. Alternatively, systems must use spiking tests to demonstrate that the system can achieve 5-log inactivation of the virus surrogate, bacteriophage MS2 (CDPH, 2014; Bae and Shin, 2016).

Showing that anaerobic membrane bioreactor effluent can be treated for unrestricted non-potable use is key for the adoption of anaerobic technologies. Anaerobic membrane bioreactors feature built-in membranes (Smith et al., 2012), thereby producing effluent that meets Title 22 filtration requirements. However, since anaerobic effluents are not "oxidized", it is important to demonstrate that the disinfection system can achieve 5-log inactivation of spiked MS2 bacteriophage and maintain a total chlorine residual for distribution. The high concentrations of sulfides and ammonia in anaerobic effluents render this difficult. Anaerobic biological sulfate reduction converts sulfate (SO_4^{2-}) to sulfides (H_2S/HS^-) (Lens et al., 1998; Sarti et al., 2010). Sulfides are strong odorants, hindering public acceptance of non-potable reuse waters. Sulfides also rapidly quench both chlorine and chloramines, preventing the use of these disinfectants for pathogen inactivation and maintenance of a residual. Oxidation of sulfides requires four molar equivalents of total chlorine (Eq. (1)) (Cadena and Peters, 1988). For an anaerobically-treated water containing 30 mg-S/L of sulfides (Lens et al., 1998), ~280 mg-Cl_2/L of total chlorine would be required. Even without sulfides, the high ammonia concentrations in anaerobic effluents (e.g., 50 mg-N/L (Szczuka et al., 2019)) react rapidly with free chlorine to form chloramines *in situ* (Eq. (2)). Chloramines are less potent disinfectants than free chlorine (NRC, 2012; Furst et al., 2018), rendering it difficult to achieve pathogen inactivation goals. A 50 mg-N/L ammonia concentration would require impractically high free chlorine doses (> 400 mg-Cl_2/L) to exceed the breakpoint and achieve a free chlorine residual (Pressley et al., 1972). These chlorine doses are far in excess of the ~10 mg-Cl_2/L typically employed to achieve the 450 mg-min/L CT value targeted by Title 22 (Furst et al., 2018).

$$H_2S + 4\,HOCl \rightarrow SO_4^{2-} + 6\,H^+ + 4\,Cl^- \quad (1)$$

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \quad (2)$$

Hydrogen peroxide (H_2O_2) is an alternative to chlorine for sulfide oxidation. Hydrogen peroxide has been used in conventional wastewater treatment to control sulfides, BOD_5, and foaming during and after aerobic biological wastewater treatment (Steiner and Gec, 1992; Ksibi, 2006). The products of sulfide oxidation are pH dependent (Eq. (3) and Eq. (4)) (Hoffman, 1977). Below the pK_a of hydrogen sulfide (pK_a = 7.1), elemental sulfur (S) formation is favored, while oxidation to sulfate is favored above the pK_a. Although lower H_2O_2 doses are required at pH < 7.1, filtration would be required to remove the particulate elemental sulfur. Even though sulfide oxidation to sulfate requires the same molar equivalents of H_2O_2 and chlorine, H_2O_2 is nearly half the cost of chlorine (Zhang et al., 2019; City of Oxnard, 2012). Chlorine addition after sulfide oxidation by H_2O_2 would form chloramines *in situ*. While this would provide a disinfectant residual, the ability to achieve sufficient MS2 inactivation is unclear. UV disinfection offers an alternative route to MS2 inactivation that should not be affected by interference from ammonia.

$$H_2S + H_2O_2 \rightarrow S + 2\,H_2O \quad pH < 7.1 \quad (3)$$

$$HS^- + 4\,H_2O_2 \rightarrow SO_4^{2-} + H^+ + 4\,H_2O \quad pH > 7.1 \quad (4)$$

The goal of this study was to evaluate the feasibility of treating a sulfide-containing, filtered anaerobic effluent using a train based on: 1) H_2O_2 for sulfide oxidation, 2) UV disinfection to inactivate MS2 bacteriophage, and 3) chlorine addition to provide a chloramine residual for distribution. In this study, we dosed H_2O_2 to authentic pilot-scale SAF-MBR effluent spiked with sulfides. We evaluated reaction kinetics and oxidation products (e.g., sulfate) in this matrix as a function of pH. Sulfides and their oxidation products absorb light at 254 nm, the emission wavelength of the low pressure mercury lamps typically used for UV disinfection. This study further characterized the effects of sulfides and their oxidation products on inactivation of MS2 coliphage during subsequent UV disinfection. Finally, this study evaluated the chlorine dose required to achieve a chloramine residual for distribution after H_2O_2 and UV treatment. These results were used to develop a preliminary cost comparison between the H_2O_2/UV/chlorine treatment scheme for anaerobic effluents and the conventional application of chloramine disinfection of aerobic effluents.

Materials and methods

Materials

Stock solutions of 30% H_2O_2 and 5.6%–6.5% sodium hypochlorite (NaOCl) were diluted with deionized water and standardized spectrophotometrically at 254 nm ($\varepsilon_{254\ nm}$ = 18.6 M^{-1} cm^{-1} (Morgan et al., 1988)) and 292 nm ($\varepsilon_{292\ nm}$ = 365 M^{-1} cm^{-1} (Feng et al., 2007)), respectively. Sulfide stocks were prepared daily by dissolving sodium sulfide nonahydrate in deoxygenated deionized water. Sulfide stocks were standardized by reacting the stock solution with a standardized free chlorine stock and measuring the chlorine demand based on a 4:1 NaOCl:sulfide stoichiometry for sulfide oxidation to sulfate. Thiosulfate, sulfite, and sulfate stock solutions were prepared in deoxygenated deionized water. MS2 coliphage (ATTC 15597-B1) was propagated using *E. coli* (ATCC 700891) as the host organism and purified using methods previously described (King et al., 2020; Szczuka et al., 2020), and stored at −80 °C prior to use.

Water sample and buffer preparation

Anaerobically treated secondary effluent samples were collected from a pilot-scale SAF-MBR system treating micro-screened sewage from the Stanford University campus. The pilot reactor and operation have been described previously (Szczuka et al., 2019). Briefly, micro-screened primary effluent (chemical oxygen demand (COD) = 450–1500 mg/L) was treated by two anaerobic fluidized bed reactors in series, with the second reactor outfitted with polyvinylidene fluoride (PVDF) membranes (0.03 μm pore size; Cheil Industries, South Korea); ~0.2 m^3/h was treated with an ~12 h HRT. A 20 L sample of secondary effluent was collected from the reactor, filtered through 0.7-μm glass fiber filters (Whatman), and stored at 4 °C before use. At the time of use, concentrations of all sulfur species of interest were below detection. Alternatively, phosphate buffer was prepared in deionized water and deoxygenated by boiling and sparging with nitrogen gas.

Kinetics experiments

Samples (250 mL) of SAF-MBR effluent were spiked with sulfides. Hydrochloric acid or sodium hydroxide was used to adjust sample pH; pH was measured using a pH probe (Fisher Accumet). Once the target pH was reached, the 250 mL samples were aliquoted into 25 mL vials and capped headspace-free. Control experiments indicated that sulfide concentrations in each vial were

within ~5% of each other, and sulfide concentrations did not decrease over the ~2 h time frame of the kinetics experiments. To initiate the reaction, H_2O_2 was injected into samples using a syringe. At each timepoint, 25 mL vials were sacrificed for immediate absorbance and total sulfide analysis. The remainder of each 25 mL vial was treated with 5 mM $ZnCl_2$ to precipitate ZnS; for low pH samples, NaOH was added to promote ZnS precipitation. H_2O_2 and sulfate concentrations were measured by colorimetric methods immediately after $ZnCl_2$ treatment. Samples were then treated with 2 mg/L catalase (250 units/mg) to degrade residual H_2O_2, and were saved for sulfite and thiosulfate analysis by ion chromatography. Control experiments showed that $ZnCl_2$ did not affect H_2O_2, sulfate, sulfite, and thiosulfate concentrations, and that quenching of H_2O_2 by catalase did not affect the analysis of sulfate, sulfite, and thiosulfate by ion chromatography. Experiments were conducted in duplicate.

UV experiments

SAF-MBR or phosphate-buffered deionized water samples were placed in 5-cm depth open-top cylindrical dishes and spiked with sulfides, sulfate, sulfite, or thiosulfate under different conditions. Hydrochloric acid or sodium hydroxide was used to adjust sample pH. MS2 was spiked into the samples targeting an initial concentration of ~10^6 PFU/mL. H_2O_2 was spiked into some samples. Quartz lids were placed on each jar, and the samples were placed on a stir plate and exposed to 254 nm light under a semi-collimated beam apparatus consisting of three 15 W Philips low pressure mercury lamps shining down onto the jars through a shutter. The SAF-MBR effluent samples had been filtered after collection to control turbidity. The incident UV fluence (mJ cm^{-2}) associated with specific illumination times was measured using iodide-iodate actinometry (Rahn et al., 2003). One objective of the study was to evaluate the extent to which sulfides and their oxidation products absorb UV light, thereby requiring higher incident UV fluence (and thus higher costs) to achieve the same level of disinfection. Therefore, we report the incident UV fluence rather than correcting the incident fluence for solution absorbance (i.e., the average UV fluence experienced by the solution). For perspective, the UV absorbance at 254 nm (UV_{254}) for the anaerobic effluent was 0.044 cm^{-1}(UV transmittance (UVT) = 90.4%) in the absence of sulfides. For a 5 cm depth of solution, the average UV fluence within the solution would be ~80% of the incident UV fluence (Jin et al., 2006). At desired intervals, subsamples for MS2 analysis were taken from the jars, stored on ice, and plated within two hours of collection. Control experiments showed that (1) sulfide concentrations at the end of experiments remained within ~5% of the initial concentrations in dark controls in the absence of H_2O_2, and (2) MS2 concentrations were not affected by H_2O_2, sulfides, thiosulfate, sulfite, or sulfate in dark controls. Experiments were conducted in duplicate or triplicate, except where noted. As an indication of the error associated with these experiments, the relative standard deviation of the pseudo-first order MS2 inactivation rate constants fit to triplicate experiments involving MS2 spiked into SAF-MBR effluent at pH 9.2 without sulfides (Fig. 3B) was 10.7%.

Analyses

UV_{254} and UV absorbance spectra (200–400 nm) were measured using an Agilent Cary 60 UV–Vis spectrophotometer (minimum reporting level (MRL) = 0.01 cm^{-1}). H_2O_2 concentrations were measured by the peroxidase catalyzed oxidation of N,N–diethyl-p-phenylenediamine (DPD) (Bader et al., 1988). HACH colorimetric methods were used to measure sulfides (method 8131; MRL = 1.0 μM), sulfate (method 8051; MRL = 2.0 μM), chemical oxygen demand (COD; method 8000; MRL = 1 mg/L), ammonia (method 10031; MRL = 0.4 mg-N/L), nitrate (method 10206; MRL = 0.2 mg-N/L), nitrite (method 10207; MRL = 0.02 mg-N/L), and monochloramine (method 10200; MRL = 0.05 mg-Cl_2/L). Sulfite (MRL = 2.0 μM) and thiosulfate (MRL = 5.0 μM) concentrations were determined using an ion chromatograph (IC; Dionex Integrion HPIC system) equipped with a Dionex IonPac AS19 column (Thermo Scientific), using a method adapted from Zhang et al. (2020). Direct determination of sulfite via IC is a challenge due to oxidation of sulfite to sulfate in the eluent (Hansen et al., 1979) and poor separation of sulfite and sulfate peaks (Sunden et al., 1983). As such, sulfite concentrations were inferred by subtracting the sulfate concentration measured using HACH method 8051 and the coeluting sulfite and sulfate concentration measured on the IC. Coliphage MS2 was enumerated using a double-agar layer assay (MRL = 10 plaque forming units (PFU)/mL), as described previously (Szczuka et al., 2020).

Results and discussion

General water quality

General water quality parameters for the pilot-scale SAF-MBR unit effluent are listed in Table S1. The chemical oxygen demand (COD; superset of BOD_5) of the effluent (25 mg/L) was < 30 mg/L, meeting discharge criteria. Ammonia (62.6 mg-N/L) was the only inorganic nitrogen species present in the effluent; inorganic nitrogen oxidation is not expected during anaerobic treatment. At the 62.6 mg-N/L ammonia concentration, a > 571 mg-Cl_2/L chlorine dose would be needed to achieve a free chlorine residual (1.8:1 chlorine: ammonia molar ratio). The effluent pH (7.2) and UV_{254} absorbance (0.044 cm^{-1}) were similar to values previously reported for this pilot unit (Szczuka et al., 2019). The chloride concentration (51.5 mg/L) was < 70 mg/L, the most restrictive recommendation for non-potable water reuse (US EPA, 2012), and < 250 mg/L, the U.S. EPA's Secondary Maximum Contaminant Level (MCL) established to avoid salt-associated taste issues in potable water (US EPA, 2016).

Since sulfate reduction to sulfides precedes methanogenesis (Lens et al., 1998), we expect nearly quantitative conversion of sulfate to sulfides in SAF-MBR effluent. Thus, sulfide concentrations ultimately depend on sulfate concentrations in the sewage influent. The drinking water supply serving the area contributing sewage to the SAF-MBR pilot facility is the Hetch Hetchy reservoir, a low-sulfate surface water overlaying granite bedrock. Sulfide concentrations in the SAF-MBR pilot effluent typically are ~2 mg-S/L (Szczuka et al., 2019), but total sulfides, sulfate, sulfite, and thiosulfate were below detection limits for the effluent employed for this study. This low-sulfate sewage enabled the isolation of the effect of sulfides by spiking sulfides into the SAF-MBR effluent.

Sewage at other facilities can feature higher sulfate concentrations resulting from minerals (e.g., gypsum) in groundwater-derived municipal drinking water supplies (e.g., 84 mg/L sulfate (880 μM) in well water from Dayton, Ohio (Snoeyink and Jenkins, 1980)). The sulfate levels within municipal drinking water are supplemented by 20–50 mg/L sulfate (~200–500 μM) from household and industrial discharges (Metcalf and Eddy, 1991). Lastly, saltwater infiltration into sewers can increase sulfate loads in coastal areas. For example, sulfate concentrations in sewage increase from ~600 μM in the summer to ~1000 μM in the winter at Silicon Valley Clean Water (Redwood City, CA) when the winter rainy season promotes saltwater infiltration from San Francisco Bay (Hansen, 2021). Previous pilot-scale research on anaerobic membrane bioreactors has treated sewage with up to ~3 mM sulfate (Gimenez et al., 2011). While removal of sulfate prior to anaero-

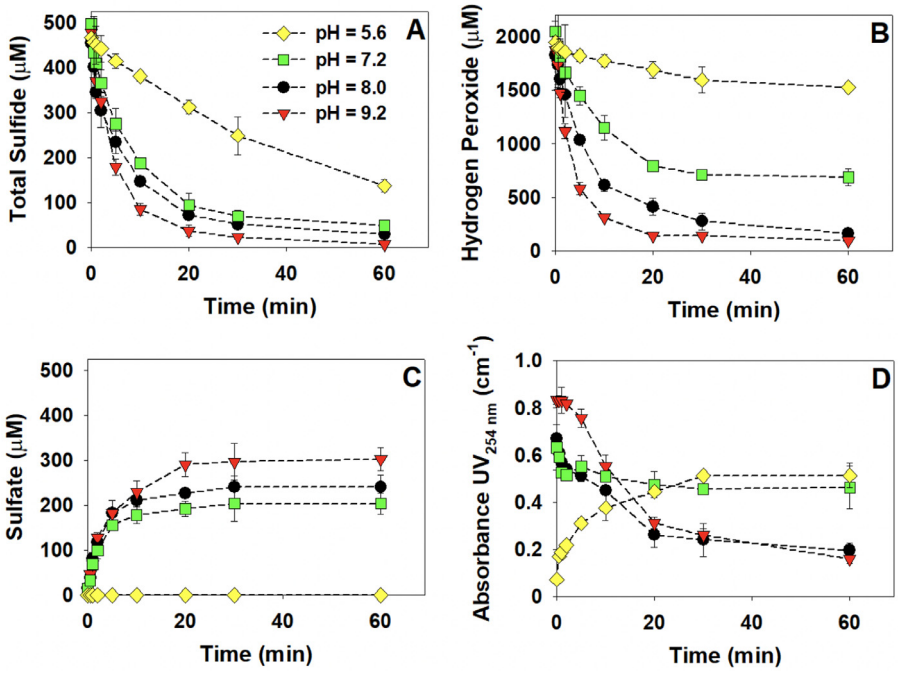

Fig. 1. Concentration of (A) total sulfide, (B) hydrogen peroxide, (C) sulfate, and (D) UV_{254} when 500 μM sulfide and 2000 μM hydrogen peroxide were spiked into SAF-MBR effluent over a one hour reaction time. Error bars represent the range of experimental duplicates.

bic treatment would avoid sulfide formation and enhance methane production, techniques such as ion exchange are challenging within a primary effluent matrix.

Timescale and products of sulfide oxidation by H_2O_2

Previous research conducted in deionized water demonstrated that the stoichiometry, products, and kinetics of sulfide oxidation by H_2O_2 are pH-dependent Eqs. (3) and (4) (Hoffmann, 1977; Millero et al., 1989). At pH below the 7.1 pK_a of H_2S, H_2O_2 oxidation of H_2S favors elemental sulfur formation over timescales of hours (k = 0.48 M^{-1} min^{-1} (Hoffmann, 1977)), consuming one molar equivalent of H_2O_2. At pH > 7.1, H_2O_2 oxidation of HS^- favors sulfate formation over timescales of minutes (k = 29 M^{-1} min^{-1} (Hoffmann, 1977)), consuming four molar equivalents of H_2O_2. However, this previous research employed H_2O_2 at high molar excess (10–20-fold) and focused on low pH conditions (< 7 with limited experiments at pH ~8).

We evaluated H_2O_2 oxidation of 500 μM sulfides spiked into SAF-MBR effluent to mimic sulfide concentrations expected in SAF-MBR effluents at typical water reuse facilities (i.e., sewage sulfate concentrations ~50 mg/L). The first objective of these experiments was to evaluate the kinetics of sulfide oxidation, focusing on higher pH conditions within the range (5.6–9.2) feasible for pH adjustment during wastewater treatment, and on H_2O_2:sulfide molar ratios (1–10) closer to the expected stoichiometric requirements in order to limit reagent supply costs. Conducting these experiments within SAF-MBR effluent was important to incorporate the H_2O_2 demand of the SAF-MBR effluent matrix. The second objective was to evaluate product formation, with a particular focus on the extent to which H_2O_2 oxidation mitigates the negative impacts on UV disinfection associated with the absorption of germicidal UV light at 254 nm (UV_{254}) by sulfides. Fig. 1 provides the loss of sulfides and H_2O_2, formation of sulfate, and change in UV_{254} for application of 2 mM H_2O_2 (i.e., the 4:1 H_2O_2:sulfide molar ratio that is stoichiometric for oxidation to sulfate) at pH 5.6 (~3% HS^-), pH 7.2 (~50% HS^-), pH 8.0 (~89% HS^-), and pH 9.2 (~99% HS^-); Figure S1 provides the concentrations of sulfite and thiosulfate.

Sulfide oxidation by H_2O_2 was slowest at pH 5.6 (Fig. 1A), accompanied by consumption of only ~360 μM H_2O_2 after 30 min (Fig. 1B). At pH 5.6, the dominance of H_2S (~97%) would favor slow kinetics and the consumption of ~360 μM H_2O_2 is close to the 500 μM expected for consumption of 1 molar equivalent of H_2O_2 to form elemental sulfur. No sulfate, thiosulfate or sulfite were observed (Figs. 1C and S1). Attempts to measure elemental sulfur by HPLC with UV detection were not successful due to the low concentration (< 500 μM) involved. However, when the experiment was conducted in deionized water buffered at pH 5.6 with 2 mM phosphate buffer, the solution turned faintly cloudy, indicative of the formation of colloidal elemental sulfur. Figure S2 provides UV spectra for sulfides spiked into SAF-MBR effluent at each of the four pH values, demonstrating that sulfides absorb UV light at 254 nm. For reaction at pH 5.6, the UV_{254} increased significantly, leveling out after ~30 min in either SAF-MBR effluent (Fig. 1D) or deionized water (Figure S3). We measured molar absorption coefficients at 254 nm of 85 M^{-1} cm^{-1} for H_2S and of 830 M^{-1} cm^{-1} for elemental sulfur on a molar S basis (Text S1), indicating that the conversion of H_2S to elemental sulfur would increase UV_{254}, as observed. The molar absorption coefficient of elemental sulfur was determined in 90% methanol and 10% deionized water due to the low solubility of elemental sulfur. Thus a portion of elemental sulfur would form a separate colloidal phase in aqueous media, as observed in the deionized water experiment. If sulfide oxidation were followed by membrane-based treatment processes (e.g., microfiltration or reverse osmosis within a potable reuse train), colloidal sulfur would contribute to membrane clogging. Regardless, the slow H_2S oxidation kinetics and increase in UV_{254} at pH 5.6 are problematic for non-potable reuse treatment.

Sulfide oxidation by H_2O_2 was significantly faster at pH ≥ 7.2 (Fig. 1A), accompanied by H_2O_2 consumption after 30 min of ~1330 μM, ~1550 μM, and ~1720 μM at pH 7.2, 8.0, and 9.6, respectively (Fig. 1B). These findings align with expectations of a shift in reaction mechanism with the change in sulfide speciation. The predominance of HS^- above pH 7.1 favors faster kinetics, and the consumption of 1330–1720 μM H_2O_2 approaches the 2000 μM ex-

pected for consumption of 4 molar equivalents of H_2O_2 to form sulfate. For the 2 mM H_2O_2 dose in these experiments, the characteristic time for HS^- oxidation would be ~17 min based on the 29 M^{-1} min^{-1} rate constant provided by Hoffmann (1977), comparable to the timescale for sulfide degradation observed for pH ≥ 7.2, where HS^- predominates. Thus, interference with H_2O_2 oxidation of sulfides by the SAF-MBR matrix was not important. The lower H_2O_2 consumption at pH 7 than at pH 8.0 and 9.2 reflects the co-occurrence of H_2S and HS^- at this pH.

Support for the change in reaction mechanism with sulfide speciation is provided by the measured concentrations of sulfate, thiosulfate and sulfite (Figs. 1C and S1). Sulfate formation was significant for pH ≥ 7.2, reaching ~200 µM at pH 7.2, ~220 µM at pH 8.0, and ~290 µM at pH 9.2 after 30 min (Fig. 1C). However, complete oxidation to sulfate (S[+6]) did not occur. Concentrations of thiosulfate ($S_2O_3^{2-}$ (S[+2])) reached ~50 μM at pH 7.2 and ~80 μM at pH 9.2 after 30 min (Figure S1A). Sulfite (SO_3^{2-} (S[+4])) was also observed at pH ≥ 7.2, but at lower concentrations (maximum ~10 μM) and declined to negligible levels after 30 min (Figure S1B). The detection of thiosulfate and sulfite demonstrate incomplete oxidation of sulfides, and concur with previous reports of thiosulfate formation during H_2O_2 oxidation of sulfides in deoxygenated deionized water at pH 9.0 (Takenaka et al., 2003).

Figure S2 provides UV spectra (200–400 nm) for 500 μM of sulfides, sulfate, thiosulfate or sulfite spiked into SAF-MBR effluent at each of the four pH values. Sulfides feature absorbance peaks with maxima near 230 nm but extending to 254 nm (Figure S2A). We calculated molar absorption coefficients at 230 nm and 254 nm for HS^- (Text S1). The 7570 M^{-1} cm^{-1} value for the HS^- molar absorption coefficient at 230 nm agrees with the 8000 M^{-1} cm^{-1} value determined previously by Zuman and Szafranski (1976). Since the UV absorbance at 254 nm by HS^- (ε_{254} = 950 M^{-1} cm^{-1}) is stronger than by H_2S (ε_{254} = 85 M^{-1} cm^{-1} (Text S1)), the UV_{254} increases strongly as pH increases from 5.6 to 7.2, and then moderately for further pH increases, reaching ~2.5 cm^{-1} at pH 9.2 (Figure S2A). While sulfate does not absorb UV light (Figure S2B), thiosulfate and sulfite both absorb UV at ~200–250 nm without pH dependence, although to a lesser degree than HS^- (Figures S2C and S2D). The molar absorption coefficients at 254 nm we calculated for thiosulfate and sulfite were 200 M^{-1} cm^{-1} and 20 M^{-1} cm^{-1}, respectively (Table S2).

The SAF-MBR effluent exhibited ~0.044 cm^{-1} (UVT = 90.4%) UV_{254} background absorbance (i.e., without sulfides; Table S1). For the treatment of 500 μM sulfides in SAF-MBR effluent with 2000 μM H_2O_2, the initial UV_{254} was highest (~0.8 cm^{-1}; UVT ~ 16%) at pH 9.2 (Fig. 1D), reflecting the predominance of HS^-. At pH 8.0 and 9.2, the UV_{254} declined to ~0.25 cm^{-1} (UVT = 56%) after 30 min. This decline reflects the conversion of HS^- to sulfate and thiosulfate, the latter contributing to the residual absorbance above the SAF-MBR background. At pH 7.2, where H_2S and HS^- co-occur, the UV_{254} decreased from ~0.65 cm^{-1} to ~0.5 cm^{-1}, reflecting the oxidation of H_2S to elemental sulfur and HS^- to sulfate and thiosulfate. Overall, the results indicate that pH adjustment to 8.0 would facilitate sulfide oxidation within 30 min while minimizing UV_{254} for subsequent UV disinfection.

Effect of H_2O_2 dose

For 500 μM sulfides spiked into SAF-MBR effluent, we tested the effect of H_2O_2:sulfide molar ratio (1–10) on the concentrations of reactants, products, and UV_{254} after 30 min (Fig. 2), the time at which reactant degradation and product formation leveled out for pH ≥ 7.2 (Fig. 1). At pH = 5.6, ~125 μM sulfides were consumed at a 1:1 molar ratio, leaving a low H_2O_2 residual (Fig. 2). At a 4:1 molar ratio, sulfide consumption increased to ~200 μM, while consuming ~360 μM H_2O_2. However, at higher molar ratios, each additional molar equivalent of H_2O_2 removed ~12 μM sulfides, while leaving an additional ~480 μM H_2O_2. No sulfate, thiosulfate or sulfite was observed (Figs. 2 and S3). These results reflect the slow oxidation of H_2S to elemental sulfur by H_2O_2 oxidation, with no further significant oxidation of the elemental sulfur. Accordingly, additional H_2O_2 accumulates with some modest consumption by reaction with the SAF-MBR effluent matrix constituents. The increase in the UV_{254} from 0.15 cm^{-1} at a 1:1 molar ratio to 0.45 cm^{-1} at a 4:1 molar ratio is associated with absorbance by elemental sulfur with only modest further increases in UV_{254} at higher molar ratios (Fig. 2D).

At pH 7.2, 8.0 and 9.2, sulfides were reduced to ~150 μM at a 1:1 molar ratio, leaving negligible H_2O_2 residuals. At a 4:1 molar ratio, sulfides declined to ~30 μM, with residual H_2O_2 concentrations ranging from ~200 μM at pH 9.2 to ~800 μM at pH 7.2 (Fig. 2B). Further increases in the molar ratio produced only modest further reductions in residual sulfide concentrations (down to ~11 μM at a 10:1 molar ratio), but at a cost of ~460 μM increase in residual H_2O_2 for each additional 500 μM H_2O_2 (i.e., each unit increase in the molar ratio). The ~40 µM consumption of the additional H_2O_2 indicates reactions of H_2O_2 with other constituents of SAF-MBR effluent; H_2O_2 has been shown to readily react with organic matter in aerobically treated wastewater (Ksibi, 2006).

Both sulfate (Fig. 2C) and thiosulfate (Figure S4) were observed. Complete oxidation of HS^- should form ~500 µM sulfate. The detection of thiosulfate and the formation of sulfate at concentrations < 500 μM, even at a 10:1 molar ratio and pH 9.2, indicates that complete oxidation did not occur. Sulfate concentrations increased between molar ratios of 1 and 4, leveling out at higher molar ratios, with the highest concentrations (~300 μM) observed for pH 8.0 and 9.2, but ~200 μM at pH 7.2. Thiosulfate concentrations declined with increasing molar ratio from ~120–150 μM at a 1:1 molar ratio to ~40 μM at a 10:1 molar ratio. Thiosulfate is expected to form under alkaline conditions, but to decline when H_2O_2 is in stoichiometric excess (Takenaka et al., 2003). At the lowest molar ratios, the highest thiosulfate concentrations were observed at pH 7.2, concurring with expectations that the lower molar ratios and the slower kinetics associated with the mixture of H_2S and HS^- at this pH would favor the formation of this intermediate.

Given that elemental sulfur, thiosulfate and sulfides absorb UV light at 254 nm (Figure S2), UV_{254} was minimized (~0.2 cm^{-1}; UVT = 63%) at H_2O_2:sulfide molar ratios ≥ 6 at pH ≥ 8.0 (Fig. 2D). The higher UV_{254} observed at pH 7.2 (~0.45 cm^{-1}; UVT = 36%, similar to pH 5.6), despite concentrations of sulfides and thiosulfate comparable to those at pH 8.0 and 9.2 is attributable to elemental sulfur. Thus, a 6:1 molar ratio at pH 8.0 would minimize the reagent costs for pH adjustment and potentially minimize the UV fluence required for pathogen inactivation by minimizing UV_{254}. However, the UV_{254} at pH 8.0 and a 4:1 molar ratio was only 25% higher (0.25 cm^{-1}; UVT = 56%) than at the 6:1 molar ratio. Thus at pH 8.0, the lower cost of the H_2O_2 reagent at the 4:1 molar ratio must be weighed against the lower cost associated with UV fluence to achieve pathogen inactivation at the 6:1 molar ratio.

Effect of sulfides on log inactivation of MS2

Fig. 3A shows that UV inactivation of bacteriophage MS2 in phosphate buffer in the presence of 500 μM sulfides is pH dependent. In the absence of sulfides, a UV fluence of 175 mJ cm^{-2} achieved a 4.5-log removal value (LRV) of bacteriophage MS2, regardless of pH (data for pH 7.2 shown). In the presence of sulfides at pH = 5.6, MS2 inactivation was similar to the no sulfide control. However, 175 mJ cm^{-2} UV fluence achieved only 1.5 and 1.3 MS2 LRVs at pH 7.2 and 9.2, respectively. Approximating MS2 inactivation by first order kinetics, UV fluence-based first order inactivation rate constants would be 0.055, 0.022, and 0.017 cm^2 mJ^{-1}

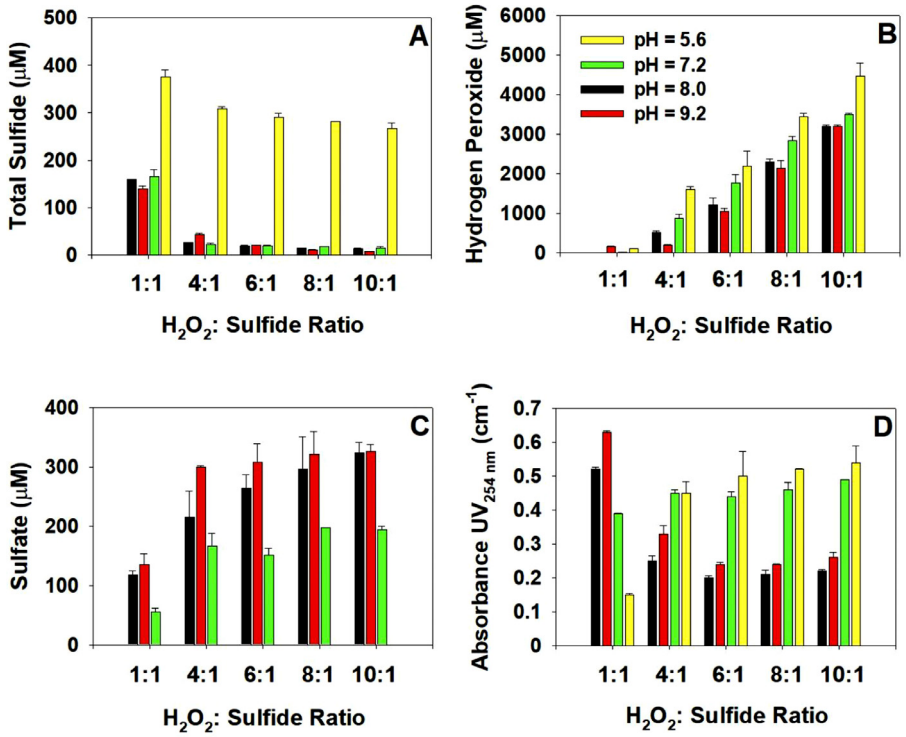

Fig. 2. . Concentrations of (A) total sulfide, (B) H_2O_2, (C) sulfate, and (D) UV_{254} measured 30 min after addition of H_2O_2 at various molar ratios relative to 500 μM sulfides spiked into SAF-MBR effluent. Error bars represent the range of experimental duplicates.

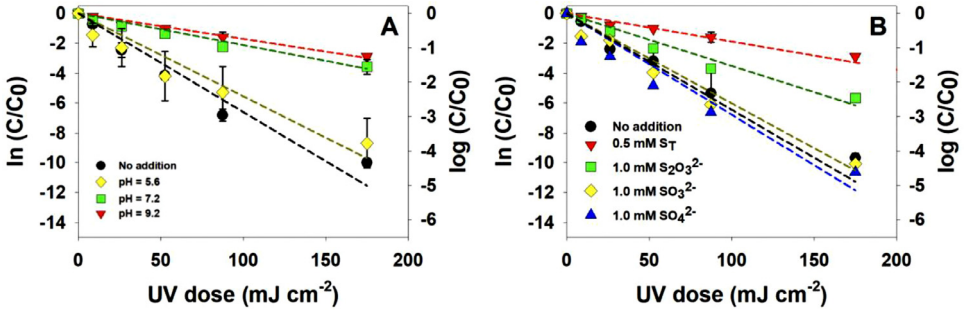

Fig. 3. Inactivation of coliphage MS2 in phosphate buffer by UV light (A) in the presence of 0.5 mM sulfides at pH 5.6, 7.2, and 9.2 and (B) in the presence of 0.5 mM sulfides (S_T), 1 mM thiosulfate ($S_2O_3^{2-}$), 1 mM sulfite (SO_3^{2-}), or 1 mM sulfate (SO_4^{2-}) buffered at pH 9.2. The UV only control (no addition) in panel A was conducted at pH 7.2 and at pH 9.2 for panel B. In panel A, error bars represent the range of duplicate (pH 5.6, 7.2, no addition), and triplicate (pH 9.2) experimental measurements. In panel B, error bars represent the range of triplicate (0.5 mM sulfides, no addition) experimental replicates, and the range of duplicate analytical measurements for the thiosulfate, sulfite, or sulfate conditions.

at pH 5.6, 7.2, and 9.2, respectively. The ~0.06 cm^2 mJ^{-1} values measured in the absence of sulfides concurs with previous determinations for treatment of groundwater, among other water types (Templeton et al., 2006; Hinjen et al., 2006). Extrapolating from this data, UV doses of 530 and 670 mJ cm^{-2} would be required to achieve a 5-log inactivation for bacteriophage MS2 at pH 7.2 and 9.2, respectively. For comparison, the National Water Research Institute (NWRI) recommends that UV systems deliver a 90 mJ cm^{-2} UV fluence for non-potable reuse of membrane-filtered municipal effluents treated by conventional, aerobic secondary biological treatment processes (NWRI, 2012).

Fig. 3B shows the effect of sulfides and sulfide oxidation products on UV inactivation of bacteriophage MS2 in phosphate buffer at pH 9.2. MS2 inactivation rates were within 18% for 1 mM sulfite (0.061 cm^2 mJ^{-1}), 1 mM sulfate (0.067 cm^2 mJ^{-1}), and the no addition control (0.057 cm^2 mJ^{-1}). However, the inactivation rate decreased to 0.035 cm^2 mJ^{-1} for 1 mM thiosulfate, such that a 330 mJ cm^{-2} UV fluence would be required to achieve 5-log inactivation of MS2.

UV inactivation of MS2 occurs predominantly by photo-oxidation of the genome, which absorbs UV light at 254 nm (Ye et al., 2018). The inhibition of bacteriophage MS2 inactivation by UV in the presence of HS^- (i.e., sulfides at pH ≥ 7.2) and thiosulfate may relate to shielding of MS2 by absorption of 254 nm light by HS^- and $S_2O_3^{2-}$, or to reversal of the photo-oxidation reactions by these potent reductants. To test the importance of photon shielding, we supplemented samples with N-acetyl-tyrosine, which absorbs UV light at 254 nm, but is not a potent reductant. Fig. 4 shows UV inactivation of MS2 in phosphate buffer at pH 9.2 in the presence and absence of 0.5 mM sulfides (predominantly HS^-at pH 9.2), 2.9 mM N-acetyl-tyrosine, and 1 mM thiosulfate with 2.0 mM N-acetyl-tyrosine. These solutions of N-acetyl-tyrosine, sulfides and thiosulfate mixed with N-acetyl-tyrosine exhibited a common UV absorbance (UV_{254} = 0.8 cm^{-1}). The MS2 inactivation rates in the presence of sulfides (0.017 cm^2 mJ^{-1}), N-

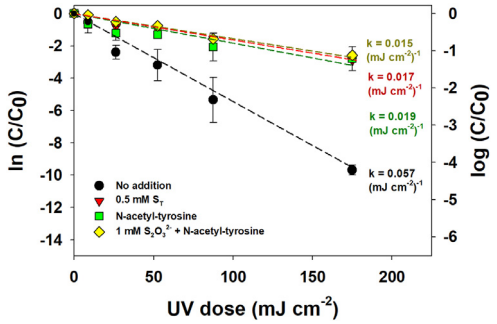

Fig. 4. . Inactivation of coliphage MS2 in phosphate buffer (pH 9.2) by UV light in the presence of 0.5 mM sulfides (S_T), 2.9 mM N-acetyl-tyrosine, and 1 mM thiosulfate with 2.0 mM N-acetyl-tyrosine. N-Acetyl-tyrosine was added at concentrations such that the total absorbances of solutions were equal at 0.8 cm^{-1} (except for the no addition control). Error bars represent the range of experimental triplicate (no addition, sulfide conditions) and duplicate (N-acetyl-tyrosine and thiosulfate + *N*-acetyl-tyrosine conditions) measurements.

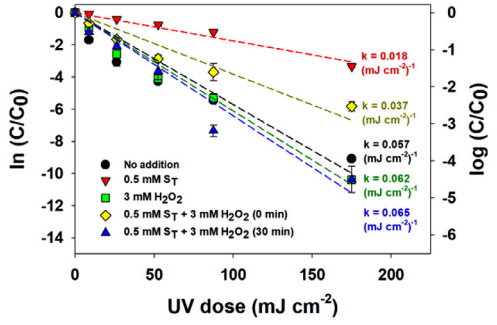

Fig. 5. . Inactivation of bacteriophage MS2 in SAF-MBR effluent by UV light. Samples were spiked with 0.5 mM sulfide, 3 mM peroxide, or a combination 0.5 mM sulfide and 3 mM peroxide at pH 8.0. Samples treated with both sulfide and peroxide were treated with UV immediately (0 min) or held for 30 min prior to UV treatment. Error bars represent the range of experimental duplicates.

acetyl-tyrosine (0.019 cm^2 mJ^{-1}), and the N-acetyl-tyrosine and thiosulfate mixture (0.015 cm^2 mJ^{-1}) were comparable and ~4-fold lower than for the no-addition control. These results indicate that photon shielding is predominantly responsible for the reduction in UV inactivation rates by HS^- and thiosulfate. Overall, the results suggest the need to achieve complete oxidation of sulfides to sulfate to minimize the UV fluence needed to achieve 5-log inactivation of MS2.

Effect of H_2O_2 pre-treatment on MS2 inactivation

As can be seen in Fig. 2, UV_{254} of the SAF-MBR effluent spiked with 500 μM sulfides is minimized when the sample pH is adjusted to 8.0 and 3 mM H_2O_2 is added to achieve a 6:1 H_2O_2:sulfide molar ratio. At pH 8.0, the rate of MS2 inactivation by UV (k = 0.057 cm^2 mJ^{-1}; Fig. 5) in SAF-MBR effluent (UV_{254} = 0.044 cm^{-1}; Table S1) was within the range of MS2 inactivation in phosphate buffer (k = 0.064 cm^2 mJ^{-1}; data not shown) in the absence of sulfides or H_2O_2. For addition of 3 mM H_2O_2 to the SAF-MBR effluent without sulfides, the rate of MS2 inactivation (0.062 cm^2 mJ^{-1}) was similar to that in the absence of H_2O_2. These results indicate that neither direct reaction with H_2O_2 nor reactions with hydroxyl radical formed by UV photolysis of H_2O_2 are important for MS2 inactivation. Although previous research has indicated that hydroxyl radical production by UV photolysis of H_2O_2 can increase the rate of MS2 inactivation during UV treatment, the importance of hydroxyl radical-mediated inactivation depends on the matrix. For example, (Sun et al., 2016) showed that the addition of 0.3 mM H_2O_2 increased MS2 inactivation by ~15-fold in phosphate buffer, but did not increase inactivation appreciably in wastewater, likely due to hydroxyl radical scavenging by dissolved organic matter.

We added 3 mM H_2O_2 to SAF-MBR effluent spiked with 0.5 mM sulfides and irradiated the sample with UV light either immediately after H_2O_2 addition or after a 30 min reaction time to permit maximum oxidation of sulfides to products (Figs. 1 and 2). When irradiated after a 30 min reaction time, the MS2 inactivation rate (k = 0.065 cm^2 mJ^{-1}) slightly exceeded the inactivation rate of the SAF-MBR effluent control containing neither sulfides nor H_2O_2 (k = 0.057 cm^2 mJ^{-1}). When irradiated immediately after H_2O_2 addition to the sulfide-containing effluent, the MS2 inactivation rate was lower (k = 0.037 cm^2 mJ^{-1}), yet H_2O_2 addition nearly doubled the rate of MS2 inactivation relative to the sulfides-containing effluent without H_2O_2 addition (k = 0.018 cm^2 mJ^{-1}). MS2 concentrations did not change over the 30 min reaction period prior to irradiation, indicating that direct reaction with H_2O_2 did not contribute to MS2 inactivation. Rather, the increase in inactivation MS2 rate can be attributed to H_2O_2 oxidizing sulfide to products with lower UV absorbance. In fact, the sulfide concentration after UV irradiation was lowest in the sample that was spiked with H_2O_2 and irradiated after a 30 min reaction time. In the sulfide-only control, ~420 µM sulfides were present after UV irradiation, compared to ~180 µM and ~5 µM when the samples were treated with H_2O_2 and irradiated with UV light immediately or after 30 min, respectively. For SAF-MBR effluent containing 0.5 mM sulfides, adjustment of the pH to 8.0 and pre-treatment with 3 mM sulfides for 30 min would reduce the UV fluence needed to achieve 5-log inactivation of MS2 from 640 mJ cm^{-2} to 180 mJ cm^{-2}, a reduction of 460 mJ cm^{-2}. When the SAF-MBR effluent containing 0.5 mM sulfides was treated with 2 mM sulfides (i.e., a 4:1 H_2O_2:sulfide molar ratio) for 30 min at pH 8.0, the UV_{254} was 0.25 cm^{-1} (Fig. 2D), such that 5-log inactivation would require an applied UV fluence of 225 mJ cm^{-2}.

Free chlorine doses to achieve total chlorine residuals for distribution

Lastly, we evaluated the free chlorine doses needed to attain 5 mg-Cl_2/L (70 μM) total chlorine residuals after 24 h to provide residuals for distribution; given the 62.6 mg-N/L (4.5 mM) ammonia concentration, the total chlorine residual consisted of chloramines. The SAF-MBR sample spiked with 0.5 mM sulfides was treated at pH 8.0 with 2 mM H_2O_2 (i.e., a 4:1 H_2O_2:sulfide molar ratio) for 30 min, and then with 225 mJ cm^{-2} UV fluence, the applied fluence needed to achieve 5-log MS2 inactivation. The residual H_2O_2 concentration was 0.4 mM. The total chlorine residuals measured 24 h after application of 25 and 50 mg-Cl_2/L were 0.3 and 29 mg-Cl_2/L, respectively, suggesting that an ~30 mg-Cl_2/L applied free chlorine dose (0.42 mM) would leave an ~5 mg-Cl_2/L residual (Table S7). Similarly, the sulfide-spiked sample was treated with 3 mM H_2O_2 (i.e., a 6:1 H_2O_2:sulfide molar ratio) for 30 min, and then with the 180 mJ cm^{-2} applied UV fluence needed to achieve 5-log MS2 inactivation. The residual H_2O_2 was 1.2 mM, and the free chlorine needed to achieve a 5 mg-Cl_2/L total chlorine residual was ~80 mg-Cl_2/L (1.1 mM) (Table S7).

For both H_2O_2:sulfide molar ratios, the applied chlorine dose needed to achieve the residual was lower than expected based upon the 1:1 stoichiometry (Eq. (5)) just to quench the residual H_2O_2. Additional experiments conducted in deionized water demonstrated that a portion of the free chlorine reacts with ammonia to form chloramines prior to being quenched by reaction with H_2O_2 (Text S2). Chloramines are degraded by reaction with H_2O_2 more slowly than is free chlorine (Zhang et al., 2019), such that chloramine formation reduces consumption of the total chlorine residual via reactions with H_2O_2.

$$HOCl + H_2O_2 \rightarrow O_2 + H^+ + Cl^- + H_2O \quad (5)$$

Table 1
Treatment costs for reuse of an aerobically treated effluent or anaerobically treated effluent spiked with 500 µm sulfide and treated with H_2O_2 dosed at either a 6:1 or 4:1 H_2O_2:sulfide ratio.

	Cost ($ m^{-3})		
	Conventional train	SAF-MBR based train	
		6:1 H_2O_2: sulfide ratio	4:1 H_2O_2: sulfide ratio
Conventional activated sludge	0.04	–	–
Microfiltration	0.05	–	–
SAF-MBR treatment	–	0	0
pH adjustment (NaOH)	–	0.02	0.02
H_2O_2 addition	–	0.17	0.11
UV treatment	–	0.01	0.01
Chlorine addition	0.02	0.14	0.05
Total	0.11	0.33	0.19

Comparison of treatment costs

The experimental results indicate that operating at a H_2O_2:sulfide molar ratio closer to 4 rather than 6 would reduce the cost of H_2O_2 supply and, by reducing the H_2O_2 residual, the cost of chlorine supply. However, these savings in reagent costs must be weighed against the increased energy cost associated with the higher UV fluence needed to achieve pathogen inactivation, since the UV_{254} was higher at the 4:1 molar ratio (0.25 cm^{-1}) than at the 6:1 molar ratio (0.20 cm^{-1}) (Fig. 2).

We conducted an initial comparison of the energy and chemical costs associated with H_2O_2/UV/chlorine treatment of SAF-MBR effluent (for both 4:1 and 6:1 H_2O_2:sulfide molar ratios) against the conventional treatment of aerobically-treated effluent by filtration (here microfiltration) and chlorine disinfection (Figure S6). Table 1 summarizes the results, while Text S3 details the cost estimates. For the conventional treatment of aerobic effluents, the estimate considered the energy costs associated with 1) activated sludge secondary treatment ($0.039/$m^3$) and 2) microfiltration ($0.052/$m^3$) and 3) the cost for addition of chlorine for disinfection ($0.017/$m^3$), for a total cost of $0.11/$m^3$. For H_2O_2/UV/chlorine treatment of SAF-MBR effluent, the estimates considered 1) the energy cost associated with SAF-MBR treatment (energy-neutral or $0.00/$m^3$), 2) the cost of NaOH for adjusting the effluent to pH 8 ($0.016/$m^3$), 3) the cost for H_2O_2 addition at 4:1 ($0.122/$m^3$) and 6:1 ($0.168/m^3) H_2O_2:sulfide molar ratios, 4) the energy cost for an incident UV fluence of 225 mJ cm^{-2} ($0.0098/$m^3$) for the 0.25 cm^{-1} UV_{254} associated with a 4:1 H_2O_2:sulfide molar ratio and 180 mJ cm^{-2} ($0.0078/$m^3$) for the 0.20 cm^{-1} UV_{254} associated with a 6:1 H_2O_2:sulfide molar ratio, and 5) the cost to provide 30 mg/L as Cl_2 chlorine for the 4:1 H_2O_2:sulfide molar ($0.052/$m^3$) and 80 mg/L as Cl_2 chlorine for the 6:1 H_2O_2:sulfide molar ($0.138/$m^3$). As an emerging technology, SAF-MBR treatment has not been fully optimized with respect to energy consumption. The assumption that SAF-MBR treatment would be energy-neutral incorporates the potential to harvest methane for energy production, reflects expectations of improved energy efficiency going from laboratory to full-scale, and aligns with recent evaluations indicating that six of eleven pilot-scale anaerobic membrane bioreactors treating domestic sewage were net energy positive (Shin and Bae, 2018). Regardless, the energy costs were modest relative to the chemical costs (Table 1). The overall energy and chemical cost to treat SAF-MBR effluent would be $0.19/$m^3$ for the 4:1 H_2O_2:sulfide molar ratio and $0.33/$m^3$ for the 6:1 H_2O_2:sulfide molar ratio. The reduction in chemical costs for H_2O_2 and chlorine associated with the 4:1 H_2O_2:sulfide molar ratio outweighed the higher energy cost for UV treatment needed to overcome the higher UV_{254} for this molar ratio.

However, for treatment of wastewater featuring 0.5 mM sulfate (48 mg/L), which could form 0.5 mM sulfides in the anaerobic reactor, H_2O_2/UV/chlorine treatment of SAF-MBR effluent at either H_2O_2/sulfide molar ratio would not be cost-competitive with the conventional approach of treating wastewater by activated sludge followed by filtration and chlorine disinfection. However, the chemical and energy costs for H_2O_2/UV/chlorine treatment of SAF-MBR effluent decrease with decreasing sulfide (and thus sewage sulfate) concentration. Further calculations (Text S3) indicate that the sulfide concentration at which H_2O_2/UV/chlorine treatment of SAF-MBR effluent becomes cost-competitive with the conventional aerobic treatment train for non-potable reuse would be 285 μM (27 mg/L sewage sulfate) for the 4:1 H_2O_2:sulfide molar ratio and 150 μM (14 mg/L sewage sulfate) for the 6:1 H_2O_2:sulfide molar ratio.

Conclusion

We evaluated treatment of secondary anaerobic biological treatment effluent using H_2O_2 to oxidize sulfides, UV disinfection and chlorine addition to provide a residual for distribution. Treatment of anaerobic effluent containing 0.5 mM sulfides at a 4:1 H_2O_2:sulfide molar ratio for 30 min at pH 8 achieved significant sulfide oxidation to sulfate. Bisulfide (HS^-) shields UV light at 254 nm, but a 225 mJ cm^{-2} applied UV fluence could achieve 5-log MS2 inactivation after sulfide oxidation at a 4:1 H_2O_2:sulfide molar ratio. Addition of 30 mg-Cl_2/L chlorine could provide a 5 mg-Cl_2/L total chlorine residual for distribution. For non-potable reuse, H_2O_2/UV/chlorine treatment of anaerobic effluent for non-potable reuse would be cost-competitive with conventional treatment of aerobic treatment for sulfide concentrations < 285 μM (i.e., sewage sulfate concentrations < 27 mg/L).

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.

Acknowledgements

The authors would like to thank researchers associated with the Codiga Resource Recovery Center (CR2C), including Chungheon Shin, Felipe Chen, and Sebastien Tilmans for help with effluent collection. Funding for this work was provided by the California Energy Commission (EPC-16–009) and the National Science Foundation Engineering Research Center for Reinventing the Nation's Urban Water Infrastructure (ReNUWIt; EEC-1028968). A.S. acknowledges support from the Abel Wolman Fellowship (American Water Works Association) and the National Science Foundation Graduate Research Fellowship Program (DGE-114747).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.wroa.2021.100097.

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