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3 **Effect of Matrix Components on UV/H₂O₂ and**
4 **UV/S₂O₈²⁻ Advanced Oxidation Processes for Trace**
5 **Organic Degradation in Reverse Osmosis Brines from**
6 **Municipal Wastewater Reuse Facilities**
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Abstract

When reverse osmosis brines from potable wastewater reuse plants are discharged to poorly-flushed estuaries, the concentrated organic contaminants are a concern for receiving water ecosystems. UV/hydrogen peroxide (UV/H₂O₂) and UV/persulfate (UV/S₂O₈²⁻) advanced oxidation processes (AOPs) may reduce contaminant burdens prior to discharge, but the effects of the high levels of halide, carbonate and effluent organic matter (EfOM) normally present in these brines are unclear. On the one hand, these substances may reduce process efficiency by scavenging reactive oxygen species (ROS), hydroxyl ([•]OH) and sulfate (SO₄^{•-}) radicals. On the other, the daughter radicals generated by halide and carbonate scavenging may themselves degrade organics, offsetting the effect of ROS scavenging. UV/H₂O₂ and UV/S₂O₈²⁻ AOPs were compared for degradation of five pharmaceuticals spiked into brines obtained from two reuse facilities and the RO influent from one of them. For UV/H₂O₂, EfOM scavenged ~75% of the [•]OH, reducing the degradation efficiency of the target contaminants to a similar extent; halide and carbonate scavenging and the reactivities of associated daughter radicals were less important. For UV/S₂O₈²⁻, anions (mostly Cl⁻) scavenged ~93% of the SO₄^{•-}. Because daughter radicals of Cl⁻ contributed to contaminant degradation, the reduction in contaminant degradation efficiency was only ~75-80%, with the reduction driven by daughter radical scavenging by EfOM. Conversion of SO₄^{•-} to more selective halogen and carbonate radicals resulted in a wider range of degradation efficiencies among the contaminants. For both AOPs, 250 mJ/cm² average fluence achieved significant removal of four pharmaceuticals, with significantly better performance by UV/S₂O₈²⁻ treatment for some constituents. Accounting for the lower brine flowrates, the energy output to achieve this fluence in brines is comparable to that often applied to RO permeates. However, much higher fluence was required for the least reactive pharmaceutical. Comparing AOP application to the RO influent or brine, equal or greater removal was achieved for brine treatment for comparable energy input. AOP treatment of brines could be applied to reduce, but not eliminate, contaminant burdens prior to discharge.

Keywords: brine; reverse osmosis; advanced oxidation; hydroxyl radical; sulfate radical

1. INTRODUCTION

Membrane technologies such as reverse osmosis (RO) have been favored to treat municipal wastewater effluents for potable reuse because they can remove a wide range of chemical contaminants, salts and pathogens. However, safe disposal of the concentrated waste brines is emerging as a significant issue (USBR, 2003). Roughly 48% of impaired-water reclamation facilities discharge brines to surface waters untreated, and a further 40% discharge brines to receiving waters via municipal wastewater treatment plants (USBR, 2003). Because salts and hydrophilic chemical contaminants are not adequately removed in these treatment plants, there have been concerns about the negative impacts of brine discharges into poorly-flushed receiving water ecosystems. Although similar contaminant mass loadings to receiving waters are expected in RO brines as from conventional discharges, contaminant concentrations in poorly-flushed receiving waters may increase because the volume of water in the RO permeate is no longer available for dilution.

The US National Research Council's report, *Desalination: A National Perspective*, identified deep well injection, evaporation basins, and thermal evaporation zero liquid discharge systems as alternatives to brine discharge to surface waters or discharge via municipal treatment plants (NRC, 2008). Evaporation basins are capital intensive (e.g., land acquisition) and thermal evaporation systems are energy intensive (NRC, 2008). While estimated costs vary widely depending on site-specific conditions, some zero liquid discharge systems are more costly than the corresponding desalination system (NRC, 2008). Accordingly, development of cost-effective concentrate management strategies was identified as one of three research priorities (NRC, 2008). Similarly, the US Bureau of Reclamation's *Desalination and Water Purification Technology Roadmap* (USBR, 2003) indicated that "cost effective and environmentally sensitive concentrate management is recognized as the significant hurdle to widespread adoption of desalination technologies, especially for inland regions that seek to make productive use of brackish water resources. It is a question that must be solved for the nation to be able to meet its future water needs."

In high population growth areas RO brines are often discharged to poorly-flushed estuaries. In such cases, contaminants may be of higher concern than salts. Engineered treatment wetlands

may provide a low-cost treatment alternative prior to discharge. However, since wetlands often are magnets for wildlife, oxidation to partially degrade organic contaminants prior to wetland treatment may mitigate impacts on wildlife and enhance further degradation within the wetland. Advanced Oxidation Processes (AOPs) that generate radicals, such as hydroxyl ($\cdot\text{OH}$) or sulfate radicals ($\text{SO}_4^{\cdot-}$) that can react rapidly with the wide variety of compounds expected in brines may be attractive for this purpose (Buxton et al., 1988; Neta et al., 1988). Previous research has demonstrated that partial degradation of the pharmaceutical carbamazepine by a $\cdot\text{OH}$ -based AOP promoted its mineralization by biodegradation (Keen et al., 2012), suggesting that AOP pretreatment may enhance contaminant removal within wetlands.

Hydroxyl-based AOPs have received some attention for treating brines, but $\text{SO}_4^{\cdot-}$ -based AOPs have received none. UV/titanium dioxide AOP treatment of a brine achieved ~67% removal of dissolved organic carbon (DOC), and reduced pharmaceutical concentrations below detection limits (Westerhoff et al., 2009). Justo et al. (2013) observed significant pharmaceutical removal in a brine from a wastewater recycling plant with UV/hydrogen peroxide (H_2O_2) treatment. Both Justo et al. (2013) and Benner et al. (2008) evaluated pharmaceutical removal from brines by ozonation; O_3 can react with contaminants either directly, or via $\cdot\text{OH}$ produced during ozone decomposition (von Gunten, 2003). Degradation of beta blockers was dominated by direct ozone reactions (Benner et al., 2008). Pharmaceutical degradation in conventional wastewater effluents by UV/ H_2O_2 AOP (Rosario-Ortiz et al., 2010) or O_3 (Buffle et al., 2006; Lee et al., 2013) has also been studied.

Municipal wastewater effluents and RO brines feature far higher concentrations of organic matter and salts than the drinking water or RO permeate matrices targeted by prior AOP applications. Previous research has not systematically evaluated the effects of these matrix components on AOP treatment. When matrix effects were addressed at all, researchers tended to equate any reduction in contaminant degradation in RO brines (Benner et al., 2008) or conventional effluents (Lee et al., 2013; Keen et al., 2014) to a reduction in steady-state $\cdot\text{OH}$ concentrations ($[\cdot\text{OH}]_{\text{ss}}$) due to scavenging. Effluent organic matter (EfOM) was a particular target (Buffle et al., 2006; Rosario-Ortiz et al., 2010; Lee et al., 2013; Keen et al., 2014), as it is regarded as the most efficient $\cdot\text{OH}$ -scavenger (~65-95% in conventional effluents). However, considering only EfOM, carbonates and nitrite as $\cdot\text{OH}$ scavengers in conventional effluents, Rosario-Ortiz et

al. (2010) and Keen et al. (2014) calculated that carbonates scavenged ~5-15% and ~0-30% of $\cdot\text{OH}$, respectively. Lee et al. (2013) calculated that carbonates scavenged 9-30% of $\cdot\text{OH}$ in wastewaters, but that bromide could scavenge up to 9% of $\cdot\text{OH}$ in a wastewater that contained a high bromide concentration (940 $\mu\text{g/L}$).

Prior calculations of $\cdot\text{OH}$ scavenging neglect the production of daughter radicals, particularly carbonate and halogen radicals (e.g., $\text{CO}_3^{\cdot-}$, $\text{Br}_2^{\cdot-}$; equations 1-6), that can participate in contaminant degradation. In previous work related to seawater matrices, we employed kinetic modeling of UV/ H_2O_2 or UV/ $\text{S}_2\text{O}_8^{2-}$ (equation 7) treatment of model contaminants in synthetic seawater containing only carbonates, chloride and bromide (no dissolved organic matter) to demonstrate that $\text{CO}_3^{\cdot-}$ and halogen radical concentrations could exceed those of $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ by several orders of magnitude (Grebel et al., 2010; Yang et al., 2014). Experiments with a range of model contaminants confirmed that degradation rates were faster than predicted based on reduction of $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ concentrations alone due to reaction of $\text{CO}_3^{\cdot-}$ and halogen radicals with the contaminant (Grebel et al., 2010; Yang et al., 2014). While $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ react rapidly with many organic compounds (rate constants typically 10^9 - $10^{10} \text{ M}^{-1} \text{ s}^{-1}$), $\text{CO}_3^{\cdot-}$ and halogen radicals are more selective oxidants (rate constants 10^5 - $10^9 \text{ M}^{-1} \text{ s}^{-1}$) (NIST, 2015). In these model systems, we observed that seawater levels of carbonates and halides in some cases resulted in an increase in the degradation rate of the most reactive components due to conversion of the non-selective $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ radicals to more selective $\text{CO}_3^{\cdot-}$ and halogen radicals which focused the oxidizing power of the solution on the more reactive components (Grebel et al., 2010; Yang et al., 2014).

The previous research indicated that, under organic matter-free seawater conditions, the daughter radicals formed by $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ scavenging by halides and carbonates offset this scavenging by contributing to contaminant degradation (Grebel et al., 2010; Yang et al., 2014). The goal of the current research was to systematically evaluate the extent to which matrix constituents of RO brines from municipal wastewater treatment, including salts and EfOM, affect the efficacy of UV/H₂O₂ and UV/S₂O₈²⁻ AOPs for contaminant degradation. In particular, we evaluated whether the halide and carbonate effects observed in seawater are still important in authentic RO brines, despite the lower concentrations of these anions in brines and the high concentration of EfOM. Although the high absorbance of brines would challenge UV-based AOPs, we targeted these systems because their common usage for treatment of RO permeate at potable reuse plants facilitates comparison, and the lower brine volume relative to permeate can partially offset the impact of absorbance. Additionally, we characterized whether significant contaminant removal could be achieved at reasonable energy input (incident UV fluence), despite the high level of scavengers. Specific contaminants driving the toxicity of RO Brines to ecosystems have not been identified. We evaluated the effect of the brine matrix on the degradation of five model organic contaminants spiked into authentic brines. These contaminants were selected to illustrate the range of effects of matrix components on the degradation of contaminants. With a wide array of organic contaminants likely in these brines, the primary focus was on the effect of the brine matrix on AOP process efficiency, rather than on the destruction of specific contaminants.

2. Materials and Methods

2.1. Materials and samples. BioXtral NaCl (Sigma-Aldrich) contained 0.0038% Br⁻ (Grebel et al., 2010) and $\leq 0.001\%$ I⁻ on a molar basis. All other chemicals were reagent grade or higher. The Supporting Information (SI) provides suppliers and details on reagent standardization. Grab samples of RO brines were collected from two municipal wastewater recycling facilities in California. At facility B, a grab sample of the RO influent was also collected. Table 1 provides basic water quality characteristics. EfOM was isolated from RO Brine A by solid-phase extraction, achieving 53% recovery of dissolved organic carbon. While the characteristics of the fractions of EfOM that were recovered or lost differed somewhat (see SI for details), the EfOM isolation was

necessary to differentiate the effects of EfOM from inorganic ions.

2.2. Experimental procedures. Experiments were performed on authentic RO influent or brine samples, as well as on samples of deionized water amended with salts and buffered at pH 8.3 with 10 mM phosphate. Each sample was spiked to achieve 5 μ M of each of five pharmaceuticals (Table 2): the antibiotic sulfamethoxazole (SMX), the beta blocker propranolol (PPL), the anti-convulsant carbamazepine (CBZ), and the antivirals acyclovir (ACV) and lamivudine (LMVD). They were selected as model compounds based on preliminary experiments demonstrating that their mixture could illustrate some of the selective targeting of contaminants by daughter $\text{CO}_3^{\bullet-}$ or halogen radicals. With the enormous number of possible contaminants in RO brines, we did not attempt to develop a structure-activity relationship for contaminant destruction. While we previously developed such a relationship (Hammett constant correlation) for UV/ H_2O_2 AOP treatment of model compounds in the absence of salts, no relationship was found in synthetic carbonate and halide solutions (Grebel et al., 2010), likely due to the mixture of radicals involved. The pharmaceuticals were quantified by HPLC with UV detection (example chromatogram in Figure S1). While 5 μ M is higher than the native concentrations expected for these pharmaceuticals in RO brines (Benner et al., 2008; Justo et al., 2013), EfOM would still dominate as an organic constituent. Experimental results, described below, confirm the dominance of EfOM for scavenging $\cdot\text{OH}$ or $\text{SO}_4^{\bullet-}$. The chloride concentration exceeded the total pharmaceutical concentration by 1,300-2,300-fold.

UV was applied using a semi-collimated beam system consisting of four 15 W low pressure mercury lamps emitting at 254 nm shining down onto a 250 mL crystallization dish (pathlength = 3.9 cm), as described previously (Yang et al., 2014). Samples were withdrawn at selected times, and quenched by excess sodium sulfite for H_2O_2 or ascorbic acid for $\text{K}_2\text{S}_2\text{O}_8$. Incident UV fluence impinging on the solution (mJ/cm^2) was determined by chemical actinometry (see SI). The average fluence experienced by a water parcel is less than the incident fluence due to photon absorbance with increasing solution depth (inner filter effect); average UV fluence was calculated by accounting for solution absorbance at 254 nm, as described previously (Bolton and Linden, 2003; Jin et al., 2006; Shah et al., 2011). All experiments were conducted in duplicate at ambient temperature (20 ± 2 °C). The range of experimental duplicates generally was <10%.

Initial experiments with UV/H₂O₂ or UV/S₂O₈²⁻ treatment of RO brine A indicated pseudo-first order behavior in each pharmaceutical (Figure S4). The observed pseudo-first order degradation rate constants (k_{obs}) increased with H₂O₂ or K₂S₂O₈ dose over the range 0.5-5 mM (17-170 mg/L H₂O₂ or 96-960 mg/L S₂O₈²⁻; Figure S5). Only ~15% loss of H₂O₂ was observed over experimental timescales. Interference prevented analysis of residual K₂S₂O₈, but residual concentrations likely were similar.

2.3. Modeling. Since analytical methods for quantifying halogen radicals are not available, steady-state inorganic radical concentrations were modeled using a kinetic model described previously (Yang et al., 2014). Briefly, the model contains 188 reactions and was implemented with Kintecus v4.55 (Ianni, 2012) using rate constants obtained from the literature when available or estimated based upon analogy with similar reactions (Table S2). Previous modeling of the degradation of phenol, for which reaction rate constants with many daughter radicals were available, indicated agreement with experimental results within ~20% for chloride, bromide and carbonate concentrations up through their seawater-relevant concentrations (Grebel et al., 2010). The modeling did not consider reactions with the pharmaceuticals because rate constants were unavailable in some cases. As noted above, concentrations of EfOM and inorganic constituents generally far exceeded pharmaceutical concentrations. Inorganic radical concentrations were modeled 5 min after initiation, a timescale that minimizes loss of H₂O₂ or S₂O₈²⁻ and attains pseudo-steady-state radical concentrations. Including reactions with the pharmaceuticals would alter the instantaneous radical concentrations, but would not appreciably influence the effects of different ion concentrations on relative radical concentrations, which was our aim with the model. However, for scavenging calculations, the empirically determined scavenging rate constants for the pharmaceutical mixtures with [•]OH or SO₄^{•-} were included, as described below.

3. RESULTS AND DISCUSSION

Basic water quality parameters for RO Influent B (Table 1) were similar to wastewater effluents evaluated in previous studies of ozonation (Lee et al., 2013) or UV/H₂O₂ AOP treatment (Rosario-Ortiz et al., 2010), although the 510 µg/L bromide concentration was on the high side of

the 31-940 $\mu\text{g/L}$ concentration range reported in the ozonation study (Lee et al., 2013). The two RO brines exhibited similar water quality parameters (Table 1). Because both brines exhibited pH ~ 8.3 , synthetic water experiments were buffered at this pH. Although pH affects the speciation and reactivity of target contaminants, our purpose was to illustrate the effect of matrix components on the performance of AOPs rather than characterize the degradation of specific target compounds. However, the chloride and bromide concentrations were higher in RO Brine B than in RO Brine A by 80% and 30%, respectively. The phosphate concentration was higher by 80% in RO Brine A. The RO brines featured higher carbonate concentrations (~ 10 mM) than seawater (~ 2.3 mM), but lower concentrations of chloride (33-58 mM vs. 540 mM) and bromide (28-36 μM vs. 800 μM) (DOE, 2013).

The DOC concentration, UV absorbance at 254 nm (UV_{254}), alkalinity, and bromide concentration were about six times greater in RO Brine B than RO Influent B (Table 1), in line with the six-fold concentration factor reported for RO Brine B based on water flow rates. The similar specific UV absorbance at 254 nm (SUVA_{254}) values suggest similar characteristics between EfOM in the RO influent and brine. Although RO Influent B was a well-nitrified municipal wastewater effluent, the ammonia concentration in the brine was higher than expected based upon the concentration factor because this facility adds ammonia and chlorine between the RO Influent B sampling point and the RO membranes to form chloramines to control biofouling. Facility A receives non-nitrified secondary effluent, but adds chlorine to form chloramines, as well as ozone, upstream of RO to control biofouling.

3.1. Contribution of daughter radicals to contaminant degradation. The elevated EfOM and salt concentrations in brines are anticipated to reduce contaminant degradation by scavenging $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$. However, contaminant degradation by daughter radicals (e.g., $\text{CO}_3^{\cdot-}$, $\text{ClBr}^{\cdot-}$) formed by $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ reactions with matrix ions may partially offset this loss in degradation efficiency. In addition, because many daughter radicals are more selective oxidants than $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$, their production may alter the relative rates at which contaminants are degraded. To evaluate the potential importance of daughter radicals, the degradation by UV/ H_2O_2 and UV/ $\text{S}_2\text{O}_8^{2-}$ AOPs (5 mM H_2O_2 or $\text{S}_2\text{O}_8^{2-}$) of 5 μM of each of five pharmaceuticals was evaluated in phosphate-buffered deionized water (“Control”) and four matrix scenarios: control with 36 mg-C/L EfOM isolated from RO Brine A (“Control + EfOM”); the concentrations of ions measured in RO Brine A

(“Salts”); the concentrations of ions measured in RO Brine A along with 36 mg-C/L EfOM (“Salts + EfOM”); and the full RO Brine A, which contained 68.2 mg-C/L EfOM (“Brine”).

The observed pseudo-first order loss rate constants (k_{obs}) for the pharmaceuticals represents the sum of dark reactions with H_2O_2 or $\text{S}_2\text{O}_8^{2-}$, direct UV photolysis, and indirect photolysis (i.e., degradation by radicals). Indirect photolysis generally dominated (Text S2). At 5 mM H_2O_2 or $\text{S}_2\text{O}_8^{2-}$, indirect photolysis accounted for >80% of k_{obs} , except for sulfamethoxazole, where direct photolysis accounted for 50% of k_{obs} . Above 5 mM H_2O_2 or $\text{S}_2\text{O}_8^{2-}$, these compounds became important scavengers of $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$, respectively (equations 8 and 9; Text S2). Thereafter, we applied 5 mM H_2O_2 or $\text{K}_2\text{S}_2\text{O}_8$ doses, at which H_2O_2 scavenged ~5-23% of $\cdot\text{OH}$ (Table 3) and $\text{S}_2\text{O}_8^{2-}$ scavenged ~0-1% of $\text{SO}_4^{\cdot-}$ (Table 4) for different matrix scenarios. Table S3 provides the measured k_{indirect} (s^{-1}) for each pharmaceutical and scenario, divided by the corresponding $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ production rates (M/s); these normalized k_{indirect} values ($k_{\text{indirect}}^{\text{N}}$; M^{-1}) correct for reduced radical production rates resulting from photon absorption by EfOM.

Scavenging by EfOM: Comparison of $k_{\text{indirect}}^{\text{N}}$ values for pharmaceuticals between the Control and Control + EfOM scenarios enabled calculation of the rate constants for $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ reaction with EfOM. The average $k_{\text{indirect}}^{\text{N}}$ values declined by 74% for the UV/ H_2O_2 AOP and 77% for the UV/ $\text{S}_2\text{O}_8^{2-}$ AOP, indicating significant $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ scavenging by EfOM (Figure 1 and Table S4). Because rate constants for $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ reactions with carbamazepine are known, the reduction in its $k_{\text{indirect}}^{\text{N}}$ values between Control and Control + EfOM scenarios enabled quantification of the rate constants for $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ reactions with EfOM (Text S3). The $3.33 \times 10^4 \text{ (mg-C/L)}^{-1} \text{ s}^{-1}$ rate constant for $\cdot\text{OH}$ is close to the range of $1.3\text{-}2.8 \times 10^4 \text{ (mg-C/L)}^{-1} \text{ s}^{-1}$ determined in previous studies (Westerhoff et al., 2009; Rosario-Ortiz et al., 2010; Lee et al., 2013). The rate constant for reaction with $\text{SO}_4^{\cdot-}$ was found to be $9.4 \times 10^3 \text{ (mg-C/L)}^{-1} \text{ s}^{-1}$. The total pseudo-first order scavenging rate constants for $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ by the five pharmaceuticals combined were calculated to be $2.1 \times 10^5 \text{ s}^{-1}$ and $7.0 \times 10^4 \text{ s}^{-1}$ for UV/ H_2O_2 and UV/ $\text{S}_2\text{O}_8^{2-}$, respectively (Text S3). Even with only 36 mg-C/L EfOM, scavenging by EfOM was 5.71-times and 4.83-times greater than scavenging by the combined pharmaceuticals for UV/ H_2O_2 and UV/ $\text{S}_2\text{O}_8^{2-}$, respectively (Tables 3 and 4).

Matrix Effects on UV/H₂O₂. First, we evaluated the importance of different inorganic ions for altering the UV/H₂O₂ AOP performance in the absence of EfOM. RO Brine A ions reduced $k_{\text{indirect}}^{\text{N}}$ of the pharmaceuticals by 32% on average (17-43% range) (Figure 1). Experiments conducted with each of the ionic constituents of RO Brine A alone confirmed that the anions most responsible for $\cdot\text{OH}$ scavenging (i.e., largest reduction in $k_{\text{indirect}}^{\text{N}}$) were carbonates and Br^- (Figure S8A). If only $\cdot\text{OH}$ reactions contribute to pharmaceutical degradation, the average percent reduction for each matrix scenario should match the percent reduction in $[\cdot\text{OH}]_{\text{ss}}$ resulting from scavenging. The reduction in $[\cdot\text{OH}]_{\text{ss}}$ was calculated using the rate constant for $\cdot\text{OH}$ reaction with EfOM, the total scavenging rate of the pharmaceutical mixture determined experimentally, as discussed above, and a kinetic model for the reactions of $\cdot\text{OH}$ with matrix ions. The full kinetic model is needed to accurately capture the importance of halides and carbonates due to their interactions. Scavenging by halides and carbonates was found to be approximately two times higher using the full model than when only considering individual components. For example, Cl^- significantly enhanced the importance of scavenging by Br^- (equation 10) via equation 11.

Modeling indicated a modest participation of daughter radicals in the absence of EfOM. The average indirect degradation rate of pharmaceuticals should have dropped by 40% (Figure 1 and Table S4) due to the decline in $[\cdot\text{OH}]_{\text{ss}}$, if only $\cdot\text{OH}$ contributed to pharmaceutical degradation. A slightly smaller effect was observed experimentally (i.e., only a 32% decline), suggesting that daughter radicals could participate in pharmaceutical degradation. As additional evidence for the participation of daughter radicals, pharmaceuticals varied in the extent to which matrix ions affected their degradation, likely reflecting the conversion of non-selective $\cdot\text{OH}$ to selective daughter radicals. Further modeling indicated that the concentrations of halogen radicals (1.6×10^{-13} M total, principally $\text{ClBr}^{\cdot-}$ and $\text{Br}_2^{\cdot-}$) and $\text{CO}_3^{\cdot-}$ (6.33×10^{-12} M) modestly exceed that of $\cdot\text{OH}$ (1.5×10^{-13} M) (Table S5). The relatively modest selectivity effect observed experimentally likely is attributable to the fact that halogen radical and $\text{CO}_3^{\cdot-}$ concentrations do not greatly exceed that of $\cdot\text{OH}$ (which generally features higher reaction rate constants than halogen radicals and $\text{CO}_3^{\cdot-}$), such that $\cdot\text{OH}$ remains the dominant radical responsible for pharmaceutical degradation.

These inorganic halide effects were less important in the presence of EfOM, which served as the predominant scavenger of $\cdot\text{OH}$. Addition of 36 mg-C/L EfOM in the presence of salts further reduced pharmaceutical degradation (81% on average) and the range of this decrease among pharmaceuticals was much smaller (79-82%). The results were similar for the full RO Brine A, although the average reduction in radical-mediated degradation was greater (87%), reflecting the higher EfOM concentration (68.2 mg-C/L). However, in the presence of EfOM, the modeled average reductions in pharmaceutical degradation rates considering only $\cdot\text{OH}$ reactions matched the experimental values (Figure 1 and Table S4), suggesting that daughter radical reactions with the pharmaceuticals were relatively unimportant. Previous research suggested that nitrite is an important $\cdot\text{OH}$ scavenger in wastewaters (Rosario-Ortiz et al., 2010). Although nitrite was not evaluated here, the close match between modeled (which did not consider nitrite) and experimental results for the full RO Brine A suggest that any nitrite in the full brine was not important here. The low importance of daughter radicals is also reflected in the low variance observed for the effect of the matrix between pharmaceuticals. This low importance for daughter radicals likely results from the dominance of $\cdot\text{OH}$ scavenging by EfOM (68-80% vs. 8-13% by inorganic ions) (Table 3). Although we had previously found that halogen and carbonate daughter radicals are important for the degradation of model contaminants by UV/H₂O₂ treatment in synthetic seawater matrices without other organic constituents (Grebel et al., 2010; Yang et al., 2014), the far lower concentrations of halides (2.2 mg/L vs. 64 mg/L Br⁻ and 1160 mg/L vs 18,900 mg/L Cl⁻) and higher DOC concentrations in the brine rendered daughter radicals of borderline (salts only) or negligible (salts with EfOM) importance for UV/H₂O₂ treatment of RO brines.

Matrix Effects on UV/S₂O₈²⁻. In the absence of EfOM, the impact of matrix constituents on pharmaceutical degradation by UV/S₂O₈²⁻ treatment was always significantly less than anticipated based upon the modeled decrease in [SO₄^{•-}]_{ss}, indicating the importance of daughter radical reactions. For the salts only scenario (“Salts”), modeling suggested a 99.3% decline in [SO₄^{•-}]_{ss} (Figure 1 and Table S4), but experimentally $k^{\text{N}}_{\text{indirect}}$ increased by 34% on average (Figure 1 and Table S4), suggesting that scavenging by Cl⁻ converted SO₄^{•-} to reactive daughter radicals. The wide variation observed experimentally in the extent to which salts impacted pharmaceutical degradation also suggests the importance of selective daughter radicals. For example, salts decreased $k^{\text{N}}_{\text{indirect}}$ for carbamazepine by 41%, but increased $k^{\text{N}}_{\text{indirect}}$ for acyclovir by 100% (Figure

1).

Modeling indicated that $\text{Cl}^\cdot$ was the dominant scavenger (98%; Table 4), forming $\text{Cl}^\cdot$ directly by equation 12. Modeled halogen (9.9×10^{-13} M total, principally $\text{ClBr}^\cdot$ and $\text{Br}_2^\cdot$) and $\text{CO}_3^\cdot$ (4.7×10^{-10} M) radical concentrations exceeded those of $\text{SO}_4^\cdot$ (7.2×10^{-15} M) and $\cdot\text{OH}$ (1.8×10^{-14} M) by orders of magnitude (Table S5). Note that $\cdot\text{OH}$ forms from $\text{SO}_4^\cdot$ reaction with water or hydroxide (equation 13). Experiments conducted with each brine ion alone confirmed that $\text{Cl}^\cdot$ was the predominant scavenger of $\text{SO}_4^\cdot$ (Figure S8B).

In the presence of both salts and EfOM (Salts + EfOM or full RO Brine A scenarios), chloride ion remained the dominant $\text{SO}_4^\cdot$ scavenger (>90% vs. $\leq 6\%$ for EfOM (Table 4)). The experimental indirect photochemical degradation rates of pharmaceuticals declined by 84% on average. If only $\text{SO}_4^\cdot$ were involved in contaminant degradation, the decline in pharmaceutical degradation rates would have been 99.3% based upon modeled reductions in $[\text{SO}_4^\cdot]_{\text{ss}}$ (Figure 1 and Table S4). The 62-90% decline in pharmaceutical degradation efficiency for Salts + EfOM was similar to that observed with EfOM alone. Although chloride was the dominant $\text{SO}_4^\cdot$ scavenger, EfOM plays an important role because it can scavenge the daughter radicals formed as a result of $\text{SO}_4^\cdot$ reactions with chloride (e.g., $\text{Cl}^\cdot$). For example, the rate constant for $\text{Cl}^\cdot$ reaction with natural organic matter was determined previously to be 1.3×10^4 (mg-C/L) $^{-1}$ s $^{-1}$ (Fang et al., 2014). In the presence of salts, scavenging of these daughter radicals by EfOM reduces contaminant degradation to the levels seen for EfOM without salts. However, salts still affect the relative rates at which specific compounds are degraded. Comparing the Control + EfOM and Salts + EfOM scenarios, the presence of anions promoted acyclovir and propranolol degradation efficiencies, but decreased carbamazepine degradation efficiency (Figure 1).

3.2. Practical implications. As an initial estimate of the feasibility of AOP treatment of brines, we focused on the operational cost, which for AOP treatment is driven by the energy input. Because no treatment of brines currently is required, we compared the energy input to that typically applied for AOP treatment of the RO permeate in potable reuse operations. UV fluence (mJ/cm 2) is commonly used to express UV dose and reflects the energy input to the water. In previous

research on contaminant removal by AOPs applied to brines, the UV fluence required to achieve contaminant degradation generally was not provided (Westerhoff et al., 2009; Justo et al., 2013). In our analysis we used average fluences. Whereas incident fluence reflects lamp output energy, average fluence corrects the incident fluence for solution absorbance to indicate the average fluence experienced by the solution (see Materials and Methods). Average fluence requirements are expected to be more general across brines of different absorbance (i.e., EfOM) and different reactor designs. For example, reactors with longer light paths would require higher incident fluence (lamp output) to achieve the same average fluence due to the greater photon absorbance along the light path.

The percent elimination of pharmaceuticals in RO Brines A and B was evaluated over 250-1,000 mJ/cm² average fluence using 5 mM H₂O₂ or K₂S₂O₈, (Figure 2). The average fluence needed for 50% removal of pharmaceuticals was estimated from plots of their percentage removal against average fluence (Table 2). For both AOPs and both brines, lamivudine, propranolol and sulfamethoxazole were degraded in preference to carbamazepine and, even more so, to acyclovir. For UV/H₂O₂ treatment the average fluence needed for 50% removal of lamivudine, propranolol, sulfamethoxazole or carbamazepine in either brine ranged from ~170-500 mJ/cm² (Table 2). The UV/S₂O₈²⁻ AOP required comparable average fluence for 50% removal of sulfamethoxazole (156 – 166 mJ/cm²) and carbamazepine (435 – 466 mJ/cm²), but only 56-85 mJ/cm² for propranolol, and 125-133 mJ/cm² for lamivudine. For either AOP, 50% removal of acyclovir required ~1,550 mJ/cm² for RO Brine A and ~1,100 mJ/cm² for RO Brine B. While the average performance of the AOPs was comparable, the UV/S₂O₈²⁻ AOP exhibited a wider variation in contaminant removal efficiency because it was more prone to selective daughter radical formation, as discussed previously (Figure 1).

Thus, significant removal of several pharmaceuticals was observed at ~250 mJ/cm² average fluence (Figure 2). For RO Brine B, 250 mJ/cm² average fluence would be equivalent to ~3,000 mJ/cm² incident fluence for the light path in our reactor due to the high level of photon-scavenging by the concentrated EfOM. However, accounting for the 6-fold concentration factor achieved by RO, the total energy input would be comparable to ~500 mJ/cm² applied to the RO influent or permeate, in the range of UV fluence applied for permeate treatment in potable reuse operations (Mitch et al., 2003). For less reactive contaminants (e.g., acyclovir), significant removal may not

be achievable at reasonable fluence. Thus, AOP treatment will not significantly degrade all contaminants, but it might serve as a pretreatment to decrease the contaminant loadings before discharge to engineered natural treatment systems (e.g., engineered wetlands).

The focus of this research is to evaluate the impact of matrix components on AOP process efficiency within brines, rather than to evaluate the fate of specific contaminants. Accordingly, we evaluated the potential for formation of halogenated byproducts from AOP treatment of RO brines A and B in the absence of spiked pharmaceuticals. Bromate was below the 4 µg/L quantification limit for both brines after treatment with 250, 500 or 1,000 mJ/cm² for either AOP, despite the presence of 2.2 and 2.9 mg/L Br⁻ in the samples. Additionally, none of the chlorinated or brominated analogues of trihalomethanes or dihaloacetonitriles were detected in either brine with either AOP at 500 mJ/cm² average fluence. It is likely the high ammonia concentrations would have scavenged any HOBr that may have formed, which is the precursor for the brominated compounds. When specific contaminants are identified that may drive brine toxicity, future research should identify the byproducts formed by AOP treatment within these matrices.

An alternative to AOP treatment of brines is to apply AOPs to RO influents. Degradation of contaminants upstream of RO would simultaneously reduce contaminant concentrations in brines, and reduce the burden on the RO system to reduce their concentrations in the RO permeate. Ozonation upstream of RO has received attention because ozone may degrade contaminants (von Gunten, 2003; Huber et al., 2003; Buffle et al., 2006) and reduce membrane biofouling (Stanford et al., 2011; Pisarenko et al., 2011; Zeng et al., 2014). However, ozonation of wastewater forms the potent carcinogen, N-nitrosodimethylamine (NDMA) (Gerrity and Snyder, 2011; Pisarenko et al., 2012; Sgroi et al., 2014; Dai et al., 2015), which is a key contaminant in potable reuse operations (NRC, 2012). Because NDMA is poorly rejected by RO membranes (Bellona et al., 2004; Fujioka et al., 2012, 2013), UV treatment of RO permeate is often required (Mitch et al., 2003). Application of UV-based AOPs upstream of RO would destroy nitrosamines occurring in the wastewater (Dai et al., 2015) and deactivate nitrosamine precursors (Shah et al., 2012).

Evaluation of AOP treatment of influent *versus* brine should account for the six-fold concentration factor resulting from the RO process. While a higher UV fluence is needed to treat the brine due to the higher concentrations of competitive scavengers, brine treatment involves a

lower flowrate. Table 4 compares the percent removal of each pharmaceutical in RO Influent B for an average UV fluence of 167 mJ/cm², to the percent removal in RO Brine B for a 1,000 mJ/cm² average UV fluence (i.e., six-fold higher fluence). Application of 5 mM H₂O₂ or K₂S₂O₈ to the brine achieved greater degradation than application to the influent with 1 mM H₂O₂ or K₂S₂O₈ by factors of ~2-10. For application of 5 mM H₂O₂ or K₂S₂O₈ to the influent, the difference was less dramatic, and for lamivudine and propranolol, 100% removal was achieved for UV/S₂O₈²⁻ treatment of either the influent or the brine (Figure S9). In practice, H₂O₂ or K₂S₂O₈ doses to RO influent may be closer to 1 mM because 5 mM would require a substantially higher material cost due to the higher flowrate, and because 5 mM K₂S₂O₈ would significantly increase brine salinity (i.e., by ~6,000 mg/L sulfate). The greater efficiency observed for brine treatment likely results from the greater average UV fluence for brine application; at higher fluence, greater degradation is expected for the most reactive competitive radical scavengers.

However, the energy costs for AOP treatment are more related to the UV lamp output (i.e., incident fluence). The UV₂₅₄ of Brine B was 1.35 after spiking pharmaceuticals and 5 mM H₂O₂ or K₂S₂O₈ (i.e., UV transmittance (UVT) = 4.5%), while those of Influent B with pharmaceuticals and 1 mM or 5 mM H₂O₂ or K₂S₂O₈ were 0.41 or 0.49, respectively (i.e., UVT = 39% or 32%). The incident fluence needed to achieve 1,000 mJ/cm² average fluence in the brine would be 12,221 mJ/cm² for the light path of our reactor while the incident fluence needed to achieve 167 mJ/cm² average fluence in the influent would be 620 mJ/cm² for 1 mM H₂O₂ or K₂S₂O₈, and 740 mJ/cm² for 5 mM H₂O₂ or K₂S₂O₈. The one previous study to quantify fluence requirements for pharmaceutical removal upon UV/H₂O₂ treatment of wastewater effluents (i.e., similar to RO influent) found <10-53% carbamazepine removal at 500-700 mJ/cm² incident fluence with 5 mM H₂O₂ (Rosario-Ortiz et al., 2010) comparable to the 23% removal observed here at 620 mJ/cm² incident fluence (Table 4). As a first approximation, the ~20-fold higher incident fluence required for brine treatment amounts to a ~3-fold higher energy cost, after accounting for the ~6-fold lower flowrate. Given that brine treatment achieved ~2-10-fold greater pharmaceutical removal, treatment of the brine would be at least as efficient or more efficient than treatment of the RO influent. A cost-benefit analysis would need to evaluate the increased energy cost against the increased contaminant degradation.

4. Conclusions

Overall we find that, while important in seawater, anions and their daughter radicals are of little importance in UV/H₂O₂ treatment of brines due to their relatively low concentrations. As the dominant •OH scavenger, EfOM will drive the radical exposure, and thus the UV energy input, needed to degrade target contaminants. In contrast, matrix ions are much more important in UV/S₂O₈²⁻ treatment, particularly Cl⁻, which is the dominant SO₄•⁻ scavenger. Based on the modeled reduction in [SO₄•⁻]_{ss} resulting from this scavenging, UV/S₂O₈²⁻ treatment of brines would be expected to be far less efficient than UV/H₂O₂ treatment. However, the daughter radicals produced by this scavenging replace SO₄•⁻ as the primary agents for target contaminant degradation. EfOM still drives the radical exposure needed for contaminant degradation, because EfOM is the dominant scavenger of these daughter radicals, but the degradation efficiency will be much higher than estimated based on the reduction of [SO₄•⁻]_{ss}. Because daughter radicals are more selective than SO₄•⁻, the relative rates at which target contaminants degrade may be altered.

Significant removal of many pharmaceuticals required 250 mJ/cm² average fluence by either AOP. Due to the high absorbance resulting from the concentrated EfOM in these brines, ~3,000 mJ/cm² UV output would be required for our reactor's pathlength to achieve this average fluence. Although 3,000 mJ/cm² is high, the brine flowrate is roughly 6-fold lower than the RO permeate, such that the energy input would be comparable to the ~500 mJ/cm² input currently applied to treat RO permeate in potable reuse facilities. Because destruction of some pharmaceuticals requires significantly higher average fluence, AOP treatment of brines may only degrade a portion of potential target contaminants. AOP treatment may be a suitable pre-treatment to reduce contaminant burdens to engineered treatment wetlands. While the AOPs exhibited comparable fluence requirements for the destruction of several of the target contaminants, the UV/S₂O₈²⁻ required lower fluence for destruction of certain components (e.g., propranolol and lamivudine). If future research indicates that such components drive the toxicity of RO brines in receiving waters, the UV/S₂O₈²⁻ AOP may be preferable, although the production of SO₄²⁻ may increase the salinity.

Application of these AOPs to the RO influent to reduce contaminant concentrations would simultaneously improve the quality of the RO permeate and the RO brine. Setting aside possible benefits to the RO permeate of RO influent treatment, AOP treatment of the brine was as efficient or more efficient than treatment of the RO influent. Separate treatment of the brine and the RO

permeate has the benefit of enabling tailoring the treatment of each stream for the different ecosystem or human health target applications.

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REFERENCES

- Bellona, C., Drewes, J. E., Xu, P., Amy, G., 2004. Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review. *Water Res.* 38, (12), 2795-2809.
- Benner, J., Salhi, E., Ternes, T., von Gunten, U., 2008. Ozonation of reverse osmosis concentrate: Kinetics and efficiency of beta blocker oxidation. *Water Res.* 42, (12), 3003-3012.
- Bolton, J. R., Linden, K. G., 2003. Standardization of methods for fluence (UV dose) determination in bench-scale UV experiments. *J. Environ. Eng.* 129, (3), 209-215.
- Buffle, M.-O., Schumacher, J., Salhi, E., Jekel, M., von Gunten, U., 2006. Measurement of the initial phase of ozone decomposition in water and wastewater by means of a continuous quench-flow system: Application to disinfection and pharmaceutical oxidation. *Water Res.* 40, (9), 1884-1894.
- Buxton, G.V., Greenstock, C. L., Helman, W. P., Ross, A. B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals. *J. Phys. Chem. Ref. Data* 17, (2), 513-886.
- Dai, N., Zeng, T., Mitch, W. A., 2015. Predicting N-nitrosamines: N-nitrosodiethanolamine as a Significant Component of Total N-nitrosamines in Recycled Wastewater. *Environ. Sci. Technol. Letters* 2 (3), 54-58.
- DOE, 2013. Department of Energy, Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2. http://cdiac.esd.ornl.gov/oceans/DOE_94.pdf (accessed August 27, 2013).
- Fang, J., Fu, Y., Shang, C., 2014. The Roles of Reactive Species in Micropollutant Degradation in the UV/Free Chlorine System. *Environ. Sci. Technol.* 48, (3), 1859-1868.

- Fujioka, T., Khan, S. J., Poussade, Y., Drewes, J. E., Nghiem, L. D., 2012. N-nitrosamine removal by reverse osmosis for indirect potable water reuse – A critical review based on observations from laboratory-, pilot- and full-scale studies. *Sep. Purif. Technol.* 98, 503-515.
- Fujioka, T., Khan, S. J., McDonald, J. A., Roux, A., Poussade, Y., Drewes, J. E., Nghiem, L. D., 2013. N-nitrosamine rejection by reverse osmosis membranes: A full-scale study. *Water Res.* 47, (16), 6141-6148.
- Gerrity, D., Snyder, S.A., 2011. Review of ozone for water reuse applications: toxicity, regulations, and trace organic contaminant oxidation. *Ozone Sci. Eng.* 33, (4), 253-266.
- Grebel, J. E., Pignatello, J. J., Mitch, W. A., 2010. Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters. *Environ. Sci. Technol.* 44, (17), 6822-6828.
- Hissung, A., von Sonntag, C., 1978. Radiolysis of cytosine, 5-methylcytosine and 2'-deoxycytidine in deoxygenated aqueous solution. A pulse spectroscopic and pulse conductometric study of the OH adduct. *Z Naturforsch* 33b, 321-328.
- Huber, M. M., Canonica, S., Park, G.-Y., von Gunten, U., 2003. Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. *Environ. Sci. Technol.* 37, (5), 1016-1024.
- Ianni, J. C., 2012. Kintecus, Windows Version 4.55. www.kintecus.com.
- Jin, S., Mofidi, A. A., Linden, K. G., 2006. Polychromatic UV fluence measurement using chemical actinometry, biosimetry, and mathematical techniques. *J. Environ. Eng.* 132, (8), 831-841.
- Justo, A., Gonzalez, O., Acena, J., Perez, S., Barcelo, D., Sans, C., Esplugas, S., 2013. Pharmaceuticals and organic pollution mitigation in reclamation osmosis brines by UV/H₂O₂ and ozone. *J. Hazard. Mater.* 263 Pt 2, (0), 268-74.
- Keen, O. S., Baik, S., Linden, K. G., Aga, D. S., Love, N. G., 2012. Enhanced Biodegradation of Carbamazepine after UV/H₂O₂ Advanced Oxidation. *Environ. Sci. Technol.* 46, (11), 6222-6227.
- Keen, O. S., McKay, G., Mezyk, S. P., Linden, K. G., Rosario-Ortiz, F. L., 2014. Identifying the factors that influence the reactivity of effluent organic matter with hydroxyl radicals. *Water Res.* 50, (0), 408-419.
- Lee, Y., Gerrity, D., Lee, M., Bogeat, A. E., Salhi, E., Gamage, S., Trenholm, R. A., Wert, E. C., Snyder, S. A., von Gunten, U., 2013. Prediction of micropollutant elimination during ozonation of municipal wastewater effluents: Use of kinetic and water specific information. *Environ. Sci. Technol.* 47, (11), 5872-5881.
- Masuda, T., Shinohara, H., Eda, M., Kondo, M., 1980. Reactivity of nucleotides and

polynucleotides toward hydroxyl radical in aqueous solution. J. Radiat. Res. (Tokyo) 21, (2), 173-179.

Mitch, W. A., Sharp, J. O., Trussell, R. R., Valentine, R. L., Alvarez-Cohen, L., Sedlak, D. L., 2003. N-nitrosodimethylamine (NDMA) as a drinking water contaminant: A review. Environmental Engineering Science 20, (5), 389-404.

Neta, P., Huie, R. E., Ross, A. B., 1988. Rate constants for reactions of inorganic radicals in aqueous solution. J. Phys. Chem. Ref. Data 17, (3), 1027-1284.

NIST, 2015. National Institute of Standards and Technology, NDRL/NIST Solution Kinetics Database on the Web. <http://kinetics.nist.gov/solution/> (Accessed February 13, 2015).

NRC, 2008. *Desalination: A National Perspective*. National Research Council. National Academies Press: Washington, DC.

NRC, 2012. *Water Reuse: Potential for Expanding the Nation's Water Supply through Reuse of Municipal Wastewater*. National Research Council, National Academies Press: Washington, D.C.

Pisarenko, A. N., Yan, D., Snyder, S. A., Stanford, B. D., 2011. Comparing oxidative organic fouling control in RO membrane applications. IDA Journal of Desalination and Water Reuse 3, (2), 45-49.

Pisarenko, A. N., Stanford, B. D., Yan, D., Gerrity, D., Snyder, S. A., 2012. Effects of ozone and ozone/peroxide on trace organic contaminants and NDMA in drinking water and water reuse applications. Water Res. 46, (2), 316-326.

Rosario-Ortiz, F. L., Wert, E. C., Snyder, S. A., 2010. Evaluation of UV/H₂O₂ treatment for the oxidation of pharmaceuticals in wastewater. Water Res. 44, (5), 1440-1448.

Sgroi, M., Roccaro, P., Oelker, G. L., Snyder, S. A., 2014. N-Nitrosodimethylamine Formation upon Ozonation and Identification of Precursors Source in a Municipal Wastewater Treatment Plant. Environ. Sci. Technol. 48 (17), 10308-10315.

Shah, A. D., Dotson, A. D., Linden, K. G., Mitch, W. A., 2011. Impact of UV Disinfection Combined with Chlorination/Chloramination on the Formation of Halonitromethanes and Haloacetonitriles in Drinking Water. Environ. Sci. Technol. 45 (8), 3657-3664.

Shah, A. D., Krasner, S. W., Lee, C. F. T., von Gunten, U., Mitch, W. A., 2012. Trade-offs in disinfection byproduct formation associated with precursor preoxidation for control of N-nitrosodimethylamine formation. Environ. Sci. Technol. 46, (9), 4809-4818.

Stanford, B. D., Pisarenko, A. N., Holbrook, R. D., Snyder, S. A., 2011. Preozonation effects on the reduction of reverse osmosis membrane fouling in water reuse. Ozone Sci. Eng. 33, (5), 379-388.

- 622 USBR, 2003. *Desalination and Water Purification Technology Roadmap: a Report of the*
623 *Executive Committee*. U.S. Bureau of Reclamation. Desalination & Water Purification Res. &
624 Develop. Program Report, 95.
625
626
627 von Gunten, U., 2003. Ozonation of drinking water: Part I. Oxidation kinetics and product
628 formation. *Water Res.* 37, (7), 1443-1467.
629
630 Westerhoff, P., Moon, H., Minakata, D., Crittenden, J., 2009. Oxidation of organics in retentates
631 from reverse osmosis wastewater reuse facilities. *Water Res.* 43, (16), 3992-3998.
632
633 Yang, Y., Pignatello, J. J., Ma, J., Mitch, W. A., 2014. Comparison of halide impacts on the
634 efficiency of contaminant degradation by sulfate and hydroxyl radical-based advanced oxidation
635 processes (AOPs). *Environ. Sci. Technol.* 48, (4), 2344-2351.
636
637 Zeng, T., Wilson, C. J., Mitch, W. A., 2014. Effect of Chemical Oxidation on the Sorption
638 Tendency of Dissolved Organic Matter to a Model Hydrophobic Surface. *Environ. Sci. Technol.*
639 48, (9), 5118-5126.
640

Table 1. Basic water quality characteristics.

Water	pH	DOC mg/L	UV ₂₅₄ cm ⁻¹	SUVA ₂₅₄ L /mg·m	Alkalinity mg/L as CaCO ₃	Cl ⁻ mg/L	Br ⁻ mg/L	NH ₄ ⁺ -N mg/L	NO ₃ ⁻ -N mg/L	PO ₄ ³⁻ mg/L	SO ₄ ²⁻ mg/L
RO Brine A ^a	8.3	68.2	1.03	1.51	861	1,160	2.2	8.6	8.9	11.3	1,766
RO Brine B ^a	8.4	50.6	1.02	2.02	1,171	2,015	2.9	12.7	341	6.1	1,437
RO Influent B ^a	8.1	7.5	0.17	2.27	195	284	0.51	0.05	52	1.2	181

^a Parameters were measured after filtration through 0.7-μm nominal pore size glass fiber filters

Table 2. Characteristics of pharmaceuticals.

Name	Structure	k_{OH} ($\text{M}^{-1}\text{s}^{-1}$)	UV_{50} (mJ/cm^2) ^a			
			$\text{UV}/\text{H}_2\text{O}_2$		$\text{UV}/\text{S}_2\text{O}_8^{2-}$	
			Brine A	Brine B	Brine A	Brine B
Sulfamethoxazole (SMX)		5.5×10^9 ^b	181	168	166	152
Propranolol (PPL)		1.0×10^{10} ^c	339	196	85	56
Carbamazepine (CBZ)		8.8×10^9 ^b	501	314	435	456
Acyclovir (ACV)		8.0×10^9 ^d	1541	1091	1571	1057
Lamivudine (LMVD)		6.3×10^9 ^e	417	302	133	125

^a Average UV fluence needed to achieve 50% removal; ^b Huber et al. (2003); ^c Benner et al. (2008); ^d rate constant for structurally similar guanosine (Masuda et al., 1980); ^e rate constant for cytosine functional group (Hissung et al., 1978).

Table 3. Importance of $\cdot\text{OH}$ scavenging by matrix components.

	$\cdot\text{OH}$ Rate Constant ($\text{M}^{-1} \text{s}^{-1}$)	Control + EfOM	Salts	Salts + EfOM	Brine
H_2O_2	2.7×10^7 ^a	9%	23%	8%	5%
EfOM	3.3×10^4 ^b	78%		68%	80%
HCO_3^-	8.5×10^6 ^a				
CO_3^{2-}	3.9×10^8 ^a				
NH_3	9.0×10^7 ^a				
NH_4^+	0 ^a		40% ^d	13% ^d	8% ^d
NO_3^-	0 ^a				
Br^-	1.1×10^{10} ^a				
Cl^-	4.3×10^9 ^a				
Pharmaceutical Mix	2.1×10^5 ^c	13%	37%	12%	7%

^a Buxton et al., 1988^b (mg-C/L)⁻¹ s^{-1} ; this work^c s^{-1} ; this work^d The percentage is derived from use of the full kinetic model

Table 4. Importance of SO₄^{•-} scavenging by matrix components

	SO ₄ ^{•-} Rate Constant (M ⁻¹ s ⁻¹)	Control + EfOM	Salts	Salts + EfOM	Brine
S ₂ O ₈ ²⁻	6.5 × 10 ⁵ ^a	1%	0.03%	0.03%	0.00%
EfOM	9.4 × 10 ³ ^b	82%		3.2%	5.9%
HCO ₃ ⁻	2.8 × 10 ⁶ ^a		0.24%	0.23%	0.22%
CO ₃ ²⁻	6.1 × 10 ⁶ ^a		0.01%	0.00%	0.00%
NH ₃	1.4 × 10 ⁷ ^a		0.01%	0.01%	0.01%
NH ₄ ⁺	3.0 × 10 ⁵ ^a		0.00%	0.00%	0.00%
NO ₃ ⁻	3.0 × 10 ⁴ ^a		0.00%	0.00%	0.00%
Br ⁻	3.5 × 10 ⁹ ^a		0.95%	0.92%	0.89%
Cl ⁻	3.0 × 10 ⁸ ^a		98%	95%	92.2%
Pharmaceutical Mix	7.0 × 10 ⁴ ^c	17%	0.69%	0.67%	0.65%

^a Buxton et al., 1988^b (mg-C/L)⁻¹ s⁻¹; this work^c s⁻¹; this work

Table 5. Comparison of pharmaceutical degradation efficiency for treatment of RO influent and brine. All samples were spiked with a mixture of 5 μM of each of the five pharmaceuticals.

	% Elimination of Pharmaceutical					
	UV/H ₂ O ₂			UV/S ₂ O ₈ ²⁻		
	Influent ^a	Brine ^b	Influent/ Brine	Influent ^a	Brine ^b	Influent/ Brine
ACV	8.9	46.8	0.19	2.61	45.2	0.06
LMVD	22.1	93.8	0.24	48.4	100	0.48
PPL	33.1	100	0.33	60.8	100	0.61
SMX	41.2	100	0.41	36	100	0.36
CBZ	23.3	90.7	0.26	12.9	93.4	0.14

^a 1 mM H₂O₂ or K₂S₂O₈ with an average UV fluence of 167 mJ/cm² in RO Influent B

^b 5 mM H₂O₂ or K₂S₂O₈ with an average UV fluence of 1000 mJ/cm² in RO Brine B

(A)

(B)

Fig. 1. Effect of anions and EfOM on k^N_{indirect} by A) UV/H₂O₂ or B) UV/S₂O₈²⁻. ACV = acyclovir, LMVD = lamivudine, PPL = propranolol, SMX = sulfamethoxazole, CBZ = carbamazepine, Exp Ave = experimental average, Model = model calculation assuming no participation by daughter radicals. All solutions contained 10 mM phosphate buffer at pH 8.3. Full salt = all anions at concentrations indicated in Table 1. All samples were spiked with a mixture of 5 μ M of each of the five pharmaceuticals.

Fig. 2. Percent elimination of pharmaceuticals in RO brines by UV/H₂O₂ or UV/S₂O₈²⁻ with 5 mM H₂O₂ or K₂S₂O₈ as a function of average UV fluence. ACV = acyclovir, LMVD = lamivudine, PPL = propranolol, SMX = sulfamethoxazole, CBZ = carbamazepine. All samples were spiked with a mixture of 5 μM of each of the five pharmaceuticals.

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