

## Organics and inorganics in flow back and produced water from shale gas operations: treatment and identification of glycols using gas chromatography–mass spectrometry

Seongyun Kim<sup>a</sup>, Pinar Omur-Ozbek<sup>b</sup>, Ken Carlson<sup>b</sup>, Sangchul Lee<sup>c</sup>, Eun-Sik Kim<sup>a</sup>, Min-Jin Hwang<sup>a</sup>, Ji-Hee Son<sup>d</sup> and Woochul Kang<sup>e,\*</sup>

<sup>a</sup> Department of Environmental System Engineering, Chonnam National University, Yeosu, Jeonnam 59626, Republic of Korea

<sup>b</sup> Department of Civil and Environmental Engineering, Colorado State University, Fort Collins, CO 80523, USA

<sup>c</sup> School of Environmental Engineering, University of Seoul, Dongdaemun-gu, Seoul 02504, Republic of Korea

<sup>d</sup> Green Technology Center, 17th fl. Namsan Square Bldg., 173, Toegye-ro, Jung-gu, Seoul 04554, Republic of Korea

<sup>e</sup> Department of Hydro Science and Engineering Research, Korea Institute of Civil Engineering and Building Technology, Goyang 10285, Republic of Korea

\*Corresponding author. E-mail: kang@kict.re.kr

 WK, 0000-0002-3720-8329

### ABSTRACT

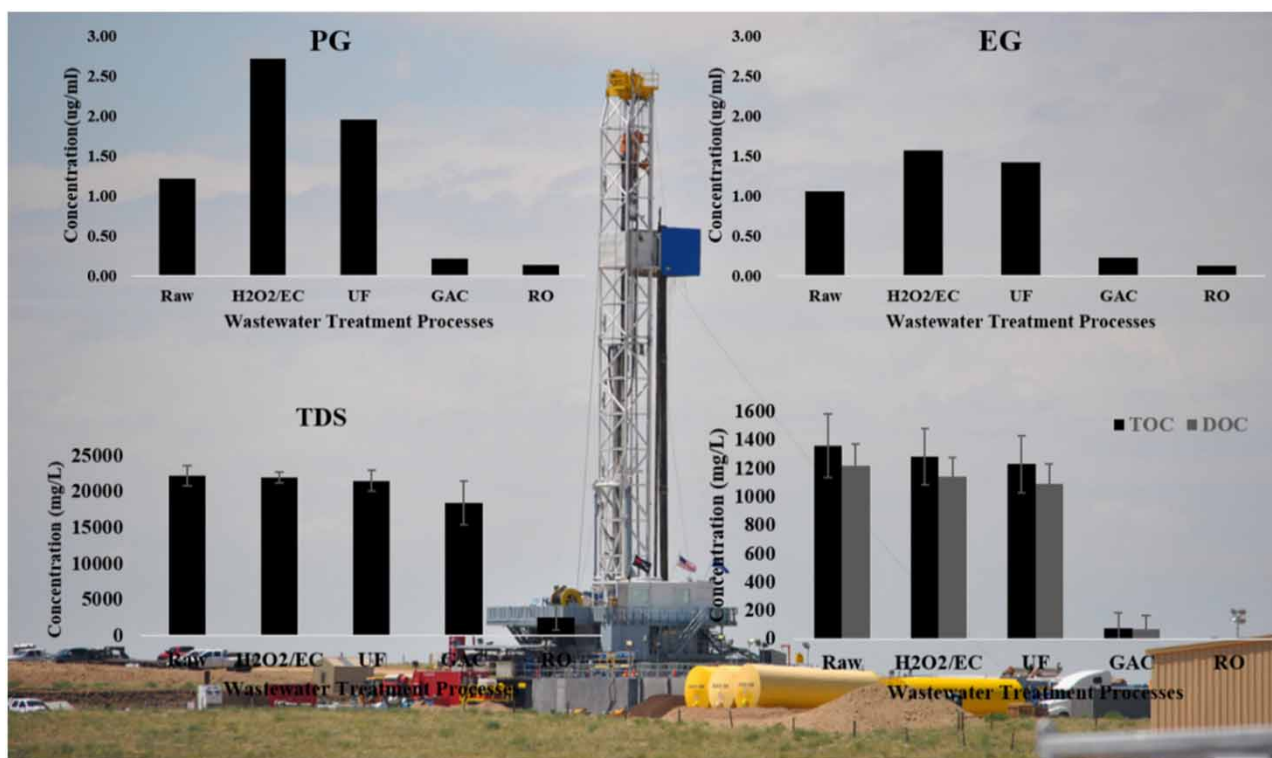
This study investigated the efficiency of different water treatment processes in reducing propylene glycol (PG), ethylene glycol (EG), ethylene glycol monobutyl ether (EGME), and other water quality parameters in flow back/produced water from a shale gas well operation. EG, PG, and EGME are the most widely used chemicals in hydraulic fracturing; however, limited investigations on these chemicals have been performed to date. Granular activated carbon (GAC) removed PG and EG to acceptable drinking water levels. Electrocoagulation was effective at decreasing turbidity (85%) as well as total petroleum hydrocarbons (TPH) (80%), while ultrafiltration removed 90% of the turbidity and TPH. GAC further removed approximately 95% of benzene, toluene, ethylbenzene, and xylene (BTEX), total organic carbon, dissolved organic carbon, and glycols but only removed 16% of total dissolved solids (TDS). Reverse osmosis removed approximately 90% of TDS (2,550 mg/L); however, this level remained high for certain purposes. Although some water quality parameters remained above the reusability threshold for most purposes, the treated water could be used on tolerant plants and permeable soils. In-depth knowledge and understanding of flow back/produced water quality characteristics, pre and post water treatment processes, can improve water treatment process strategies, reduce wastewater discharge, and improve treated water's reusability.

**Key words:** flow back/produced water, gas chromatography–mass spectrometry, glycol identification, hydraulic fracturing, organic compounds, wastewater treatment

### HIGHLIGHTS

- Glycols in flow back from a shale gas well were measured via gas chromatography–mass spectrometry.
- The efficiency of different produced water treatment processes was assessed.
- Glycols and other water quality parameters were compared before/after each treatment.
- Water quality parameters remained above the reusability threshold.
- The treated water reached a level where it could be reused on tolerant plants and permeable soils

## GRAPHICAL ABSTRACT



## INTRODUCTION

The shale gas boom in the United States (USA) will likely play an important role in meeting the current energy demand increases (Bellani *et al.* 2021). The shale oil and gas industry is the fastest-growing energy-related industry in the country owing to horizontal drilling during hydraulic fracturing (Bellani *et al.* 2021). Hydraulic fracturing requires approximately two to seven million gallons of an aqueous solution for each drilling operation (Lee *et al.* 2011; Rahm 2011; Stephenson *et al.* 2011; Nicot & Scanlon 2012; Suarez 2012; Goodwin *et al.* 2013; Hickenbottom *et al.* 2013), and this solution consists of 98–99% water along with sand and fracturing additives (Lee *et al.* 2011; Spellman 2013). After the flow back begins, approximately 20–40% of the initial water input is recovered over 4 weeks, indicating that most of the fracturing additives remain in the geological formation (Bai *et al.* 2013). It is therefore crucial to assess flow back/produced water quality and ultimately determine adequate treatment or disposal techniques. The U.S. Environmental Protection Agency (EPA) proposed total petroleum hydrocarbons (TPHs) and benzene, toluene, ethylbenzene, and xylene (BTEX) limits of less than 100  $\mu\text{g/L}$  and 5.0 ml/L, respectively, in the effluent (United States Environmental Protection Agency 2005).

Propylene glycols (PGs), ethylene glycols (EGs), and various ethoxylated compounds are considered as commonly used chemical additives for the hydraulic fracturing process (Carter *et al.* 2013). Glycols act as scale inhibitors, biocides, and friction reducers (Carter *et al.* 2013; Kim *et al.* 2020). Carter *et al.* (2013) reported that PG and EG account for more than 15% of additives used during hydraulic fracturing. Ethylene glycol monobutyl ether (EGME) and EG ranked third and fourth as the most widely used additives for hydraulic fracturing between 2005 and 2009 in the USA, respectively (Waxman *et al.* 2022). The characteristics of flow back and produced water from shale oil and gas operations vary based on the characteristics of the formation, especially total dissolved solid (TDS) concentrations (Osborn *et al.* 2012; Vengosh *et al.* 2014).

Treatment approaches for flow back and produced water may differ depending on the purpose of the effluent (Jenner & Lamadrid 2013; Lutz *et al.* 2013). Flow back water can be reused for fracturing in other wells; however, the water should meet a certain quality level for successful hydraulic fracturing. Flow back and produced water may be evaporated to decrease the total amount of waste. However, this approach is not always applicable due to unsuitable geological conditions for injection in some regions (Lutz *et al.* 2013). In other cases, untreated wastewater can be injected into subsurfaces below

groundwater formations (Rahm 2011; Jenner & Lamadrid 2013). Electrocoagulation (EC), ultrafiltration (UF), granular activated carbon (GAC), and reverse osmosis (RO) have been used to treat produced water to improve its quality and potential reuse for switch grass and canola irrigation (Pica *et al.* 2017). High levels of TDS in flow back and produced water are difficult to treat with conventional wastewater treatment processes (Lefebvre *et al.* 2004; Altaee & Hilal 2014; Lester *et al.* 2014). Due to the various chemicals used as fracturing additives, such as biocides or toxins, biological treatments are not a suitable option (Stringfellow *et al.* 2014; Rogers *et al.* 2015). High levels of total organic carbon (TOC) in flow back and produced water can harm membrane processes and reduce the effectiveness of direct treatment options (Pandey *et al.* 2012).

Coagulation is usually applied to wastewater because of its high efficiency in reducing suspended and colloidal particles (Wang *et al.* 2012). Flow back and produced water have similar characteristics, such as high total suspended solids (TSS) and TDS (Kim *et al.* 2019), and thus are frequently treated by coagulation processes (Esmailirad *et al.* 2015; Rosenblum *et al.* 2016). Activated carbon is one of the most widely used treatments for industrial and municipal wastewater due to its high ability to absorb organic compounds and relatively reasonable costs (Zhang *et al.* 2013). Activated carbon is useful for reducing hydrocarbons from saline water (Karapanagioti 2007) and surfactants in flow back and produced water (Wu & Pendleton 2001). GAC is preferred over powdered activated carbon (PAC) for shale oil and gas operations owing to the relatively low carbon usage rate and reasonable costs (Hackney & Wiesner 1996). The adsorption efficiency of activated carbon depends on a broad range of organic compounds as well as contact time, dose, activated carbon quality, size, adsorbate polarity, and salinity. However, activated carbon has significant limitations in removing poly and hydrophilic compounds. Rosenblum *et al.* (2016) investigated the application of chemical coagulants and PAC in reducing organic compound concentrations, such as TPHs, glycols, and dissolved organic carbon (DOC) from produced water in Colorado.

The guidelines for the possible treatment of produced water from conventional and unconventional oil and gas have been published (Andrew *et al.* 2005; Fakhru'l-Razi *et al.* 2009). Since limited investigations for main glycols used as hydraulic fracturing additives have been performed, this study focused not on the treatment but identified PG, EG, and EMGE in flow back and produced water after each treatment process. The objectives of this study were to assess the efficiency of EC, UF, GAC, and RO water treatment processes in reducing PG, EGME, EG, BTEX, TPH, DOC, TOC, TDS, and turbidity in flow back and produced water from shale oil and gas operations in Colorado.

## MATERIALS AND METHODS

### Sample preparation

Flow back and produced water were sampled from the Julesburg Basin in Weld County, Denver, between October 27, 2015, and April 8, 2016. Samples (20 mL) were transferred to glass vials for gas chromatography–mass spectrometry (GC–MS) and then stored at 4 °C before use. The samples represented mixed samples because flow back and produced water were collected directly from a tank located in the central processing facility.

### Treatment processes

Flow back and produced water samples were treated in a series of wastewater treatment processes, as presented in Supporting Information, Figure S1, and detailed below. After each treatment, the samples were transferred into 40 mL amber glass vials to measure the concentration of various water quality parameters.

### Electrocoagulation

Jar tests were performed using two metal plates connected to a power supply, and the system included one cathode and one anode. Continuous flow EC used the same power supply as the second-stage test and a SHURflo diaphragm pump, model No. 8000-953-238 (Flow Technologies Group of Pentair, Inc., Minneapolis, MN, USA), and the system was composed of six stacked iron plates and anode and cathode electrolytic cell linkages. Flocculation was conducted using a Phipps and Bird 900 Model Jar Tester (Phipps & Bird, VA, USA) at a speed of 15 rpm. A total of 60 L was processed with the mixer at a paddle speed of 50 rpm. The addition of deionized water with microbubbles generated pressurized microbubbles at 80 psi in the vessel.

### Ultrafiltration

UA420 E hollow fiber filters and a MANN + HUMMEL UA420-BT housing (MANN + HUMMEL, Ludwigsburg, Germany) were used during the UF process. The modified hydrophilic membrane material with a pore size of 0.05  $\mu\text{m}$  was used. The water was pumped using a SHURflo diaphragm pump, model No. 8000-953-238 (Flow Technologies Group of Pentair, Inc., Minneapolis, MN, USA) with a flow rate of 0.5 gmp.

### Granular activated carbon

GAC testing was performed using three columns composed of 3-inch diameter PVC pipes, caps, nozzles, and plastic tubing. The tubing was used to connect the bottom of each column and was located upward at the entrance for the next column. Acid-washed mesh-activated charcoal coconut shells ( $12 \times 30$ ) were applied as the adsorption medium. The volume of the columns was approximately 24,000  $\text{cm}^3$ . A Masterflex peristaltic pump (Masterflex, IL, USA) was used, pumping at 50 mL/min. The GAC1230C AW adsorption medium served as isotherms and was combined with 400 mL of UF brine using 10 different masses of GAC (5–50% of mass). The same conditions were applied to the Phipps & Bird Jar Testers (Phipps & Bird, VA, USA) as explained in the EC section. A total of 400 mL of UF brine and coconut charcoal were mixed in a beaker at a speed of 25 rpm for 1 h. The brine–GAC mixture was filtered using a Whatman filter (Cytiva, Bucks, UK) with a 6- $\mu\text{m}$  pore size to remove suspended inorganic carbon particles before analyzing the TOC content.

### Reverse osmosis

RO was performed using a Sterlitech SEPA CF cross-flow cell filter unit (Sterlitech, Auburn, WA, USA), and a GE Osmonics flat plate RO membrane (GE, Osmonics, TX, USA) was used to evaluate various materials and operating pressures. Detailed information on the AG and SE series is provided in Supporting Information in Table S1.

### GC–MS method for organic compounds

#### Sample preparation

EG (CAS No. 106-21-1) was obtained from Fisher Scientific. PG (CAS No. 57-55-6), EG butyl ether (CAS No. 111-76-2), 1,3-propanediol (CAS No. 504-63-2), and ENVI-Carb Plus were purchased from Sigma Aldrich. Solid phase extraction (SPE) was performed based on a previously reported method with minor modifications (Sidisky *et al.* 2010). First, the cartridge was conditioned after rinsing with 1 mL of methylene chloride, 2 mL of methanol, and 3 mL of LC-grade water. The solvents were transferred to the cartridge, and the plunger of a glass syringe placed on top of the cartridge was pressed. A sample (5 mL) spiked with 100  $\mu\text{L}$  of 500  $\mu\text{g}/\text{mL}$  1,3-propanediol (internal standard (IS)) in water was transferred to the cartridge and dried under a vacuum for 10 min. Glycols were eluted with 2 mL of methanol and methylene chloride in an 8:2 (volume/volume) ratio after 1 min of soaking. The elute was preserved at 4  $^{\circ}\text{C}$  until analysis and injected without adjusting the volume. The vacuum used for drying over 10 min was provided from a fume hood vacuum outlet and a syringe was used to push the liquid to the cartridge for sample loading and elution. Two samples from each treatment process were randomly selected to generate sample blanks without adding IS and extracted via SPE. Samples for the calibration curves were set by diluting authentic standards in methanol and spiking them with an equivalent amount of IS. The samples for the calibration curve were directly injected without performing SPE extraction.

#### GC–MS analysis

Trace 1310 GC coupled with a Thermo ISQ-LT MS system (Thermo Fisher Scientific, MA, USA) was used to analyze the samples after SPE extraction and calibration curve generation. Samples (2  $\mu\text{L}$ ) were injected at a ratio of 5:1, the inlet was maintained at 250  $^{\circ}\text{C}$ , and the transfer line at 240  $^{\circ}\text{C}$ . Short chain fatty acids (SCFA) separation was performed on a 30 mm DB-WAX Ultra Inert (DBWAXUI) column (J&W, 0.25 mm inner diameter, 0.25  $\mu\text{m}$  film thickness) (Agilent, CA, USA). The oven temperature was maintained at 110  $^{\circ}\text{C}$  for 1 min, increased at 10  $^{\circ}\text{C}/\text{min}$  to 160  $^{\circ}\text{C}$ , and increased further at 30  $^{\circ}\text{C}/\text{min}$  to 240  $^{\circ}\text{C}$ . Helium was used as the carrier gas and the flow was maintained at 1.2 mL/min. Selected ion monitoring (SIM) mode was applied for mass scanning at values of 31, 33, 41, 43, 45, 57, 58, 61, 62, 75, 87, and 100 at a rate of 10 scans per second. Methanol blanks were injected three times between sample runs to remove any carryover signals. The total ion chromatograms of the samples and standard are presented in Supporting Information, Figure S2. The mass spectra for PG, EMGE, EG, and IS are presented in Supporting Information, Figure S3.

### Calibration curves for PG, EG, and EGME

Initially, samples after SPE for the calibration curve were prepared using water in equivalent amounts. Concentrations of 5, 10, 15, and 30  $\mu\text{g}/\text{mL}$  were measured for the first set of calibration curves as suggested in a previous study (Sidisky *et al.* 2010). However, the results indicated that most samples had concentrations of approximately 0.1–5  $\mu\text{g}/\text{mL}$ . A second set of calibration curves was then run with concentrations of 0.2, 1, 2, 10, and 20  $\mu\text{g}/\text{mL}$  (see Supporting Information, Figure S4). All calibration curves had high coefficients of determination. The final calibration curves were generated based on the second calibration curves by applying four concentration points (0.2, 1, 2, and 10  $\mu\text{g}/\text{mL}$ ).

### Quality control

The coefficient of variation for the entire analysis, including sample preparation and data acquisition, was computed based on the three replicates. The coefficients of variations for EG and PG were 8 and 12%, respectively. Raw-produced water samples were rerun after prefiltration to reduce turbidity and remove suspended solids by using a 0.45  $\mu\text{m}$  pore size filter.

### 1,3-Propanediol signal in samples without IS spiking

The signal intensity for 1,3-propanediol in samples ranged from  $1.5 \times 10^4$  to  $4.2 \times 10^4$ , which was less than 6% of the signal intensity for the spiked IS level. Variations were observed after each treatment; hence, the background was not subtracted. A summary of the spiked IS signals is provided in Supporting Information, Table S2.

### Water quality analysis

A Shimadzu TOC-VCSH analyzer (Shimadzu, Kyoto, Japan) was used to measure the TOC. The standard method 2540 and EPA method 180.1 were used to measure TDS and turbidity, respectively. BTEX, TPH, Mg, Ca, Na,  $\text{HCO}_3^-$ , Cl, and B were measured at the ALS Global Environmental Laboratory (Fort Collins, CO, USA) using the USEPA Method 310.

### Statistical analysis

Water quality parameters (TOC, DOC, TDS, EG, and PG) were determined by Tukey's test for multiple pairwise comparisons and the analysis of variance. R version 3.20 (R Core Team 2019) was used to perform the statistical analyses. Every water quality parameter after each treatment was considered significant when *P*-values were less than 0.05.

## RESULTS AND DISCUSSION

### Water quality of flow back and produced water

Flow back and produced water samples used in the water treatment processes were obtained from the central processing facility. The water quality characteristics varied depending on the sampling date because of temporal variability in flow back and produced water quality from this facility.

Table 1 presents the characteristics of the flow back and produced water from the central processing facility.

**Table 1** | Summary of the flow back and produced water quality characteristics from the central processing facility

Variable	Minimum	Maximum	Average	# Data points	Time period
TOC (mg/L)	1,200	2,173	1,783	11	10/27/2015–4/8/2016
TDS (mg/L)	13,600	27,539	21,978	12	
pH	6.5	6.7	6.6	3	
ORP (mV)	−88	−23	−58	3	
Ca (mg/L)	190	270	227	4	
Mg (mg/L)	ND	36	22	4	
$\text{HCO}_3^-$ (mg/L)	600	750	660	3	
Na (mg/L)	6,300	6,900	6,526	4	
Cl (mg/L)	11,000	17,000	13,000	4	
B (mg/L)	19	22	25	4	

ND, not detected.

The pH value of produced water was approximately 6.6. A high TOC level indicated higher concentrations of dissolved cross-linkers remaining in the fracturing fluid. The relatively older produced water had a higher TDS level compared to the newer produced water. The relatively high fluctuations in TDS concentration may have been due to temporal variations. Bicarbonate, calcium, chloride, and sodium were considered the main ions in the produced water. Kim *et al.* (2016) showed that flow back and produced water from two different wells that used different types of fracturing fluids had similar TDS and TOC values and further assessed the temporal variations in Northeast Colorado for 200 days after flow back water production began. Magnesium and boron ions were also observed in the present study.

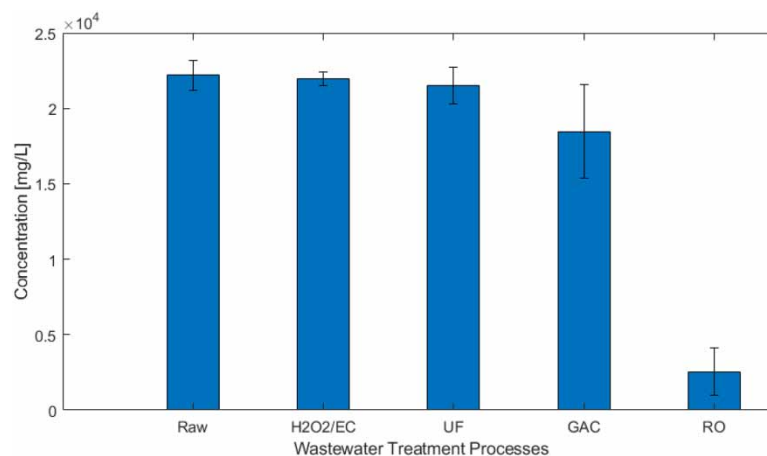
### TDS in produced water before and after treatment

EC and UF did not successfully remove TDS concentration (approximately 1% removal by EC and 3% removal by UF; see Figure 1).

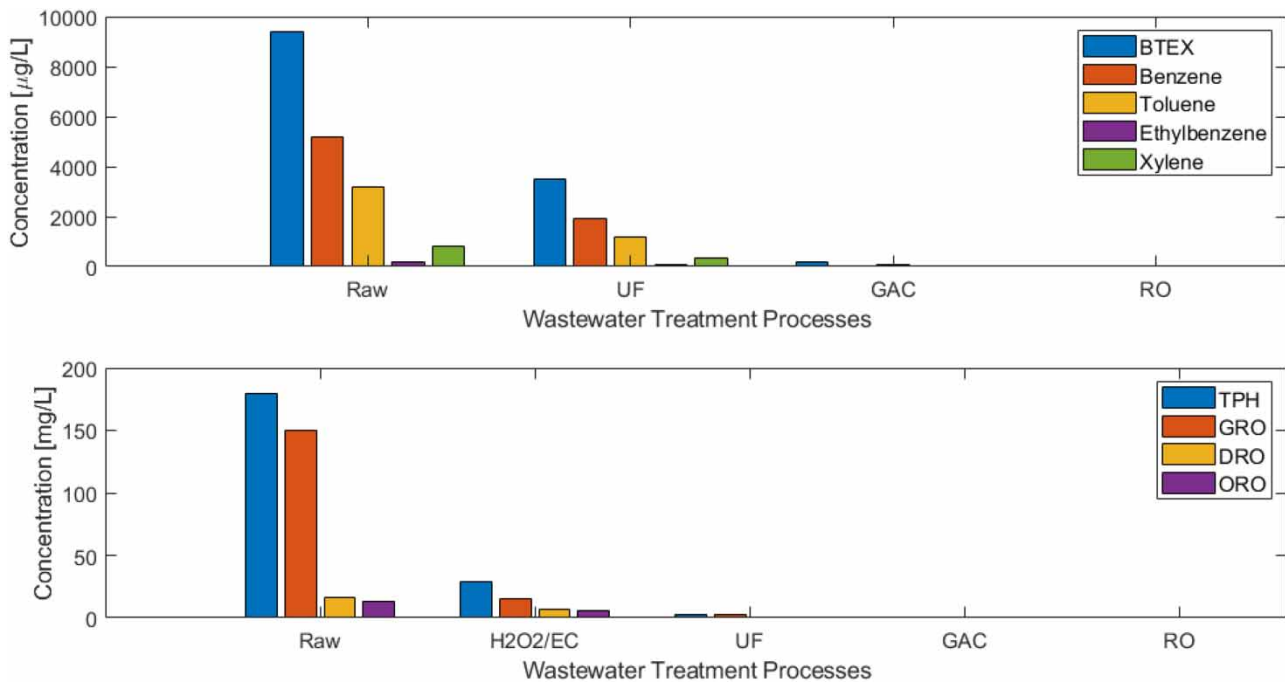
Significant differences were not observed between the raw flow back and produced water and the water samples after UF or EC treatment ( $P$ -values were higher than 0.99; see Supporting Information, Table S3). In general, activated carbon reduced the concentration of organic compounds in wastewater. However, the TDS concentration was reduced by approximately 15% after GAC (from 21,500 to 18,470 mg/L after GAC). Esmailirad *et al.* (2015) showed that divalent ions like  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , the main ions in flow back and produced water, got removed after EC treatment. However, EC removed approximately 1% of inorganic compounds in the present study. Some organic ions can be adsorbed on the GAC sorbent through accumulation based on the water quality. The most frequently adsorbed ion was  $\text{Ca}^{2+}$  (Lambert *et al.* 2002), which is considered a dominant ion in flow back and produced water (Barbot *et al.* 2013; Kim *et al.* 2016). Mg, Al, and Fe can also be adsorbed on the GAC sorbent (Lambert *et al.* 2002). The removal of approximately 15% TDS was probably due to the accumulation of these inorganic ions in the GAC bed. RO can effectively reduce more than 95% of the TDS concentration depending on factors that include membrane quality, water quality, and RO equipment condition (Funston *et al.* 2002; ALL Consulting 2003; Barrufet *et al.* 2005). Although RO reduced the TDS by approximately 90% in this study (18,470–2,550 mg/L), the TDS level was still high for reuse because recycled water with a TDS value higher than 2,000 mg/L can only be reused for the irrigation of tolerant plants and permeable soils (United States Environment Protection Agency 2004).

### Organic compounds in produced water before and after treatment

Soluble organic compounds in flow back and produced water are polar compounds consisting of relatively low carbon chains (Fakhru'l-Razi *et al.* 2009). The oil concentration in flow back and produced water varies based on the oil type, well age, and water production volume (Stephenson 1992). In general, separation techniques for oil and water do not easily remove aromatic compounds, which can cause natural environmental toxicity (Fakhru'l-Razi *et al.* 2009). The BTEX concentration can exceed 600 mg/L in flow back and produced water because of the variety of organic compounds added to the fracturing fluid during the hydraulic fracturing process (Neff & Stout 2002). Figure 2 presents the BTEX reduction efficiency of the UF, GAC, and RO treatment processes applied to flow back and produced water.



**Figure 1** | TDS results of each water treatment process (EC, UF, GAC, and RO). Error bars indicate the standard deviation.



**Figure 2** | BTEX and TPHs after each water treatment process (UF, GAC, and RO).

The BTEX concentration from the raw flow back and produced water reached approximately 9,300  $\mu\text{g/L}$  and mostly consisted of benzene (5,200  $\mu\text{g/L}$ ) and toluene (3,200  $\mu\text{g/L}$ ). GAC removed most of the BTEX by more than 95% (from 3,482 to 166  $\mu\text{g/L}$ ), which was similar to a previous finding in which approximately 95% of BTEX was removed after GAC treatment (Caetano *et al.* 2017). The GAC treatment process is usually applied to reduce organic compounds (Caetano *et al.* 2017), and the BTEX concentration complied with the discharge policy requirements except for benzene (discharge permitted: benzene (5  $\mu\text{g/L}$ ), toluene (100  $\mu\text{g/L}$ ), ethylbenzene (100  $\mu\text{g/L}$ ), and xylene (200  $\mu\text{g/L}$ )) (Nevada Division of Environmental Protection Fact Sheet). The drinking water standards were also met, except for benzene (drinking water standard: benzene (5  $\mu\text{g/L}$ ), toluene (1,000  $\mu\text{g/L}$ ), ethylbenzene (700  $\mu\text{g/L}$ ), and xylene (10,000  $\mu\text{g/L}$ )) (Water Research Center Database). Benzene has strict discharge and drinking water limits because it is considered carcinogenic (Water Research Center Database).

UF decreased BTEX by more than 60% (from 9,380 to 3,482  $\mu\text{g/L}$ ), consistent with a previous study that reported a 50% removal of BTEX from produced water in the North Sea after UF treatment (Bilstad & Espedal 1996).

Raw flow back and produced water contained 180 mg/L of TPH, which was mostly composed of gasoline range organics ((GRO); 150 mg/L; Figure 2).

The TPH concentration of raw flow back and produced water was higher than that reported by Rosenblum *et al.* (2016), who observed a TPH concentration of 8–20 mg/L from a well in Colorado and illustrated more than 90% TPH removal using a PAC dose of 1,000 mg/L.

EC removed approximately 80% TPH and 90% GRO, whereas only approximately 50% of diesel range organics (DRO) and oil range organics (ORO) were removed (DRO: from 16.0 to 7.3 mg/L; ORO: from 13 to 6.30 mg/L), indicating that smaller carbon chain TPHs (GRO (C5–C10)) were easier to remove than larger carbon chain ones (DRO (C10–C28) and ORO (C28–C36)). GRO, ORO, and DRO were decreased by more than 95% following the UF process, with ORO decreased to undetected concentration. TPH concentration following the UF process still required further treatment to comply with the discharge limits for ground remediation, which are less than 1 mg/L (Nevada Division of Environmental Protection Fact Sheet). TPH in flow back and produced water was removed by GAC. Therefore, RO was not applied for TPH removal in flow back and produced water in this study.

EC removes up to 80% of TPH under ideal working conditions (Pérez *et al.* 2016). Activated carbon is the most commonly used method for treating municipal and organic wastewater because of its ability to remove various organic compounds. Ayotamuno *et al.* (2006) showed that more than 95% TPH removal following PAC or GAC (from 9,300 to 360 and

12 mg/L, respectively) using 5–25 g of activated carbon. However, since flow back and produced water usually have high TDS and TOC levels, these waters may reduce the efficiency of the wastewater treatment process. Previously, flow back and produced water TOC concentrations were measured in water samples from unconventional oil and gas wells, and the TOC level was stabilized at approximately 2,000 mg/L based on temporal variations and fracturing fluid types (Kim *et al.* 2016).

TOC consists of suspended carbon, including oils or high carbon particles, which can be removed by the filtration process. Approximately 9.5 and 10.5% of TOC (from 1,356 to 1,229 mg/L) and DOC (from 1,220 to 1,093 mg/L) were removed after the EC and UF treatments, respectively; therefore, the TOC concentrations may have consisted primarily of dissolved carbon instead of suspended carbon (Figure 3).

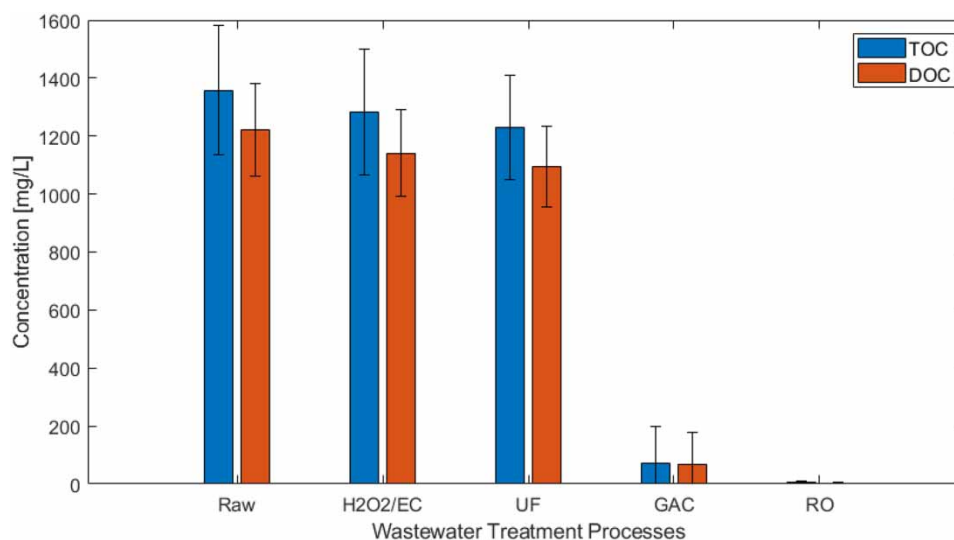
GAC removed more than 95% of TOC and DOC, confirming that activated carbon is the best method for reducing organic carbon. The *P*-values of TOC and DOC between the UF and GAC processes were lower than 0.001, meaning that TOC and DOC concentrations obtained by the UF process were statistically lower than those obtained by the GAC process (Supporting Information, Tables S4 and S5). Recent studies have reported higher TOC and DOC removal rates (95%) following GAC treatment compared with those presented by Rosenblum *et al.* (2016), who obtained reductions between 9.5 and 23.3% by PAC using a 1,000 mg/L dose from both vertical and horizontal oil and gas operations. Significant differences in the DOC (*P*-value = 0.94) and TOC (*P*-value = 0.98) values were not observed between the GAC and RO processes; however, the TOC and DOC levels decreased by 99% following the RO process; thus, the TOC removal efficiency obtained was higher than that observed in previous studies, in which TOC decreased by approximately 90% using a surfactant-modified zeolite membrane bioreactor RO system (Brookes 2005; Kwon *et al.* 2008). The EC treatment decreased TPH concentration by more than 8% and the DOC level by only 5%. Therefore, DOC accounted for a small fraction of TPH.

Five sets of wastewater samples were analyzed using GC–MS to identify EG, PG, and EGME. Figure 4 presents the rate of PG and EG reduction in the flow back and produced water after the EC, UF, GAC, and RO treatments.

EGME was not detected in any of the samples, indicating that it might have not been used as an additive in the studied well or was degraded by high temperatures and pressure during hydraulic fracturing. The PG concentration was slightly higher than the EG concentration, varying from 0.07 to 5.39 and 0.07 to 5.52 µg/mL, respectively. The highest PG and EG concentrations were found in the fourth sample set (Supporting Information, Table S6).

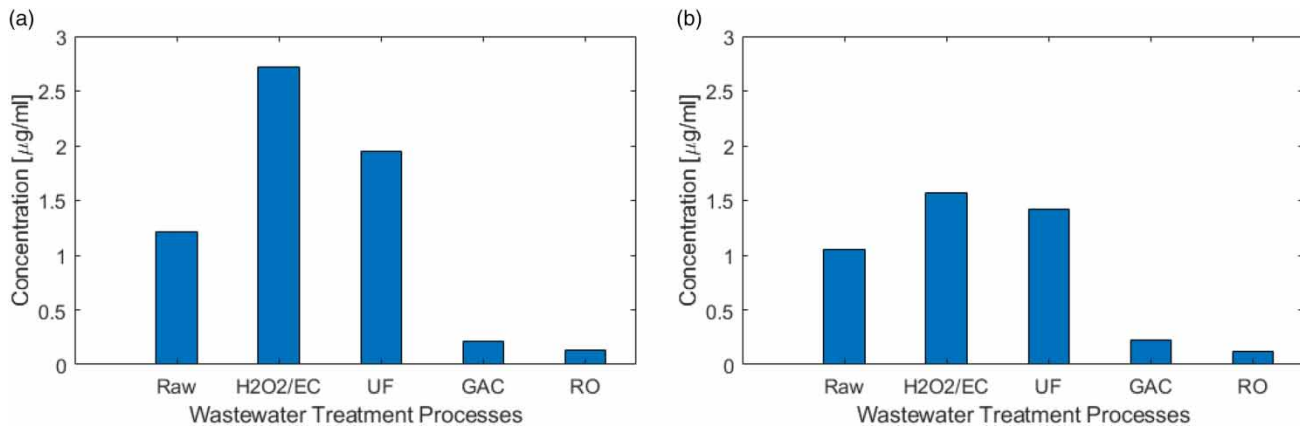
The average EG and PG concentrations presented a decreasing trend based on the treatment processes. The GAC process removed a considerable amount of EG and PG that complied with drinking water standards (less than 1 µg/mL). Significant differences were not observed in the EG and PG values between the GAC and RO processes, as the *P*-values were higher than 0.9 (Supporting Information, Tables S7 and S8).

The PG and EG concentrations in the raw flow back and produced water were lower than those after the H<sub>2</sub>O<sub>2</sub>–EC process. As the raw flow back and produced water were collected from hydraulic fracturing, interference from the geological



**Figure 3** | TOC and DOC results of each water treatment process (EC, UF, and GAC, and RO). Error bars indicate the standard deviation.





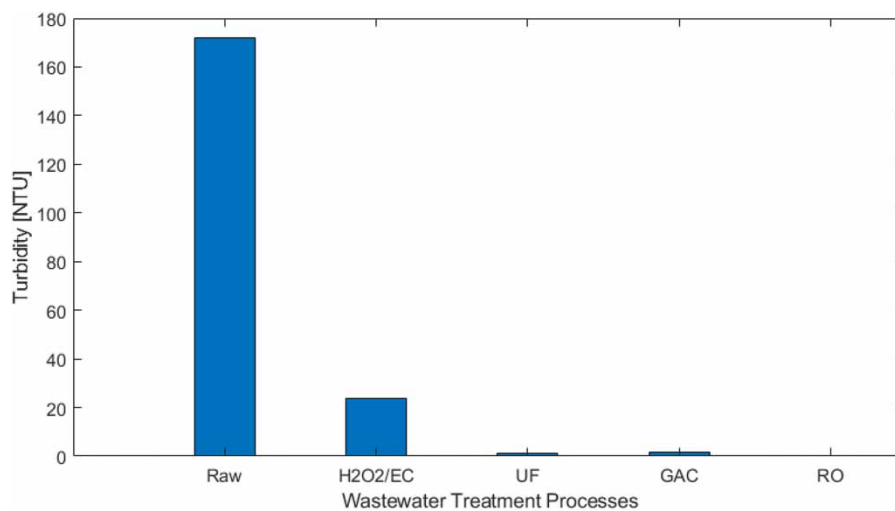
**Figure 4** | PG (a) and EG (b) of average concentrations from five sets of samples via different wastewater treatment processes.

formation or fracturing additives may have occurred that negatively impacted the chromatogram despite the application of prefiltration and the SPE method. Figure 1 shows that the TDS level was insufficiently removed by any of the processes except for RO. Hence, the salts in flow back and produced water may not significantly influence the recovery of EG and PE in the chromatogram. Moreover, DOC and TOC may not have been affected by EG and PG in the flow back and produced water due to limited decreases in these parameters after EC and UF treatments.

#### Turbidity in produced water before and after treatment

Turbidity varies based on the location of the well and the time after the commencement of flow back water production. Kim *et al.* (2019) discovered that the mean turbidity was approximately between 250 and 300 NTU for 60 days after flow back water production started, and these values were based on the type of fracturing additives. Moreover, the results showed that more than 96% of turbidity was removed after coagulation treatment using aluminum as a coagulant (Kim *et al.* 2019). The turbidity value of raw flow back and produced water was approximately 170 NTU in the present study (Figure 5).

Previous studies confirmed that the EC process can effectively remove turbidity (Kobyta *et al.* 2003; Bukhari 2008; Merzouk *et al.* 2009). Turbidity can be removed more effectively by applying a softening process prior to the EC process (Esmaeilirad *et al.* 2015). In the present study, EC reduced turbidity by 85% (from 172 to 24 NTU) and UF by approximately 99% (from 24 to 1.1 NTU).



**Figure 5** | Turbidity of each water treatment process (EC, UF, GAC, and RO).

The EC process significantly removed the TPH (Figure 3) and turbidity (Figure 5), indicating that TPH and turbidity may interfere with the raw flow back and produced water samples. The recovery of EG and PG using the GC–MS method after applying ENVI-Carb Plus cartridges for SPE was not affected by the presence of salt and oil (Sidisky *et al.* 2010). Suspended solids, which have a strong positive correlation with turbidity (Hannouche *et al.* 2011), can block SPE cartridges (Tadeo 2008), indicating that low EG and PG recovery levels may be due to high turbidity levels in the raw flow back and produced water. Prefiltration was expected to decrease the turbidity and increase the recovery of EG and PG in raw flow back and produced water. Prefiltration was applied to five sets of raw flow back and produced water samples using a 10 mL NORM-JECT with a 0.45 µm pore size; however, prefiltration did not improve the recovery of PG and EG from raw-produced water in the current study. The PG and EG concentrations in the raw flow back and produced water may be higher than those after the H<sub>2</sub>O<sub>2</sub>/EC treatment. Thus, other pre-treatment techniques are essential for PG and EG recovery in raw water samples. Moreover, the use of peroxide during H<sub>2</sub>O<sub>2</sub>/EC might result in increased PG and EG concentrations due to the formation of glycols, such as polyglycols. Previous studies have shown the presence of polypropylene glycols and polyethylene glycols in produced water in Weld County, Denver, CO, USA (Thurman *et al.* 2017).

## CONCLUSIONS

The study investigated specific organic compounds and water quality parameters in flow back and produced water and determined the effects of different treatment processes, including EC, UF, GAC, and RO. GC–MS with SPE was used to measure PG, EG, and EGME levels. EGME was not recovered in any of the raw flow back and produced water samples. However, PG and EG were recovered at values ranging from 0.07 to 5.52 µg/mL after the treatment process. The GAC treatment reduced both the EG and PG levels to values that meet acceptable levels and also reduced the levels of other organic compounds (TPH, BTEX, TOC, and DOC). TPH and turbidity were significantly removed by the EC process, and most of the TPH and turbidity were removed by the UF process. TDS values were effectively decreased by approximately 90% after the RO process. However, the TDS levels remained too high for water reuse in certain contexts.

Although some water quality parameters remained above the reusability threshold for most purposes, the treated water reached a level where it could be reused on tolerant plants and permeable soils. In-depth knowledge and understanding of flow back/produced water quality characteristics, prior and post water treatment processes, can improve water treatment process strategies, reduce wastewater discharge, and improve the consequent reusability of treated water.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

## REFERENCES

- ALL Consulting 2003 *Handbook on Coal Bed Methane Produced Water: Management and Beneficial Use Alternatives*, p. 322. Available from: [http://www.all-llc.com/publicdownloads/CBM\\_BU\\_Screen.pdf](http://www.all-llc.com/publicdownloads/CBM_BU_Screen.pdf).
- Altaee, A. & Hilal, N. 2014 Dual-stage forward osmosis/pressure retarded osmosis process for hypersaline solutions and fracking wastewater treatment. *Desalination* **350**, 79–85. <https://doi.org/10.1016/j.desal.2014.07.013>.
- American Petroleum Institute 2002 *Predictors of Water-Soluble Organics in Produced Water – A Literature Review*. Washington, District of Columbia.
- Andrew, A. S., Whitford, D. J., Berry, M. D., Barclay, S. A. & Giblin, A. M. 2005 Origin of salinity in produced waters from the Palm Valley gas field, Northern Territory, Australia. *Appl. Geochem.* **20** (4), 27–747.
- Ayotamuno, M. J., Kogbara, R. B., Ogaji, S. O. T. & Probert, S. D. 2006 Petroleum contaminated ground-water: remediation using activated carbon. *Appl. Energy* **83**, 1258–1264. <https://doi.org/10.1016/j.apenergy.2006.01.004>.

- Bai, B., Goodwin, S. & Carlson, K. 2013 Modeling of frac flow back and produced water volume from Wattenberg oil and gas field. *J. Petrol. Sci. Eng.* **108**, 383–392. <https://doi.org/10.1016/j.petrol.2013.05.003>.
- Barbot, E., Vidic, N. S., Gregory, K. B. & Vidic, R. D. 2013 Spatial and temporal correlation of water quality parameters of produced waters from Devonian-age shale following hydraulic fracturing. *Environ. Sci. Technol.* **47**, 2562–2569. <https://doi.org/10.1021/es304638h>.
- Barrufet, M. A., Burnett, D. & Mareth, B. 2005 Modeling and operation of oil removal and desalting oilfield brines with modular units. In *SPE Annual Technical Conference and Exhibition*. <https://doi.org/10.2118/95647-MS>.
- Bellani, J., Verma, H. K., Khatri, D., Makwana, D. & Shah, M. 2021 Shale gas: a step toward sustainable energy future. *J. Pet. Explor. Prod. Technol.* **11**, 2127–2141.
- Bilstad, T. & Espedal, E. 1996 Membrane separation of produced water. *Water Sci. Technol.* **34**, 239–246. [https://doi.org/10.1016/S0273-1223\(96\)00810-4](https://doi.org/10.1016/S0273-1223(96)00810-4).
- Brookes, A. 2005 *Immersed Membrane Bioreactors for Produced Water Treatment*. PhD Dissertation, Thesis, Cranfield University School of Water Sciences, Cranfield, UK.
- Bukhari, A. A. 2008 Investigation of the electro-coagulation treatment process for the removal of total suspended solids and turbidity from municipal wastewater. *Bioresour. Technol.* **99**, 914–921. <https://doi.org/10.1016/j.biortech.2007.03.015>.
- Caetano, M. O., Schneider, I. A. H., Gomes, L. P., Kieling, A. G. & Miranda, L. A. S. 2017A compact remediation system for the treatment of groundwater contaminated with BTEX and TPH. *Environ. Technol.* **38**, 1408–1420. doi:10.1080/09593330.2016.1231222.
- Carter, K. E., Hakala, J. A. & Hammack, R. W. 2013 Hydraulic fracturing and organic compounds – uses, disposal and challenges. *Soc. Pet. Eng.* 165692. <http://dx.doi.org/10.2118/165692-MS>.
- Esmailirad, N., Carlson, K. & Omur Ozbek, P. 2015 Influence of softening sequencing on electrocoagulation treatment of produced water. *J. Hazard. Mater.* **283**, 721–729. <https://doi.org/10.1016/j.jhazmat.2014.10.046>.
- Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S. & Abidin, Z. Z. 2009 Review of technologies for oil and gas produced water treatment. *J. Hazard. Mater.* **170**, 530–551. <https://doi.org/10.1016/j.jhazmat.2009.05.044>.
- Funston, R., Ganesh, R. & Leong, L. Y. C. 2002 Evaluation of technical and economic feasibility of treating oilfield produced water to create a 'New' water resource. In: *California, USA: Ground Water Protection Council Conference*. Colorado Springs, pp. 16–17.
- Goodwin, S., Carlson, K., Bai, B., Rein, L., Knox, K. & Douglas, C. 2013 Improved water use estimates for drilling and hydraulic fracturing in northeastern Colorado. *J. Water Resour. Prot.* **05**, 1262–1267. doi:10.4236/jwarp.2013.512135.
- Hackney, J. & Wiesner, M. R. 1996 *Cost Assessment of Produced Water Treatment*. Working Paper. Duke University Press, Durham, NC, USA.
- Hannouche, A., Chebbo, G., Ruban, G., Tassin, B., Lemaire, B. J. & Joannis, C. 2011 Relationship between turbidity and total suspended solids concentration within a combined sewer system. *Water Sci. Technol.* **64**, 2445–2452. doi:10.2166/wst.2011.779.
- Hickenbottom, K. L., Hancock, N. T., Hutchings, N. R., Appleton, E. W., Beaudry, E. G., Xu, P. & Cath, T. Y. 2013 Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations. *Desalination* **312**, 60–66. <https://doi.org/10.1016/j.desal.2012.05.037>.
- Jenner, S. & Lamadrid, A. J. 2013 Shale gas vs. coal: policy implications from environmental impact comparisons of shale gas, conventional gas, and coal on air, water, and land in the United States. *Energy Policy* **53**, 442–453. <https://doi.org/10.1016/j.enpol.2012.11.010>.
- Karapanagioti, H. K. 2007 Removal of phenanthrene from saltwater solutions using activated carbon. *Desalination* **210**, 274–280. <https://doi.org/10.1016/j.desal.2006.05.052>.
- Kim, S., Omur-Ozbek, P., Dhanasekar, A., Prior, A. & Carlson, K. 2016 Temporal analysis of flow back and produced water composition from shale oil and gas operations: impact of frac fluid characteristics. *J. Petrol. Sci. Eng.* **147**, 202–210.
- Kim, S., Sick, B., Omur-Ozbek, P. & Carlson, K. H. 2019 Investigating the influence of hydraulic fracturing fluid type and well age on produced water quality: chemical composition, and treatment and reuse challenges. *Desalin. Water Treat.* **146**, 39–56.
- Kim, S., Omur-Ozbek, P. & Carlson, K. 2020 Characterization of organic matter in water from oil and gas wells hydraulically fractured with recycled water. *J. Hazard. Mater.* **397**, 120551.
- Koby, M., Can, O. T. & Bayramoglu, M. 2003 Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. *J. Hazard. Mater.* **100**, 163–178. [https://doi.org/10.1016/S0304-3894\(03\)00102-X](https://doi.org/10.1016/S0304-3894(03)00102-X).
- Kwon, S., Sullivan, E. J., Katz, L., Kinney, K. A. & Bowman, R. S. 2008 Pilot-scale test of a produced water-treatment system for initial removal of organic compounds. In *SPE Annual Technical Conference and Exhibition*, Denver, CO, USA.
- Lambert, S. D., Miguel, G. S. & Graham, N. J. D. 2002 Deleterious effects of inorganic compounds during thermal regeneration of GAC: a review. *J. Am. Water Works Assn.* **94**, 109–119. <https://doi.org/10.1002/j.1551-8833.2002.tb10253.x>.
- Lee, D. S., Herman, J. D., Elsworth, D., Kim, H. T. & Lee, H. S. 2011 A critical evaluation of unconventional gas recovery from the Marcellus Shale, northeastern United States. *KSCE J. Civ. Eng.* **15**, 679–687. <https://doi.org/10.1007/s12205-011-0008-4>.
- Lefebvre, O., Habouzit, F., Bru, V., Delgenes, J. P., Godon, J. J. & Moletta, R. 2004 Treatment of hypersaline industrial wastewater by a microbial consortium in a sequencing batch reactor. *Environ. Technol.* **25**, 543–553. doi:10.1080/09593330.2004.9619345.
- Lester, Y., Yacob, T., Morrissey, I. & Linden, K. G. 2014 Can we treat hydraulic fracturing flow back with a conventional biological process? The case of guar gum. *Environ. Sci. Technol. Lett.* **1**, 133–136. doi:10.1021/ez4000115.
- Lutz, B. D., Lewis, A. N. & Doyle, M. W. 2013 Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development. *Water Resour. Res.* **49**, 647–656. doi:10.1002/wrcr.20096.

- Merzouk, B., Gourich, B., Sekki, A., Madani, K. & Chibane, M. 2009 Removal turbidity and separation of heavy metals using electrocoagulation–electroflotation technique a case study. *J. Hazard. Mater.* **164**, 215–222. <https://doi.org/10.1016/j.jhazmat.2008.07.144>.
- Neff, J. M. & Stout, S. 2002 *Predictors of water-soluble organics (WSOs) in produced water—a literature review* American Petroleum Institute, Washington, DC.
- Nicot, J. P. & Scanlon, B. R. 2012 Water use for shale-gas production in Texas, US. *Environ. Sci. Technol.* **46**, 3580–3586. <https://doi.org/10.1021/es204602t>.
- Osborn, S. G., McIntosh, J. C., Hanor, J. S. & Biddulph, D. 2012 Iodine-129, 87Sr/86Sr, and trace elemental geochemistry of northern Appalachian Basin brines: evidence for basinal-scale fluid migration and clay mineral diagenesis. *Am. J. Sci.* **312**, 263–287. <https://doi.org/10.2475/03.2012.01>.
- Pandey, S. R., Jegatheesan, V., Baskaran, K. & Shu, L. 2012 Fouling in reverse osmosis (RO) membrane in water recovery from secondary effluent: a review. *Rev. Environ. Sci. Biotechnol.* **11**, 125–145. <https://doi.org/10.1007/s11157-012-9272-0>.
- Pérez, L. S., Rodríguez, O. M., Reyna, S., Sánchez-Salas, J. L., Lozada, J. D., Quiroz, M. A. & Bandala, E. R. 2016 Oil refinery wastewater treatment using coupled electrocoagulation and fixed film biological processes. *Phys. Chem. Earth Parts A/B/C* **91**, 53–60. <https://doi.org/10.1016/j.pce.2015.10.018>.
- Pica, N. E., Carlson, K., Steiner, J. J. & Waskom, R. 2017 Produced water reuse for irrigation of non-food biofuel crops: effects on switchgrass and rapeseed germination, physiology and biomass yield. *Ind. Crops Prod.* **100**, 65–76. <https://doi.org/10.1016/j.indcrop.2017.02.011>.
- Rahm, D. 2011 Regulating hydraulic fracturing in shale gas plays: the case of Texas. *Energy Policy* **39**, 2974–2981. <https://doi.org/10.1016/j.enpol.2011.03.009>.
- R Core Team 2019 R: a language and environment for statistical computing, version 3.0. 2. R Foundation for Statistical Computing, Vienna, Austria.
- Rogers, J. D., Burke, T. L., Osborn, S. G. & Ryan, J. N. 2015 A framework for identifying organic compounds of concern in hydraulic fracturing fluids based on their mobility and persistence in groundwater. *Environ. Sci. Technol. Lett.* **2**, 158–164. <https://doi.org/10.1021/acs.estlett.5b00090>.
- Rosenblum, J. S., Sitterley, K. A., Thurman, E. M., Ferrer, I. & Linden, K. G. 2016 Hydraulic fracturing wastewater treatment by coagulation-adsorption for removal of organic compounds and turbidity. *J. Environ. Chem. Eng.* **4**, 1978–1984. <https://doi.org/10.1016/j.jece.2016.03.013>.
- Sidisky, L. M., Stenerson, K. K., Betz, W. R., Keeler, M. J., McCoy, M. & Brown, J. 2010 *The Extraction of Glycols from Water Using ENVI-Carb Plus Solid Phase Extraction Cartridge*. Sigma-Aldrich Application Note T410135.
- Spellman, F. R. 2013 *Environmental Impacts of Hydraulic Fracturing*. CRC Press, Boca Raton, FL, USA.
- Stephenson, M. T., 1992 *A survey of produced water studies*. In: *Produced Water. Environmental Science Research*, Vol. 46 (Ray, J. P. & Engelhardt, F. R., eds.). Springer, Boston, MA, pp. 1–12. [https://doi.org/10.1007/978-1-4615-2902-6\\_1](https://doi.org/10.1007/978-1-4615-2902-6_1).
- Stephenson, T., Valle, J. E. & Riera-Palou, X. 2011 Modeling the relative GHG emissions of conventional and shale gas production. *Environ. Sci. Technol.* **45**, 10757–10764. <https://doi.org/10.1021/es2024115>.
- Stringfellow, W. T., Domen, J. K., Camarillo, M. K., Sandelin, W. L. & Borglin, S. 2014 Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing. *J. Hazard. Mater.* **275**, 37–54. <https://doi.org/10.1016/j.jhazmat.2014.04.040>.
- Suarez, A. A. 2012 The expansion of unconventional production of natural gas (tight gas, gas shale and coal bed methane). *Adv. Nat. Gas Technol.* doi:10.5772/37404.
- Tadeo, J. L. 2008 *Analysis of Pesticides in Food and Environmental Samples*. CRC Press, Boca Raton.
- Thurman, E. M., Ferrer, I., Rosenblum, J., Linden, K. & Ryan, J. N. 2017 Identification of polypropylene glycols and polyethylene glycol carboxylates in flow back and produced water from hydraulic fracturing. *J. Hazard. Mater.* **323**, 11–17. doi: 10.1016/j.jhazmat.2016.02.041.
- United States Environmental Protection Agency 2004 *Manual Guidelines for Water Reuse; EPA/625/R-92/004*. Washington, District of Columbia. Available from: <http://www.ehproject.org/PDF/ehkm/water-reuse2004.pdf>.
- United States Environmental Protection Agency 2005 *Remediation General Permit Fact Sheet Excerpts: Fact Sheet Attachment A*. Available from: [https://www3.epa.gov/region1/npdes/remediation/RGP2010\\_FactSheet\\_AttachmentA.pdf](https://www3.epa.gov/region1/npdes/remediation/RGP2010_FactSheet_AttachmentA.pdf).
- Vengosh, A., Jackson, R. B., Warner, N., Darrah, T. H. & Kondash, A. 2014 A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. *Environ. Sci. Technol.* **48**, 8334–8348. doi: 10.1021/es405118y.
- Wang, X., Goual, L. & Colberg, P. J. S. 2012 Characterization and treatment of dissolved organic matter from oilfield produced waters. *J. Hazard. Mater.* **217–218**, 164–170. doi:10.1016/j.jhazmat.2012.03.006.
- Waxman, H. A., Markey, E. J. & DeGette, D. 2011 *Chemicals used in hydraulic fracturing*. United States House of Representatives Committee on Energy and Commerce Minority Staff, Washington, DC.
- Wu, S. H. & Pendleton, P. 2001 Adsorption of anionic surfactant by activated carbon: effect of surface chemistry, ionic strength, and hydrophobicity. *J. Colloid Interface Sci.* **243**, 306–312. <https://doi.org/10.1006/jcis.2001.7905>.
- Zhang, W., Yang, X. & Wang, D. 2013 Complete removal of organic contaminants from hypersaline wastewater by the integrated process of powdered activated carbon adsorption and thermal Fenton oxidation. *Ind. Eng. Chem. Res.* **52**, 5765–5771. doi: 10.1021/ie3030888.

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