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Physical-chemical evaluation of hydraulic fracturing chemicals in the context of produced water treatment

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Abstract

Produced water is a significant waste stream that can be treated and reused; however, the removal of production chemicals—such as those added in hydraulic fracturing—must be addressed. One motivation for treating and reusing produced water is that current disposal methods—typically consisting of deep well injection and percolation in infiltration pits—are being limited. Furthermore, oil and gas production often occurs in arid regions where there is demand for new water sources. In this paper, hydraulic fracturing chemical additive data from California are used as a case study where physical-chemical and biodegradation data are summarized and used to screen for appropriate produced water treatment technologies. The data indicate that hydraulic fracturing chemicals are largely treatable; however, data are missing for 24 of the 193 chemical additives identified. More than one-third of organic chemicals have data indicating biodegradability, suggesting biological treatment would be effective. Adsorption-based methods and partitioning of chemicals into oil for subsequent separation is expected to be effective for approximately one-third of chemicals. Volatilization-based treatment methods (e.g. air stripping) will only be effective for approximately 10% of chemicals. Reverse osmosis is a good catch-all with over 70% of organic chemicals expected to be removed efficiently. Other technologies such as electrocoagulation and advanced oxidation are promising but lack demonstration. Chemicals of most concern due to prevalence, toxicity, and lack of data include propargyl alcohol, 2-mercaptoethyl alcohol, tetrakis hydroxymethyl-phosphonium sulfate, thioglycolic acid, 2-bromo-3-nitrilopropionamide, formaldehyde polymers, polymers of acrylic acid, quaternary ammonium compounds, and surfactants (e.g. ethoxylated alcohols). Future studies should examine the fate of hydraulic fracturing chemicals in produced water treatment trains to demonstrate removal and clarify interactions between upstream and downstream processes.

Keywords: Hydraulic fracturing, Oil and gas production, Produced water, Wastewater treatment

1. Introduction
During the extraction of oil and gas (O&G) from geological reservoirs, water is also extracted, often in quantities that far exceed the volumes of O&G produced (Clark and Veil, 2009; Veil, 2015). Water is the O&G industry's largest volume waste stream and the volume of water produced is expected to rise from current estimated levels of approximately 13 billion gallons per day to more than 15 billion gallons per day by 2017 (BCC Research LLC, 2012). The United States alone generates approximately one trillion gallons of produced water per year (Veil, 2015). Produced water volumes tend to increase dramatically as mature fields pass peak production levels and for crude wells nearing the end of their productive existence; water production can exceed oil production by more than ten times (BCC Research LLC, 2012; Clark and Veil, 2009; Veil, 2015).

Produced water is often reused on-field for purposes such as maintaining reservoir pressure, water flooding, cyclic steam injection, and other secondary and tertiary production processes (Clark and Veil, 2009; Veil, 2015). Other beneficial uses for produced water include power plant cooling fluid, dust and ice control, and irrigated agriculture, particularly where the salt content of the produced water is naturally low (Clark and Veil, 2009; Dallbauman and Sirivedhin, 2005; Guerra et al., 2011; Veil, 2015). However, almost 50% of produced water is not reused and must be disposed, most commonly by well injection, but also by methods that could potentially contaminate surface waters and shallow aquifers (Clark and Veil, 2009; Veil, 2015).

In the face of continuing drought in the Western USA and the expanding recognition that water is an undervalued resource, there is growing interest in reclaiming produced water for beneficial reuse, particularly in arid areas where agriculture and O&G production coincide geographically. O&G production activities are under increasing regulatory scrutiny and there is mounting pressure for the industry to change water management practices and lessen potential environmental impacts from inadequately treated wastewaters. In order for produced water to be diverted to beneficial reuse in agriculture, it is important to ensure that adequate safeguards are in place.

The increased regulation and public scrutiny surrounding unconventional O&G production activities, particularly hydraulic fracturing, is an important aspect of produced water beneficial reuse. Recent studies have shown that a wide array of anthropogenic chemicals are used in O&G fields and that these chemicals and their degradation products can occur in produced water (Ferrer and Thurman, 2015a, b; Lester et al., 2015; Stringfellow et al., 2014). Since typical produced water treatment trains are designed for the separation and recovery of gaseous or hydrophobic hydrocarbons, the question rises whether commonly used treatment systems will remove hydraulic fracturing chemicals and other O&G field chemicals (M-I SWACO, 2012; Shaffer et al., 2013).
The amount of treatment produced water receives varies. Minimally, produced water is treated using gravity settling (e.g. oil-water separation) to recover oil product, separate gas, and remove particulate matter (Arthur et al., 2005; Fakhru'l-Razi et al., 2009). Additional treatment may consist of dissolved air/gas flotation or coagulation-flocculation (Arthur et al., 2005). Nut shell filters are used as coalescing media to remove residual oil (Liu and Liu, 2016; Srinivasan and Viraraghavan, 2008). Water softening is often used to reduce scale-forming minerals that are problematic in enhanced oil recovery and disposal (Fakhru'l-Razi et al., 2009). The most advanced systems use multimedia filtration (anthracite, sand, and garnet), ion exchange softening (weak acid cation softening), and cartridge filtration followed by a two-pass RO system (Liske and Leong, 2006; Orr, 2011).

Although some degree of trace contaminant removal likely occurs in even the most basic treatment processes via capture onto particle surfaces and into small oil droplets (Faksness et al., 2004), produced water treatment systems have not been designed to remove hydraulic fracturing chemicals specifically.

The use of hydraulic fracturing in O&G production contributes organic content, toxicity, and salinity that can interfere with produced water treatment (Abualfaraj et al., 2014; Barbot et al., 2013; Chapman et al., 2012; Haluszczak et al., 2013; Thacker et al., 2015). The presence of salinity, trace toxins, and recalcitrant organics present unique challenges that require a comprehensive treatment strategy (Gregory and Mohan, 2015; Shaffer et al., 2013). Produced waters from fractured wells contain high oxygen demand (Lester et al., 2015; NYS DEC, 2011; Stringfellow et al., 2014) that can interfere with physical-chemical treatment and cause fouling in membranes (Evans et al., 2014; He et al., 2014). Produced water from fractured wells appears biodegradable (Kekacs et al., 2015; Strong et al., 2014), and treatable using biological (Lester et al., 2015) and physical-chemical treatment methods (He et al., 2014; Jiang et al., 2013; Walsh, 2013). However, verification of removal of hydraulic fracturing chemicals in produced water treatment trains is needed.

Here, we use fundamental physical and chemical properties and biodegradability test results to examine treatability of hydraulic fracturing chemicals in conventionally used and widely available treatment processes. We evaluate whether technologies and processes developed for the treatment of naturally occurring hydrocarbons and salts can remove anthropogenic chemicals. Conventional produced water treatment is described elsewhere (Arthur et al., 2005; Clark and Veil, 2009; Colorado School of Mines, 2009; Fakhru'l-Razi et al., 2009; Igunnu and Chen, 2012). Here, we evaluate whether well-established physical, chemical, and biological processes can be combined into treatment trains to produce effluents suitable for disposal or beneficial uses, particularly irrigation and groundwater recharge.

2. Methods
A detailed description of the methods are available in the supplementary materials. Briefly, hydraulic fracturing chemical use in California has been previously characterized, and this reviewed and vetted data set was used here as the basis for which chemicals are used and their frequency of use (Stringfellow et al., 2015). We examined the treatability of the 193 unique chemical additives identified by Chemical Abstract Service Registration Number (CASRN).

Data on chemical additives and molecular weight were collected using TOXNET and EPISuite software (National Library of Medicine, 2013a, b). Physical-chemical data on melting point, boiling point, flash point, vapor pressure, water solubility, octanol-water partition coefficient ($K_{ow}$), soil organic carbon-water partitioning coefficient ($K_{oc}$), and Henry’s Law constant ($K_H$) were compiled.

Organic chemicals with $\log K_{ow} > 2$ were considered candidates for adsorption by activated carbon and other adsorptive media and also for removal by partitioning into the oil fraction for removal by oil-water separation (Bellona et al., 2004; Crittenden et al., 2012; U.S. EPA, 2012). Organic chemicals with $\log K_{oc} > 3$ were considered candidates for adsorption onto organic media (U.S. EPA, 2012). Organic chemicals with Henry's Law constants ($K_H$) of $1 \times 10^{-3}$ atm-m$^3$ mol$^{-1}$ or greater ($\log K_H > -3$), were considered candidates for removal by dissolved air/gas flotation (U.S. EPA, 2012; Watts, 1998). Organic chemicals were considered candidates for biological treatment based on available standardized biodegradation data (European Chemicals Agency (ECHA), 2000; National Library of Medicine, 2013c) or were shown to be biodegradable using similar protocols in published literature. Removal of chemicals by nanofiltration/reverse osmosis (NF/RO) was predicted using a molecular weight cut-off (MWCO) of 200–400 amu based on DOW Chemical FILMTEC NF membranes and 100 amu based on DOW Chemical FILMTEC RO membranes (Dow Chemical, 2015a, 2015b).

3. Results

The 193 chemical additives identified by Stringfellow et al. (2015) represent a range of functions in hydraulic fracturing. The physical-chemical properties of the additives are variable (Figs. 1–4), suggesting multiple treatment processes are needed for complete removal. Of the additives, 155 are organic and 38 are inorganic. Many of the additives have significant theoretical oxygen demand (Fig. 5), indicating oxidizing treatments such as biological treatment are needed. Available data indicate many additives are biodegradable (Fig. 6). When classified by primary function and/or chemical type (when function is not clear), potential removal in conventional produced water treatment systems is apparent based on physical-chemical properties (Table 1). Based on the results in Table 1, the most universally applicable treatment technologies are biological treatment and RO. Groups of chemicals that are most difficult to treat are acids/bases, breakers, and corrosion inhibitors (Table 1). Twenty-four of the 193 chemicals are missing...
physical-chemical data (Table S1) and these chemicals fall into the functional categories of corrosion inhibitors, scale control agents, surfactants, and other categories. The major categories of chemicals and their potential removal in treatment systems is described in more detail below.

![Histogram of logKow values](image)

**Fig. 1.** Distribution of octanol-water partition coefficient (Kow) values for chemicals used in hydraulic fracturing.

### 3.1. Treatability of biocides and QACs

Biocides used in hydraulic fracturing present a challenge for treatment due to their toxicity (Table 2). Quaternary ammonium compounds (QACs) are also a concern for the same reason although it is not always clear if QACs are being added as biocides or as surfactants (Table 3). At least one QAC identified—alkyl dimethyl benzyl ammonium chloride (68424-28-8)—is used as a biocide to control corrosion-inducing bacteria (Kahrilas et al., 2015). The most commonly used biocides in California are 2-methyl-3(2H)-isothiazolone (2682-20-4) and 5-chloro-2-methyl-3(2H)-isothiazolone (26172-55-4). These two biocides are not commonly used in others parts of the U.S.; however the other biocides are commonly used throughout the U.S. (U.S. EPA, 2015a). Biocides are expected to be a major obstacle for treating produced water from stimulated wells.
Fig. 2. Distribution of soil organic carbon-water partition coefficient ($K_{oc}$) values for chemicals used in hydraulic fracturing.

Fig. 3. Distribution of Henry's Law constant ($K_H$) values for chemicals used in hydraulic fracturing.
Fig. 4. Distribution of molecular weight values for: a) organic compounds, and b) inorganic compounds, used in hydraulic fracturing.
Based on physical-chemical data, none of the biocides and only one of the QACs (N,N-Dimethyldecylamine, 1120-24-7) are candidates for removal by volatilization. None of the biocides and only three QACs [dicoco dimethyl ammonium chloride (61789-77-3), decyltrimethylamine (1120-24-7), and alkyl dimethylbenzyl ammonium chloride (68424-85-1)] are candidates for removal by adsorption or by partitioning into the oil fraction that is removed by oil-water separators. Biological treatment is possible for many of the biocides and QACs. Isothiazolones can be treated in biological treatment systems (Jacobson and Williams, 2000; Laopaiboon et al., 2001). Biodegradability of QACs is possible under appropriate conditions (Kreuzinger et al., 2007; Tezel et al., 2012), and biological treatment has been demonstrated (Laopaiboon et al., 2002). Glutaraldehyde and formaldehyde are also biodegradable, suggesting biological treatment (Doronina et al., 1997; Laopaiboon et al., 2008; Leung, 2001). Biological treatment of 2,2-dibromo-3-nitrilopropionamide (DBNPA), commonly used in hydraulic fracturing (Kahrilas et al., 2015), is possible as long as inhibition is controlled (Choi et al., 2015). Published demonstration of the biodegradability of tetrakis hydroxymethyl-phosphonium sulfate (THPS) could not be located. Five of the biocides and four of the QACs have log $K_{oc}$ high enough to suggest sorption onto organic particles, which further suggests removal in biological treatment systems (Sarkar et al., 2010).
Only three of the biocides have molecular weights large enough for efficient removal (>90%) by NF. With the exception of formaldehyde (50-00-0) and ethaneperoxoic acid (79-21-0), the remaining biocides would be efficiently removed by RO. The organic nature of the biocides suggests that electrocoagulation and advanced oxidation processes might be useful; further testing is warranted.

3.2. Treatability of breakers

Breakers can be organic enzymes or inorganic oxidants. In California, the most commonly used breaker is ammonium persulfate (7775-27-1), used in 85% of treatments. With the exception of hydrogen peroxide (7722-84-1), inorganic breakers are added as salts that increase the salinity of fracturing fluids. The inorganic breakers are strong oxidants that readily decay and are unlikely to be found in produced water. Organic breakers include hemicellulose enzyme (9025-56-3), which is used in 68% of treatments. None of the breakers have log $K_H$ or log $K_{ow}$ values that would suggest removal by volatilization or adsorption, although ammonium ions (originating from ammonium persulfate) can be volatilized to ammonia for removal by air stripping. Ammonium ions can also be removed by adsorption onto activated carbon media (Boopathy et al., 2013), oxidation in biological treatment systems (Tchobanoglous et al., 2013), and removal by either NF or RO (Hayrynen et al., 2009).
While physical/chemical data could not be located for the organic breakers, these chemicals are expected to be biodegradable and are candidates for biological treatment (Chauhan et al., 2012; Qing and Wyman, 2011). The salinity added by inorganic breakers suggests the need for RO for their efficient removal. Enzymes are likely candidates for removal by either NF or RO due to their large molecular structures, although bio-fouling potential may be increased in membrane systems.

### 3.3. Treatability of clay stabilizers

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Biocide used for hydraulic fracturing in California. a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical name</td>
<td>CASRN</td>
</tr>
<tr>
<td>2-Methyl-3(2H)-isothiazolone</td>
<td>2682-20-4</td>
</tr>
<tr>
<td>5-Chloro-2-methyl-3(2H)-isothiazolone</td>
<td>26172-55-4</td>
</tr>
<tr>
<td>Tetralin hydroxymethyl-phosphoninate sulfonate</td>
<td>55566-30-8</td>
</tr>
<tr>
<td>Ampicillin</td>
<td>69-53-4</td>
</tr>
<tr>
<td>Glutaraldehyde</td>
<td>111-30-8</td>
</tr>
<tr>
<td>DBNPA (2,2-dibromo-3-nitropropionamide)</td>
<td>10222-01-2</td>
</tr>
<tr>
<td>MBNPA (2-Bromo-3-nitropropionamide)</td>
<td>1113-55-9</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>50-00-0</td>
</tr>
<tr>
<td>Ethanolperoxoic acid</td>
<td>79-21-0</td>
</tr>
</tbody>
</table>

a Based on FracFocus v1/2 data from January 30, 2011 to May 19, 2014. The list only contains chemical additives with CASRN.
Clay stabilizers consist of ammonium compounds, including salts and organic polymeric chemicals. The most common clay stabilizer in California was 1,2-Ethanediaminium, N1,N2-bis(2-(bis(2-hydroxyethyl)methylammonio)ethyl)-N1,N2-bis(2-hydroxyethyl)-N1,N2-dimethyl-, chloride (1:4) (138879-94-4), a large molecule (506.14 g mol\(^{-1}\)) used in 66% of treatments. None of the clay stabilizers are volatile based on log \(K_H\) data; however, ammonium ions can be volatilized to ammonia for removal. None of the clay stabilizers have log \(K_{ow}\) values that would suggest removal by adsorption although three of the clay stabilizers [ammonium chloride (12125-02-9), 2-propen-1-aminium, N, N-dimethyl-N-2-propen-1-yl-, chloride (1:1), homopolymer (26062-79-3), and ammonium sulfate (7783-20-2)] have high enough log \(K_{oc}\) values to suggest sorption onto organic particles. As mentioned above, ammonium ions can be removed via activated carbon adsorption, biological treatment and NF or RO. Choline chloride (67-48-1), a QAC used for clay stabilization, is readily biodegradable, making it a candidate for removal by biological treatment. Based on molecular weights, polymeric clay stabilizers and choline chloride would likely be removed in NF or RO while RO would be necessary for removal of inorganic salts.

3.4. Treatability of corrosion inhibitors

Corrosion inhibitors consist of organic chemicals that include formaldehyde polymers, chelating agents, and other chemicals (propargyl alcohol and thioglycolic acid). The use of formaldehyde polymers in corrosion control is well-documented (Singh et al., 2014) although fate in treatment systems including degradation pathways and the resulting by-products does not appear well known. None of the corrosion inhibitors were used in more than 3% of hydraulic fracturing treatments in California. Based on log \(K_H\) and log \(K_{ow}\) data, corrosion inhibitors are not candidates for removal by volatilization, adsorption, or partitioning into the oil fraction for removal in oil-water separators. The log \(K_{oc}\) values indicate half of the corrosion inhibitors will sorb onto organic particles.

Biodegradability data are mixed for the corrosion inhibitors, indicating some potential for removal in biological treatment. Sodium erythorbate (6381-77-7) is biodegradable, while propargyl alcohol, thioglycolic acid, and trisodium nitrilotriacetate (5064-31-3) are somewhat biodegradable and EDTA compounds [tetrasodium ethylenediaminetetraacetate (64-02-8) and
trisodium ethylenediaminetetraacetate (150-38-9)] can be recalcitrant (Bernhard et al., 2006; Sykora et al., 2001; U.S. EPA, 1989). Four formaldehyde polymers were identified: 4,1,1-dimethylethyl phenomethyl oxirane (29316-47-0), formaldehyde, polymer with 2- methyloxirane, 4-nonylphenol and oxirane (63428-92-2), formaldehyde, polymer with 4-nonylphenol and oxirane (30846-35-6), and thiourea, polymer with formaldehyde and 1-phenylethanone (68527-49-1). Only two of the corrosion inhibitors have molecular weights less than 100 g mol\(^{-1}\), propargyl alcohol (107-19-7) and thioglycolic acid (68-11-1), suggesting that most of the corrosion inhibitors would be removed by either NF or RO. Given that the corrosion inhibitors are organic, electrocoagulation and advanced oxidation may be appropriate—additional study is warranted.

3.5. Treatability of crosslinkers

The most commonly used crosslinkers in California were boron compounds (e.g. boron sodium oxide, sodium tetraborate decahydrate), which were used in 92% of treatments. Organic crosslinkers were also used. None of the crosslinkers have log \(K_H\) values that suggest removal by volatilization. Based on log \(K_{ow}\) data, only zirconium oxychloride (7699-43-6) is a candidate for removal by adsorption or partitioning into the oil fraction. Five of the crosslinkers have log \(K_{oc}\) values high enough to suggest sorption onto organic particles.

Only two of the organic crosslinkers have data indicating biodegradability and possible removal in biological treatment: Dglucitol (50-70-4) and glyoxal (107-22-2). Given that most crosslinkers are inorganic salts, desalination appears most appropriate for removal. Based on molecular weight data, four of the crosslinkers could be removed by NF, while three of the crosslinkers have molecular weights below the MWCO for RO: boric acid (10043-35-3), glyoxal (107-22-2), and boron oxide (1303-86-2). Removal of boron compounds by RO is improved by first raising the pH above 10 to convert compounds to borate (Xu and Jiang, 2008). Ion exchange resins can also be used for boron removal (Xu and Jiang, 2008). Electrocoagulation, conventional coagulation, and other technologies appear effective for boron removal although further demonstration is needed (Ezechi et al., 2014; Xu and Jiang, 2008).

3.6. Treatability of friction reducers

No friction reducers were identified in the dataset. Friction reducers are used infrequently in California because cross-linked gelled treatments are preferred over slickwater treatments due to geologic conditions (CCST, 2015). Three friction reducers were identified without CASRN: a polyacrylamide copolymer, a polyacrylate, and a non-specified commercial product. Polyacrylamide can be removed using biological treatment (Liu et al., 2012), or advanced oxidation (Lu et al., 2012). Polyacrylamides and the associated polymers are used as coagulants (Chatterjee et al., 2009), and as adsorbents (Rahchamani et al., 2011), so coagulation and adsorption based
treatment methods are likely to be effective. Membrane treatments, such as NF and RO, may be impractical due to bio-fouling (Matin et al., 2011).

3.7. Treatability of gelling agents

Only one gelling agent was identified, guar gum (9000-30-0), which was used in 97% of treatments. Guar gum adsorbs onto media (Liu et al., 2000), although adsorption-based removal may be impractical due to media clogging. Guar gum is readily biodegradable (Lester et al., 2013) and contributes to the oxygen demand of produced water from fractured wells (Stringfellow et al., 2014; Thacker et al., 2015), suggesting that biological treatment is appropriate for its removal (Kekacs et al., 2015; Lester et al., 2015; Strong et al., 2014). Guar gum is a natural flocculant (Singh et al., 2000), so coagulation-flocculation methods are likely effective for removal. However, chemical treatments are only practical when guar gum is present in low concentrations (50–300 mg L\(^{-1}\)); highly concentrated gelled fluids (>5000 mg L\(^{-1}\)) require excessive chemical doses (Evans et al., 2014). Membrane-based treatment (in NF or RO systems) may be impractical due to bio-fouling (Matin et al., 2011).

3.8. Treatability of iron control agents

Iron control agents, used in 16% of treatments, consist of organic acids and bases that function as chelating agents. With the exception of recalcitrant EDTA compounds [tetrosodium ethylenediaminetetraacetate (64-02-8) and trisodium ethylenediaminetetraacetate (150-38-9)], most iron control agents are carboxylic acids that are biodegradable including acetic acid (64-19-7), citric acid (77-92-9), erythorbic acid (89-65-6), thioglycolic acid (68-11-1), and sodium erythorbate (6381-77-7). The prevalence of carboxylic acids in fracturing fluids is evident by the large quantity of acetic acid observed in produced water from fractured wells that increases oxygen demand (Lester et al., 2015). Trisodium nitrilotriacetate (5064-31-3) is somewhat biodegradable and may be partially removed in treatment systems (Bernhard et al., 2006; Sykora et al., 2001). Six of the eight iron control agents have log \(K_{oc}\) values suggesting sorption onto organic particles, although removal by adsorption and oil-partitioning is not suggested by log \(K_{ow}\) values.

3.9. Treatability of scale inhibitors

Scale inhibitors, used in 60% of treatments, consisted mostly of organic chemicals, although two inorganic chemicals were also listed. The most commonly used scale inhibitor was phosphonic acid (13598-36-2), used in 49% of treatments. The log \(K_{ow}\) and log \(K_{H}\) data of the scale inhibitors do not suggest removal by adsorption or volatilization. Six of the seven chemicals have log \(K_{oc}\) values that suggest sorption onto organic particles. Although phosphonic acid and its salts adhere to biological flocs, they are not readily biodegradable (Nowack, 1998).
Carboxylic acids used as scale inhibitors are biodegradable (e.g. sodium erythorbate (6381-77-7)) although EDTA compounds are recalcitrant and nitrilotriacetate (NTA) compounds have limited biodegradability (Bernhard et al., 2006; Sykora et al., 2001). All but two of the scale inhibitors [phosphonic acid (13598-36-2) and 2-propenoic acid/ammonium salt (1:1) (10604-69-0)] have molecular weights higher than 100 g mol⁻¹, suggesting efficient removal by either NF or RO.

3.10. Treatability of solvents

Solvents were used in 99% of treatments in California. Frequently used solvents include ethylene glycol (107-21-1), hydrotreated light petroleum distillates (64742-47-8), and hydrotreated light petroleum distillates, paraffinic (64742-55-8). Of the 36 solvents identified, 11 have log \( K_H \) values high enough to suggest removal by volatilization. Fifteen of the solvents have log \( K_{ow} \) values that suggest adsorption onto media or removal by partitioning into the oil fraction. Many of the solvents with high log \( K_{ow} \) values are hydrocarbon-based solvents. Seventeen of the solvents have log \( K_{oc} \) data that indicates adsorption onto organic particles.

Twenty-four of the solvents have data indicating biodegradability. Biological treatment is generally effective for solvents provided that the microbial consortia is appropriate (Margesin and Schinner, 2001). Biological treatment of solvents can be improved by oxidative pre-treatments (Nam et al., 2001).

3.11. Treatability of surfactants

Surfactants were used in 95% of treatments in California. The most commonly used surfactant was isotridecanol, ethoxylated (9043-30-5), used in 72% of treatment. Of the 44 surfactants identified, eight have log \( K_H \) values high enough to suggest removal by volatilization. Twenty-five of the surfactants have log \( K_{ow} \) values high enough to suggest removal by adsorption or partitioning into the oil fraction for removal. Many of the surfactants with high log \( K_{ow} \) values are ethoxylated surfactants.

Sixteen of the surfactants are biodegradable, suggesting biological treatment would be appropriate. Treatment of surfactants has been demonstrated using advanced oxidation (Ikehata and ElDin, 2004; Lin et al., 1999), biological treatment (Di Gioia et al., 2008), and biological treatment combined with oxidative pretreatments (Nakai et al., 2015).

4. Discussion

4.1. Dissolved air/gas flotation

Only 10% of the hydraulic fracturing chemicals with data are volatile enough for efficient removal by dissolved air/gas flotation. The low volatility of hydraulic fracturing chemicals stems from the fact that most additives are salts, gelling agents, acids/bases, polymers, resins, etc. that are not volatile. Although solvents are used extensively in fluid formulations, the volatility of these solvents is not sufficiently high enough to warrant removal by
volatilization. Minimal volatilization of fracturing fluids is consistent with the results of Kekacs et al. (2015) where volatilization of organic carbon accounted for only 7% of carbon loss in biodegraded hydraulic fracturing fluid mixtures.

Despite the low volatility of hydraulic fracturing chemicals, dissolved air/gas flotation is likely to be used for produced water treatment to remove conventional contaminants (Arthur et al., 2005; M-I SWACO, 2012). Removal of trace chemicals in air/gas flotation could be improved by upstream chemical addition (Crittenden et al., 2012). An immiscible layer at the water surface could further increase removal of contaminants in dissolved air/gas flotation units (Bayati et al., 2011; Thoma et al., 1999).

4.2. Adsorption

Only one-third of hydraulic fracturing chemicals with data are candidates for removal by adsorption or partitioning into oil for removal. Adsorption potential onto organic surfaces is slightly less expected—only 22% of chemical additives with data are expected to sorb onto organic surfaces. Although adsorption-based technologies (e.g. activated carbon) are effective for many organic contaminants (Crittenden et al., 1999), adsorption-based treatment is only partially effective here. Prediction of adsorption potential could be improved using quantitative structure-property relationships (Blum et al., 1994; de Ridder et al., 2010; Magnuson and Speth, 2005). Modeling and experimental data could also provide better predictions of equilibrium contaminant loading onto adsorptive media (Crittenden et al., 1999), although realistic estimates of media life would need to be done using field trials. An adsorption media successfully demonstrated for conventional produced water is surfactant-modified zeolite, which removes hydrocarbons and is regenerated with air sparging (Altare et al., 2007; Kwon et al., 2011; Ranck et al., 2005)—this media should be investigated for its ability to remove hydraulic fracturing chemicals.

4.3. Biological treatment

Thirty-seven percent of organic chemical additives were biodegradable in bench-scale tests, suggesting these additives would be removed in biological treatment (Struijs and Vandenberg, 1995). Preliminary investigations of produced water from fractured wells indicate biodegradability, even with high salinity and trace toxicants present (Kahrilas et al., 2015; Lester et al., 2013; Strong et al., 2014). Produced water from fractured wells contains high oxygen demand and microbial populations capable of degrading the organic matter present, suggesting the suitability of biological treatment (Cluff et al., 2014; Mohan et al., 2013a, 2013b).

Biological treatment has been demonstrated for many saline wastewaters, including conventional produced water (Janson et al., 2015; Kose et al., 2012; Kwon et al., 2011; Li et al., 2010). Biological treatment of saline wastewaters is possible under both aerobic and anaerobic conditions.
provided that an appropriate halophilic bacterial consortium is present (Xiao and Roberts, 2010). Biological treatment has been demonstrated in conventional produced water for salt concentrations up to 100,000 mg/L TDS, although removal efficiency decreases with increasing salinity (Pendashteh et al., 2012). The salinity of produced water from many—although not all—fractured wells is less than 100,000 mg/L TDS (Barbot et al., 2013), low enough to permit biological treatment. Although residual chemical additives such as biocides can contribute toxicity that interfere with biological processes (Kahrilas et al., 2015; Kassotis et al., 2014; Maguire-Boyle and Barron, 2014; Orem et al., 2014), biological treatment remains possible in the presence of toxicants such as DDAC at concentrations up to 80 mg/L (Laopaiboon et al., 2002). Fixed-film treatment technologies (Laopaiboon et al., 2002, 2008, 2001) and microbial acclimation can improve treatment efficacy (Leung, 2001). Various forms of biological treatment systems—utilizing combinations of reactor designs—appear promising for contaminants in produced water: an example is two-phase partitioning bioreactors that allow for biodegradation of recalcitrant substrates (Piemonte et al., 2016; Tomei et al., 2012).

4.4. Reverse osmosis

The most universally applicable treatment method for produced water from fractured wells is RO, based on its ability to remove most compounds (Alzahrani et al., 2013; Malaeb and Ayoub, 2011). RO is effective for reducing salts in produced water (Xu et al., 2008). Given that RO fouling is a major problem with high-strength organic wastewaters (Matin et al., 2011; Mondal and Wickramasinghe, 2008; Xu and Drewes, 2006), alternatives such as nanofiltration (NF), low-pressure RO, and forward osmosis have been rigorously pursued (Mondal and Wickramasinghe, 2008; Thiel et al., 2015; Xu and Drewes, 2006), as have combinations of these technologies (Shanmuganathan et al., 2015). The alternatives are not as efficient as RO (Thiel et al., 2015), suggesting that extensive pre-treatment followed by RO may be most appropriate treatment (Cakmakci et al., 2008; Ozgun et al., 2013; Pramanik et al., 2015; Shanmuganathan et al., 2015). Pre-treatment is used to reduce particulate matter, minerals, and organics that can cause scaling and bio-fouling on membrane surfaces (Gregory et al., 2011; He et al., 2014; Shaffer et al., 2013). Candidate pre-treatment technologies are biological treatment, microfiltration, activated carbon, etc.

Contaminant removal in RO is a function of contaminant properties, membrane properties, and feed water quality (Malaeb and Ayoub, 2011). Physical-chemical properties (e.g. molecular weight, hydrophobicity) are useful for predicting removal by RO and NF (Bellona et al., 2004; Chen et al., 2004; Kiso et al., 2001; Van der Bruggen et al., 1999). Modeling and bench-scaling testing can confirm preliminary predictions (Shahmansouri and Bellona, 2013). Based on the molecular weights of chemical additives and a molecular weight cut-off (MWCO) of 100 g mol\(^{-1}\) for RO membranes (Dow Chemical, 2015a), approximately 70% of organic chemical additives are
expected to be rejected by RO (Fig. 4). In contrast, only 26% of organic chemicals are expected to be rejected by NF membranes, given a MWCO of 200–300 g/mol (Dow Chemical, 2015b). Actual removal rates will vary based on membrane fouling, which affects effective pore size and membrane surface charge (Xu et al., 2006). Removal rates of inorganic compounds will vary according to the extent of ionization, which is altered according to pH. For example, boron removal by RO is improved at higher pH (Alzahrani et al., 2013; Cengeloglu et al., 2008).

4.5. Emerging technologies

Technologies under development for treatment of conventional produced water could be effective for treating hydraulic fracturing wastes (Arthur et al., 2005; Fakhru’l-Razi et al., 2009; M-I SWACO, 2012). Some of these technologies lack full-scale demonstration. Electrocoagulation is currently under development—it can reduce COD, trace metals, and boron from produced water (Esmaeilirad et al., 2015; Ezechi et al., 2014). Evaporation-based desalination methods [e.g. mechanical vapor compression (MVP)] are also being developed for treatment of produced water although the economic feasibility of such technologies is not certain. Advanced oxidation is useful for oxidizing recalcitrant trace organics (Liu et al., 2009), and could be useful for oxidizing hydraulic fracturing additives (Stringfellow et al., 2014). Advanced oxidation can remove polyacrylamide (Lu et al., 2012), an additive used nationally (U.S. EPA, 2015b) although not frequently used in California (Stringfellow et al., 2015). Advanced oxidation can remove chelating agents (Sillanpaa et al., 2011), which are used extensively in oil/gas production for control of iron, scaling, and corrosion (Stringfellow et al., 2015). Duran-Moreno et al. (2011) used advanced oxidation to improve the efficacy of biological treatment of oil refinery wastewater—a similar approach could be used for produced water from fractured wells.

5. Conclusions

Physical-chemical data available for hydraulic fracturing chemicals indicate these chemicals are largely treatable using combinations of treatment technologies. However the most common, currently-applied treatment technologies (gravity separation, sedimentation, gas floatation, and filtration) are unlikely to remove significant amounts of hydraulic fracturing chemicals. Biological treatment appears a viable choice for reducing oxygen demand and removing many hydraulic fracturing chemicals. Reverse osmosis or evaporation-based technologies are appropriate choices for desalination. Nanofiltration does not appear to be a viable treatment since it is only predicted to remove a portion of the hydraulic fracturing chemicals. Advanced oxidation and electrocoagulation are promising technologies although demonstration is needed. Further research and pilot studies are needed demonstrated removal of hydraulic fracturing chemicals in produced water during treatment, especially prior to beneficial reuse that results in environmental release.
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Appendix A. Supplementary data
Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2016.08.065.

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