Reducing the water intensity of hydraulic fracturing: a review of treatment technologies

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ABSTRACT

A novel thermal treatment technology is presented that can separate multitudes of dissolved solids, volatile contaminants, and azeotropes from wastewater, and may be able to fill a gap that currently exists in hydraulic fracturing wastewater treatment technologies. The vast majority of wastewater treatment methods are tuned to extract only certain contaminants; however, it can be difficult to predict the composition of hydraulic fracturing wastewater. This introduces a major technical challenge to design a treatment system that is largely composition agnostic. The novel technology presented in this paper uses humidification–dehumidification in nozzle-demister assembly to separate clean water from dissolved solids, suspended solids, and various volatile compounds. Several review papers already exist that discuss the difficulties and options around the treatment of hydraulic fracturing wastewater. These tend to focus on variations of existing desalination technologies which are adopted for hydraulic fracturing wastewater treatment. These reviews are also devoid of discussion of azeotrope removal from wastewater. This paper, in addition to discussing the difficulties and existing treatments for hydraulic fracturing wastewater, analyzes the treatment options for the separation of volatile contaminants and azeotropes, and illustrates the advantages of a thermal-based treatment. Treating hydraulic fracturing wastewater is different from treating seawater or other types of wastewater due to the higher concentration and variety of contaminants. The unique challenges as well as the necessity of treating hydraulic fracturing wastewater are explained. The relative merits of several existing treatment technologies are discussed. The existing literature on the topic lacks discussion of azeotropes in hydraulic fracturing wastewater as well as which technologies can be used to remove them. This paper addresses all of the above with particular focus on separation of contaminants and water-based azeotropes.

Keywords: Hydraulic fracturing; Wastewater; Wastewater treatment; Azeotrope separation

1. Introduction

Hydraulic fracturing is the practice of injecting high-pressure fluid into shale rock formations to break open the rock and gain access to the oil and gas trapped within. This process, while less water intensive than conventional oil and gas extraction methods, still uses large volumes of fresh water per well [1–3]. Additionally, not all of the water used to fracture the well returns to the surface, thus the

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Most common components in hydraulic fracturing wastewater and their concentration in the wastewater 5 days after the well was drilled. Between 2005 and 2014, 9.4 billion m$^3$ of water were used to hydraulically fracture wells in the United States [7]. Fracturing a single well uses anywhere from 7,000 to 21,000 m$^3$ of fresh water [2,6]. Further reducing the water intensity of oil and gas extraction methods is necessary to reduce the total water load of energy production—especially considering the fact that ~15% of global water consumption is used for energy production [8]. The water consumption for hydraulic fracturing should be reduced whenever possible, especially in arid regions where water scarcity is already an issue.

There has been a rapid increase in unconventional oil and gas development since the beginning of the millennium, particularly in the United States [2–4,7,9–12]. In 2018, there were 139,977 hydraulically fractured wells in the United States. This is 12,846 more wells than there were in 2017 and 131,492 more wells than there were in 2000 [13]. The largest by-product of hydraulic fracturing is wastewater. Between 2004 and 2013, the annual wastewater production from hydraulic fracturing increased 570% in Pennsylvania [1]. Additionally, water use per unit length of well has increased in recent years [4]. Natural gas production is projected to increase by 45% by 2040 [9]. As natural gas production increases, so will the consumption of water used to hydraulically fracture wells and the associated production toxic wastewater—posing serious environmental and health threats [7,12,14,15].

The contaminants in hydraulic fracturing wastewater typically come from two sources: the chemicals added to the water used to frac the well, also called hydraulic fracturing fluid, and the water native to the rock formation, also called formation water (also known as connate water). Hydraulic fracturing fluid is typically made up of 90% clean water, 8% sand, and 2% other additives [16,17]. Additives to the hydraulic fracturing fluid typically include gelling agents, friction reducing polymers, corrosion and scale inhibitors, surfactants, acids, and biocides, all used to increase the efficiency of the hydraulic fracturing process [1,18]. Table 1 summarizes common chemicals in hydraulic fracturing wastewater as well as their concentrations are a function of the additives used per well [18]. The actual chemicals added to the water vary from company to company and well to well. The chemicals in the injected fluid may return to the surface in wastewater, may remain in the formation, or may degrade [19]. Additionally, chemical reactions may take place between the additives and formation water which create compounds more toxic than the parent compounds [7]. In the well, the chemical additives are exposed to high temperatures, pressures, and salinities, as well as a range of pH levels [20,21]. The conditions in the well, or downhole conditions, are extremely variable and may even differ between wells in the same shale play [20]. Some common additives have been studied in downhole conditions to determine how the reaction mechanisms may differ from near-surface environment reactions. One of the most commonly used biocides in hydraulic fracturing is glutaraldehyde. The downhole reactions of glutaraldehyde were found to be a function of temperature, pH, and salinity [20]. Additionally downhole decomposition of some corrosion inhibitors has been shown to produce hydrogen sulfide gas [21]. Given the extreme and unpredictable nature of downhole well conditions it can be difficult to predict the downhole reactions of hydraulic fracturing additives [20].

Wastewater may contain salts, metals, metalloids, organics, or naturally occurring radioactive materials at various concentrations. The contaminants in the wastewater as well as their concentrations are a function of the additives in the hydraulic fracturing fluid, the local geology, and the time [3,7]. The salinity of the wastewater can vary from nearly that of fresh water to 14 times that of seawater, and the pH can be lower than that of produced water from oilfields or coalmine drainage [22,23].

Wastewater is typically separated into two types: flowback water and produced water. Flowback water is the wastewater produced immediately after the well is drilled and is produced at a relatively high flowrate, up to 1,000 m$^3$/d. It typically has contaminants that are very similar to that of the hydraulic fracturing fluid. After the flowback period ends (~2–3 weeks), produced water is then recovered from the well for the remaining life of the well (~30–40 y) at a relatively low and constant flowrate, between 2 and 8 m$^3$/d [25,26]. Produced water typically has characteristics similar to that of the brackish formation water, or water that was contained within the rock formation before the well was drilled, and therefore is more saline than the flowback water [1,27]. While flowback and

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling point (°C)</th>
<th>Density (g/mL)</th>
<th>Concentration 5 days (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dissolved solids (TDS)</td>
<td>–</td>
<td>–</td>
<td>94,000</td>
</tr>
<tr>
<td>Ammonia</td>
<td>–33</td>
<td>0.77</td>
<td>70</td>
</tr>
<tr>
<td>Benzene</td>
<td>80</td>
<td>0.89</td>
<td>625</td>
</tr>
<tr>
<td>Toluene</td>
<td>100</td>
<td>0.88</td>
<td>833</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>197</td>
<td>1.11</td>
<td>29,700</td>
</tr>
<tr>
<td>2-Butoxyethanol</td>
<td>171</td>
<td>0.9</td>
<td>10,000</td>
</tr>
<tr>
<td>Other: chlorides, sulfates, Na, B, Sr, Ba, trace compounds</td>
<td></td>
<td></td>
<td>Chlorides + Na: 98,000</td>
</tr>
</tbody>
</table>
produced waters are considered to be different by the oil and gas industry, they are both ultimately wastewater that will be disposed of or treated [7]. On average, produced water tends to be extremely saline with salt concentrations greater than 100,000 mg/L [28]. The most common salt in the wastewater is NaCl. The salt concentration tends to increase with time as the wastewater is in contact with the native brine for more extended periods of time. As the salt concentration increases, the concentration of naturally occurring radioactive material increases as well. The naturally occurring radioactive material is typically radium [16,29–33]. The change from flowback to produced wastewater is relevant to treatment because it demonstrates the temporal change in composition of the wastewater. A treatment that is well suited to the treatment of flowback water may not be suitable to treat produced water, or vice versa.

Hydraulic fracturing wastewater composition varies significantly [34]. Produced waters from the Marcellus (PA), Eagle Ford (TX), and Barnett (NM) shale plays were tested and the ten most common chemicals in produced waters were found to be sodium, potassium, lithium, magnesium, calcium, strontium, iron, silicon, sulfur, and phosphorus. However, even among the most common chemicals in produced water the concentration of the chemicals varies by orders of magnitude between plays [35]. Over 1,000 organic compounds have been identified in wastewater samples [34]. Volatile organic compounds, such as toluene and benzene, have also been found in wastewater samples [36]. Volatile organic compounds are toxic and may cause health issues even in low concentrations if not properly removed and disposed of [37].

2. Hydraulic fracturing wastewater management

Due to the toxicity, high levels of salinity, total dissolved solids (TDS), and total suspended solids (TSS), proper management of hydraulic fracturing wastewater is difficult. The concentration of TDS tends to be much higher for wastewater produced by hydraulic fracturing as compared to other types of oil and gas production [38]. The range of TDS levels as well as its average level will vary based on local geology. For example, the Denver-Julesberg formation has TDS levels ranging from 20,000 to 65,000 mg/L, and the Bakken formation has values ranging from 150,000 to 300,000 mg/L [39]. Wastewater from the Marcellus formation in Pennsylvania has TDS levels ranging from 8,000 to 360,000 mg/L, with an average around 100,000 mg/L [6,25,27]. The suspended solids in the wastewater are largely made up of the sand used as proppant in the hydraulic fracturing fluid. TSS levels in wastewater range from 300 to 3,000 mg/L [40].

High salinity wastewater is not suitable to be treated by traditional wastewater treatment operations, among other reasons because the salt can harm the biological treatment processes that are common to municipal wastewater plants and therefore specialized methods of wastewater treatment are necessary [41]. About 95% of the wastewater produced in the United States is temporarily stored in surface pools before being transported to deep injection wells for disposal [42]. Deep injection disposal wells, also called Class II disposal wells, are geologically isolated from the hydraulic fracturing wells and are solely used for injection of wastewater, as shown in Fig. 1. Numerous production wells utilize the same disposal well. There are about 36,000 deep injection disposal wells in the United States, so the wastewater from a hydraulic fracturing well will be transported, sometimes across state lines, to a disposal well. Approximately 7.5 million m³ of wastewater are disposed of in deep injection wells every day in the United States [43].

The annual cost associated with the transportation of hydraulic fracturing wastewater is estimated to have reached $2.1B in 2020 [10]. The transportation of wastewater to centralized disposal wells represents a significant expense for the industry, as well as an environmental risk. Approximately half of the wastewater produced over the lifetime of a well is produced in the first few weeks given the high flowrate of flowback water [44]. If a low cost on-site treatment approach was available, it would be more economical to treat wastewater where it is produced than at a central facility. Also, the on-site treatment of the wastewater may reduce many of the concerns about the management and potential risks of the wastewater [28]. Table 2 lists the approximate cost ranges of some disposal and treatment methods used in the industry. Such figures tend to be proprietary information and are extremely difficult to find in publicly-accessible resources. Table 2 shows figures based on one source [45].

Surface pools, transportation, and disposal wells all represent potential environmental and health risks. If the water seeps into the ground from a surface pool or leaks out of a disposal well, the contaminants can affect local ecosystems or water supplies. The most common sources of contamination from hydraulic fracturing wastewater are surface leaks and spills, illegal disposal, and inadequate treatment and discharge of wastewater [29,46]. Additionally, deep well injection has been shown to induce seismicity in the region of the disposal well [47–50]. In the central United States, where approximately 85% of all Class II injection wells are located, there has been an 804% increase in the number of earthquakes per year between 1973–2008 and 2009–2014 [48,51]. Fortunately, with the right approach,
treatment and reuse can be an attractive alternative to surface storage and deep well injection.

The most common form of reuse is using wastewater as the hydraulic fracturing fluid for a new well. However, some treatment is still required. Without any treatment, wastewater would typically be unsuitable for fracturing new wells due to high concentrations of salt, hydrocarbon, grease, and biological matter [35]. Typically, the wastewater is filtered to remove the TSS and then mixed with fresh water before being used as hydraulic fracturing fluid [6]. While there are no uniform standards for the quality of the wastewater used to hydraulically fracture new wells, the water typically would not be reused when the TDS concentration is greater than 50,000–60,000 mg/L [3,17]. The treatment requirements vary based on what components are present in the wastewater, as well as the new well’s geology and hydraulic fracturing company. This form of reuse is only feasible while new wells are being hydraulically fractured. When more wastewater is being produced than can be reused to hydraulically fracture new wells, a new reuse or treatment option will be necessary [6,52].

Beneficial reuse of the wastewater could help alleviate water scarcity issues rather than adding to them; however, nearly all beneficial reuse applications require significant treatment. One of the only cases of untreated wastewater being used outside of the oil and gas industry is dust suppression. Some states, including North Dakota, South Dakota, Nebraska, Kansas, Wyoming, Michigan, Indiana, Ohio, New York, Pennsylvania, and West Virginia, allow untreated wastewater to be sprayed on roads for dust control [28,53–55]. Beneficial reuse of treated water would include agricultural irrigation or livestock watering. All of these applications have minimum water quality standards. Agricultural irrigation is the most common application for beneficial reuse for treated wastewater from other industries [56].

### 3. Hydraulic fracturing wastewater treatment

Treatment options for hydraulic fracturing wastewater often utilize well-established desalination technologies, such as reverse osmosis (RO), forward osmosis (FO), membrane distillation (MD), multistage flash distillation (MFD), multi-effect distillation (MED), and mechanical vapor compression (MVC) [57]. However, hydraulic fracturing wastewater and the seawater for which these technologies are optimized are very different. A desalination technology that works well for seawater treatment will not necessarily work well for wastewater treatment. The treatment of hydraulic fracturing wastewater poses unique challenges. Many technologies are limited by the TDS levels in the wastewater. Membrane based technologies (RO, FO, MD, etc.) also face the issue of fouling. Membrane processes rely on membranes that are specifically designed to work with a particular wastewater or separate specific contaminants. Hydraulic fracturing wastewater is highly variable and therefore it is difficult to design a membrane or draw solution that can treat all wastewaters. Additionally, azeotropic mixtures may exist in the wastewater which are mixtures that cannot be separated by simple distillation. One example is the binary azeotropic mixture of n-heptane and isooamyl alcohol in the chemical industry wastewater [58]. Another example is the wastewater from isopropanol industries. Such wastewater contains benzene and isopropanol which can form different azeotropes (i.e., binary or ternary, and heterogeneous or homogenous) with water [59]. Most analyses of hydraulic fracturing wastewater are focused on organic compounds and further investigation is necessary in order to quantify the most common azeotropes in this kind of wastewater [19,34,35].

#### 3.1. Membrane-driven technologies

Membrane-driven technologies have the benefit of successfully filtering suspended solids and volatiles, but have the drawbacks of membrane fouling and the fact that it is not feasible to tailor membranes and draw solutions to each hydraulic fracturing wastewater stream due to their high compositional variability. Osmotic backwashing cleaning via the circulation of deionized water on both sides of a membrane has been shown to effectively restore water flux through membranes that has been reduced by fouling [60–63]. Additionally, backwash using ultrafiltration permeate, reverse osmosis concentrate and permeate, nanofiltration permeate, and forward osmosis draw solutions have been used to membrane reduce fouling due to hydraulic fracturing wastewater [64]. To alleviate fouling issues, membrane-driven technologies typically utilize pretreatment to slow the fouling of the membrane [65,66]. Additionally, membrane treatments may be used to reduce membrane fouling in place of pretreatment. Use of double skinned membranes and zwitterionic polymers has been shown to significantly reduce membrane fouling and maintain water flux through the membrane [67]. There has also been anti-fouling progress using superhydrophilic ceramic membranes that have been shown to maintain permeate flux for at least 10 days [68].

#### 3.1.1. Reverse osmosis for wastewater treatment

Reverse osmosis uses high pressure to force clean water through a semi-permeable membrane. Clean water is collected on one side of the membrane and concentrated brine effluent is collected on the other side. This process is shown in Fig. 2a. However, for wastewater applications, this process is of limited applicability. Unfortunately, conventional RO is not economically attractive at TDS levels greater than 30,000–33,000 mg/L [69], and conventional RO is not capable of treating water with TDS levels in excess of 40,000 mg/L [10]. RO accounts for about...
60% of the desalination of seawater and brackish water worldwide [70].

There are modifications to the traditional RO process that can increase the maximum treatable TDS level. Closed circuit desalination (CCD) increases the pressure on the feed side of the membrane with time, so as the concentration of the feed side increases the pressure used to overcome the osmotic pressure of the membrane also increases [71]. Given that hydraulic fracturing wastewater salinity also increases with time, the increase in pressure of CCD may help to treat the higher salinity produced water later in the life of the well. CCD RO was evaluated for hydraulic fracturing wastewater, and a TDS removal of 99.6% was obtained [72]. Additionally, a permeate side sweep, which uses fresh water to reduce the osmotic pressure gradient across the membrane, can be used. This is called osmotically assisted RO, which has been experimentally shown to increase the maximum TDS level to 100,000 mg/L–140,000 mg/L [73]. Given the TDS limits, RO alone may be limited to a pre- or post-treatment, but when modifications such as CCD or osmotic assistance are made to the process it may be suitable as a standalone treatment for hydraulic fracturing wastewater.

3.1.2. Forward osmosis for wastewater treatment

Forward osmosis utilizes a draw solution on one side of a semi-permeable membrane to draw clean water through the membrane, leaving a concentrated effluent. The water that permeates through the membrane mixes with the draw solution and must then be separated from the draw solution, as shown in Fig. 2b. The limiting factor for this process is the concentration of the draw solution. The osmotic pressure across the membrane must push water to the draw solution, or more concentrated side of the membrane. If the wastewater is more concentrated than the draw solution, the FO will not purify water. There needs to be a draw solution that works for even the most contaminated wastewater. In order to maintain the concentration of the draw solution, another process, such as RO or distillation, must be used to separate the treated water from the draw solution [74,75]. For FO, the TDS limit of treatment is typically 70,000 mg/L, but can be as high as 200,000 mg/L depending on the membrane [3,6,74]. A drawback of FO is that it is a relatively slow process. In the absence of high pressure forcing fluid motion through the membrane, the water permeates through the membrane very slowly [66]. On the other hand, a significant advantage to FO is that it has been shown to be capable of producing treated water that meets surface discharge and drinking water standards [66,76,77].

Alternatively, if purity of the treated water is not critical, the draw solution and treated water may not need to be separated; this is called osmotic dilution mode. For this type of operation, there is no re-concentration of the draw solution, instead the dilute draw solution is the product of this process and new draw solution is constantly introduced to the system [78,79]. Osmotic dilution may be well suited to the treatment of hydraulic fracturing wastewater as the draw solution concentration will not decrease with time. Osmotic dilution FO has been applied to the treatment of oil and gas wastewater in the Haynesville shale formation via the Green Machine, developed by Hydration Technology Innovations (Albany, OR) and Bear Creek Services (Shreveport, LA) [66,80]. The Green Machine treats over 80% of the wastewater from any given well. This water has been internally reused to hydraulically fracture other wells [66].

3.1.3. Membrane distillation for wastewater treatment

Unlike other membrane separation processes, membrane distillation (MD) is a thermally-driven process and the driving force for each component to pass through the membrane pores is its partial pressure gradient in the vapor phase inside the pores due to the temperature difference across each pore [81]. The hydrophobic, microporous membrane prevents liquids or solutions from entering its pores due to the surface tension forces. In the MD process a liquid feed mixture at relatively high temperature, typically 60°C–90°C, will be in contact with one side of a porous membrane which separates the warm solution of feed mixture and the permeate that then enters into a cooling chamber [81]. The more volatile component moves as vapor phase, from the feed mixture to the permeate side of the membrane. At the permeate side this vapor is either condensed or convected away from the membrane module, depending on the MD configuration. As a result, the feed side will be concentrated. MD is a thermally-driven technology, but because it utilizes a membrane, it is susceptible to fouling [82]. However, because the membrane in MD is not a physical barrier to contaminants, rather a
support for the vapor-liquid interface, membrane fouling is less of an issue than it is for other membrane technologies, like RO and FO [81]. When MD was tested with hydraulic fracturing wastewater, iron-based deposits formed on the membrane, but was shown to have negligible effects on the performance of the membrane [31].

MD has been used to treat wastewater from a number of industries, including textile and pharmaceutical, as well as wastewater containing heavy metals and wastewater containing sulfuric acid solutions [83–86]. One of the benefits of using MD as a hydraulic fracturing wastewater treatment is that it is not significantly affected by salinity [3,6]. Therefore, the temporal change in salinity of hydraulic fracturing wastewater would not significantly impact the operation of MD. This process is capable of treating wastewater with TDS levels up to 350,000 mg/L [65]. MD has been shown to outperform RO and evaporative crystallization for hydraulic fracturing wastewater treatment, with ion removal efficiencies above 99.9% [87]. Additionally, MD tends to operate at temperatures near those typical of produced water [3]. In some cases MD has been paired with other technologies, such as precipitative softening and walnut shell filtration, to treat hydraulic fracturing wastewater with water recovery rates greater than 80% [88].

3.1.4. Other membrane technologies

RO, FO, and MD are by far the most common membrane driven treatment technologies, but there are a number of other, less common, membrane technologies that may be used for this application, at least as a pre- or post-treatment. Ultrafiltration (UF) and microfiltration (MF) are low pressure membrane-driven processes. Given the low pressure demand of these processes, they have a relatively small footprint which makes them suitable for on-site treatment [65]. UF & MF operate at pressures ranging from 0.5 to 5 bar [89]. UF & MF are rarely used as independent processes, but are commonly used as a pretreatment for RO, FO, or membrane distillation [90–92].

Electrodialysis is an electrically-driven membrane process that has been shown to treat wastewater with TDS levels, below 5,500 mg/L, to drinking or livestock watering quality, making it a promising post-treatment option for treatment processes not capable of reducing TDS levels so dramatically [93]. For example, electrodialysis could be used as a secondary treatment after RO or FO to increase the quality of the clean water.

3.2. Thermally-driven technologies

Thermally-driven technologies are better able to deal with high levels of salinity and avoid issues with membrane fouling or the need of specifically tailored membranes or draw solutions. However, due to the lack of a physical filter, these processes do not always remove volatiles. Evaporation or crystallization have been suggested as the only ways to successfully treat high salinity wastewater in a single process [5,94]. Additionally, for on-site hydraulic fracturing wastewater treatment applications, thermal processes can take advantage of otherwise waste thermal energy from the flared gas [95].

3.2.1. Mechanical vapor compression for wastewater treatment

In a MVC system, heat is transferred to the wastewater from superheated compressed vapor in a tube evaporator. The wastewater is sprayed over the tube evaporator and the steam is then mechanically compressed and the distillate is collected in condenser channels. The main demand of energy for this process is the electricity or mechanical energy required to compress the vapor [96]. The heat required to evaporate the wastewater, on one side of the tube evaporator is supplied by the condensation of the distillate on the other side of the tube evaporator [97]. Additionally, the hot condensate is used to preheat the incoming wastewater to increase the energy efficiency of the system. A schematic of an MVC system is shown in Fig. 3a. The main advantages of MVC are that it does not require pre-treatment because it is not prone to fouling or clogging, and that it can treat wastewater with TDS levels up to 200,000 mg/L [3].

3.2.2. Multi-effect distillation for wastewater treatment

MED is a process in which feed water is sprayed over a hot tube bank. Some of the water will evaporate and will move to the next effect where the clean steam will be used as the heat source for the tube bank. Concentrated brine will be collected at the bottom of the system. Some of the steam will condense inside the tubes and will be collected as clean product water. The number of times the steam is used as the heat source for a tube bank defines the number of effects, as the number of effects is limited by the temperature difference between the condensate temperature at the first effect and the condensate temperature at the last effect [98]. Each successive effect will take place at a lower temperature and pressure. This process is shown in Fig. 3b.

MED is one of the oldest desalination technologies and can effectively treat high salinity feeds [98–100]. MED has been tested as a hydraulic fracturing wastewater treatment only after significant pretreatment. The pretreatments were done to remove organics and oils from the wastewater prior to the MED process. The number of effects in MED is important to the operation of the process as the number of effects becomes a trade-off between the cost of the process and the quality of the treated water [101].

4. Azeotrope separation techniques

There are a number of reviews on the topic of hydraulic fracturing wastewater [1,5,7,11,12,17,29], however, these reviews do not mention the formation of azeotropic mixtures in hydraulic fracturing wastewater. Removing contaminants that form azeotropes in the wastewater requires specialized methods beyond desalination treatments adapted to hydraulic fracturing wastewater. Therefore, there is a gap in existing review literature on this particular type of contamination and its removal methods.

An azeotropic mixture is one in which the equilibrium compositions of the vapor and liquid phases are the same and do not change with simple distillation. Consequently, conventional distillation cannot be used to separate azeotropic constituents. Non-ideal behavior of some components
in a mixture can yield azeotropic systems. If the components are dissimilar, repulsion forces are very strong, and activity coefficients are greater than unity, then minimum-boiling azeotropes can form. Alternatively, if the components are similar, attract each other, and activity coefficients are less than unity, then maximum-boiling azeotropes can form [102]. The separation techniques used for azeotropic separation can be divided into two main categories: enhanced distillation techniques and membrane processes; however, there are other emerging techniques which have been investigated in some studies but are not yet industrialized. Also, there are treatment systems which take advantage of the combination of multiple separation methods. The most significant distillation techniques suitable for azeotropic separation, which are discussed in later sections, include azeotropic distillation, extractive distillation, pressure swing distillation and fixed-bed adsorption distillation; while suitable membrane processes include pervaporation, vapor permeation, membrane distillation and frictional diffusion.

4.1. Distillation

Azeotropic distillation and extractive distillation are techniques based on the addition of a third component called an entrainer that alters relative volatility of components of the original azeotropic mixture. In azeotropic distillation, this leads to the formation of a new azeotrope with properties that differ from the target compound and enables separation. According to the number of phases present in the new azeotrope mixture, the azeotropic distillation will be either homogeneous or heterogeneous [103].

Considering a binary azeotropic mixture as a reference, in heterogeneous azeotropic distillation, adding the entrainer will increase the volatility of one of the two components, leading to a mixture of two liquid phases after the vapor from overhead is condensed. In this case, the process will consist of two distillation columns and a decanter to separate the entrainer from the other component [104–106]. In homogeneous azeotrope separation, however, the overhead product is one liquid phase, so a liquid-liquid extraction column is needed after the first column to separate the overhead product from the entrainer [107]. In industrial applications of azeotropic distillation, it is more common to form a heterogeneous minimum temperature azeotrope. In this way one of the components and the entrainer will be carried to the overhead of the column and then a decanter is applied to separate the two liquid phases [104]. Pla-Franco et al. [103] used Aspen Hysys to simulate azeotropic distillation for a binary mixture of 1-propanol and water at 101.3 kPa, using diisopropyl ether as the entrainer. They showed that it is an effective entrainer for 1-propanol dehydration. In an experimental study, Gomis et al. [107] studied different potential entrainers for ethanol dehydration in azeotropic distillation. They performed the experiments in a pilot scale azeotropic distillation column and showed that naphtha is an effective entrainer for such azeotropic separation. Shi et al. [108] also proposed two azeotropic distillation processes for the separation of azeotropic mixture of 2,2,3,3-tetrafluoro-1-propanol and water, using chloroform and p-xylene as two potential entrainers. They showed their experimental results are in good agreement with those from the simulation.

4.2. Extractive distillation

The extractive distillation method is similar to azeotropic distillation in terms of adding a third component to the azeotropic mixture, but they are different processes. In azeotropic distillation, the entrainer is a more volatile component than the azeotropic solution. Therefore, it changes the volatility of one of the two components and will be taken from the overhead of the column along with that component. Adding the third component in azeotropic distillation forms a new azeotrope, however, in extractive distillation adding the third component (solvent agent) only increases the relative volatility and does not form an azeotrope with any of the components of the original mixture. The other important difference is that the solvent agent added into an extractive distillation process is a heavy substance with a high boiling point which will be recovered from the bottom of the second column; while in azeotropic distillation, the entrainer added to the separation process is a low boiling point substance that will be recovered from the top of the column. Azeotropic distillation, compared to extractive distillation, uses more energy to vaporize the entrainer at the top of the column [103,106,109].

In extractive distillation, a sufficient change of relative volatility is essential within the separated components.
when the solvent agent is added to the feed mixture. The solvent agent can be either solid salt, liquid solvent, a combination of solid salt and liquid, or ionic liquid. Selecting a suitable solvent is important to ensure effective and economical separation. Using solid salt as the solvent agent has the advantage of high separation ability; however, such salts be decomposed at high temperatures and can corrode the equipment. Liquid solvents may not have the same high separation capacity as solid salt, but are widely used due to the ease of their transport and recovery [110,111]. Extractive distillation using a mixture of solid salt and liquid solvent is a promising method for separation, since it integrates the advantages of solid salt and liquid solvent techniques, but it needs to be economically viable. Extractive distillation with ionic liquids has many advantages, including negligible vapor pressure (which means it does not pollute the top product of the column), as well as high thermal and chemical stability under the operating conditions of extractive distillation columns. However, distillation using liquids is not very common in industry due to material cost [111]. Yong et al. [112] carried out some experiments to study the effect of deep eutectic solvents (DES) on the elimination of mixture’s azeotropic point in an extractive distillation process. They used an ethanol-water system as it is a typical industrial azeotropic mixture and showed that adding ChCl/urea as the entrainer can increase the relative volatility of the mixture to more than 4.7 times and eliminate the azeotropic point [112]. In another study, Wang et al. [113] used the UNIQUAC model to investigate the separation of acetone and chloroform mixture by adding N-methyl-2-pyrrolidone (NMP) as the heavy entrainer in an extractive distillation column. They compared their results with those from previous works that used dimethyl sulfoxide or ethylene glycol as the entrainer to show that using NMP is more economic in separation of this maximum-boiling azeotropic mixture.

4.3. Pressure swing distillation

Another distillation technique for azeotrope separation is pressure swing distillation which takes advantage of the fact that the azeotrope point can be shifted by changing the pressure when the azeotropic mixture is pressure sensitive. In this way, a homogeneous azeotropic mixture whose azeotrope point changes with pressure can be separated. This method applies two distillation columns working at two different operating pressures: one at low pressure and the other at high pressure. Depending on the type of azeotrope (i.e., maximum boiling or minimum boiling) the products are collected from the top or bottom of the column [59,105,114,115]. Fig. 4 shows a schematic of pressure swing distillation for a minimum boiling azeotropic mixture.

Yue et al. [59] studied the separation of a ternary mixture of benzene, isopropanol, and water. They compared the simulation results for two different techniques: pressure swing distillation and heterogeneous azeotropic distillation. The results from their study showed that total annual cost for pressure swing distillation is almost half of the combination of both techniques, so it is a more economic and energy efficient method. They also showed that pressure swing distillation is an effective method for wastewater treatment containing benzene and isopropanol. Luyben [116] applied Aspen to simulate and optimize the separation of a binary mixture of methanol and trimethoxysilane in a pressure swing distillation process. The above mixture forms a maximum-boiling homogeneous azeotrope at 1 bar and 87.94°C when the concentration of methanol reaches to 28.65 mol%. In this study, they showed the optimum operating condition for the low pressure and high pressure columns are 0.25 and 7 bar, respectively. Furthermore, Liang et al. [117] have explored various aspects of pressure swing distillation, especially the application of this method in azeotrope separation, and published their review study in 2017.

There are other distillation techniques that are applicable for azeotrope separation, such as fixed-bed adsorption distillation which applies molecular sieves as active packing material in a packed-bed distillation column instead of the conventional inert packing materials. Molecular sieves can alter the vapor-liquid equilibrium of feed components and improve the relative volatility to help azeotropic mixture separation [118]. An azeotrope dividing wall column is another enhanced distillation column technique useful in azeotrope separation. The dividing wall column reduces the number of required columns by installing a partition wall inside the column which leads to a significant reduction in energy consumption and capital cost.

4.4. Membrane distillation for azeotrope separation

Conventional distillation and membrane distillation both depend on vapor-liquid equilibrium as the basis for separation. However, the most significant difference between these processes is the feed water temperature. Membrane distillation does not require heating the feed to its boiling temperature, which is necessary for conventional distillation. Moreover, the target components to be separated can have similar boiling points or form azeotropes. There are four different configurations developed to perform membrane distillation: direct contact membrane distillation, air gap membrane distillation, sweeping gas membrane distillation, and vacuum membrane distillation. They differ in the way in which the vapor is condensed and/or removed from the membrane distillation module. Sarita et al. [119] carried out experimental studies on the separation of HCl-water azeotropic mixture (20.2 wt.% HCl) using

Fig. 4. Schematic of pressure swing distillation for a minimum boiling azeotropic mixture.
air gap membrane distillation. Specifically, they investigated the effects of parameters such as feed temperature, air gap widths and selectivity on the permeation and total flux. Their experimental results also showed there is an increase in permeate flux by decreasing air gap thickness and increasing temperature at the air gap. They showed that 31 wt.% is the maximum concentration level of HCl achievable at 45°C of feed temperature. They also developed heat and mass transfer correlations for this separation process [119]. Li et al. [120] introduced a methodology for designing and optimizing a membrane-assisted distillation process for dehydrating ethanol which is a common example of aqueous azeotrope dehydration in industry. They showed that enriching the ethanol up to 99.6 wt.% is achievable by using their methodology to define the optimum hybrid configuration. More information can be found in [121].

4.5. Pervaporation

Membrane-based processes are cleaner than conventional distillation because they require less energy and do not need additional chemicals. Pervaporation is an effective membrane technique for azeotropic separation. Unlike distillation, it is not limited by the thermodynamic vapor-liquid equilibrium. In distillation, separation is based on the difference in relative volatilities of the components. However, in pervaporation the driving force for separation is the difference in chemical activity and diffusion rate of the components into a membrane [122,123]. Pervaporation is an energy efficient process compared to most conventional separation methods such as distillation because only the latent heat of minor component that permeates within the membrane must be supplied. Also, pervaporation units often have small footprints and do not require entrainers [123,124]. Kanse et al. [122] built up an experimental setup to study the pervaporation separation of two azeotropic mixtures: ethanol/water and acetonitrile/water. They performed experiments to investigate the effects of feed temperature and solution concentration on the separation process. They also carried out experiments for two different membranes: poly vinyl alcohol (PVA) and PVA-poly ether sulfone (PES). Results from their experiments revealed that the flux of both membranes increases by increasing the feed temperature and concentration. They showed for both binary systems, using PVA-PES membrane in pervaporation leads to a higher flux [122]. Pervaporation has been proven to be one of the most promising techniques for azeotrope separation. However, choosing a suitable membrane is crucial, as it affects the efficiency of the separation. In this regard, Ong et al. [124] have accomplished a review study on recent development of membranes in pervaporation processes.

4.6. Vapor permeation

Vapor permeation is similar to pervaporation, except that in vapor permeation the feed is a gaseous as opposed to a liquid mixture. In the vapor permeation process, the feed temperature and the driving force do not reduce within the vapor permeation module, so there is no need for a heat exchanger after each module. A vacuum is often needed on the permeate side to run the process at lower pressures which leads to lower condensation temperatures. Consequently, it has high operating costs due to the need for low operating pressure and is usually not used as a standalone separation unit. In many applications, because of high operating costs of the pervaporation technique, a more economical way is to use pervaporation or vapor permeation only to break the azeotropes and then couple that with a secondary separation process such as distillation columns [125,126]. Čihál et al. [127] carried out experiments to compare pervaporation and vapor permeation techniques with different membranes. They examined the separation of an azeotropic mixture of dimethyl carbonate and methanol, and asserted that vapor permeation using PIM-1 membranes is the most selective membrane-based technique in removing the dimethyl carbonate from this azeotropic mixture.

4.7. Frictional diffusion

In 2007, Geboers et al. [128] introduced a novel separation technique for azeotropic mixtures. They claimed that by using a gas that has a higher binary diffusive friction with one of the two components of a binary azeotropic mixture, diffusion of the gas leads to the separation. They modeled this concept and performed the experiments in a shell and tube module with a counter current configuration similar to what is shown in Fig. 5. In order to prevent the mixing of feed mixture with the enhancer gas (sweep gas), they applied a porous barrier. Using CO₂ as the enhancer gas for the separation of ethanol/water mixture, they performed the experiments and provided results to support this novel concept which they named frictional diffusion [128]. Frictional diffusion (also called friction difference

![Fig. 5. Schematic of frictional diffusion.](image-url)
or FricDiff) is based on the difference in diffusion rates of the constituents of a gas or vapor mixture when they diffuse through an enhancer gas. In this separation technique, flow of the feed mixture and that of enhancer gas are separated by a porous barrier. The feed mixture passes through this nonselective barrier and gasses diffuse due to the concentration difference of the components on each side. For example, heavier components in the feed mixture have lower diffusion rates as they have larger molecular weights. So they have more friction with the sweep gas. This leads to enrichment of the target product either on the feed or sweep side. One of the advantages of this separation process is low energy consumption and absence of hazardous solvents [106,126]. However, pressure drop across the porous barrier should be minimized as it causes convective mass transfer and adversely affects the separation. Breuer et al. were another group who examined using FricDiff for the separation of an azeotropic mixture of 2-propanol and water. They studied the effects of operating conditions and the porous barrier on the separation process using a detailed numerical model [126].

Table 3 shows a summary of separation techniques that can be useful in azeotrope separation.

5. Humidification–dehumidification nozzle-demister

We are developing a new wastewater treatment technology which uses humidification–dehumidification in a subsonic swirling nozzle combined with an in-line demister to reclaim clean water from wastewater (US Patent Application 16/985,043). The method takes advantage of a widely-observed trend in water azeotropes as well as the thermodynamics of the humid streams to efficiently separate and selectively condense water vapor. The technology is largely insensitive of the composition of the feed wastewater. It can be containerized and mobilized from site to site with minimal mounting and dismounting time and expense. Supersonic swirling nozzle-demisting is used in the oil and gas industry to dehydrate natural gas after extraction [144]. By taking advantage of the same principles of operation, but at subsonic velocities, the nozzle-demister will treat hydraulic fracturing wastewater while utilizing technology that is already familiar to the oil and gas industry.

5.1. Azeotrope separation

The prevalent method of separation is to break an azeotrope by introducing a compound that forms a stronger azeotrope with one/some of the constituents, as previously discussed. However, this approach is not practical for hydraulic fracturing wastewater due to the vast variety of chemicals and azeotropes. The new treatment approach, which avoids this limitation, relies on two observations:

- Hundreds of water azeotropes have been documented, and in a large majority of cases the saturation temperature deviates significantly from that of water (Fig. 6). Our process will operate narrowly around the saturation point of water such that azeotropes with saturation temperatures that are different from that of water are separated from the treated water. This will be accomplished by heating the wastewater to nominally 1°C above the saturation temperature of water and then cooling the vapor to nominally 1°C below the saturation temperature, as discussed further below. If the process is controlled within ±1°C of water’s saturation temperature, only 2.5% of azeotropes may remain; some of which have not been reported in hydraulic fracturing wastewater and some are innocuous, such as butyric acid-water.
- Hydraulic fracturing wastewater is by-and-large made of dissolved solids and low-volatility compounds. Many of these contaminants are likely to be present in concentrations which are orders of magnitude smaller than their respective azeotropic mixtures with water. As little as 2% of all contaminants may evaporate and even fewer form a water-based azeotrope. Furthermore, in that 2%, the mass ratio of water in the azeotrope is relatively small; in almost half of its azeotropes, water makes up less than 30% of the total mass. This means that the vast majority of water is not engaged in an azeotrope and is recoverable.

Fig. 6 shows the saturation temperature of 280 common azeotropes vs. the water ratio in each azeotrope. The saturation temperature of water is shown as a red line. In the new treatment, first the wastewater will be heated to 1°C above the saturation temperature of water. The waste vapor will contain all the azeotropes shown in the red box. The azeotropes in the white box will remain in the wastewater tank. Then, the vapor will be cooled to 1°C below the saturation temperature of water. Only the azeotropes in the narrow blue band will condense with the clean water. Thus, by carefully controlling the temperature of the process, 98% of potential azeotropes can be separated from the treated water.

5.2. Operation

The process schematic is shown in Fig. 7. Dry air is drawn into the nozzle, shown as point 0 in Fig. 7, and is heated via low-grade heat. Next, the fast-moving hot air comes into contact with a vortex generator (labeled as point 1) which swirls the incoming stream. Then, wastewater vapor enters the nozzle (point 2) and mixes with the air (point 3), the wastewater vapor is at a temperature 1°C above the saturation temperature of water. The humid air mixture, at point 3, continues through the converging nozzle. As the velocity of the air increases due to the reduction in cross-sectional area, the temperature of the air will decrease as the thermal energy is converted to kinetic energy. As the temperature drops to the saturation point, clean water will condense out of the humid air. As the water condenses, the latent heat of condensation is released and rejected to a jacket heat exchanger with cold feed wastewater flowing over the nozzle. The jacket heat exchanger allows the temperature in the nozzle to be maintained at 1°C below the saturation temperature despite the latent heat of condensation being released. The flowrate of cold feed wastewater through the jacket heat exchanger can be adjusted in order to control the temperature. As the water condenses into suspended droplets, the flow becomes misty. The swirling motion pushes the droplets to the
<table>
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<th>Separation processes</th>
<th>Description</th>
<th>Advantages</th>
<th>Drawbacks</th>
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| Distillation processes | Azeotropic distillation | A third component (entrainer) is added to the mixture. The entrainer is more volatile than the azeotropic solution and increases the volatility of one of the two components, facilitating the separation | • Well understood process  
• Abundant theoretical and practical knowledge | • Energy-intensive  
• Large column diameter  
• More difficult control  
• Need for a secondary distillation of the entrainer | [103–105, 107, 109, 114, 115, 129, 130] |
| | Azeotrope dividing wall column | Only requires one column for separation. This leads to energy savings and significantly reduces the capital and operating cost | • Low capital cost | High actual steam cost due to combining two reboilers into one | [131, 132] |
| | with solid salt | A third component (separating agent) is used to change relative volatility of the components and overcome the azeotrope. For binary feed, one pure component exits as the top product of the first column and the other component plus solvent agent accumulate at the bottom and can be separated in a second distillation column | • High separation ability  
• Easy operation  
• No problems of dissolution, reuse and transport | Corrosion  
High consumption of energy in case of large solvent ratio  
Impurities in the top product because of volatile solvents  
Impurities in the top product because of volatile solvents  
Corrosion and salt decomposition at higher temperature  
Impurities of solvent in the products  
High cost  
Impurities of solvent in the products  
Large energy consumption and capital investment  
Difficulty of controlling the process due to the use of a third component  
Need for a secondary distillation of the auxiliary solvent  
Complexity of operation and process control  
Decomposition of heat-sensitive components with increasing pressure  
Higher operating cost in case of using a vacuum pressure | [110, 111, 133–137] |
<p>| | with liquid solvent | | | |
| | with a mixture of solid salt and liquid solvent | | | |
| | Distillation processes | Distillation processes | Distillation processes | Distillation processes | Distillation processes |
| | Extractive distillation | It takes advantage of the sensitivity of the azeotrope point to pressure variation in order to accomplish the separation in a two-column process operating at different pressures | • Low contamination in the product due to the absence of a third component | | [59, 102, 117, 138–140], [141] |
| | with ionic liquid | | | | | (Continued) |</p>
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| Fixed-bed adsorption distillation | Molecular sieves or ion-exchange resins are used as separating agents. The molecular sieves alter the vapor-liquid equilibrium of the mixture's components. It is a combination of two mechanisms: permeation and evaporation. Components of a liquid mixture permeate through a membrane and evaporate into the other side. It is useful in azeotropic separation, because it is based on the difference in sorption and diffusion of the components, not the relative volatility. | • Environmentally friendly  
• No extra organic solution  
• No solvent loss  
• Small footprint  
• Environmentally friendly  
• Simplicity and flexibility  
• Low energy consumption  
• Independent of relative volatility, so suitable for azeotrope separation  
• No additional impurities in the final product | • Difficulty to regenerate the molecular sieves  
• Lower separation effect than the separating agent used in the extractive distillation  
• High capital cost  
• Relatively low permeate fluxes (i.e., large membrane areas)  
• Low condensation temperatures (i.e., high operating costs)  
• Need for integration with conventional separation units | [118, 123, 122–124, 142] |
| Pervaporation | It is similar to the pervaporation, except that in vapor permeation the feed is a mixture of vapors or vapor and gas. | • Simple operation and control  
• Reliable performance and high flexibility  
• High product purity (no contamination by entrainer)  
• Small footprint | • Rather expensive  
• Relatively low permeate fluxes (i.e., large membrane areas)  
• Low condensation temperatures (i.e., high operating costs)  
• Need for integration with conventional separation units | [125, 127] |
| Vapor permeation | It is similar to the pervaporation, except that in vapor permeation the feed is a mixture of vapors or vapor and gas. | • Simple operation and control  
• Reliable performance and high flexibility  
• High product purity (no contamination by entrainer)  
• Small footprint | • Rather expensive  
• Relatively low permeate fluxes (i.e., large membrane areas)  
• Low condensation temperatures (i.e., high operating costs)  
• Need for integration with conventional separation units | [125, 127] |
| Membrane distillation | It is based on thermal gradient across a porous membrane that only passes the vapors. Nonvolatile components remain on the feed side; so there will be neither solid nor nonvolatile components in the product. | • Relatively low cost and low energy consumption  
• Large vapor-liquid interface area per unit volume compared with conventional distillation  
• Possible under mild operating conditions (i.e., not necessary to increase feed temperature to its boiling point) | • Low permeate flux  
• Relatively small thermal efficiency in direct contact membrane distillation configuration | [120, 121, 143] |
| Membrane evaporation | It is based on thermal gradient across a porous membrane that only passes the vapors. Nonvolatile components remain on the feed side; so there will be neither solid nor nonvolatile components in the product. | • Relatively low cost and low energy consumption  
• Large vapor-liquid interface area per unit volume compared with conventional distillation  
• Possible under mild operating conditions (i.e., not necessary to increase feed temperature to its boiling point) | • Low permeate flux  
• Relatively small thermal efficiency in direct contact membrane distillation configuration | [120, 121, 143] |
| Frictional diffusion | It is based on differences in diffusive velocities of the feed components when diffusing through a sweep gas. | • Relatively low energy consumption and absence of hazardous solvents | • Need to avoid pressure drop across the porous barrier (it causes convective mass transfer and adversely affects the separation) | [106, 126, 128] |
periphery of the nozzle where the clean water is collected by an in-line demister (point 5). The dry air and gaseous contaminants pass through the demister and flow through a diffuser to reduce the velocity and increase the temperature of the flow (points 7 & 8), thus allowing more energy to be recouped from the waste stream via heat exchangers. Both the clean water and contaminants flow through heat exchangers in the wastewater pool before collection (point 9). Heat is also added to the wastewater pool (point 13) to generate the waste vapor that is the feed stream entering the nozzle. All points and what they indicate in the nozzle-demister are shown in Table 4. Based on the energy consumption of the treatment our process is projected to treat hydraulic fracturing wastewater at a cost of $7/m³.

Component-level testing has proven the concept of the treatment system. The nozzle uses the Venturi effect to suck the wastewater vapor into the nozzle. Experimental-validated simulations have shown that the nozzle can achieve a suction ratio of air to steam ranging from 5 to 1 up to 1 to 1, which is ideal for the humidity in the nozzle before condensation. In-house experiments on azeotrope separation have shown that over 95% of the azeotropes can successfully be separated from the clean water. Additionally, the demister has been proven collect 99% of the clean water. Details of these results are outside the scope of this article and will be the subjects of upcoming publications.

The control of the system is critical to the quality of the resulting treated water. If the temperature in the nozzle is controlled within ±1°C, then only 2.5% of potential contaminants would remain in the treated water. Controlling the temperature within that level of accuracy is complicated by the thermal mass and inertia as well as variability in the fluid composition, thus making traditional control insufficient for this system. The temperature in the nozzle will be controlled using a digital twin. A physics-based model of the system will be paired with real-time experimental data to
create a digital twin that will use machine learning to predict the performance of the nozzle, as well as the temperature. The predictions from the digital twin will then be used to adjust the operation of the system to maintain a temperature of 1°C above the saturation temperature of water.

6. Conclusions

Although membrane-driven technologies have the advantage of filtering out suspended solids and volatiles, the TDS limits for membrane technologies are significantly lower than those of thermally-driven technologies. Additionally, vaporization has been suggested as the best way to treat wastewater. Of the thermally-driven technologies, membrane distillation is capable of dealing with the highest TDS levels; however, the use of a membrane in this process makes it susceptible to fouling. Additionally, few treatment processes are capable of removing azeotropes from the hydraulic fracturing wastewater. Membrane distillation is the main common treatment technology that separates azeotropes. A humidification–dehumidification nozzle-demister process that is not susceptible to fouling or clogging was described. This process has the advantage of high TDS limits and azeotrope separation. The next steps for the new design are fabrication and experimental validation. Component validation has been completed. Thermal-based processes show promise for treating the highly variable and toxic hydraulic fracturing wastewater, and a process that does not require pretreatment or fouling treatment would be ideal. Given the difficulties of hydraulic fracturing wastewater treatment, a hybrid or novel treatment system may be best suited as treatment methods.

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