Hydraulic Fracturing Wastewater Treatment by Coagulation-Adsorption for Removal of
Organic Compounds and Turbidity

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Abstract

Waters produced from fracturing operations in the oil and gas industry are a complex mixture of fracturing fluids and formation water. Closing the water cycle loop in this industry depends on the effective reuse of these wastewaters, and therefore treatment. This study investigated the application of chemical coagulants and powder activated carbon (PAC) to reduce turbidity, dissolved organic carbon (DOC), total petroleum hydrocarbons (TPH), and polyethylene glycols (PEGs) in four hydraulic fracturing wastewaters. Jar tests were performed to evaluate both the PAC and coagulants. Treatment goals were operationally defined targeting 90% reduction of turbidity, PEGs,

and TPH. PAC was found to be effective at removing both PEGs and TPH from the wastewaters, but would not settle without the addition of a coagulant. Ferric chloride achieved a 90% reduction in turbidity at a lower dose than aluminum chlorohydrate, in the presence and absence of PAC. The optimized coagulant dose by itself had little to no effect upon concentrations of DOC and PEGs, while greater than 80% removal of TPH, a minor component of DOC, was observed in three of the waters. PAC at 1000 mg L⁻¹ achieved greater than 80% reductions of the total ion chromatogram, while DOC removals were from 9.5 to 48.3%. These results suggest that coagulation with ferric chloride at doses as low as 5 mg L⁻¹ is an effective process for turbidity and TPH reduction in hydraulic fracturing wastewaters, and when coupled with PAC can also remove DOC and targeted organic contaminants such as PEGs.

Keywords: Hydraulic Fracturing, Produced Water, Coagulation, and Activated Carbon

Highlights:

- 1) Frac waters from the same formation can have vast differences in water quality
- 2) Metal salts (5ppm) can reduce turbidity and hydrocarbon levels of frac waters
- 3) Powder activated carbon can sorb PEGs and hydrocarbons in frac waters
- 4) Coagulation-adsorption can reduce turbidity, DOC, PEGs, and TPH in frac waters

1. Introduction

Hydraulic fracturing is a well stimulation method used to extract oil, natural gas, and geothermal energy from geological formations [1]. The recent use of this process has generated a surge of oil and natural gas development in the U.S., and its use is expected to increase as new formations are identified [2]. Hydraulic fracturing occurs after a well bore has been drilled and the formation perforated, by pumping fracturing fluids at high pressures through the well bore to improve access for oil and natural gas extraction from the formation [6]. This process, which uses around 15 to 23 million liters of water per well, has further involved the oil and gas industry into the water management business [2,3] since it requires the acquisition of large volumes of fresh water and the management of large amounts of wastewater that return to the surface as flowback or produced water.

The treatment and re-use of these wastewaters is important to the long-term sustainability of hydraulic fracturing. However, hydraulic fracturing wastewaters are challenging to treat, as they can have vast compositional differences and flow rates from one formation to the next, and may contain a multitude of known and unknown chemicals used within fracturing fluids [4,5,6,7]. Hydraulic fracturing across different formations can produce wastewater with markedly different water quality characteristics, specifically total dissolved solids (TDS) levels (Marcellus Shale $\sim 180 \text{ g L}^{-1}$, Barnett $\sim 60 \text{ g L}^{-1}$, to Denver-Julesburg $\sim 35 \text{ g L}^{-1}$; [8,9]). High TDS levels can negatively impact several treatment technologies, like biological processes, and can also be higher than brines used in some osmotic methods [10,11,12]. Formational differences and their impacts on treatment are also magnified by water quantity (ratio of water-to-oil) and flow-rates (which decline

over the life of a well), since these can change how one might handle or treat the wastewaters. Further complicating the treatment of these waters is the use of various chemicals within the fracturing fluids, which are either toxic (2-butoxyethanol, ethylene glycol, etc.) or inhibit microorganisms (biocides e.g., glutaraldehyde), presenting issues for biological treatment approaches [13,14]. The problems presented by the existence of these chemicals, along with the high TDS levels, is further compounded by high levels of total organic carbon, which create issues for certain membrane processes (e.g., fouling; [15]) and ultimate reuse. As a result of these factors, methods for the treatment and reuse of flowback and produced waters are not well established.

The removal of the total suspended solids (TSS), dissolved organic carbon (DOC), and TDS can be challenging and expensive. However, the removal of all three of these components may not be needed for certain end uses of the water, instead being required only for agricultural uses and environmental discharge. With hydraulic fracturing only expected to increase in the coming years, well-to-well reuse could be a means at reducing the water needs of the industry. Targeted treatments that aim to remove specific contaminants, TSS, or just organics might be used as a cost-effective strategy to improve water reuse and bring down water associated costs in the industry. Coagulation-based treatments for the removal of TSS, colloidal particles, and some DOC are one such option.

Coagulation-based treatments are widely implemented within both classical wastewater and industrial treatment processes, as they are a steadfast and proven method for reducing

suspended and colloidal particles [16,17]. Chemical coagulation-flocculation involves the addition of chemicals to change the physical state of suspended and dissolved particles in order to aid their removal through settling and filtration [18]. There are an array of coagulants used to accelerate sedimentation, with their effectiveness being dependent upon the coagulant type, coagulant dose, mixing conditions, pH, alkalinity, ionic strength, and temperature [16,18,19,20]. Coagulation-flocculation practices have been applied for various industrial wastewaters. Notably, they have been used successfully to treat landfill leachates, which can have similar water quality characteristics to hydraulic fracturing wastewaters, such as high TSS, DOC, and TDS [21]. Therefore, applying coagulation-flocculation practices to hydraulic fracturing wastewaters could provide the solids removal needed for the reuse of these waters from well-to-well, if suspended solids removal was the only target for reuse.

During coagulation-flocculation processes, further treatment can be achieved by the addition of an adsorbent such as activated carbon. Activated carbon is the most frequently used adsorbent in the treatment of water, landfill leachates, municipal and industrial wastewater, due to its ability to adsorb a wide array of organic contaminants, as well as its associated costs [22]. It has also been shown to be effective in the removal of hydrocarbons from hypersaline salt waters [23]. Activated carbon has also been used in the removal of surfactants, which are frequently found within hydraulic fracturing wastewaters [24]. Powder activated carbon (PAC), a finely ground activated carbon, has been shown to be an effective adsorbent and is frequently used during coagulation-flocculation processes. The ability of PAC to remove contaminants from high-strength

wastewaters [19] illustrates the potential for PAC to potentially remove organic contaminants from hydraulic fracturing wastewaters.

The objective of this study was to evaluate the ability of coagulation-flocculation coupled with PAC to remove suspended solids (turbidity), DOC, total petroleum hydrocarbons (TPH), and polyethylene glycols (PEG) within different produced and flowback waters. Turbidity and DOC were chosen as general water quality indicators, while TPH is generally used for oil and gas (O&G) wastewater. In addition to these general indicators, the study identified PEGs as a unique hydraulic fracturing wastewater marker [26]. The output from this study was used to determine the following: 1) if PAC can remove PEGs and TPH in this high-strength wastewater; 2) if an increased dose of PAC would increase the removal of PEGs and TPH; and 3) if metal salts (coagulant) could reduce the turbidity of these wastewaters along with both PEGs and TPH in the absence and presence of PAC.

2. Methods

2.1. Water Characteristics

Four hydraulically fractured wastewaters from the Denver-Julesburg basin (Weld County, CO) were studied in this experiment. Three of the waters were from vertically fractured wells, while the fourth sample was from a horizontally fractured well. Vertically fractured well number one and two (VF1, VF2) were fractured over two years

ago, and the produced water samples were taken from the holding tanks onsite. The third site (VF3) was a vertical well that was recently re-fractured (120 days) prior to sample collection, and was also taken from the holding tank onsite. The last water tested was from a horizontally fractured well that was flowed back less than 30 days prior to sampling (HF). The HF water sample was also taken from a holding tank on-site. All of the water samples were collected and stored at 4°C prior to treatment and analysis.

2.2. Experimental Procedure

A Phipps & Bird stirrer six paddle jar tester (Model 7700; Richmond, VA) was utilized for the coagulation-flocculation experiments. All jar tests were performed using 2 L jars filled with 1 L of raw produced water at room temperature ($22^{\circ}\text{C} \pm 2^{\circ}\text{C}$). Jar tests were performed with a rapid mix of 300 RPM for 1 minute, followed by a three-stage tapered flocculation period: first at 55 RPM for 10 minutes, second at 35 RPM for 10 minutes, and third at 15 RPM for 10 minutes. Each jar was then allowed to settle for 30 minutes. Upon conclusion of settling, samples were immediately collected from the middle of the jar (two inches below the water surface) for analysis.

The first jar test utilized six different concentrations of PAC (WPH, Calgon Corp.; PA, USA)—50, 150, 300, 500, 750, and 1000 mg L⁻¹—to determine the ability of the PAC to remove TPH and PEGs. The PAC dose that achieved at least a 90% reduction of TPHs and PEGs was utilized for the second set of jar tests that included coagulant addition. In the event that 90% reductions were not achieved, 1000 mg L⁻¹ of PAC was used. Ferric

chloride (FeCl_3 ; Fisher Scientific) and aluminum chlorohydrate (ACH; Spectrum Chemicals) were the metal salts used, and were prepared each week of the study. Coagulants were added simultaneously (second set of jar tests) with the chosen PAC dose (VF1, 1000 mg L^{-1} ; VF2, 750 mg L^{-1} ; VF3, 1000 mg L^{-1} ; and HF, 1000 mg L^{-1}) at nine different concentrations (5, 15, 30, 45, 60, 90, 120, 240, and 500 mg L^{-1}). The lowest coagulant dose that achieved a 90% reduction in turbidity for each water sample was determined, and used for the third set of jar tests, looking at coagulant performance in the absence of PAC (VF1, $5 \text{ mg L}^{-1} \text{ FeCl}_3$; VF2, $5 \text{ mg L}^{-1} \text{ FeCl}_3$; VF3, $500 \text{ mg L}^{-1} \text{ ACH}$; and HF, $45 \text{ mg L}^{-1} \text{ FeCl}_3$).

2.3. Analytical Methods

Dissolved organic carbon (DOC) was determined by filtering samples through a 25 mm $0.45 \mu\text{m}$ nylon filter (VWR Int.; PA, USA), followed by dilution and analyses using a TOC-V_{SCH} analyzer (Schimadzu Corp., Japan). Turbidity was determined using a HACH 2100N Turbidimeter (Loveland, CO). Total dissolved solids (TDS), total suspended solids (TSS), and volatile suspended solids (VSS) were determined using standard methods [27]. Chemical oxygen demand (COD) was measured using HACH (Loveland, CO) COD kits and a DR5000 spectrophotometer, after dilution to avoid chloride interferences. Total alkalinity was determined using HACH method 8203. The analyses for inorganic ions and metals were done at the Laboratory for Environmental and Geological Studies (LEGS, Department of Geological Sciences, University of Colorado at Boulder, CO) using a Perkin Elmer SCIEX inductively coupled plasma mass

spectrometer (ICP-MS, Elan DRC-e), ion Chromatograph (Dionex Series 4500I), and an inductively coupled plasma optical emission spectrometry (ICP-OES; ARL 3410+, Thermo Scientific).

Total petroleum hydrocarbons (TPH) were extracted from 50 mL of hydraulic fracturing wastewater with 5 mL of methylene chloride in 60 mL vials. After methylene chloride addition, samples were manually inverted for 2 minutes, and then placed upon a mechanical shaker for 10 minutes at 300 RPM. The samples were then manually inverted for another 2 minutes, and then placed within a sonication bath for 5 minutes. Following sonication, the samples were allowed to settle for 5 minutes. The solvent layer was then extracted and passed through a glass wool and sodium sulfate filter to remove any remaining water, and the recovered solvent was then concentrated down to 2 ml (Turbovap LV; Uppsala, Sweden) and analyzed with an Agilent 7890a gas chromatograph using a flame ionization detector (GC-FID; Agilent Technologies, Santa Clara, California). The column used was a Restek Rxi-1ms model (20m, 0.18mm ID, 0.18 μ m). The GC was operated with a 4 μ L injection volume, carrier gas (helium) pressure of 14.505 psi, splitless flow of 10 ml min⁻¹, injector temperature of 275°C, detector (FID) temperature of 350°C. The ramp program was run at 40°C for 2 minutes followed by 20°C minute⁻¹ to 330°C and held for 20 minutes. TPH concentrations were determined as described by Lu et al. [28]. Extraction efficiency was verified for all samples using o-terphenyl and phenanthrene as internal standards, with recoveries ranging from 50-65% for both compounds.

Polyethylene glycols (PEGs) were determined using ultrahigh pressure liquid chromatography (1290 Agilent UHPLC; Agilent Technologies, CA) coupled with an ultra high definition quadrupole time-of-flight mass spectrometry (6540 Agilent Q/-TOF; Agilent Technologies, CA). The detailed method used can be found in Thurman et al. [26], and is summarized here. Samples were filtered through a surfactant-free 0.2 μm filter (Acrodisc), with 10 μL being injected onto a reverse phase C8 analytical column (Zorbax Eclipse XDB-C8). Mobile phase A was water with 0.1% formic acid, while mobile phase B was acetonitrile. The chromatographic method entailed, 5 minutes (10% B), followed by linear gradient to 100% B after 30 minutes, with a flow rate of 0.6 mL/min. Ions were generated using electrospray Jet Stream Technology, operating in positive ion mode. The data was processed using MassHunter software (version 6.1).

3. Results and Discussion

3.1. Water Characteristics

The four-wastewater samples tested exhibited chemical characteristics that varied from well-to-well, especially in regards to time since flowed back (i.e., well age; Table 1). All of the samples had a nearly neutral to slightly acidic pH along with similar metal concentrations for Si, K, and Ba. Otherwise, the samples had diverse chemical characteristics. HF had the highest TOC value (758 mg L^{-1}), followed by VF3, VF1, and VF2. TDS levels also varied widely, with VF1 and VF2 having levels greater than 40,000 mg L^{-1} , while VF3 (21,255 mg L^{-1}) and HF (24,700 mg L^{-1}) had roughly half the TDS

concentration. Other variables of note were alkalinity (decreased with well age), nitrate (not found in HF), and phosphate (only found in HF).

Well age clearly had a significant effect on levels of TOC, DOC, COD, TDS, alkalinity, and most of the inorganic ions and metals. Generally, the most recent well (HF, 30 days since flowback) had the highest levels of COD, TOC, DOC alkalinity, and turbidity, followed by VF3, VF1, and VF2. This trend, with regards to well age, was nearly reversed (VF2, VF1, HF, VF3) for TDS, TSS, and most inorganic ions and metals aside from PO_4^{-3} , SO_4^{-2} , barium, manganese, and iron. VF3 did not display this same trend, having the lowest TDS levels, as well as the lowest inorganic ions (except, SO_4^{-2}) and metals (Mn, Fe, K, Si) concentrations. This relationship between well age and the variables discussed above was likely due to the newer waters consisting of significant portions of fracturing fluid, resulting in higher TOC, DOC, and COD. In contrast, the older waters had minimal fracturing fluid present and were similar to what one might expect of formation water. Esmailirad et al. [29] had similar findings regarding water quality characteristics in their flowback and produced waters, which were sampled from different wells at different stages of production in Northeast, Colorado (2 to 183 days). Lastly, all four of the waters studied contained toxic heavy metals (Cr, Cu, Ni, etc.) often found within industrial waters, but at concentrations less than 1 mg L^{-1} , similar to the other Colorado-based hydraulic fracturing wastewater reported in the literature [30].

Table 1: Raw water characteristics of the four-wastewater samples investigated

Variable	HF	VF1	VF2	VF3
General Indicators				
pH	6.84	6.59	6.93	6.93
TDS (mg/L)	24700	41645	44520	21255
COD (mg/L)	2145	775	617.5	1545
TOC (mg/L)	758	164	117	412
DOC (mg/L)	680	118	47	313
Alkalinity (mg/L)	392	70	112	275
TSS (mg/L)	847.5	1140	1297.2	710
VSS (mg/L)	780	33.3	57.18	156.67
Turbidity (NTU)	322.5	118	126.5	140
TPH (mg/L)	8.76	16.9	12.2	20.1
Inorganic Ions				
PO ₄ (mg/L)	7.2	DL	DL	DL
SO ₄ (mg/L)	8.5	DL	DL	26.63
NO ₃ (mg/L)	DL	89.9	53.3	30.7
Chloride (mg/L)	17497	24955	27103	12724
Bromide (mg/L)	191.6	244.4	265.1	81.3
Metals				
Barium (mg/L)	41.39	41.07	31.55	14.15
Calcium (mg/L)	550	1081.4	1204.2	365.5
Magnesium (mg/L)	71.4	119.3	130	40.5
Strontium (mg/L)	78	179	202	47
Manganese (mg/L)	1.03	0.19	0.33	0.29
Iron (mg/L)	2.71	6	4.8	19
Potassium (mg/L)	51.6	75.9	65.4	52.9
Silicon (mg/L)	31.96	42	29	41
Sodium (mg/L)	10461	14215	14794	7472

DL: Detection Limit (PO₄ and SO₄, 0.05 mg/L)

3.2. PEGs

PACs ability to remove PEGs from hydraulic fracturing wastewater is illustrated in Figure 1. There is a clear dose response between PAC and PEG removal for both HF and VF3. As expected, the highest dose of PAC (1000 mg L⁻¹) achieved the greatest removals, with PEG10 removals of 99.6% and 71.7%, for HF and VF3 respectively (Figure 1). The removals of PEGs from the wastewaters were apparently the result of

adsorption to the activated carbon as demonstrated by ACH and FeCl_3 inability to remove PEGs (no reduction in peak area of PEGs or the total ion chromatogram), when performed in the absence of PAC.

These results were not anticipated because the adsorption of PEGs on activated carbon has been shown to be dependent upon pH, PEG molecular weight, and water quality [31]. Therefore, the water quality characteristics (high levels of organics and solids) of HF and VF3 were anticipated to severely inhibit the removal of PEGs. However, this was not seen, given the clear dose response between PAC and PEGs (Figure 1, insert) that demonstrates the previous finding of Gajdos et al. [32] that PEGs have a strong affinity for PAC.

PEGs are one of the most ubiquitous chemicals used in hydraulic fracturing [33], and have been suggested as a fingerprinting tracer for fracturing fluids [26]. Their universal presence was part of the rationale for this study focusing on PEGs as a fracturing fluid and flowback water constituent. It should also be noted that at 1000 mg L^{-1} of PAC, reduced the total ion chromatogram (TIC) by 86.3% and 82.5% for HF and VF3, respectively (Figure 1). This demonstrates the ability of PAC to remove PEGs and other water soluble organic compounds from this high strength wastewater. This is especially important since the removal of PEGs through biological processes (biodegradation) decreases with increasing molecular weight [34]. This, coupled with recent findings on anti-estrogenic activity of ethylene glycols (the monomers of PEGs), further illustrates

the need to remove both PEGs and their monomer from these high strength wastewaters [25].

[Figure 1 Goes here]

3.3. Total Petroleum Hydrocarbons (TPH)

Powdered activated carbon has been shown to readily adsorb hydrocarbons [36]. However, given the hydraulic fracturing wastewater quality, inhibition of the hydrocarbon sorption to the PAC was anticipated due to competition for active sites from other organics present in the wastewater. However, this was not observed and the dose response for TPH was similar to the PEGs, with an increased dose of PAC resulting in an increased TPH removal for VF1, VF2, and HF (Figure 2). These three wastewaters all exhibited greater than 90% removal of TPH (VF1, 93%; VF2, 93%; and HF, 96%), while VF3 only achieved a 43% removal (20.1 mg L⁻¹ of TPH to 11.4 mg L⁻¹). Increasing the PAC dose for VF3 above 500 mg L⁻¹ did not yield a greater reduction in TPH (illustrated in Figure 2), suggesting the remaining 11.4 mg L⁻¹ were associated with colloidal and suspended particles. This appears to be confirmed for VF3, since the coagulation alone jar tests yielded a 10.9 mg L⁻¹ (55% removal) reduction in TPH, while the combined (PAC and coagulant) resulted in a residual of 1.67 mg L⁻¹ TPH (92% removal). In the other waters, the coagulant alone was able to achieve 82%, 85% and 81% reduction for VF1, VF2 and HF waters, respectively. This is likely the result of the TPH forming micro-emulsions, which through coagulation can be removed from the water sample. The

PAC and coagulant together yielded 99%, 96%, and 99% removals for VF1, VF2, and HF, respectively. These results suggest that TPH is highly associated with suspended and colloidal particles, and that much of TPH found in these hydraulic fracturing wastewater could be removed by coagulation alone.

[Figure 2 goes here]

3.4. Turbidity

The turbidity results for PAC alone and the subsequent coagulation results are summarized in Figure 3. The first set of jar tests used PAC alone which did reduce the turbidity from the raw waters as illustrated in Figure 3, with resulting turbidity values of 38, 38, 128, and 180 NTU for VF1 (1000 mg L⁻¹ PAC), VF2 (750 mg L⁻¹ PAC), VF3 (1000 mg L⁻¹ PAC), and HF (1000 mg L⁻¹ PAC), respectively. However, the PAC would not settle in our 30 minute settling time, without the aid of a coagulant, even at 1 g L⁻¹ of PAC.

The turbidity levels achieved by coagulant addition in combination with PAC are illustrated in Figure 3. VF1, VF2, and HF data indicate classic coagulant dose versus turbidity plots. VF1 and VF2 both saw a 90% reduction in turbidity with a dose of 5 mg L⁻¹ FeCl₃ in conjunction with 1000 mg L⁻¹ of PAC for VF1 and 750 mg L⁻¹ for VF2, while it took a dose of 15 mg L⁻¹ of ACH to achieve a similar turbidity level for both VF1 and VF2. HF attained a 90% reduction of turbidity with a dose of 5 mg L⁻¹ of both FeCl₃ (24.5 NTU) and ACH (40.9 NTU) in combination with 1000 mg L⁻¹ of PAC. However,

FeCl₃ addition resulted in a considerably lower turbidity value of 5 NTU with a dose of 45 mg L⁻¹ of FeCl₃. VF3 was the only water that did not see a 90% reduction in turbidity until a dose of 500 mg L⁻¹ of ACH. This turbidity reduction is likely the result of colloidal particles becoming entrapped by sweep floc. This phenomenon occurs when concentrations of FeCl₃ and ACH reach levels that precipitate metal hydroxides that enmesh the colloidal particles, resulting in reductions of turbidity but significant amounts of sludge [36]. It should also be noted that there was almost no pH change for the optimal coagulant dose in VF1, VF2, and HF (high alkalinity levels), while VF3 at 500 mg L⁻¹ dropped 1.2 pH units to 5.8.

The low doses required for VF1, VF2, and HF could be the result of these waters' ionic strength (VF1, 0.791 M; VF2, 0.745 M; HF, 0.522 M; VF3, 0.381 M), as increased ionic strength is known to compress the electrical double layer and to positively influence floc formation [36]. The low optimum coagulant doses could also result from high concentrations of divalent cations in these waters (Ca²⁺ and Mg²⁺; Table 1), which impact resulting chemical bond interactions and their saturation, leaving an excess of cations and other counter ions to aid in electrical double layer compression [37]. The ionic strength of VF3 (0.381 M) was the lowest of the three waters, and also had the fewest divalent cations, which could partially explain its inability to form flocs below 240 mg L⁻¹ for either coagulant.

FeCl₃ was able to achieve the greatest reductions with the lowest doses for three of the four waters tested: VF1, VF2, and HF. VF3 was the exception, with ACH achieving the

lowest turbidity level compared to FeCl_3 . These results demonstrate the ability of both ACH and FeCl_3 to coagulate hydraulic fracturing wastewaters. However, when choosing a coagulant, another variable to consider is its solubility and how it might impact downstream processes. In that regard, aluminum based coagulants have a relatively high solubility compared to iron, and so aluminum can remain in solution and potentially affect downstream processes (e.g., perceptive scaling) [20]. Thus, iron-based coagulant was more efficient for reducing turbidity in three of the waters investigated.

[Figure 3 goes here]

3.5. Dissolved Organic Carbon

There was a clear dose response between PAC and the removal of DOC in the PAC-only experiment. The total DOC removed from 1000 mg L^{-1} of PAC was 23.3%, 9.5%, and 14.6% for VF1, VF3, and HF, respectively. 750 mg L^{-1} of PAC removed 48.3% of the DOC for VF2. Interestingly, the total DOC removed by PAC was similar for all the vertically fractured wastewaters (~28 mg/L removed). In the case of HF, which had the greatest total amount of DOC removed, 99.2 mg L^{-1} by 1000 mg L^{-1} of PAC, this accounted for only 14.6% of the total DOC within the sample.

These total DOC removals in the PAC only experiments illustrate the paucity that TPH and PEGs make up of the total fraction of DOC within VF1, VF3, and HF. Since these waters are field samples, it would be challenging to determine exactly the specific DOC

fractions that were removed. TPH accounted for half of the DOC removed for both VF1 and VF2 by PAC. TPH removal by 1000 mg L⁻¹ of PAC for VF3 accounted for a third of the total DOC removed, while only a tenth of the DOC from HF appears to be the result of TPH removal. This illustrates the affinity of TPH for the PAC used, while also illustrating the small fraction that TPH makes up of the total DOC within three out of the four waters. These results highlight the need to further characterize the organic constituents of hydraulic fracturing wastewaters. The LC-MS TIC was reduced more than 80% for both HF and VF3 in addition to TPH being reduced more than 90% for both HF and VF3 (combined coagulation-adsorption), yet the total DOC was only reduced by 9.5% (VF3) and 14.6% (HF). This remaining fraction for HF (85.4%) and VF3 (90.5%) requires further investigation, to help target treatments and better characterize these high strength wastewaters.

4. Conclusion

The variability of water quality between the wastewaters studied illustrates the substantial differences between hydraulic fracturing wastewaters from different wells and their ages, even when those wells are in the same formation. This study demonstrated the ability of PAC to remove both PEGs and TPH from hydraulic fracturing wastewaters. As expected, an increased dose of PAC resulted in an increase of PEG removal for the waters tested, and the same trend existed for TPH removal with three of the four waters tested. The exception was VF3, which had a maximal removal of 43% of TPH at a dose of 500 mg L⁻¹, with increasing dose not yielding increased removal. However, the majority of the

remaining fraction of TPH in VF3 was bound to the particulates, since the combination of both PAC and coagulant resulted in a 92% TPH removal. The association of TPH with suspended and colloidal particles was further illustrated by the coagulant only jar tests, which had more than 80% of the TPH removed by coagulation alone (for VF1, VF2, and HF), suggesting that the majority of TPH is associated with the suspended and colloidal particles. Turbidity results illustrate the low coagulant doses required for 90% reduction in turbidity for VF1, VF2, and HF (5 mg L^{-1} of FeCl_3), while VF3 required nearly 500 mg L^{-1} of either coagulant to achieve significant turbidity reductions. These differences in floc formation and turbidity reduction could be the result of the wastewaters ionic strengths and the ability of ionic strength to compress the electric double layer, thereby reducing the coagulant dose needed to achieve a 90% reduction in turbidity. This study's results (lower FeCl_3 doses needed for 90% reduction in turbidity), along with solubility concerns of aluminum based coagulants on downstream processes, would suggest that FeCl_3 might be the desired coagulant (of the two) for coagulation-flocculation of hydraulic fracturing wastewaters. The study shows that low doses of either coagulant are able to remove greater than 90% of the turbidity, illustrating the potential of chemical coagulants for turbidity and TPH removal. However, it should be noted, that the dose of PAC required for 90% removal of TPH and PEGs (1000 mg L^{-1}) could be cost prohibitive of this combined process. If PAC costs were potentially reduced through the use of biochar or other low cost alternatives, it would be more plausible to incorporate PAC for the removal of both PEGs and TPH.

Acknowledgments

This work was supported by the AirWaterGas Sustainability Research Network, and was funded by the National Science Foundation under Grant No. CBET-1240584. Opinions, findings, recommendations, and conclusions conveyed in this paper are those of the author(s) and do not necessarily reflect the views of the National Science Foundation. The authors would like to thank Dr. R. Scott Summers and Dr. Tzahi Cath for their technical support, and Kelsey Bennett and Ian Morrissey for their laboratory assistance. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

References

- 1) US Environmental Protection Agency. 2010. Hydraulic Fracturing Research Study. <http://epa.gov/tp/pdf/hydraulic-fracturing-fact-sheet.pdf>
- 2) Malakoff, D. (2014). The gas surge. *Science*, 344, 1464.
doi:10.1126/science.344.6191.1464
- 3) Dahlen E. (2013). Hydraulic Fracturing – Managing the Risk of Produced Water. *Journal of Environmental Hydrology*, 21, 4.
- 4) Gregory, K. B., Vidic, R. D., & Dzombak, D. A. (2011). Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing. *Elements*. doi:10.2113/gselements.7.3.181
- 5) Arthur, A. J. D., Consulting, A. L. L., Bohm, B., Layne, M., & Ph, D. (2008). Hydraulic Fracturing Considerations for Natural Gas Wells of the Marcellus Shale. *Environmental Protection*, 1–19.
<http://www.thefriendsvillegroup.com/HydraulicFracturingReport1.2008.pdf>

- 6) Barbot, E., Vidic, N. S., Gregory, K. B., & Vidic, R. D. (2013). Spatial and temporal correlation of water quality parameters of produced waters from Devonian-age shale following hydraulic fracturing. *Environmental Science and Technology*, 47, 2562–2569.
- 7) Ferrer I. and Thurman E. M. Chemical constituents and analytical approaches for hydraulic fracturing waters. *Trends in Environmental Analytical Chemistry*, 2015, 18-25
- 8) Vengosh A., Jackson R.B., Warner N., Darrah T.H., Kondash A. 2014. A Critical Review of the Risks to Water Resources from Unconventional Shale Gas Development and Hydraulic Fracturing in the United States. *Environmental Science and Technology*,
- 9) Osborn, S.G.; McIntosh, J.C.; Hanor, J.S; Biddulph, D. Iodine-129 $^{87}\text{Sr}/^{86}\text{Sr}$, and trace element geochemistry of Northern Appalachian Basin brines; Evidence for basinal-scale fluid migration and clay mineral diagenesis. *Am. J. Sci.* 2012, 312, 263-287.
- 10) Lester Y., Yacob T., Mossissey I., Linden K. Can we Treat Hydraulic Fracturing Flowback with a Conventional Biological Process? The Case of Guar Gum. *Environ. Sci. Technol. Lett.*, 2014, 1 (1), pp 133-136
- 11) Lefebvre, O., Habouzit, F., Bru, V., Delgenes, J. P., Godon, J. J., & Moletta, R. (2004). Treatment of hypersaline industrial wastewater by a microbial consortium in a sequencing batch reactor. *Environmental Technology*, 25, 543–553. doi:10.1080/09593330.2004.9619345

- 12) Altaee A. and Hilal N. (2014). Dual-stage forward osmosis/pressure retarded osmosis process for hypersaline solutions and fracking wastewater treatment. *Desalination* 350, 79-85.
- 13) Rogers, J. D., Burke, T. L., Osborn, S. G., & Ryan, J. N. (2015). A framework for identifying organic compounds of concern in hydraulic fracturing fluids based on mobility and persistence in groundwater. *Environmental Science & Technology Letters*.
- 14) Stringfellow, William T., et al. "Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing." *Journal of hazardous materials* 275 (2014): 37-54.
- 15) Pandey S., Jegatheesan V., Baskaran K., Shu L. (2012). Fouling in reverse osmosis (RO) membrane in water recovery from secondary effluent: a review, *Reviews in Environmental Science and Biotechnology* 11 (2012) 125-145.
- 16) Alexander, Jonathan T., Faisal I. Hai, and Turki M. Al-aboud. "Chemical coagulation-based processes for trace organic contaminant removal: Current state and future potential." *Journal of environmental management* 111 (2012): 195-207.
- 17) Wang, Yufeng, et al. "Optimization of coagulation–flocculation process for papermaking-reconstituted tobacco slice wastewater treatment using response surface methodology." *Journal of Industrial and Engineering Chemistry* 20.2 (2014): 391-396.
- 18) Duan, Jinming, and John Gregory. "Coagulation by hydrolysing metal salts." *Advances in colloid and interface science* 100 (2003): 475-502.

- 19) Mahtab A., Tariq M., Shafiq T., Nasir A. Coagulation/adsorption combined treatment of slaughterhouse wastewater. *Desalination and Water Treatment*, 12: 1-3. 270-275
- 20) Edzwald J.K. and Haarhoff J. (2011). Seawater pretreatment for reverse osmosis: Chemistry, contaminants, and coagulation. *Water Research*, 45, 5428-5440.
- 21) Mukherjee S., Mukhopadhyay S., Hashim M.H, Gupta B.S. (2015) Contemporary Environmental Issues of Landfill Leachate: Assessment and Remedies, *Critical Reviews in Environmental Science and Technology*, 45:5, 472-590
- 22) Zhang W., Yang X., Wang D. (2013) Complete Removal of Organic Contaminants from Hypersaline Wastewater by the Integrated Process of Powder Activated Carbon Adsorption and Thermal Fenton Oxidation. *Ind. Eng. Chem. Res*, 52, 5765-5771.
- 23) Karapanagiotic H.K. Removal of phenanthrene from saltwater solutions using activated carbon. *Desalination* 210 (2007), 274-280
- 24) Wu, S. H. and Pendleton, P., (2001) “Adsorption of Anionic Surfactant by Activated Carbon: Effect of Surface Chemistry, Ionic Strength, and Hydrophobicity, *J. of Colloid and Interface Science*, 243, 306
- 25) Kassotis, C. D., Tillitt, D. E., Davis, J. W., Hormann, A. M., & Nagel, S. C. (2014). Estrogen and androgen receptor activities of hydraulic fracturing chemicals and surface and ground water in a drilling-dense region. *Endocrinology*, 155, 897–907. doi:10.1210/en.2013-1697

- 26) Thurman E.M., Ferrer I., Blotvogel J., Borch T. (2014). Analysis of Hydraulic Fracturing Flowback and Produced Waters Using Accurate Mass: Identification of Ethoxylated Surfactants. *Analytical Chemistry*, 84, 9653-9661
- 27) APHA, AWWA, & WEF. (1999). *Standard Methods for the Examination of Water and Wastewater. Standard Methods for the Examination of Water and Wastewater* (p. 1496).
- 28) Lu, L., Yazdi, H., Jin, S., Zuo, Y., Fallgren, P. H., & Ren, Z. J. (2014). Enhanced bioremediation of hydrocarbon-contaminated soil using pilot-scale bioelectrochemical systems. *Journal of Hazardous Materials*, 274, 8–15. doi:10.1016/j.jhazmat.2014.03.060
- 29) Esmaeilirad N., Carlson K., Ozbek P.O. Influence of softening sequencing on electrocoagulation treatment of produced water (2015). *Journal of Hazardous Materials*, 721-729
- 30) Lester Y., Ferrer I., Thruman E.M., Sitterley K., Korak J.A., Aiken G., Linden K.G. (2015). Characterization of hydraulic fracturing flowback water in Colorado: Implications for water treatment. *Science of the Total Environment*, 512-513, 637- 644
- 31) Pietrelli, Loris. "Effect of MW and pH on poly (ethylene glycol) adsorption onto carbon." *Adsorption* 19.5 (2013): 897-902.
- 32) Gajdos, L., Pietrelli, L., Ciccarello, A., Derco, J.: Elimination of polyethylene glycol from aqueous solution using activated carbon. *Polish J. Environ. Stud.* 16, 385–388 (2007)
- 33) United States House of Representatives Committee On Energy And Commerce,

535 Minority Staff, April 2011 Chemicals Used In Hydraulic Fracturing.
 536 [http://democrats.energycommerce.house.gov/sites/default/files/documents/Hydraulic](http://democrats.energycommerce.house.gov/sites/default/files/documents/Hydraulic%20Fracturing%20Report%204.18.11.pdf)
 537 [lic%20Fracturing%20Report%204.18.11.pdf](http://democrats.energycommerce.house.gov/sites/default/files/documents/Hydraulic%20Fracturing%20Report%204.18.11.pdf)
 538 34) Watson, G.K., Jones, N. (1976) The biodegradation of polyethylene glycol by
 539 sewage bacteria. *Water Res.* 11, 95–100
 540 35) Ayotamuno, M. J., Kogbara, R. B., Ogaji, S. O. T., & Probert, S. D. (2006).
 541 Petroleum contaminated ground-water: Remediation using activated carbon.
 542 *Applied Energy*. doi:10.1016/j.apenergy.2006.01.004
 543 36) Metcalf, E., & Eddy, H. (2003). *Wastewater engineering: treatment and reuse*.
 544 *McGraw-Hill Publishing Company Limited, 4th edition*.
 545 37) Duan J., Niu A., Shi D., Wilson F., Graham N.J.D. (2009). Factors affecting the
 546 coagulation of seawater by ferric chloride. *Desalination and Water Treatment*
 547 11:1-3, 173-183
 548
 549

Figure Titles

Figure 1: Total ion chromatogram for raw HF (black), HF treated with 300 mg L⁻¹ PAC (green), and HF treated with 1000 mg L⁻¹ of PAC (red). PEG10 accurate mass (m/z) for the ammonium adduct is presented. Insert: Dose response curve for PEG10 peak area versus PAC.

Figure 2: Dose response of TPH as a function of PAC concentration for the four hydraulic fracturing wastewaters investigated

Figure 3: Turbidity results for each water following treatment conditions of: PAC dose alone (VF1, 1000 mg L⁻¹; VF2, 750 mg L⁻¹; VF3, 1000 mg L⁻¹; and HF, 1000 mg L⁻¹), optimized coagulant dose alone, and both coagulants from 5 to 500 mg L⁻¹ with each water's optimized PAC dose (combined jar test).

Figure 1

Figure 2

Figure 3

Treated
Flowback Wastewater

Raw
Flowback Wastewater

Coagulation-Adsorption
Treatment
for
Well-to-Well
Reuse