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Removal of organic compounds from shale gas flowback water

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ABSTRACT

Ozonation, sorption to granular activated carbon and aerobic degradation were compared as potential treatment methods for removal of dissolved organic carbon (DOC) fractions and selected organic compounds from shale gas flowback water after pre-treatment in dissolved air flotation unit. Flowback water was characterised by high chemical oxygen demand and DOC. Low molecular weight (LMW) acids and neutral compounds were the most abundant organic fractions, corresponding to 47% and 35% of DOC respectively. Ozonation did not change distribution of organic carbon fractions and concentrations of detected individual organic compounds significantly. Sorption to activated carbon targeted removal of individual organic compounds with molecular weight >115 Da, whereas LMW compounds remained largely unaffected. Aerobic degradation was responsible for removal of LMW compounds and partial ammonium removal, whereas formation of intermediates with molecular weight of 200–350 Da was observed. Combination of aerobic degradation for LMW organics removal with adsorption to activated carbon for removal of non-biodegradable organics is proposed to be implemented between pre-treatment (dissolved air floatation) and desalination (thermal or membrane desalination) steps.

1. Introduction

The negative impact on the quality of surface and ground water is one of the major environmental consequences of shale gas production (Brantley et al., 2014; Ferrar et al., 2013; Jackson et al., 2013; Osborn et al., 2011; Vidic et al., 2013). Shale gas producers use a combination of horizontal drilling and hydraulic fracturing to recover gas from formations. Hydraulic fracturing implies high pressure well injection of large volumes of water mixed with inert solid material (proppant) and chemical additives. This mixture, called fracturing fluid, creates fissures in the shale increasing its permeability and gas recovery. The mixture of the injected fracturing fluid together with the connate water of the formation, which returns to the surface within few weeks after pressure being released, is called flowback water (Olmstead et al., 2013). The connate water of the formation, which continues flowing upwards for years after fracturing has been completed, is called produced water (Vidic et al., 2013).

Both flowback and produced waters (FPW) are contaminated with high concentrations of total dissolved solids (TDS), oil and grease, natural radioactive materials (NORM), and dissolved organic matter (DOM) (Gregory et al., 2011). Injection into disposal wells was the most widely used shale gas wastewater management strategy until 2010 (EPA, 2016; Rahm et al., 2013). However, the limited availability of disposal wells, increased uncertainties about risks related to deep well injection, and legislative constrains make the industry turn towards reuse and discharge of FPW (Gregory et al., 2011; Mauter et al., 2014; Rahm et al., 2013; Silva et al., 2017). Removal of contaminants is required before FPW can be discharged. FPW reuse also requires removal of certain compounds, e.g. potential scalants and foulants. Treatment technologies typically include separation for removal of total suspended solids (TSS), oil and grease, adsorption for removal of organics, NORM and heavy metals, membrane or thermal desalination for TDS removal (Drioli et al., 2015; Igunnu and Chen, 2014; Jiménez et al., 2018; Saba, 2014). Desalination is a crucial step in the FPW treatment, because of the high TDS concentrations that often equal or exceed sea water salinity (Shaffer et al., 2013). Membrane and thermal

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desalination technologies for oil and gas produced water are well established and can remove TDS and majority of contaminants mentioned above (Abousnina et al., 2015; Fakhru'l-Razi et al., 2009). However, concentrations of organic carbon in shale gas FPW often exceed 1000 mg/L, causing fouling on the membranes and distillation equipment (Alzahrani and Mohammad, 2014; Chen et al., 2015; Thiel and Lienhard, 2014). In addition, desalination technologies are effective towards high molecular weight polar compounds, such as polycyclic aromatic hydrocarbons (PAHs), but poorly remove low molecular weight non-polar organics, that may also pose threats to the environment and human health (Annevelink et al., 2016; Butkovskyi et al., 2017; Ferrar et al., 2013; Shaffer et al., 2013). Despite that only few studies attempt to characterize the nature of organic compounds in FPW and evaluate potential treatment strategies for their removal (Butkovskyi et al., 2017; Camarillo et al., 2016).

Components of the fracturing fluid, including heterocyclic biocides, cocamidopropyl surfactants, ethylene glycol and derivatives, as well as natural constituents of shale, including aliphatic and aromatic hydrocarbons, alkanes, resins, asphaltenes, heterocyclic and halogenated organics were detected in FPW from U.S. shale basins using gas and liquid chromatography coupled to mass spectrometry (GC-MS and LC-MS) (Annevelink et al., 2016; Butkovskyi et al., 2017; Ferrar et al., 2013; Hayes, 2009; Lester et al., 2015; Maguire-Boyle and Barron, 2014; Orem et al., 2014). Lester et al. (2015) reported low removal of DOM from shale gas flowback water by advanced oxidation, whereas aerobic treatment removed >50% of DOM at flowback water TDS of 22.5 g/L. Other authors demonstrated that microbial mats are capable to decrease COD at TDS as high as 100 g/L (Akyon et al., 2015). Neither the fate of different DOM fractions nor the removal of individual organic compounds were studied in these works, moreover, Akyon et al. (2015) did their experiments with synthetic flowback water. Several authors reported high biodegradability of fracturing fluid components, including poly(ethylene glycol) surfactants and biocide glutaraldehyde (Kekacs et al., 2015; McLaughlin et al., 2016; Mouser et al., 2016). However, the degradation of compounds was studied in fracturing fluids, which composition is very different from FPW. High potential of granular activated carbon (GAC) for adsorption of fracturing fluid chemicals furfural and 2-butoxyethanol and powdered activated carbon (PAC) for adsorption of polyethylene glycols was also shown (Manz et al., 2016; Rosenblum et al., 2016). So far these are the only two studies focused on application of activated carbon for removal of organic chemicals from flowback water.

This paper aims to assess the removal of different fractions of dissolved organic carbon and individual organic compounds present in flowback water using typical primary treatment process (dissolved air flotation) followed by one of the common processes for organics removal (ozonation, adsorption to activated carbon or aerobic degradation). Flowback water is studied because, in comparison to produced water, this stream has typically high concentrations of organic carbon and contains potentially harmful components of fracturing fluids. The most promising treatment strategy for organic compounds removal is proposed and its integration with existing treatment processes is discussed.

2. Materials and methods

The shale gas flowback water was obtained from a Baltic shale gas basin (Poland) under non-disclosure agreement regarding location, storage conditions and composition of the fracturing fluid used at the production site. The water was sampled within two months after commencement of the first fracturing operation. It was transported in 20 L plastic containers and stored at 4 °C until the experiments. The flowback water was pre-treated in a dissolved air flotation (DAF) unit assisted by coagulation in order to remove TSS, oil and grease. DAF-treated flowback water was used for ozonation, adsorption to GAC and aerobic degradation experiments.

2.1. Experimental set-up

2.1.1. Dissolved air flotation/coagulation

Flowback water ($V = 80$ L) was treated by $FeCl_3$-assisted DAF in a stainless steel tank ($V = 200$ L). $FeCl_3$ (100 mg Fe/L) was added as a coagulant and pH was adjusted to 8.0 by addition of NaOH (0.5 g/L) (Megid et al., 2014). Flocculation was observed within 40 min and 3 L of water saturated with air was released to the stainless steel vessel from the adjacent pressurized tank ($p = 5$ bar). Flotation contact time was 10 min. DAF-treated flowback water ($V \approx 63$ L) was collected excluding precipitate and scum ($V \approx 20$ L) and stored at 4 °C until ozonation, GAC sorption and aerobic degradation tests were performed.

2.1.2. Ozonation

Ozonation was performed in batch mode in a glass vessel ($V_{liquid} = 2$ L) with ozone supplied through a bubble diffuser during 60 min. Ozone was produced from pure oxygen using a Fischer 503 ozone generator. The gas flow was maintained at 0.1 m^3/h, and the ozone concentration in the reactor inlet at 6.3 g/m^3. Ozone concentrations in the gas phase of the reactor inlet and outlet were measured by BMT ozone analyser 961TC and 961, respectively.

An ozone dosage of 0.3 g/L was applied to DAF-treated flowback water. Additionally, control tests with air supplied instead of ozone at the same flow rate were run to correct for volatilization. To correct for ozone losses in the system, a blank test with milliQ was run until stabilization of ozone concentrations in the reactor inlet (≈ 6.0 g/m^3) and outlet (≈ 5.5 g/m^3) has been reached. The ozone losses were taken into account when calculating ozone consumption of the flowback water. Liquid samples were filtrated through 0.45 µm pore size filters directly after the test and stored at −20 °C until the analyses.

2.1.3. Sorption to GAC

Sorption tests were performed with DAF-treated flowback water and three different types of GAC. Granular types of activated carbon were chosen because they are preferred to powdered by oil and gas industry due to lower carbon usage rates and operational costs (Arthur et al., 2005; Hackney and Wiesner, 1996). The tests were performed in stirred glass vessels ($V_{liquid} = 1$ L) using three different fresh GAC types typically used in municipal and industrial wastewater treatment, Chemviron F400, Norit GAC 830W and Norit C GRAN (Table S1) and dosage of 2000 mg/L. The adsorption tests were run for 6 weeks at 20 °C to reach the equilibrium state. Liquid samples were filtrated through 0.45 µm pore size filters directly after the test and stored at −20 °C until the analyses.

2.1.4. Aerobic degradation

Batch aerobic degradation test was adapted from OECD method 301A (OECD, 1992). The test was performed in triplicate in 250 mL glass bottles holding a liquid volume of 120 mL and headspace volume of 130 mL. Activated sludge adapted to high salinities was obtained from a wastewater treatment plant (WWTP) at Delfzijl (the Netherlands) which treats industrial wastewater with high Cl^- concentrations (2–20 g Cl^-/L) (van der Marel and de Boks, 2014). The sludge (volatile suspended solids (VSS) = 3.5 g/L) was collected from the aerobic nitrification basin and stored at 4 °C until the experiment. Sludge liquor had low COD (170 mg/L), no ammonium nitrogen and comparatively high chloride concentrations