



Investigating the effects of heat activated persulfate on the degradation of furfural, a component of hydraulic fracturing fluid chemical additives



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HIGHLIGHTS

- Degraded furfural using persulfate activated through heat, acidic pH, and iron.
- Furfural removal achieved with hydraulic fracturing chemical additives present.
- Reaction by-products and potential degradation pathways identified.

ARTICLE INFO

Article history:

Received 22 March 2017
Received in revised form 16 June 2017
Accepted 28 June 2017
Available online 29 June 2017

Keywords:

Furfural
3-Furaldehyde
Heat-activated persulfate
Oxidation
Fe (III)
Hydraulic fracturing chemical additives
Breaking agents

ABSTRACT

Improper well casings and produced water handling can lead to hydraulic fracturing fluid migration and groundwater pollution. Interactions among the chemical components can cause compositional changes in hydraulic fracturing fluids. This study focuses on degradation or transformations of 3-furfuraldehyde (or furfural) by activated-persulfate oxidation, two chemicals reported in hydraulic fracturing additives. As hydraulic fracturing conditions may be conducive to persulfate activation, the degradation of furfural was examined using elevated temperatures, varying persulfate dosing and Fe (III) concentration, initial pH, and the presence of other chemical additives (e.g., a gelling agent and an enzyme breaking agent).

Experiments showed furfural degradation using activated persulfate followed pseudo-first order kinetics with respect to the furfural concentration. Impacts of pH and ferric sulfate concentrations were investigated at different temperatures and the results were fit to the Arrhenius model to establish the activation energy. Decreasing the pH to 2.54 caused an increase in the furfural removal. The addition of ferric sulfate to solutions with pH 5.4 had no impact on the activation energy of furfural oxidation, which was 107 kJ mol^{-1} , while decreasing the pH to 2.54 allowed for the activation energy to decrease to 75 kJ mol^{-1} . Quenching with methanol and tert-butyl alcohol indicated significant hydroxyl radical contributions to furfural degradation compared to sulfate radicals during thermal persulfate activation in the presence of iron and acidic conditions. Furthermore, furfural degradation was monitored in the presence of other hydraulic fracturing chemical additives establishing furfural degradation does not occur as rapidly. However, furfural does still degrade in this matrix and this indicates that persulfate may break down other chemicals in hydraulic fracturing fluids more preferentially than the target gelling agent.

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1. Introduction

Hydraulic fracturing, along with horizontal drilling, has permitted economical natural gas extraction from shale reserves [1,2]. The hydraulic fracturing process utilizes chemical additives, water,

and sand at high pressures to produce fractures in the shale and stimulate the recovery of natural gas [3,4]. The chemical additives have various purposes (e.g., friction reducers, biocides, gelling agents and breaking agents) and contain a myriad of chemical compounds that are environmental concerns including methanol, ethoxylated surfactants, and formaldehyde [5–7]. Much of the current hydraulic fracturing research focuses on identifying chemical components of hydraulic fracturing fluids [6,8–11]. In the U.S. Environmental Protection Agency's (EPA) 2015 "Draft Assessment

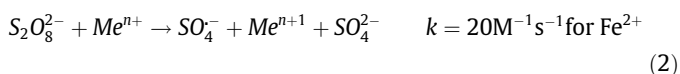
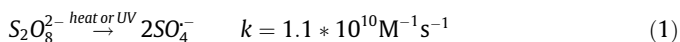
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of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources,” transformation processes are considered important to understanding how hydraulic fracturing can affect the environment [12,13]. Currently, little is known about chemical additive transformation in hydraulic fracturing. Only recently have researchers begun to study chemical additive and shale transformation in abiotic and biotic conditions [13,14]. These studies have shown that chemical transformations do occur under hydraulic fracturing conditions, potentially causing more harmful or persistent byproducts that pose severe human health and environmental risks. However, the use of strong oxidizers, such as sodium persulfate, have not yet been considered in the research shift to transformation studies. Oxidizers likely play a strong role in chemical additive transformation, especially if they react with other constituents rather than the gelling agent they were intended to target.

Hydraulic fracturing companies use sodium persulfate as a “delayed” breaking agent and are used to decompose the gelling agents [15]. Persulfate salts are also used for contaminated groundwater remediation through *in situ* chemical oxidation (ISCO) because they do not decay rapidly or harm native microorganisms [16]. Of the commercially available persulfate salts (ammonium, sodium, and potassium), sodium persulfate has the greatest solubility (73 g/100 g H₂O at 25 °C) and is the most stable at 25 °C, making it the most preferable for hydraulic fracturing companies [17]. While the concentration of sodium persulfate used in fracturing depends on the conditions of the formation, site location, and hydraulic fracturing, concentrations as low as 0.125 mmol L⁻¹ up to as much as 47 mmol L⁻¹ have been reported [18–20].

Persulfate possesses an oxidation potential (E⁰) of 2.01 V; however, once activated, it produces strong oxidizing sulfate radicals (E⁰ = 2.7 V) as seen in reactions 1, 2, and 3 [21–23]. Persulfate activation occurs through electron transfer from transition metals such as iron, cobalt, or manganese, as well as through the use of heat, ultraviolet (UV) light, acidic conditions, or a combination of these activators [16,23–27]. Persulfate activation has also been shown to occurring using the oxidized form, Meⁿ⁺¹, of the transition metals manganese and iron, as shown in Reaction (4) [28–30]. When Fe (III) is present, a persulfate radical and Fe (II) are generated. The Fe (II) produced may further react with persulfate anions as shown in Reaction (2), enabling further organic contaminant removal. Organic compounds may also participate in iron recycling, reducing Fe (III) to Fe (II) as shown in Reaction (5) [31].



The conditions faced in hydraulic fracturing provide an adequate environment for persulfate activation. Over the course of a fracture, downhole temperatures may exceed 140 °C [32]. Hydrochloric acid, one of the most common additives used in hydraulic fracturing [33], may influence the extent of persulfate reactions. Concentrations of hydrochloric acid used may range from 0.012% to 15% of the total water [34–37], but is reported as 0.07% by FracFocus.org [38–40]. The dissolved iron content in hydraulic fracturing fluids ranges between 0.1 and 222 mg L⁻¹, while total iron can range between 2.6 and 321 mg L⁻¹ [41]. A

previous study regarding the quality of flowback water determined the total iron content as 16 mg L⁻¹, while Fe²⁺ content was below the detection limits of the study (0.2 mg L⁻¹) [42]. This suggested that the predominant oxidation state of iron was either Fe (III) or Fe(0) for the flowback fluid samples from this study [42]. The presence of Fe (III) likely arises from the fluid’s interaction with shale rock, as shale contains various iron oxides (e.g., hematite (Fe₂O₃)) [43–46]. In addition, ferric sulfate has also been found in at least 7 different chemical products added by hydraulic fracturing companies [47]. The potential combination of persulfate activators and conditions present in hydraulic fracturing fluids of the shale formation may provide an environment for the breakdown of chemical additives other than the target gelling agent. Therefore, the objective of this research is to investigate the reaction of persulfate exposed to elevated temperatures, pH changes, and the chemical additives in hydraulic fracturing fluids and to determine if these conditions are conducive to persulfate transformation of organic contaminants in produced waters [3,6,32,47,48].

This study is to systematically determine how a hydraulic fracturing chemical additive interacts with persulfate in different conditions and ultimately investigate if persulfate preferentially attacks the additive or the target gelling agent. Furfural, or 3-furaldehyde, was identified as a contaminant of interest in the components of a hydraulic fracturing enzyme breaker and used to study hydraulic fracturing fluid interactions with sodium persulfate. In addition, furfural has also been used as a coating polymer for proppants in hydraulic fracturing fluids [47,49,50] because it is highly resistant to heat, acid, and water [51]. Furfural’s interactions with sodium persulfate are investigated in the presence of different activators which may be encountered during hydraulic fracturing and include heat (20 to 60 °C), ferric sulfate, and pH variations. Oxidation reaction by-products were determined using gas chromatography mass spectrometry (GC/MS). Finally, this study goes a step further by examining the impact other organic compounds have on furfural degradation when present in hydraulic fracturing fluids by comparing reaction kinetics when an enzyme breaking agent and a gelling agent are present in solution. Insight into the interactions between furfural and sodium persulfate enables the understanding of how the oxidizing breaking agent used in hydraulic fracturing fluids impact the quality and treatability of the flowback/produced water returning to the surface.

2. Materials and methods

2.1. Chemicals

All solutions were prepared using deionized water from a Milli-Q Plus water purification system (Darmstadt, Germany). Furfural was purchased from Sigma Aldrich (St. Louis, MO 63103). Optima grade hexane, methylene chloride, ethyl acetate, methanol, tert-butanol (TBA) and toluene were purchased from Fisher Scientific (Pittsburgh, PA 15275, USA). Inorganic salts, including sodium persulfate (>98%), sodium bicarbonate (>99%), and potassium iodide (>99%), were purchased from Fisher Scientific (Pittsburgh, PA 15275, USA). pH was adjusted with hydrochloric acid (35–38%) and sodium hydroxide (>97%), which were obtained from Fisher Scientific (Pittsburgh, PA 15275, USA). LEB-10X, an enzyme breaker, and WGA, a gelling agent, were obtained from Weatherford International (Houston, Texas, USA).

2.2. Experimental procedures

2.2.1. Batch heat-activated oxidation experiments

Furfural solutions were prepared 24 h prior to starting the experiment and mixed using a magnetic stir bar. The initial

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