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Adsorption of hydraulic fracturing fluid components 2-butoxyethanol and furfural onto granular activated carbon and shale rock

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HIGHLIGHTS

- 2-BE and furfural adsorption assessed for solutions with varying salt concentration.
- Various temperatures were evaluated to determine the isosteric heat of adsorption.
- Adsorption appeared to be endothermic in nature for solutions in DI water.

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ABSTRACT

The objective of this study was to understand the adsorption ability of a surfactant and a non-surfactant chemical additive used in hydraulic fracturing onto shale and GAC. Experiments were performed at varying temperatures and sodium chloride concentrations to establish these impacts on the adsorption of the furfural (a non-surfactant) and 2-Butoxyethanol (2-BE) (a surfactant). Experiments were carried out in continuously mixed batch experiments with Langmuir and Freundlich isotherm modeling. The results of the experiments showed that adsorption of these compounds onto shale does not occur, which may allow these compounds to return to the surface in flowback and produced waters. The adsorption potential for these chemicals onto GAC follows the assumptions of the Langmuir model more strongly than those of the Freundlich model. The results show uptake of furfural and 2-BE occurs within 23 h in the presence of DI water, 0.1 mol L^{-1} sodium chloride, and in lab synthesized hydraulic fracturing brine. Based on the data, 83% of the furfural and 62% of the 2-BE was adsorbed using GAC.

1. Introduction

Water reuse and recycling is a major issue surrounding the extraction of natural gas from shale rock formations via hydraulic fracturing. For each well fractured, hydraulic fracturing companies use two to ten million gallons of water (Boudet et al., 2014). According to Howarth et al., approximately 200,000 L of chemical additives are added to this water, making a chemical slurry (Howarth et al., 2011). Hydraulic fracturing fluids contain surfactants, acids, biocides, scale inhibitors, friction reducers, corrosion inhibitors, clay stabilizers, breaking agents, and iron controllers (FracFocus.org). Once a well is completed, a portion of the original injected volume returns to the surface as flowback and produced waters (Clark et al., 2012). Flowback and produced waters contain fluids naturally occurring in the shale formation, resulting in high TDS content ranging from 66,000 to 261,000 mg L^{-1} or more (Gregory et al., 2011).

Treating these waters is largely dependent on the chemical additives used in the fluids and their interactions with chosen treatment methods. Previously, hydraulic fracturing companies have used GAC as a treatment method for removing organic and toxic metal compounds (Cheremisinoff and Davletshin, 2015). Not only are all of the chemical additives and naturally occurring constituents able to interact with the chosen treatment method, it is also plausible that these additives may interact with the shale formation surrounding the well or migrate through the shale into drinking water aquifers (Birdsell et al., 2015).

Furfural, a non-surfactant, and 2-BE, a surfactant, are chemical

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additives used in hydraulic fracturing fluids and a variety of industries (Waxman et al., 2011). Furfural is produced through the decomposition of plant biomass and is used as a preservative, fungicide, herbicide, disinfectant, a precursor to other compounds and synthetic resins, and as a demulsifying agent in petroleum refining (Peters, 1939; Hoydonckx et al., 2000; Xin-tong, 2011). Furfural is a strong inhibitor of dark fermentation process, which is one of the first steps of anaerobic digestion (Monlau et al., 2014) and is found in the resin material of proppants because of its high resistance to heat, acid, and water (Zoveidavianpoor and Gharibi, 2015; Liang et al., 2016).

2-BE has been used in herbicides, pesticides, food additives, corrosion resistant coatings, cosmetics, and as a dispersant in solutions used by the EPA to clean up oil and gas spills (Smith, 1984; Johnson, 2002; Kroes et al., 2007; Ramirez et al., 2013). 2-BE is a well-known surfactant and has the ability to lower surface tension between two liquids. For this reason, 2-BE is used as a product stabilizer in hydraulic fracturing fluids (FracFocus.org). Both furfural and 2-BE have become a concern due to evidence that hydraulic fracturing fluids have penetrated drinking water via leaks in the steel and cement casings of wells and their potential health risks (OSHA, 1996; Proctor et al., 2004; Cal/OSHA, 2007; EPA, 2010; Llewellyn et al., 2015).

Understanding the potential for chemical constituents from hydraulic fracturing to migrate through shale formations offers insight into their potential to cause groundwater contamination, while evaluating the ability to remove these chemicals is necessary to provide effective treatment strategies should contamination occur. Previously conducted adsorption studies have found activated carbon, zeolites, nanoporous silica based MCM-48 material, and polymeric resins are capable of adsorbing furfural (Gupta et al., 2001; Lucas et al., 2004; Sahu et al., 2008; Sulaymon and Ahmed, 2008; Anbia and Mohammadi, 2009; Ranjan et al., 2009), however; review of literature shows that no adsorption data currently exists for 2-BE. Therefore, the objectives of this study were 1) to determine if adsorption onto granular activated carbon (GAC) may be used to remove the chemical additives, 2-BE and furfural, from solution; 2) to understand how these two compounds may compete for adsorption sites; and 3) to better understand the interaction between these chemical additives with shale.

2. Materials and methods

Optima grade dichloromethane, sodium chloride, and ≥95% practical grade 2-butoxyethanol (2-BE) were purchased from Fisher Scientific (Pittsburgh, PA 15275, USA). 99% furfural and ≥85 wt % phosphoric acid in water were purchased from Sigma-Aldrich (St. Louis, MO 63178, USA). The activated carbon, NORIT® GAC 1240, with a 12–40 mesh size was obtained from ACROS Organics (New Jersey, USA) and was used as received. This material was chosen because it is commercially available and has previously been shown to remove furfural from aqueous solutions (Sahu et al., 2008). WV7 shale rock from a depth of 6582.5 m was obtained from the West Virginia Geological Survey (Morgantown, WV 26508) and was crushed and sieved using a No. 10 and 18 mesh with a mean diameter of 1.00–2.00 mm. Deionized water was produced using a Milli-Q Plus water purification system (Darmstadt, Germany).

The total organic carbon (TOC) of the shale and GAC used was measured with a Shimadzu TOC analyzer equipped with an ASI autosampler and a SSM-5000A solid sample module (Kyoto, Japan). TOC was calculated by subtracting inorganic carbon (IC) from the total carbon (TC). For TC analysis, solid samples were heated in a 900 °C oven that was connected to the detector. For IC analysis, samples were acidified in the sample boat using 1 part ≥85 wt % phosphoric acid mixed with 2 parts water and immediately introduced into a 150 °C oven attached to the detector. Samples of GAC and shale were measured in triplicate and standard error for these samples were less than 2%. The TOC content of the shale used in this study was 4.4%, whereas the TOC of the GAC was 70%.

Aqueous solutions of 2-BE, furfural, and both 2-BE and furfural were prepared in 2-L glass volumetric flasks using deionized water. The solutions were prepared in DI water, a 0.001 mol L^{-1} sodium chloride solution, a 0.1 mol L^{-1} sodium chloride solution, or with hydraulic fracturing brine. The hydraulic fracturing brine was composed in the laboratory and its chemical make-up has been previously described (Manz and Carter, 2016). All solutions were mixed using a magnetic stir bar at least 24 h prior to the experiment. The initial and final pHs were measured using a Fisher Scientific Accumet XL benchtop meter (Pittsburgh, PA 15275, USA). Initial concentration of 2-BE and furfural ranged from 500 to 700 mg L^{-1}. Adsorption isotherms by GAC or shale were performed in small batch experiments using 125 mL volume borosilicate glass serum bottles closed with a rubber septum and aluminum crimped seal. GAC or shale was added to each vial in weights of 0, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, and 0.5 g. The vessel containing 0 g of GAC was used to account for volatilization and losses of the compounds not due to adsorption. The vials were stirred continuously using a water bath shaker at constant temperatures of 20, 35, 45, 55, and 65 °C (New Brunswick Scientific Co, Inc, Model G76, Edison, NJ USA) for 24 h in order to achieve equilibrium between the solid and liquid phases were reached (Sahu et al., 2008; Sulaymon and Ahmed, 2008; Carter and Farrell, 2010). Samples were taken after 24 h to measure the 2-BE and/or furfural concentration. The absorbed amount was calculated using Equation (1):

$$q_A = \frac{V}{M} * (C_i - C_A) \qquad (1)$$

where q_A is the adsorbent-phase concentration of 2-BE or furfural at equilibrium, V is the volume, M is the weight of GAC, C_i is the concentration of 2-BE or furfural, and C_A is the concentration of furfural or 2-BE in solution.

2-BE concentrations were determined using GC/MS. The liquid-liquid extraction procedure and GC/MS parameters have been previously described (Manz and Carter, 2016). 15 mL samples from each experiment were collected in borosilicate scintillation vials with silicon-lined caps. 3 mL of the sample was used for extraction and quantification of 2-BE and the rest was used for pH measurements. Dichloromethane (DCM) was used as the extraction solvent. 3 mL of DCM was added to the sample vial and the sample was vortexed using a 115 V Mini Vortex Mixer (Fisher Scientific, Pittsburgh, PA 15275, USA). The solution was allowed to equilibrate for 10 min and separated using a 6 mL polypropylene syringe (Fisher Scientific, Pittsburgh, PA 15275, USA). The extraction was repeated 3 times and after each extraction the DCM fraction was collected in a separate scintillation vial and weighed to determine the total volume of DCM used. The 2-BE concentration was determined using calibration curves made from analysis of 2-BE standards at the start of each GC/MS run and a detailed description of this method and quantification procedure for 2-BE was previously described (Manz and Carter, 2016).

An Agilent 7890B Gas Chromatograph (GC) equipped with 5977A Mass Selective Detector (MSD) system, 7963 auto-sampler, and an Agilent J&W DB-1 capillary column, with dimensions of 60 m × 0.25 mm inner diameter and 0.25-μm film thickness, was used to determine the 2-BE concentrations (Santa Clara, CA 95051, USA). Ultra-high purity helium purchased from Airgas Corporation (Knoxville, TN 37921, USA) was used as the carrier gas with the flow rate maintained at 2.5 mL min^{-1}. The GC was operated in split-less mode and the pressure maintained in the instrument was 33.974

psi. Each sample was injected using a 10 μL needle with an injection volume of 3.5 μL. The initial temperature of the GC was 40 °C and was held for 4 min. The temperature ramp was 10 °C per min to 230 °C, which was held for 3 min. The 2-BE peak on the chromatogram was between 9.5 and 10 min.

Furfural concentrations were determined using a ThermoFisher Scientific Evolution 600 UV/Vis spectrophotometer (Madison, WI 53711, US). The maximum wavelength for furfural was determined to be at 258 nm. For samples containing 2-BE and furfural, 2-BE was determined to have no maximum wavelength and, therefore, did not interfere with furfural measurements. The furfural concentration was calculated using calibration curves made by measuring standards of known furfural concentrations. Standards were created by dissolving a known amount of furfural in distilled water or salt water, depending on the sample matrix, and successively diluting the stock solution with the same solvent.

3. Results and discussion

3.1. 2-BE and furfural adsorption onto shale analysis

Fig. S1a and b in the Supplementary Materials display the uptake of furfural by shale at 20 and 65 °C in 0 and 0.1 mol L^{-1} sodium chloride. As seen in these figures, for both temperatures, the concentration of furfural remained consistent as the mass of shale rock increaseed. In addition to these conditions, experiments were also performed at 35, 45, 55 °C and with 0, 0.001, and 0.1 mol L^{-1} sodium chloride at all temperatures. Similar results were observed for these experimental conditions; as the mass of shale increased, the concentration of furfural remained constant.

Similar experiments were performed with 2-BE and the shale. The results for the 2-BE experiments displayed similar trends at the same temperatures and salt concentrations and are shown in Supplementary Materials Fig. 1c and d. These results imply that neither 2-BE nor furfural adhere or adsorb to the shale because the shale does not contain enough organic matter or the sites available are not sufficient for adsorption of the chemicals (Martinez et al., 2006; Milner et al., 2010; Curtis et al., 2011). The TOC content of the shale used in this study was 4.4%. The results also suggest that these two chemical additives in hydraulic fracturing fluids may migrate with the flowback and produced waters through shale formations when present in these fluids (Llewellyn et al., 2015).

3.2. Analysis of 2-BE and furfural adsorption onto GAC in separate reaction vessels

3.2.1. Time dependence of 2-BE and furfural adsorption

Fig. 1a and b displays the decrease in concentration over the course of 21 days for furfural and 2-BE, respectively, in reaction vessels containing water, 0.1 mol L^{-1} sodium chloride, and hydraulic fracturing brine with 0.5 g GAC. Adsorption/desorption equilibrium was achieved within 23 h for both furfural and 2-BE. For 2-BE, maximum adsorption in all solution matrices occurred within 4.75 h. Decreasing 2-BE concentrations occurred after 22.3 h in the presence of GAC and was determined to be due to the hydrolysis half-life, which is 5.55 days (Manz and Carter, 2016). Adsorption of 2-BE in hydraulic fracturing brine mimicked adsorption from water and sodium chloride. At 22.3 h, the overall removal of 2-BE is 64, 60, and 62% in water, hydraulic fracturing brine, and sodium chloride. For furfural, the overall removal was 85, 83, and 86% in water, hydraulic fracturing brine, and sodium chloride, respectively, after 22.3 h.

3.2.2. Effects of temperature and salt concentration

Figs. S2 and S3 in the Supplementary Material display the percent removal of furfural and 2-BE from solutions containing different salt concentrations using GAC at 20, 35, 45, 55 °C, and 65 °C. For furfural, greater percent removal was obtained at lower temperatures, which agrees with the findings of Sahu et al.'s studies on furfural adsorption to commercial grade activated carbon (AAC) (Sahu et al., 2008). In addition to temperature effects, the influence of salt concentrations was observed. At room temperature, the highest percent of furfural removal was observed when no sodium chloride was present in solution, as seen in Supplementary Materials Fig. S2a. At each temperature, the percent of furfural removed is approximately the same, independent of salt concentration as shown in Figs. S2 and S3. The average difference between the percent removal at one mass of GAC and for all 3 salt concentrations was 3.7%, while the highest percent difference was 7.76% for 0.4 g of GAC at 20 °C, the lowest percent difference was 0.09% for 0.3 g of GAC at 35 °C.

Maximum adsorption of 2-BE at each weight of GAC varied with temperature and sodium chloride concentration. The greatest percent removal of 2-BE was observed in the solution containing 0.1 mol L^{-1} of sodium chloride. Increasing the salt concentration also had little to no effect on the adsorptive properties of 2-BE. At 35, 45, 55, and 65 °C, furfural adsorption is not affected by salt concentration. Studies have shown that the sodium chloride concentration has variable effects on adsorption capacity, enhancing adsorption capacity for anionic organic molecules and having little to no effect on non-ionized compounds (Randtke and Jepsen, 1982).

However, increasing temperature did impact 2-BE adsorption. At 65 °C, a greater proportion of 2-BE is absorbed than at room temperature for all salt concentrations. 2-BE is classified as a small-size surfactant (Elizalde et al., 1988) and is zwitterionic, having both cationic and anionic centers within the neutral molecule (Acton, 2013). In the presence of ionic solutions, surfactant adsorption is accompanied by counter-ion adsorption (Kralchevsky et al., 1999) suggesting that, in addition to the adsorption monolayer being formed at the surface of the GAC, an electric double layer may also form at the cationic or anionic center of 2-BE that is not already attached to the GAC, thus providing additional adsorption of 2-BE. Double layers have been shown to result due to the varying electric potentials, which are not necessarily uniform and can vary with temperature (Stojek, 2010). Therefore, the variation of adsorption at different temperatures may be due to this differences in the electric double layer. The variation in 2-BE adsorption may also be due to the stability of 2-BE as shown in the Supplementary Material Fig. S4. Fig. S4 shows that as the temperature increases, the half-life of 2-BE decreases.

3.2.3. Isotherms

Langmuir and Freundlich isotherms models were applied to the data for both furfural and 2-BE (Clark, 2011; Crittenden et al., 2012). Fig. 2 displays the Langmuir isotherms for furfural and 2-BE experiments. The Langmuir isotherm assumes that the absorbent is uniform with a fixed number of adsorption sites, reversible equilibrium with the aqueous phase, monolayer adsorption with no interactions between the molecules (Crittenden et al., 2012).

The Langmuir parameters for furfural and 2-BE are shown in Table 1. These parameters were found by fitting the data to the linearized form of the Langmuir isotherm, as shown in Equation (2):

$$\frac{C_A}{q_A} = \frac{1}{K_L Q_M} + \frac{C_A}{Q_M} \tag{2}$$

where C_A is the concentration of furfural or 2-BE in solution, q_A is the adsorbent-phase concentration of 2-BE or furfural at equilibrium, Q_M is the maximum absorbent phase concentration of 2-BE or furfural when the absorbent is saturated, and K_L is the Langmuir

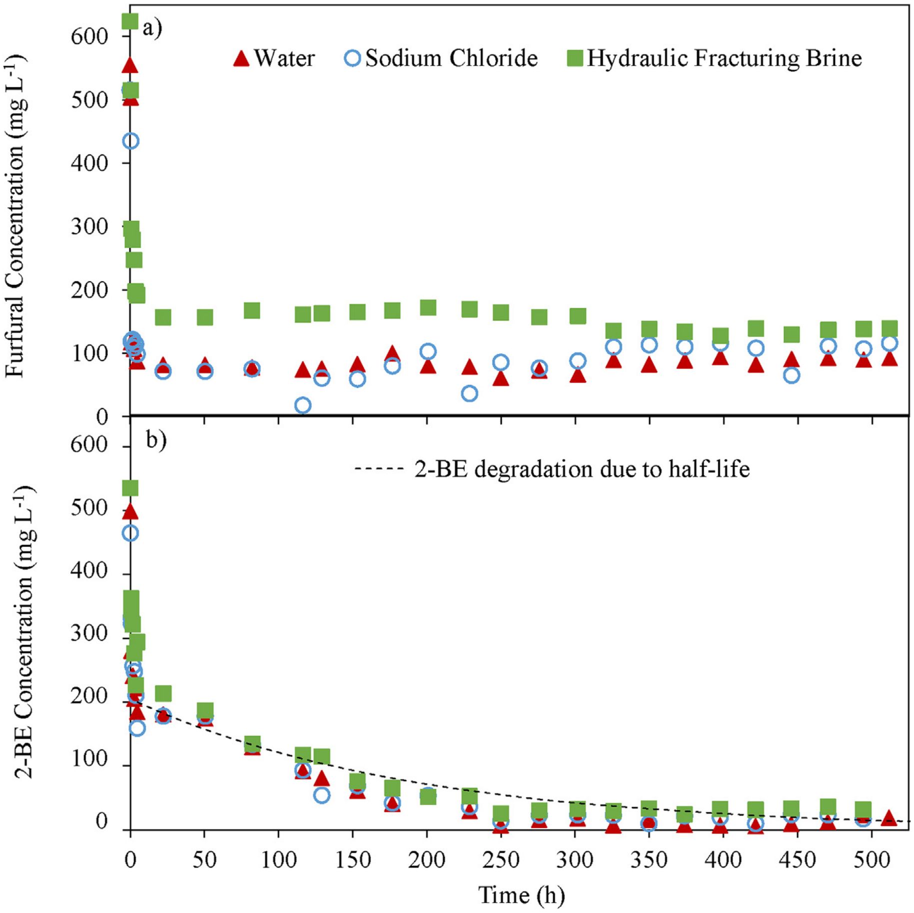

Fig. 1. Decreasing a) furfural and b) 2-BE concentrations due to adsorption onto GAC are shown for water, 0.1 mol L^{-1} sodium chloride, and lab synthesized hydraulic fracturing brine. The data was taken over the course of 511 h (21.3 days). The dashed line in b) represents the 2-BE half-life and shows that this decrease in concentration was due to 2-BE decay. Furfural and 2-BE adsorption occurred within 24 h.

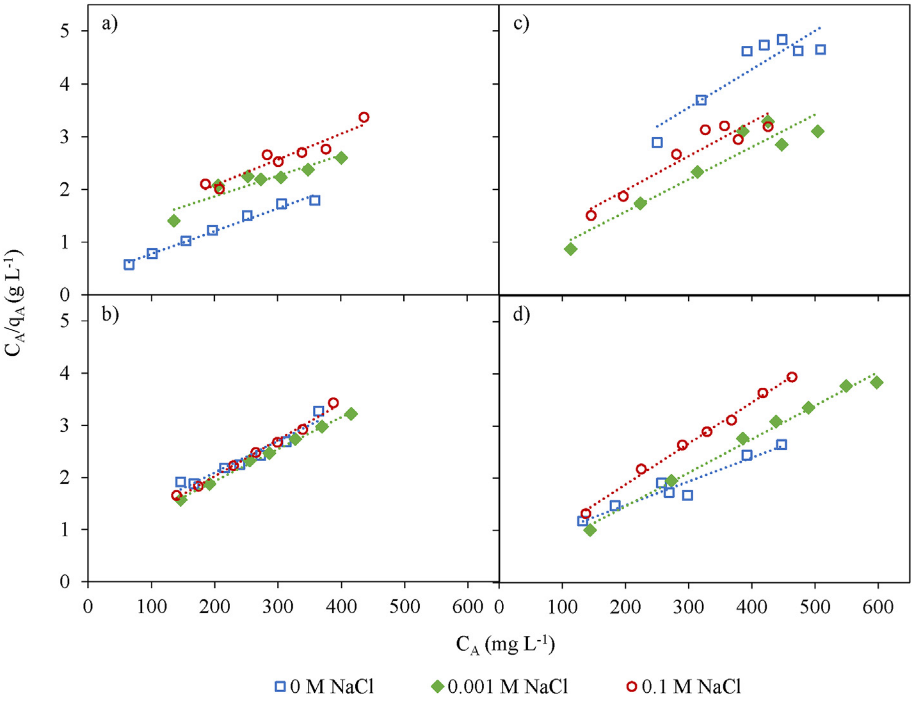

Fig. 2. Langmuir isotherm for furfural at a) 20 and b) 65 °C and 2-BE at c) 20 and d) 65 °C with 0, 0.001, and 0.1 mol L^{-1} sodium chloride is shown.

Table 1
Langmuir and Freundlich Isotherm parameters for furfural and 2-BE at indicated temperatures and sodium chloride concentrations.

Constituent	[NaCl] (mol L^{-1})	T (°C)	Langmuir			Freundlich		
			Q_M (mg g^{-1})	$K_L \times 10^{-3}$ (L mg^{-1})	R^2	$\frac{1}{n}$	KF $\left(\left(\frac{mg}{g}\right)\left(\frac{L}{mg}\right)^{\frac{1}{n}}\right)$	R^2
Furfural	0	20	231	12.6	0.98	0.308	31.6	0.98
		35	450	2.05	0.96	0.818	1.53	0.88
		45	254	3.97	0.96	0.489	8.43	0.97
		55	139	14.0	0.95	0.301	20.4	0.77
		65	205	4.34	0.98	0.514	6.20	0.97
	0.001	20	256	3.59	0.86	0.482	8.41	0.89
		35	387	2.12	0.92	0.643	3.81	0.97
		45	312	2.88	0.91	0.608	4.52	0.93
		55	207	4.87	0.99	0.476	8.11	0.97
		65	163	8.72	0.99	0.309	20.0	0.99
	0.1	20	283	2.71	0.90	0.562	5.10	0.93
		35	347	2.51	0.85	0.641	3.85	0.94
		45	270	5.07	0.93	0.503	9.26	0.95
		55	93.9	160	0.94	0.129	45.3	0.44
		65	143	11.1	0.99	0.298	20.1	0.94
2-BE	0	20	138	5.27	0.83	0.278	17.6	0.51
		35	422	2.17	0.94	0.904	1.07	0.93
		45	194	24.7	0.99	0.078	109	0.60
		55	207	4.87	0.99	0.476	8.11	0.97
		65	219	8.07	0.94	0.358	20.0	0.78
	0.001	20	163	17.7	0.92	0.0971	78.9	0.91
		35	609	2.26	0.91	0.594	8.16	0.96
		45	196	24.8	0.99	0.114	89.4	0.93
		55	252	6.11	0.89	0.444	12.9	0.95
		65	155	37.2	0.99	0.0339	119	0.94
	0.1	20	155	9.32	0.95	0.244	28.2	0.90
		35	145	33.9	0.94	0.145	57.7	0.71
		45	183	63.6	0.95	0.180	64.3	0.91
		55	195	7.87	0.93	0.487	11.7	0.95
		65	127	25.9	0.95	0.115	58.1	0.98

adsorption constant of 2-BE or furfural (Crittenden et al., 2012). For furfural, values of K_L ranged from 2.05 × 10^{-3} to 160 × 10^{-3} L mg^{-1}. For 2-BE, values ranged from 2.17 × 10^{-3} to 63.6 × 10^{-3} L mg^{-1}.

As shown by the data plotted in Fig. 2 using the Langmuir model, the sodium chloride concentration had a more significant impact on the adsorption of 2-BE than furfural. At 20 and 65 °C, the slope of each furfural line varies only slightly for all salt concentrations. For 2-BE at room temperature, the isotherm with the greatest slope is the one with no sodium chloride present in solution. However, at 65 °C, the isotherm with the greatest slope occurred when 0.1 mol L^{-1} of sodium chloride was present in solution. The slope of the Langmuir plot is the inverse of Q_M, which means that the slope of this plot is equal to the mass of absorbent per mass of adsorbate. The higher slope at 65 °C and 0.1 mol L^{-1} sodium chloride is likely due the decreased stability of 2-BE at higher temperatures as shown in Supplementary Materials Fig. S4.

Fig. S5 in Supplementary Materials displays Freundlich isotherms for furfural and 2-BE at 20 and 65 °C with 0, 0.001, and 0.1 mol L^{-1} sodium chloride. Freundlich isotherms are used to model heterogeneous adsorption and assume, unlike the Langmuir model, that individual sites have different energies and more than one layer of adsorption can occur (Clark, 2011; Crittenden et al., 2012). Freundlich isotherms were plotted using Equation (3)

$$\log q_A = \log K_F + \frac{1}{n} \log C_A \tag{3}$$

where $1/n$ is the unit-less adsorption intensity parameter (Crittenden et al., 2012). The Freundlich parameter values at all temperatures and salt concentrations for furfural and 2-BE are displayed in Table 2. The slope, 1/n, of the Freundlich isotherm indicates the adsorption intensity. For both Furfural and 2-BE, the highest adsorption intensity was observed at 35 °C. This indicates that adsorption is more favorable at this temperature. Overall, Freundlich isotherms exhibited lower R^2 values than the Langmuir isotherms for both 2-BE and furfural. This suggests that the assumptions made in the Langmuir model are better suited for these contaminants.

Table 2
Isosteric heats of adsorption for 2-BE and furfural in solutions containing 0, 0.001, 0.1 mol L^{-1} of sodium chloride.

[NaCl] (mol L^{-1})	Mass of GAC (g)	Q_{iso} (kJ mol^{-1})	
		Furfural	2-BE
0	0.1	11.09	6.20
	0.15	10.23	7.30
	0.2	8.49	15.0
	0.25	9.30	13.8
	0.3	14.28	12.5
	0.4	14.26	14.8
	0.5	18.85	14.0
0.001	0.1	5.65	−3.30
	0.15	5.73	−5.27
	0.2	5.10	−0.166
	0.25	4.91	−0.551
	0.3	3.72	−0.995
	0.4	2.86	−0.565
	0.5	2.87	−3.66
0.1	0.1	9.01	1.55
	0.15	9.90	0.423
	0.2	3.77	2.42
	0.25	5.87	5.80
	0.3	4.14	4.97
	0.4	−5.70	0.611
	0.5	−3.45	1.84

3.2.4. Isosteric heats of adsorption

Van't Hoff plots for furfural at 0, 0.001, and 0.1 mol L^{-1} of sodium chloride are displayed in Fig. 3. Isosteric heats of adsorption (Q_{iso}) for each GAC loading were calculated using the Van't Hoff plots and the following Equation (4):

$$Q_{iso} = R\left[\frac{d(\ln K_D)}{d\left(\frac{1}{T}\right)}\right]_{loading} \tag{4}$$

where R is the universal gas constant, T is the temperature, and K_D is the partitioning coefficient of the adsorbate (Clark, 2011). For all weights of GAC used, at 0 and 0.001 mol L^{-1} sodium chloride, the Van't Hoff plots display negative slopes, indicating that the adsorption reaction is endothermic, thus requiring energy for the adsorption to take place. For solutions with 0.1 mol L^{-1} sodium chloride, all weights of GAC displayed negative slopes with the exception of the plots for 0.4 (3.2 g L^{-1}) and 0.5 g (4 g L^{-1}) GAC. For these doses of GAC, the Van't Hoff plot displays a positive slope, indicating an exothermic reaction. Sahu et al. have previously reported furfural adsorption as an endothermic process, with the isosteric heat of adsorption as -12.45 kJ mol^{-1} in a solution of 10 g L^{-1} commercial grade activated carbon and no sodium chloride in solution (Sahu et al., 2008). The differences in these values may be attributed to the amount of GAC in solution. At the lower weights of GAC tested in this study, there are less adsorption sites, requiring more energy input for furfural adsorption. Table 3 displays furfural Q_{iso} values for each weight of GAC and sodium chloride concentration tested in this study.

Table 3 also displays Q_{iso} values for 2-BE at all salt concentrations. Van't Hoff plots used to determine Q_{iso} may be found in Supplementary Material Fig. S6. The adsorption processes with 2-BE are endothermic when there is 0.001 mol L^{-1} sodium chloride in solution. For all doses of GAC tested with 0 and 0.1 mol L^{-1} sodium chloride, the adsorption process of 2-BE onto GAC is exothermic.

3.3. Analysis of competitive 2-BE and furfural adsorption onto GAC

3.3.1. Analysis of the effects of temperature and salt concentration on competitive adsorption

Fig. 4 displays percent recovery of 2-BE and furfural at 20 and 65 °C and salt concentrations of 0, 0.001, and 0.1 mol L^{-1} sodium chloride. Table 3 displays the Langmuir and Freundlich constants for these experiments with both 2-BE and furfural in solution. At 65 °C, more 2-BE appears to be adsorbed than furfural. This is due to the poor stability of 2-BE at high temperatures. At room temperature, a greater percentage of furfural is removed than 2-BE. This indicates that furfural adsorption onto GAC occurs more preferentially than 2-BE, since heat stability is not a factor in this case. This was not expected since GAC favors adsorption of nonpolar compounds (Sulaymon and Ahmed, 2008). Furfural is a polar molecule, while 2-BE has both polar and nonpolar ends. However, at low temperatures and low concentrations, 2-BE is more susceptible to aggregates (Elizalde et al., 1988). If the 2-BE is aggregating at these lower temperatures, less 2-BE will adsorb to the GAC.

When GAC is used in water treatment for hydraulic fracturing fluids, 2-BE and furfural are of importance because their degrees of adsorption vary when other compounds, including salts, are in solution. Despite the known surfactant properties of 2-BE, in many of the tested conditions, 2-BE has less adsorption capacity than furfural. Rather than adsorbing to the GAC, the 2-BE forms aggregates with itself at low temperatures. This leaves more open sites on the GAC for the furfural to adsorb. At high temperatures, 2-BE is

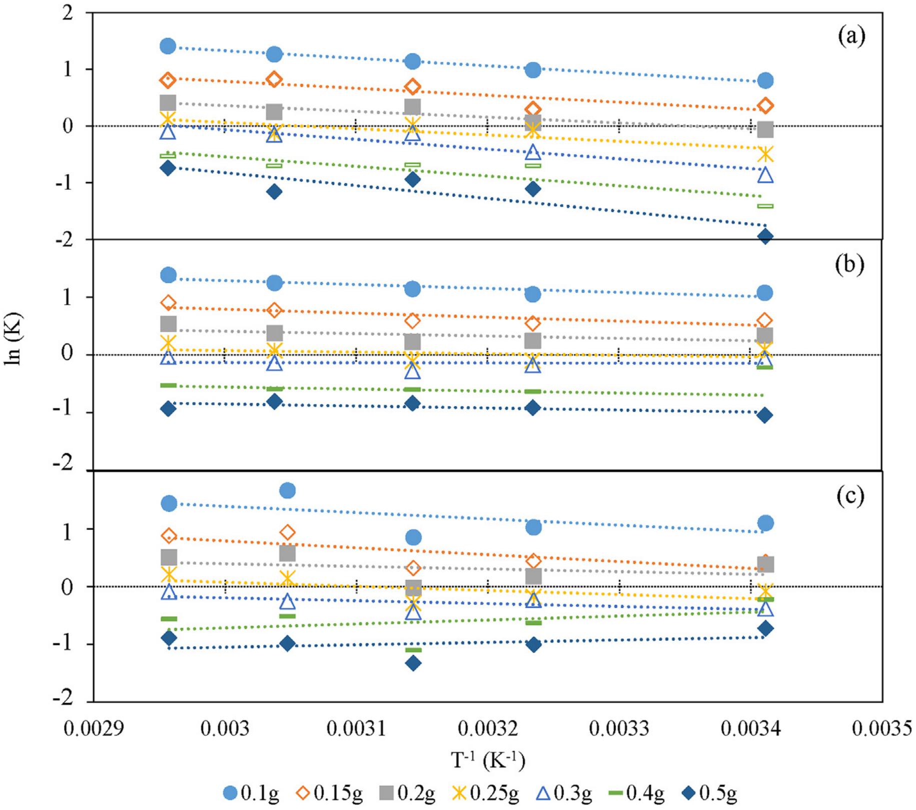

Fig. 3. Van't Hoff plot for experiments containing furfural in solution with a) 0 mol L^{-1} NaCl, b) 0.001 mol L^{-1} NaCl, and c) 0.1 mol L^{-1} NaCl is shown.

Table 3
Langmuir and Freundlich isotherm parameters for experiments containing both furfural and 2-BE at 20 and 65 °C and 0, 0.001, and 0.1 mol L^{-1} sodium chloride.

[NaCl] (mol L^{-1})	Constituent	T (°C)	Langmuir			Freundlich		
			Q_M (mg g^{-1})	K_L ($\times 10^{-3}$ L mg^{-1})	R^2	$\frac{1}{n}$	K_F $\left(\left(\frac{mg}{g}\right)\left(\frac{L}{mg}\right)^{\frac{1}{n}}\right)$	R^2
0	Furfural	20	530	5.84	0.32	0.808	0.956	0.85
		65	106	9.74	0.97	0.194	27.2	0.72
	2-BE	20	82.9	17.1	0.71	0.204	18.9	0.15
		65	101	11.8	0.84	6.00×10^{-4}	94.9	0.19
0.001	Furfural	20	371	14.9	0.18	0.707	1.56	0.69
		65	516	2.06	0.94	0.117	38.8	0.77
	2-BE	20	59.4	204	0.18	0.283	6.21	0.17
		65	648	1.62	0.95	–	–	–
0.1	Furfural	20	328	19.4	0.16	0.759	0.972	0.71
		65	58.1	18.3	0.94	0.0614	39.2	0.18
	2-BE	20	1570	1.03	0.62	0.665	1.53	0.90
		65	164	13.4	0.46	0.316	13.9	0.24

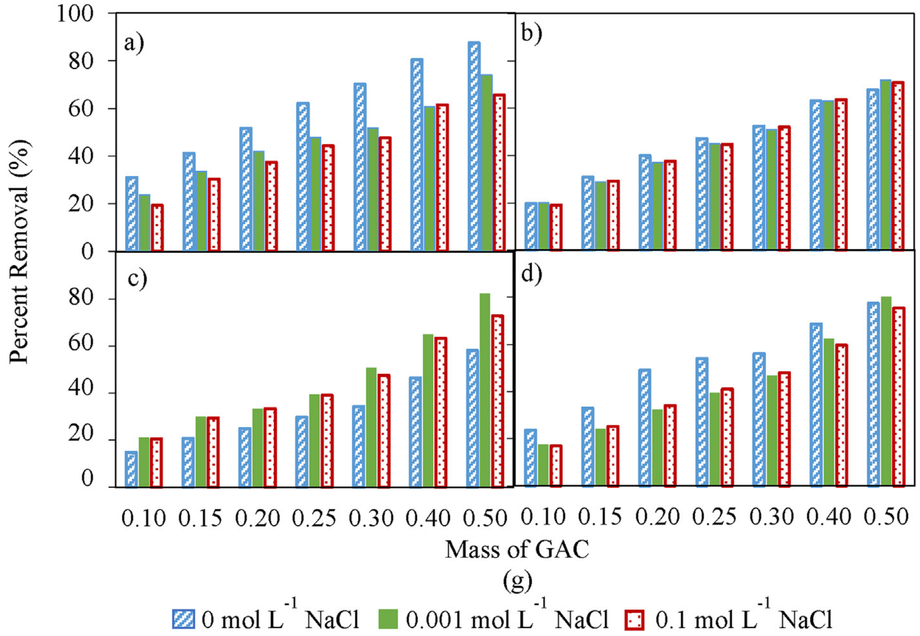

Fig. 4. Percent recoveries of experiments with both furfural and 2-BE in solution at 0, 0.001 0.1 mol L^{-1} sodium chloride. The conditions in each experiment are: a) furfural, 20 °C, b) furfural, 65 °C, c) 2-BE, 20 °C, and d) 2-BE, 65 °C.

unstable, making it appear that 2-BE adsorbs to GAC more preferentially than furfural.

4. Conclusion

In summary, hydraulic fracturing chemical additives furfural and 2-BE interact differently with GAC and shale and are very dependent on the temperature of the solutions that they are in. Conclusions from this study were:

- Neither 2-BE nor furfural adsorb to shale rock. This implies that these chemical additives may be able to migrate through shale formations and into water resources.
- GAC may be used to adsorbed 2-BE and furfural from hydraulic fracturing fluids. Adsorption onto GAC occurs within 23 h for both contaminants. Adsorption is even quicker for 2-BE, occurring within 4.75 h.
- 2-BE and furfural compete for adsorption sites. At lower temperatures, furfural adsorption takes place to a greater degree than 2-BE adsorption.
- 2-BE adsorption is influenced by temperature and salt concentration. High temperatures are best for 2-BE adsorption, which is most likely due to 2-BE's surfactant properties and poor stability at high temperatures.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.09.010.

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