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Can We Treat Hydraulic Fracturing Flowback with a Conventional Biological Process? The Case of Guar Gum

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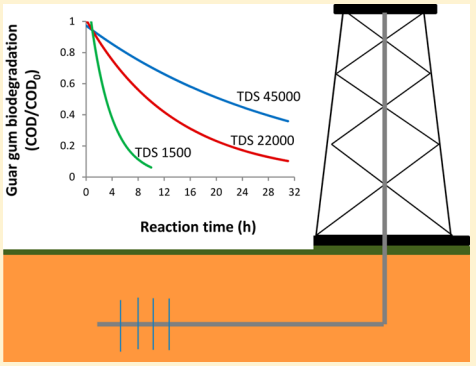
ABSTRACT: Hydraulic fracturing of unconventional gas wells utilizes large volumes of water-based fluid to increase formation permeability and, as a result, generates large amounts of wastewater as flowback. This water requires suitable treatment before being reused or discharged into the environment. A principal ingredient of flowback water is guar gum (a gelling agent), which may adversely affect advanced flowback water treatment such as membrane separation. This study demonstrates the potential of an activated sludge mixed liquor to degrade guar under typical flowback conditions [i.e., high concentrations of total dissolved solids (TDS)]. Guar was efficiently degraded at a TDS concentration of 1500 mg/L, with more than 90% of the dissolved chemical oxygen demand (COD_d) having been removed after 10 h. Increasing the TDS concentration to 45000 mg/L inhibited COD_d degradation to 60% removal after 31 h. A high TDS concentration additionally resulted in an increased effluent level of total suspended solids and turbidity; however, these were efficiently reduced using ferric chloride coagulation followed by sedimentation and filtration. Biological reduction of the guar concentration increased the flux of a bench-scale ultrafiltration membrane, demonstrating the potential of the process to treat flowback water prior to membrane separation.



INTRODUCTION

The production of natural gas from unconventional sources (i.e., shale gas, tight sand, and coalbed methane) has rapidly developed over the past decade.[1,2] Unconventional gas exploration typically requires hydraulic fracturing techniques, in which large volumes of water-based fluid (fracturing fluid) are injected into a drilled well to initiate and expand fractures in the formation, as well as to transport proppant (e.g., sand) to maintain open fractures during well operation.[1]

Typically, 10−70% of the fracturing fluid is subsequently recovered as flowback water, generating an unavoidable stream of wastewater that requires suitable treatment before being reused or discharged into the environment.[3] At present, the most popular disposal method is underground injection into salt water wells.[4] Other alternatives include treatment at a municipal wastewater treatment plant or at a private industrial facility and partial treatment for reuse as fracturing fluid.[5] In the past several years, however, growing pressure by authorities and public opinion has led the gas industry to search for alternative treatment solutions, allowing beneficial water reuse.[5]

The physical and chemical characteristics of flowback water, influencing the choice of treatment technology, largely depend on the composition of the fracturing fluid. The principal ingredients of fracturing fluid are gelling agents,[6] which increase the fluid's viscosity to allow an efficient transport of proppant into the fractures. Among those agents, guar gum and guar derivatives are the most abundant.[6−9] Guar is a high-molecular weight polysaccharide, produced from guar beans, which is used in many different industries as a thickener. After fracturing is complete, some of the guar is degraded inside the well by chemical additives (gel breakers) to facilitate the fluid's recovery, while some is recovered in the flowback.[10]

Although guar is considered nontoxic,[8] it is nonetheless important from a flowback treatment point of view. Because of its gel-like nature, it may adversely affect advanced treatment technologies such as membrane separation processes, as demonstrated previously by Carrere and co-workers.[11] Membrane separation [e.g., reverse osmosis (RO)] is often considered as a solution for treating water with a high level of dissolved solids (TDS), as in the case of flowback water. Thus, removing guar from flowback may be essential for beneficial reuse, particularly if the water is subsequently treated with membrane filtration.

The goal of this study was to demonstrate the potential of conventional activated sludge, as a pretreatment for membrane filtration, to degrade guar gum under typical flowback conditions (i.e., high TDS concentration). The examined TDS concentration was up to 45000 mg/L, representing the upper limit for an economic RO membrane treatment.[12] Although this TDS concentration is in the lower range for flowback water, it nevertheless represents a large volume of potentially treatable water.[12]

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MATERIALS AND METHODS

Synthetic Wastewater. Synthetic wastewater was prepared by mixing 3 g/L guar gum with deionized water (Millipore Milli-Q purification system, resistance of 18.2 MΩ cm), followed by a settling period of 12 h. The supernatant was filtered through a 15 μm glass-fiber filter (Fisherbrand P8), to achieve a chemical oxygen demand (COD) of approximately 2500 mg/L (within the range of guar concentrations in fracturing fluid[6]). Nutrients were added to optimize the biological process as follows: phosphorus (K_2HPO_4/KH_2PO_4) and ammonia (NH_4Cl) at a 30:4:1 C:N:P ratio and calcium ($CaCl_2{\cdot}2H_2O$), magnesium (MgCl), and yeast extract at 50 mg/L each. The pH of the solution was set to 7, using NaOH. Sodium chloride (NaCl) (typical for flowback water[12]) was used to increase the TDS concentration. All chemicals were obtained from Sigma-Aldrich (>98%) and were used as received.

Experimental Setup. The activated sludge experiments were conducted using three bench-scale sequencing batch reactors (SBRs) operated in parallel. The first reactor functioned as a control, with the TDS concentration maintained at approximately 1500 mg/L, while the second and third reactors operated at TDS levels of 22000 and 45000 mg/L, respectively. All reactors had a liquid capacity of 2 L and an additional 2 L of head space, to prevent the loss of solids from the top of the reactor because of foaming. Mixing (100 rpm) was conducted using a standard Jar Tester (Phipps and Bird, Richmond, VA) to achieve a homogeneous activated sludge suspension. Air was continuously sparged through a diffuser located at the bottom of each reactor, to maintain a dissolved oxygen level of >3 mg/L.

The influence of guar on membrane filtration was assessed using a bench-scale dead-end ultrafiltration (UF) cell (model XFUF07601 from Millipore Corp.), operating at a constant nitrogen pressure of 80 psi. The volume of the cell was 300 mL, and the effective membrane area was 13.4 cm^2. The accumulated permeate water was weighed using a calibrated analytical balance (Ainsworth DE310), and the flux was further calculated, as described previously by Dror-Ehre et al.[13]

Experimental Procedure. Experiments began with the mixing of 1 L of activated sludge [mixed liquor suspended solids (MLSS), ~2500 mg/L] from the Boulder, CO, municipal wastewater treatment plant with 1 L of synthetic wastewater, followed by a 2 week acclimation period. During the first acclimation stage (1 week), the TDS concentration was kept constant in all the reactors (1500 mg/L) to facilitate an efficient acclimation of the sludge culture to guar. In the second acclimation stage, the TDS concentration was gradually increased in the second and third reactors, to final concentrations of 22000 and 45000 mg/L, respectively. The reactors were typically operated in a 36 h batch cycle, consisting of a fill period of 0.5 h, a reaction period of 32 h, a settle period of 3 h, and a decant period of 0.5 h. At the end of each cycle, 1 L, equal to half of the filled volume, was replaced by new synthetic wastewater. No sludge was removed from the reactors during acclimation, yielding a dense culture of microorganisms. After acclimation, the MLSS concentration was maintained at 3500−4000 mg/L by controlled wasting of solids before the settling period. The solids retention time (SRT) was estimated as 20−30 days; however, because of the unsteady increase in the MLSS concentration, this value was highly variable and might not represent the actual field-scale SRT, achieved after a longer period of treatment. Samples (5 mL) were taken periodically for dissolved COD_d analysis (filtered at 0.45 μm), used to monitor guar degradation.

Analytical Methods. Chemical oxygen demand (COD_d), TDS, and MLSS analyses were conducted as specified in ref 14. To avoid interference by chlorides, COD samples were diluted with deionized water. The turbidity and level of dissolved oxygen were measured using a HACH turbidimater (2100N) in Nephelometric Turbidity Units (NTU) and ORION 3-Star DO meter (Thermo Scientific), respectively.

RESULTS AND DISCUSSION

Biodegradation of Guar. Figure 1 presents the removal of COD_d as a function of reaction time, for TDS concentrations of

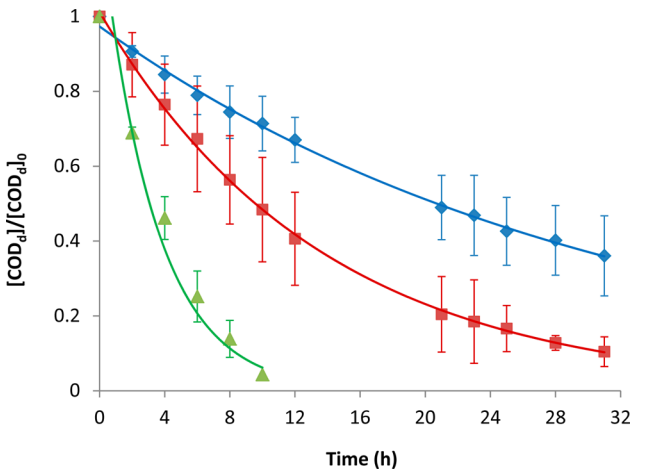

Figure 1. COD_d removal as a function of time, at TDS concentrations of (△) 1500, (□) 22000, and (◇) 45000 mg/L. The SBRs were seeded with the same activated sludge and acclimated at the time of the study.

1500, 22000, and 45000 mg/L. Results are the average of two cycles taken during the postacclimation period. In all cases, COD_d decay exhibited first-order kinetics. COD_d was readily degraded at a TDS concentration of 1500 mg/L, with more than 90% removal after 10 h. This degradation rate is within a typical range for SBR treatment of both municipal and industrial wastewaters,[15] indicating that guar is biodegradable. Increasing the salt concentration inhibited the degradation of COD_d, with 60% removal after 31 h at a TDS concentration of 45000 mg/L. The first-order degradation rate constants were 0.302, 0.074, and 0.032 h^{-1} for TDS levels of 1500, 22000, and 45000 mg/L, respectively.

A high TDS concentration (>10000 mg/L) is known to adversely affect the performance of biological treatments, because of plasmolysis and/or loss of cell activity.[16−18] For example, Kargi and Dincer[19] showed that COD removal decreased from 85 to 59% when salinity increased from 0 to 5%, treating synthetic wastewater with activated sludge. The inhibitory effect of salts can nevertheless be minimized by optimizing the sludge acclimation period.[20] It was shown that a sudden increase in salt concentration causes a drastic decrease in microbial activity,[21] while a gradual increase in salinity results in adaptation of the microorganisms.[22] Different sludge acclimation periods have been used in previous work. For example, Tokuz and Eckenfelder[20] increased the concentration of NaCl from 8 to 45 g/L over a 1 month period, whereas

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Deorsola et al.[18] used 15−20 days to increase the NaCl concentration by 2 g/L. The optimal acclimation period depended mainly on the final salt concentration.[22] Because no optimization was attempted in our case, we suspect that the obtained degradation rate merely represents the lower range of guar degradation.

The influence of TDS on turbidity and TSS of the biologically treated effluent was further examined (Figure 2).

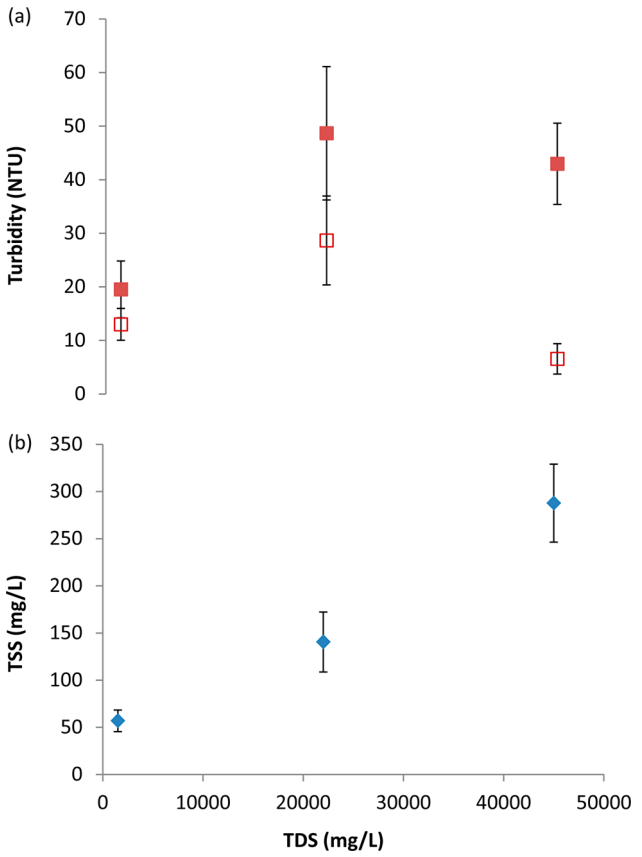

Figure 2. (a) Turbidity and (b) TSS concentration of the effluent as a function of TDS concentration. Filled symbols represent data for the biologically treated effluent; empty symbols represent data for the biological treatment followed by coagulation and sedimentation.

The level of turbidity increased from a TDS concentration of 1500 to 22000 mg/L but then remained constant when the TDS concentration increased to 45000 mg/L; the TSS concentration steadily increased with the TDS concentration over the entire range of TDS concentrations examined. A high salt concentration in biological wastewater treatment reduces the populations of protozoa and filamentous organisms, resulting in low sedimentation efficiencies and high effluent TSS concentrations and turbidities.[16] This phenomenon was previously observed by different researchers.[18,20] Furthermore, the relative concentration of cations plays an important role in the sludge characteristics; high sodium to calcium and magnesium ratios (>2) may weaken the sludge's settling properties.[23]

The effluent's high turbidity could be decreased by up to 85% using coagulation and sedimentation, with ferric chloride ($FeCl_3 \cdot 6H_2O$) at a concentration of 60 mg/L as Fe (Figure 2a, empty symbols). This decrease is particularly noticeable at the highest TDS level, possibly because of residual guar in the effluent, influencing the coagulation process.[24] An additional reduction in turbidity was achieved by 1.6 μm glass-fiber filtering (Millipore) of the sedimentation supernatant, with final turbidity values of <5 NTU for the low and medium TDS concentrations (1500 and 22000 mg/L) and <1 NTU for the highest TDS level (results not shown).

Implication for Membrane Filtration. Guar gum is expected to adversely affect membrane filtration of flowback water through fouling and reducing of permeate flux.[11] The potential of guar biodegradation to improve subsequent membrane filtration treatment was assessed using a UF membrane apparatus (regenerated cellulose 10 kDa membrane, Millipore) by tracking the change in permeate flux versus time. UF was selected because it is frequently used as pretreatment to RO in wastewater effluent applications.[25] Effluent samples were taken from the high-TDS concentration reactor at reaction times of 0.5 and 31 h, subjected to coagulation, sedimentation, and filtration as described in the previous section, and filtered with the UF system. Concentrations of COD_d in the samples (prior to UF) were 1260 and 440 mg/L for the 0.5 and 31 h treatments, respectively. The turbidity was approximately 0.9 NTU in both samples (after 1.6 μm filtration and prior to UF).

A decrease in flux is observed in the first 10 min of membrane filtration for both samples (more noticeable at high COD levels) (Figure 3). The stabilized flux is ~2-fold higher at a COD level of 440 mg/L, compared to 1260 mg/L, implying that reducing the guar concentration improves the efficiency of UF.

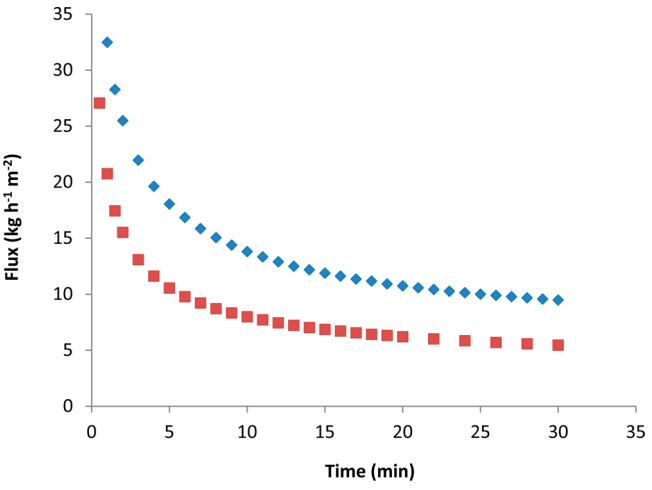

Figure 3. Membrane permeate flux (10 kDa UF membrane) as function of time for COD_d concentrations of (◇) 440 and (□) 1260 mg/L. Effluent samples were taken from the high-TDS concentration reactor (45000 mg/L) and subjected to coagulation, sedimentation, and filtration (1.6 μm). Results are the average of two separate experiments (for each COD_d concentration), and standard errors were <5%.

The results suggest that a treatment train that includes a biological process, coagulation, sedimentation, and filtration (Figure 4), has a strong potential to degrade guar, improve

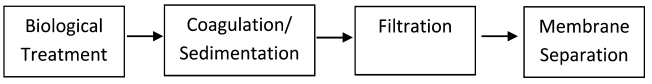

Figure 4. Schematic diagram of the proposed treatment train.

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flowback quality, and, as a consequence, increase the efficiency of subsequent membrane filtration. Moreover, the low cost and small footprint of an SBR system, relative to those of other biological systems,[26,27] make it an attractive solution for on-site flowback water treatment. The efficacy of biological treatment may be affected by the complex mixture of chemicals typically present in flowback water. These chemicals include high concentrations of ions (other than NaCl) such as calcium, magnesium, iron, sulfate, etc., oil and grease, and trace organic compounds.[12] In addition, different biocides such as glutaraldehyde are known to be used in fracturing fluid[6] and can potentially inhibit a biological treatment process. Therefore, because of the proprietary nature of fracturing water constituents and flowback water quality that varies with the nature of the geological formation, further studies with actual field waters should be performed to more precisely predict site-specific biological treatment efficacy.

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Notes

The authors declare no competing financial interest.

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