BIODIESEL WASTE FLUID AS AN INEXPENSIVE CARBON SOURCE FOR BIOREACTORS TREATING ACID MINE DRAINAGE (CALIFORNIA-NEVADA, UNITED STATES)

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Abstract
Acid drainage remains the largest source of environmental pollution from mining in the western United States. An un-related waste material, the fluid left after production of biodiesel fuel, is becoming a disposal issue as more biodiesel is manufactured. Semi-passive bioreactors treating acid mine drainage waters may be able to use the waste from biodiesel production as a feed for the sulfate-reducing bacteria cultivated in reactors, thus involving one waste material in the remediation of another. The success of laboratory columns using biodiesel waste led to a limited field experiment at a reactor treating acid-mine drainage in the state of California, U.S.

Introduction
Biodiesel was produced in 23 states in the U.S. as of Jan. 2006 (National Biodiesel Board 2006), resulting in an estimated 2.1 million gallons (7,949,000 L) of waste glycerol. Due to the amount and caustic nature of this waste, disposal has become an issue (McCoy 2005; Soap and Detergent Association 2005). A potential application is as a carbon source for bioreactors treating acid mine drainage (AMD). The University of Nevada, Reno has been treating AMD from the Leviathan mine, a Superfund site in the Sierra Nevada mountains, since 1993 (Tsukamoto and Miller 1999). A system of four constructed ponds serves as a bioreactor treatment system (Fig.1).

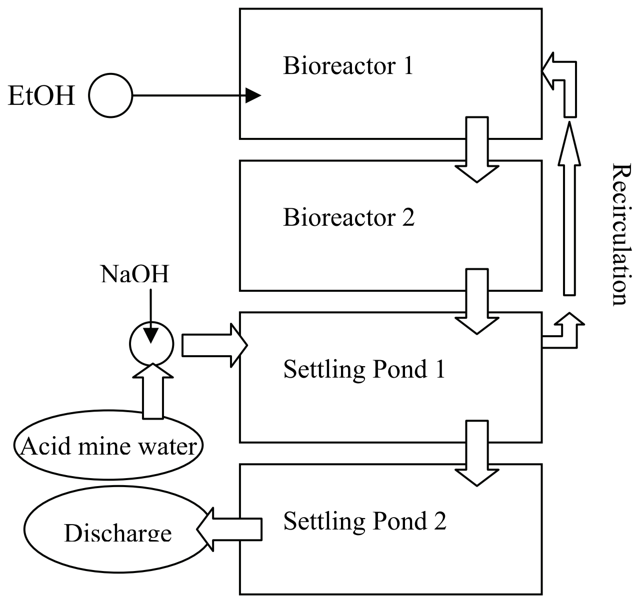

Figure 1. Constructed pond reactor system. Ponds have dimensions 10m x 3.5m x 3.5m deep; Bioreactor ponds are filled with 25 cm rock. Ethanol is provided at Bioreactor 1, NaOH is added to mine water just prior to entering Settling Pond 1, and water from Settling Pond 1 (neutral pH high in sulfate) is pumped to Bioreactor 1. Settling Pond 2 acts as a backup for sludge precipitation and storage. Water leaving Settling Pond 2 enters a basin prior to final discharge to the watershed.

Sulfuric acid in mine water is converted by sulfate-reducing bacteria (srb) to hydrogen sulfide during oxidation of provided ethanol (Equation 1), promoting the precipitation of dissolved metals as metal sulfides.

$$3\ SO_4^{2-} + 2\ CH_3CH_2OH + 2H^+ \rightarrow 3\ H_2S + 4\ HCO_3^- + 2\ H_2O \quad (1)$$

The cost of ethanol is a factor in the operational costs of alcohol-fed bioreactors. This study was initiated to determine if low cost biodiesel waste (bdw) could serve as a carbon source. Biodiesel is manufactured by adding methanol and sodium- or potassium-hydroxide to vegetable oil, including waste cooking oil, resulting in trans-esterification of the fatty acids to form biodiesel, the methyl ester of the fatty acid component. Glycerol, hydroxides, methanol, and traces of fatty acids remain in the bottom waste fraction. Glycerol and methanol are known to be carbons srb can utilize.

Methods

Two laboratory column studies were conducted. The first compared columns fed biodiesel waste with columns fed laboratory-grade glycerol to determine if any material in bdw negatively impacted sulfate reduction. The second compared columns fed biodiesel waste with columns fed ethanol, and how columns then reacted to switching carbons to determine how the field bioreactor might react to having ethanol replaced with bdw.

In the first experiment, seven columns with dimensions 6.4 cm i.d. and 40.1 cm length were filled with 5 cm river rock (Fig. 2). Triplicate columns received biodiesel waste (1a, 1b, 1c) or reagent-grade glycerol (2a, 2b, 2c) and one control column received no carbon. Influent water containing 900 mg/L of sulfate as Na_2SO_4 was held in 20 L carboys and gravity-fed into columns; a peristaltic pump removed water from the bottom of the columns at a rate of 1 ml/min for a retention time of 13 hours. Influent water pH was maintained at near neutrality after the addition of the carbon source. Nutrients (Fe, N, P, Ca, Mg and trace minerals) and vitamins (Wolfe's Vitamin Solution, ATCC 2002). were provided as injections to ports immediately above the columns.

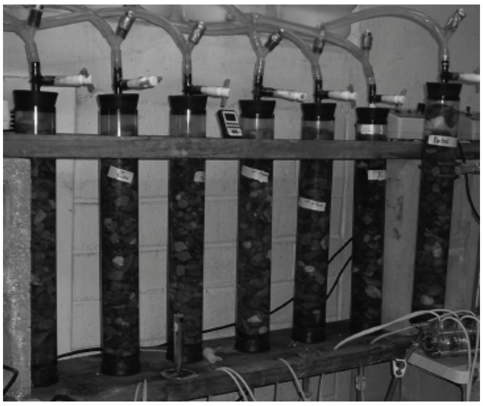

Figure 2. Experimental columns.

Reagent-grade glycerol or bdw was added based on the stoichiometric amount of glycerol required to reduce 50% of the 900 mg/L sulfate in the influent water. Although bdw contains methanol and fatty acids, it was added as the glycerol equivalent rather than the carbon equivalent. The reduction of sulfate by glycerol occurs at a 7: 4 ratio, therefore, reduction of 450 mg of sulfate (0.0047 moles) requires 246 mg of glycerol (0.0027 moles). The biodiesel waste contained 64% glycerol; therefore, columns in triplicate (1a, 1b, 1c) were fed 383 mg/L of biodiesel waste fluid to provide 246 mg/L of glycerol. The control column received no carbon. The second experiment was set up similarly, with the exception that duplicate columns were used and iron was provided with the influent sulfate rather than as injections. Columns were again fed enough carbon to reduce 50% of the 900 mg/L of sulfate provided in influent (383 mg/L of bdw or 152 mg/L of 95% ethanol).

In the field study, a set of four constructed ponds serves as a bioreactor. The ponds have been operating in the current configuration, and on ethanol feed, since 2004. In summer 2006, they were provided with intermittent biodiesel waste in addition to the usual ethanol feed, and from August to October 2006, the ethanol was removed and replaced with bdw. Ethanol had been provided through a gravity drip system. Biodiesel waste is a more viscous material, and was fed to the system using a peristaltic pump to provide consistent delivery.

Results and Discussion

In comparison of columns fed biodiesel waste v glycerol, sulfate reduction was consistently better in columns fed bdw, indicating that constituents in bdw improved rather than detracted from the attractiveness of this material to sulfate reducers (Fig. 3).

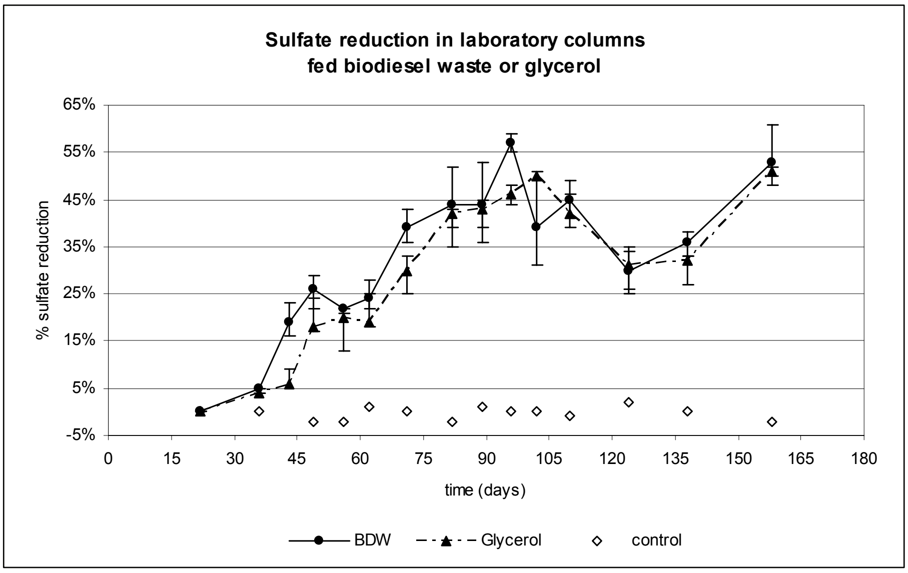

Figure 3. Columns fed biodiesel waste reduced more sulfate than columns fed glycerol, when bdw was provided in concentrations of glycerol equivalents to reduce 50% of influent sulfate water. The sharp decrease after day 105 occurred when columns were not fed enough iron, resulting in sulfide toxicity; when provided with iron after day 120, they recovered quickly.

In a comparison of columns that were started on bdw and switched to ethanol v columns started on ethanol and switched to bdw, columns were able to transition from bdw to ethanol more easily than from ethanol to bdw when provided with a very short transition time. Analysis of alcohols and metabolic acids indicates that sulfate reducers, once acclimated to the carbon source, use metabolic acids produced during the oxidation of biodiesel waste more completely than they use the acetate produced during oxidation of ethanol (Fig. 4). This is of importance to the field bioreactor in that feeding bdw could result in requiring the neutralization of less total acid; currently both the acid from mine water and the acetic acid produced by sulfate reduction via ethanol need to be neutralized.

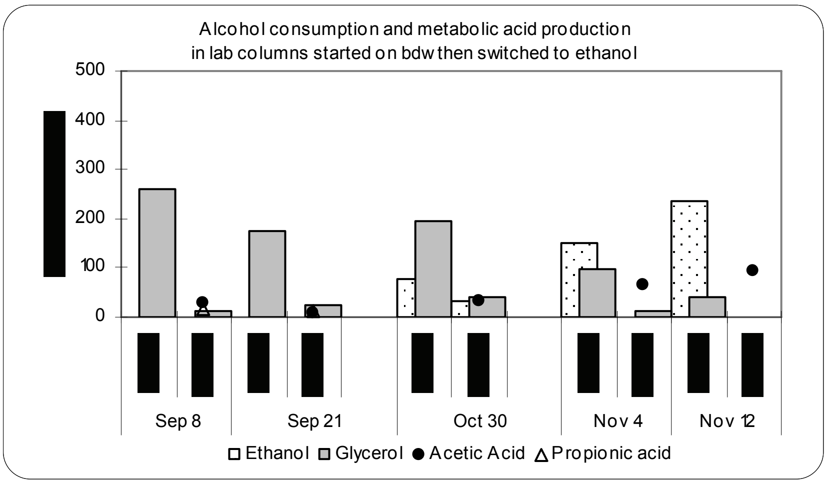

Figure 4. Columns started on biodiesel waste were transitioned to ethanol Oct 27-30. Residual glycerol remained until Nov 12, although no bdw was fed after Oct 30. Metabolic acid production increased when columns were fed ethanol.

Results in the field experiment were complicated by the transition of operation and maintenance of the reactor from UNR to a private contractor, which occurred at the time of the experiment. Several upsets occurred such that we cannot consider our results to be valid for typical operation. However, it was evident that the bioreactor was able to operate on biodiesel waste, and potentially will produce less metabolic acid than ethanol (Fig. 5).

We had difficulty with consistent delivery of biodiesel waste; the material is too caustic to be able to use peristaltic pump tubing.

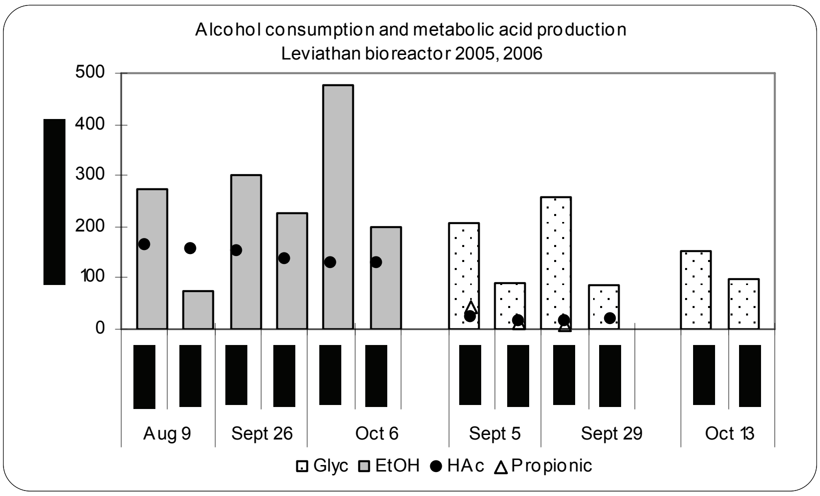

Figure 5. A comparison of alcohol consumption and metabolic acid production in the Leviathan bioreactor when provided with ethanol (left end of x-axis: Aug, Sept, Oct 2005) and when provide with bdw (right end of x-axis: Aug, Sept, Oct 2006). Bars at each date represent the alcohol and acid concentrations entering bioreactor 1 and at system discharge. Metabolic acid production was less when bdw was provided (glycerol bars), but glycerol was not used as well as ethanol. The reactor had been operating on ethanol since 2003, and was provided with biodiesel waste as the sole carbon source from Aug 18 2006 - October 21 2006.

Conclusions

Biodiesel waste shows evidence of being a very good material for use in bioreactors that utilize sulfate-reducing bacteria. Although a reactor operating on ethanol may take time to transition fully to bdw, it is an inexpensive waste material that provides a complex carbon source, and is potentially utilized more fully than ethanol. However, due to the viscous and caustic nature of bdw, a method for consistent delivery needs to be developed. In addition, testing needs to be conducted under winter conditions to ensure that the delivery system continues to be stable under winter conditions, and that the bacterial community that uses bdw contains psychrotolerant members such that winter bioreactor operations will not fail.

Acknowledgements

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