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Effect of electron donors on the performance of haloalkaliphilic sulfate-reducing bioreactors for flue gas treatment and microbial degradation patterns related to sulfate reduction of different electron donors

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ABSTRACT

Haloalkaliphilic microorganisms were used to treat wastewater from adsorption alkaline solution of flue gas characterized by high pH and salinity. Lactate, glucose, methanol, ethanol, formate, and acetate were used to investigate the effect of different electron donors on the performance of haloalkaliphilic sulfate-reducing bioreactors. At pH 9.5 and 1.0 M of Na^+, the optimum electron donor was found to be ethanol with the shortest lag period (31 days) and the highest sulfate removal rate (8.60 ± 0.129 kg m^{-3} d^{-1}). Bioreactors were stable after they were successfully started up. High sulfide concentration (3294 ± 18.8 mg l^{-1}) did not inhibit the activity of sulfate-reducing bacteria (SRB). Microbial degradation patterns related to sulfate reduction of different electron donors were determined. Oxidation process of propionate was coupled with sulfate reduction process in the lactate- and glucose-fed bioreactor. Glucose can be directly utilized by haloalkaliphilic SRB. The pathway of ethanol to pyruvate and Wood–Ljungdahl pathway were found in the ethanol- and formate-fed bioreactor, respectively. Some haloalkaliphilic SRB of the complete oxidation type may be present in the formate-fed bioreactor.

1. Introduction

A group of microorganisms known as sulfate-reducing bacteria (SRB) play an important role in the biological sulfate reduction process [1]. SRB include diverse bacterial and archaeal lineages [2,3]. They can use sulfate as terminal electron acceptor for the respiration of hydrogen or diverse organic substances, resulting in the production of sulfide, a highly toxic end product [4].

As previous studies have found, sulfur dioxide in the flue gas can be treated by biological methods in three steps [5,6]. Alkaline $NaHCO_3$ solution is used to absorb sulfur dioxide in flue gas, which is converted into sulfate. The alkaline solution containing sulfate is then treated by SRB to generate sulfide. Finally, sulfide is oxidized into sulfur by sulfur-oxidizing bacteria. Sulfide is toxic to SRB at pH about 6.0, which necessitates sulfide stripping with N_2, increasing the cost of the process [5,6]. However, no sulfide inhibition exists in the haloalkaliphilic system, obviating the need for stripping sulfide with N_2 [5,6]. From an engineering perspective, if the flue gas is treated with haloalkaliphilic microorganisms at pH about 9.5, fewer treatment cycles will be required due to the higher gas absorption efficiency, thereby reducing costs [5,6]. So far, few research studies have investigated sulfate reduction by haloalkaliphilic bioreactors, and the use of haloalkaliphilic microorganisms to treat flue gas adsorption wastewater is still a novel method.

Biological treatment is an attractive replacement of conventional treatments because of its economy, efficacy, and thoroughness [7]. It is necessary to add suitable carbon sources to the alkaline absorption liquid of flue gas to reduce sulfate. Electron donors used by SRB are usually low-molecular-weight organic compounds [1]. In this case, fermentative bacteria firstly convert macro-molecular-weight organic compounds into volatile fatty acids (VFAs), lactate, ethanol, or hydrogen, followed by SRB with sulfate reduction [8]. Different types of carbon sources give rise to different microbial communities, which can influence the performance of bioreactors, such as start-up, operation, accumulation of sulfide, etc. [1,9]. Start-up is important for establishing proper microbial communities in sulfate-reducing bioreactors. Poor start-up of a bioreactor may lead to a prolonged period of acclimation, ineffective removal of sulfate, and low accumulation of sulfide [10].

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Table 1
Gibbs free energies of methane production and sulfate reduction with different electron donors.

Number	Equation	$\Delta G^{\circ\prime}$ (kJ reaction^{-1})	References
Methane production			
1	$Acetate^- + H_2O \rightarrow CH_4 + HCO_3^-$	−31.0	[3,11]
2	$4H_2 + H^+ + HCO_3^- \rightarrow CH_4 + 3H_2O$	−135.6	[3,11]
3	$4Methanol \rightarrow 3CH_4 + HCO_3^- + H_2O + H^+$	−316	[1,11]
Sulfate reduction			
4	$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$	−152.2	[11,12]
5	$4Formate^- + SO_4^{2-} + H^+ \rightarrow HS^- + 4HCO_3^-$	−146.7	[1,5,11]
6	$Acetate^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^-$	−47.3	[1,11,12]
7	$4Propionate^- + 3SO_4^{2-} \rightarrow 3HS^- + 4HCO_3^- + 4Acetate^- + H^+$	−150.6	[3,11,12]
8	$4Propionate^- + 7SO_4^{2-} \rightarrow 7HS^- + 12HCO_3^- + H^+$	−341	[11,12]
9	$4Butyrate^- + 10SO_4^{2-} \rightarrow 10HS^- + 16HCO_3^- + 2H^+$	−492	[11,12]
10	$2Butyrate^- + SO_4^{2-} \rightarrow HS^- + 4Acetate^- + H^+$	−55.5	[3,11,12]
11	$4Methanol + 3SO_4^{2-} \rightarrow 3HS^- + 4HCO_3^- + 4H_2O + H^+$	−361.7	[1,11]
12	$2Methanol + SO_4^{2-} \rightarrow HS^- + 2Formate^- + 2H_2O + H^+$	−108.3	[1,11]
13	$2Ethanol + SO_4^{2-} \rightarrow HS^- + 2H_2O + H^+ + 2Acetate^-$	−132.7	[1,5,11]
14	$2Ethanol + 3SO_4^{2-} \rightarrow 3HS^- + 4HCO_3^- + H^+ + 2H_2O$	−227.3	[11]
15	$Glucose + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- + 3H^+ + 2Acetate^-$	−358.2	[1,11]
16	$Glucose + 3SO_4^{2-} \rightarrow 3HS^- + 6HCO_3^- + 3H^+$	−452.5	[1,11]
17	$2Lactate^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- + H^+ + 2Acetate^-$	−160.1	[3,11,12]
18	$2Lactate^- + 3SO_4^{2-} \rightarrow 6HCO_3^- + H^+ + 3HS^-$	−255.3	[11,12]

Thus, it is important to select a suitable electron donor for haloalkaliphilic SRB.

There are many advantages and drawbacks to different electron donors for sulfate reduction, and several factors should be considered before selecting a suitable electron donor. These include thermodynamic or kinetic parameters (Table 1) [1,11,12], treatment efficiency or ability (Table 2) [13], cost [18], availability, and residual chemical oxygen demand (COD) [1]. Thermodynamic or kinetic parameters can affect the competition between SRB and methane-producing archaea, which can subsequently influence the treatment efficiency. Molasses is much cheaper than other organic substances; however, it offers lower sulfate removal rate [15,16]. Complex organic substances such as lactate, molasses, and hydrocarbons cannot be completely oxidized by SRB with acetate as the end product, generating high COD levels in the effluent [1]. For biological treatment of flue gas, incomplete oxidization of electron donors increases costs and causes secondary pollution. By accounting for these factors, choosing a suitable electron donor for biological treatment of flue gas is particularly important. However, no studies have yet reported optimum electron donors for biological treatment of flue gas by haloalkaliphilic SRB.

Shortening start-up duration (the period before the bioreactor achieves a stable state) and improving treatment efficiency are essential. This study tested different electron donors to start up parallel bioreactors and investigated their effect on the performance of haloalkaliphilic sulfate-reducing bioreactors. Microbial degradation patterns related to sulfate reduction of different electron donors were also determined.

Table 2
Summary of sulfate removal rates with different electron donors.

Bioreactor type	Electron donor	Sulfate removal rate (kg m^{-3} d^{-1})	References
UASB[a]	Molasses	6.40	[14]
UASB–MFC–BAF[b]	Molasses	3.21	[15]
Packed bed	Molasses/mine water	1.36	[16]
Gas-lift	H_2	4.89	[17]
Gas-lift	$H_2 + CO_2$	30.0	[18]
Gas-lift	$H_2 + CO_2$	25.0	[19]
Packed bed	$H_2 + CO$	1.20	[20]
Gas-lift	$H_2 + CO$	1.63	[21]
Gas-lift	Synthesis gas	15.0	[22]
DFFB[c]	Volatile fatty acids	5.48	[12]
MBR[d]	Formate	13.7	[23]
Plug flow	Lactate	0.41	[24]
Fluidized-bed	Ethanol	4.30	[25]
MBR	Ethanol + acetate	6.62	[26]
Fluidized-bed	Ethanol + lactate	12.0	[27]
Baffled reactor	Sucrose + peptone	23.5	[28]
Anaerobic digester	Glucose + acetate	1.92	[29]
AFR[e]	Lactate	3.38	This study
AFR[e]	Glucose	5.0	This study
AFR[e]	Methanol	0	This study
AFR[e]	Ethanol	8.60	This study
AFR[e]	Formate	8.17	This study
AFR[e]	Acetate	0	This study

[a] Up-flow anaerobic sludge blanket.
[b] Up-flow anaerobic sludge blanket reactor-Microbial fuel cells-Biological aerated filter.
[c] Down-flow fluidized bed.
[d] Membrane bioreactor.
[e] Anaerobic filter reactor.

2. Materials and methods

2.1. Bioreactor setup

Twelve parallel laboratory-scale anaerobic filter reactors (1 l volume) were started up (Fig. 1). Seed sludge was collected from salt-lake sediments in Qinghai, China. Experiments were conducted in duplicate. Each pair of bioreactors was fed with a different electron donor: lactate, glucose, methanol, ethanol, formate, or acetate. Influent synthetic wastewater (1000 ml) consisted 31.8 g of Na_2CO_3, 21 g of $NaHCO_3$, 0.5 g of yeast extract, 0.5 g of NH_4Cl, 2 g of KH_2PO_4, 6 g of NaCl corresponding to Na_2SO_4 and carbon sources with a COD/SO_4^{2-} ratio of 2.0. In the presence of bicarbonate buffer, the pH could be maintained at about 9.5. The oxidation–reduction potential (ORP) of each bioreactor was measured using an acidity voltmeter (pHS-25; Shanghai, China) [6]. Each reactor was fed continuously with a hydraulic retention time of 24 h and covered with a water jacket to keep the operational temperature at 37.0 ± 0.5 °C. During start-up, sulfate loading improved gradually when the performance of the bioreactors was stable, as shown in Table 3. The reactor headspace was swept with N_2 gas with a flow rate of 0.1 l min^{-1}.

2.2. Analytical methods

The amount of sulfide was determined by colorimetry [30] with a spectrophotometer (U-2910; Hitachi, Tokyo, Japan). Sulfate concentration was quantified using an ICS-900 ion chromatograph system (Dionex, Sunnyvale, CA, USA) equipped with a Dionex IonPac™ AS14A analytical column (4 × 250 mm). For sulfate