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Inhibition of sulfate reduction by iron, cadmium and sulfide in granular sludge

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ABSTRACT

This study investigated the inhibition effect of iron, cadmium and sulfide on the substrate utilization rate of sulfate reducing granular sludge. A series of batch experiments in a UASB reactor were conducted with different concentrations of iron (Fe^{2+}, 4.0–8.5 mM), cadmium (Cd^{2+}, 0.53–3.0 mM) and sulfide (4.2–10.6 mM), the reactor was fed with ethanol at 1 g chemical oxygen demand (COD)/L and sulfate to yield a COD/SO_4^{2-} (g/g) ratio of 0.5. The addition of iron, up to a concentration of 8.1 mM, had a positive effect on the substrate utilization rate which increased 40% compared to the rate obtained without metal addition (0.25 g COD/g VSS-d). Nonetheless, iron concentration of 8.5 mM inhibited the specific substrate utilization rate by 57% compared to the substrate utilization rate obtained in the batch amended with 4.0 mM Fe^{2+} (0.44 g COD/g VSS-d). Cadmium had a negative effect on the specific substrate utilization rate at the concentrations tested; at 3.0 mM Cd^{2+} the substrate utilization rate was inhibited by 44% compared with the substrate utilization rate without metal addition. Cadmium precipitation with sulfide did not decrease the inhibition of cadmium on sulfate reduction. These results could have important practical implications mainly when considering the application of the sulfate reducing process to treat effluents with high concentrations of sulfate and dissolved metals such as iron and cadmium.

1. Introduction

Sulfate reduction is an anaerobic biological process that can be used for metal precipitation and sulfate removal. This process is carried out by sulfate reducing bacteria (SRB); the generation of sulfide and alkalinity (Eq. (1)) is the key for its application to precipitate metals from solution as metal sulfides (Eq. (2)).

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \quad (1)$$

where CH_2O = electron donor (organic matter).

$$H_2S + M^{2+} \rightarrow MS(s) + 2H^+ \quad (2)$$

where M = metal.

Acid mine drainage (AMD) and the wastewaters from metal processing, mining and petrochemical industries contain high concentrations of sulfate and dissolved metals. Such characteristics make these effluents candidates for the application of biological sulfate reduction for metal precipitation, to minimize the environmental risk caused when these effluents are deposited in aquatic or terrestrial ecosystems [1]. The main advantage of the biological treatment over the chemical treatment of effluents with dissolved metals is the reduction of the bulky sludge that is generated, when hydroxides and carbonates are used to precipitate metals. Moreover, under anaerobic conditions metal sulfides are more insoluble than the corresponding hydroxides or carbonates according to the low solubility product constants of most metal sulfides. For example and as reference, the solubility product constants (K_{sp}) of iron carbonate and iron hydroxide are 2.0×10^{-11} and 7.9×10^{-16}, respectively, whereas the solubility product constant of iron sulfide is 7.9×10^{-19} ($T = 25\,^{\circ}C$, ionic strength = 0) [2], being more insoluble the metal compound with the lowest solubility product constant. Another aspect of AMD treatment to take into account is low pH, however the potential toxic effect of treating an effluent with low pH may be avoided using reactors with water recycling, as this will reduce direct contact between the acidic influent and the microorganisms [3].

The majority of the metals present in AMD are inhibitory or toxic (depending on their concentration) to anaerobic microorganisms including SRB, responsible of the sulfate reduction process. Heavy metals have the tendency to deactivate enzymes because they may react with functional groups, such as sulfhydril (−SH), and can replace cofactors such as Cu(II), Zn(II), Co(II), Ni(II) causing a negative effect over the growth (toxicity) or the metabolic activity of microorganisms (inhibition) [4].

The inhibitory effects of heavy metals, such as zinc and copper, on sulfate reduction have been widely studied [4–7]. Related to cadmium, for a mixed culture of SRB the concentration that

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inhibited sulfate reduction was 0.18 mM [5]; and for a coccus-like, Gram-positive SRB isolate a cadmium concentration of 0.174 mM yielded a sulfate consumption of only 16%, compared with the sulfate consumption obtained (26%) when manganese was present [8]. Cadmium showed to be highly toxic or inhibitory to sulfate reduction compared to other metals such as Zn, Cu, Ni or Mn [5,8]. In contrast, the information concerning the potential inhibitory effect at high concentrations of iron towards sulfate reduction is rather scarce, in spite of being the predominant element present in AMD. Therefore, a better understanding between iron and sulfate reduction is necessary to employ the biological sulfate reducing process effectively for the treatment of mining effluents with high concentrations of iron and sulfate [9].

To what extent SRB are able to tolerate the presence of metals, without the reduction of their metabolic capacity (sulfate reducing activity), highly depends on the metal and its concentration. Moreover is not only the dissolved metal which may cause inhibition, in experiments with zinc and copper it was found that the insoluble metal sulfides can inhibit the biological sulfate reduction process as well [4].

The objective of this work was to investigate the inhibitory effect caused by iron and cadmium in combination with sulfide on the sulfate reducing process of granular sludge. In addition, this study may contribute to a better understanding of metal inhibition towards the sulfate reducing process.

2. Materials and methods

2.1. Bioreactor

Experiments were carried out in one lab-scale upflow anaerobic sludge blanket reactor (UASB) made of glass with a working volume of 840 mL. The UASB reactor was operated during 238 days under two different regimens: in batch for the determination of the kinetic parameters and inhibition experiments, and in continuous mode between the individual batch experiments. The duration of the batch assays was variable between 8 and 11 h, after each batch experiment the reactor was operated in continuous mode for at least 36 h. The rationale, for the operation in continuous mode after each batch assay, was to conduct each batch experiment under similar pseudo-steady state conditions. When operated in continuous mode the reactor was fed using a peristaltic pump, in batch mode the feed line was closed and the liquid contained in the reactor was recirculated at a flow of 44 mL/min equivalent to a superficial upward velocity of 1 m/h. All experiments were performed at ambient temperature 25 °C (±2 °C). Fig. 1 shows the experimental set-up.

2.2. Inoculum and basal mineral medium

The reactor was inoculated with 154 g of granular sludge to yield 20 g of volatile suspended solids (VSS) per liter of reactor. The sludge was obtained from a laboratory scale UASB reactor that was operated under sulfate reducing conditions at a chemical oxygen demand (COD) to sulfate (SO_4^{2-}) ratio of 0.66 (g/g).

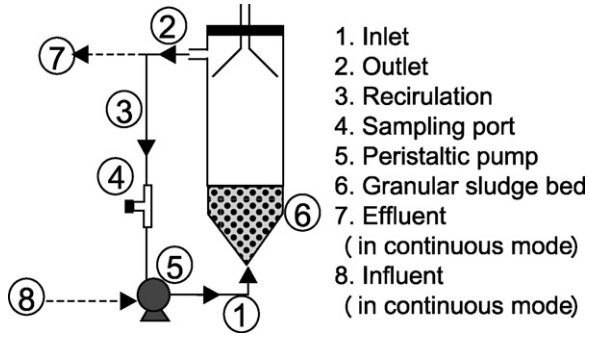

Fig. 1. Diagram of the UASB reactor set-up. Dashed line corresponds to the continuous mode configuration, when reactor operated in this mode there was not recirculation of the effluent.

The composition of the basal mineral medium was as follows (g/L): NH_4Cl (0.3), $CaCl_2{\cdot}H_2O$ (0.015), KH_2PO_4 (0.2), $MgCl_2{\cdot}6H_2O$ (0.098), KCl (0.25), yeast extract (0.02) and for the continuous mode operation 0.1 mL/L of trace elements solution as follows (g/L): $FeCl_2{\cdot}4H_2O$ (1.5), $MnCl_2{\cdot}4H_2O$ (0.1), EDTA (0.5), H_3BO_3 (0.062), $ZnCl_2$ (0.07), $NaMoO_4{\cdot}2H_2O$ (0.036), $AlCl_3{\cdot}6H_2O$ (0.04), $NiCl_2{\cdot}6H_2O$ (0.024), $CoCl_2{\cdot}6H_2O$ (0.07), $CuCl_2{\cdot}2H_2O$ (0.02), HCl 36% (1 mL/L).

2.3. Continuous flow reactor operation

The continuous operation was divided in four periods each one corresponds to the period when a set of batch experiments was performed: Period 1 corresponds to the kinetic parameters determination; period 2 to the experiments with sulfide; period 3 to the experiments with iron and period 4 to the experiments with cadmium. The reactor was fed with a synthetic wastewater that consisted of basal mineral medium (pH 5) supplemented with ethanol (1 g COD/L) and sulfate (2 g SO_4^{2-}/L as Na_2SO_4) to obtain a COD/SO_4^{2-} ratio (g/g) of 0.5, this ratio was chosen to avoid limitation of the electron acceptor (SO_4^{2-}) during the experiments. The hydraulic retention time was 10 h and the organic loading rate was constant at 2.5 g COD/L-d. Sulfide concentration was analyzed in the effluent; pH and COD were analyzed in the effluent and influent.

2.4. Batch assays

Batch experiments were conducted to obtain the maximum specific substrate utilization rate (q_{max}), the affinity constant (K_s) of ethanol oxidation, and to evaluate the inhibitory effect of sulfide, iron or cadmium on sulfate reduction with ethanol as electron donor. For this purpose, the feed flow of the reactor was discontinued and the liquid was recirculated by means of a peristaltic pump. Each batch experiment started with a shot of 140 mL at low pH (3–3.5), introduced into the reactor through the sampling port (Fig. 1). The content of the shot varied depending on the experiment to reach the initial concentrations according to Table 1. Each shot contained 14 mL of 10 times concentrated basal mineral medium, the corresponding amounts of ethanol, sulfate, and depending on the inhibition experiment different concentrations of sulfide, iron

Table 1
Concentrations of ethanol and sulfide, iron or cadmium added to the UASB reactor in the batch assays for the determination of the kinetic parameters (q_{max} and K_s) and the inhibition effect of sulfide, iron or cadmium on the sulfate reducing granular sludge.

Batch assay	Ethanol (g COD/L)	Iron (mM Fe^{2+})	Cadmium (mM Cd^{2+})	Sulfide (mM)
Kinetic parameters determination	0.26; 0.37; 0.55; 0.59; 0.69; 0.72; 0.80; 0.92; 0.96; 1.62; 2.8	NA	NA	NA
Inhibition with sulfide	1	NA	NA	4.7; 8.0; 10.2; 13.2
Inhibition with iron	1	4.0; 7.4; 8.1; 8.5	NA	NA
Inhibition with cadmium	1	NA	0.53; 2.14; 3.0	NA

NA: not added.