

Study of immobilization methods for sulfate-reducing sludge characterization through H₂S production evaluation

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Abstract

Immobilized sulfate reducing sludge present a solution for fast analysis of H₂S production and accurate mass transfer studies using amperometric microsensors. For this purpose, polymer carrier alginate, PVA and agar were mixed with sludge and placed in a flat plate bioreactor. Kinetic rates were calculated and long-term assays were performed to evaluate sulfate consumption, COD removal and resistance in order to select the optimal immobilization method. The selected method was also validated following the activity of immobilized sulfate-reducing sludge in the monitoring platform.

Keywords: Immobilization, Sulfate-reducing bacteria, H₂S monitoring, COD removal, sulfate removal.

1. Introduction

Bioscrubbers are an environmentally-friendly alternative for the treatment of SO_x emissions from waste incineration or coal-based power generation plants (Mora et al. 2018). The SONOVA process (Mora et al. 2020) has been successfully implemented for the valorisation of SO₂ as elemental sulfur. This treatment technology is based on the absorption of SO₂ from flue gases as a mixture of sulfite/sulfate, followed by two bioprocesses consisting of the sulfite/sulfate reduction to H₂S and its partial oxidation to elemental sulfur.

The bottleneck of SO₂ scrubbing relies on the heterotrophic reduction of SO₂ to obtain sulfide (Mora et al. 2020). However, this stage cannot be optimized from direct measurements or the in-situ characterization due to the lack of monitoring technologies available for in-situ H₂S measurement. To this aim a procedure for sulfate-reducing sludge characterization has been proposed in order to obtain relevant information about biomass dynamics and increase sulfide production rates. The characterization procedure is based on an immobilization of the sludge to be characterized, coupled to a monitoring platform for H₂S measurement during characterization assays. The results obtained in the study and selection of three different immobilization procedures and the validation of the selected one are presented in this work.

2. Materials and Methods

2.1. Sludge Immobilization

The study of the optimal procedure for the immobilization of the sulfate-reducing sludge has been performed assessing three different methods, using agar, PVA and alginate as carriers. The procedure followed in each case is detailed in Table 1.

Table 1. Procedure for the immobilization of sulfate-reducing sludge.

Immobilization method	Preparation procedure
Agar	Agar solution (2% w/w) was prepared and heated until 100°C and cool down to 60°C. Then it was mixed with sludge (2,2 mg VSS/L) in a 1:1 proportion (Okabe et al. 2002)
PVA	Polyvinyl alcohol solution (7%w/w) was prepared and autoclaved at 120°C for 20 min. Cooled down PVA solution was mixed with sludge in equal proportions, stored at -15°C for 12h for crosslinking and stored 4 h at 4°C (Magrí et al. 2012).
Alginate	3% w/w)alginate solution was mixed with sludge in equal proportions and after dropped on CaCl ₂ solution (2% w/w) to obtain beads with 1 cm diameter (Patel and Gupte 2015)

2.2. Kinetic study

The influence of the immobilization on the sludge activity was assessed estimating sulfate reduction rates of agar-bacteria, PVA-bacteria, alginate-bacteria mixtures and non-immobilized sludge. In this sense, 50 ml of immobilization mixture was placed in 500 ml bottles adding 250 ml of mineral medium containing pure glycerol as the sole carbon source and sulfate in a C/S rate of 6,25 (Mora et al.2018). Bottles were bubbled with nitrogen and sealed to obtain an anoxic environment and the assay was performed for 72 h at 32 °C. Sulfate consumption rate was calculated.

2.3. Long term assays

Immobilization mixture of sludge and polymer was placed in a flat plate bioreactor (FPB) designed in accordance with Guimerà et al. (2015). The reactor was manufactured in methacrylate (PMMA), 20 cm in length, 3.5 cm in width, and 1.3 cm in depth, hermetically closed with a cover connected to a nitrogen bag to allow gas exchange. A peristaltic pump (MCP Standard, Ismatec, Germany) was used to feed the reactor with a nutrient solution containing pure glycerol as the sole carbon source and sulfate

in a C/S rate of 6,25 (Mora et al. 2018). The assay was carried out at room temperature, to evaluate start-up time and removal of sulfate and COD. Besides, a control assay was performed with non-immobilized sludge using recirculation of inoculum to promote biofilm formation.

2.4. Monitoring platform

The selected method was validated for the monitoring of sulfate-reducing sludge through the analysis of H₂S production. The monitoring platform consisted of a methacrylate reactor, 7 cm length, 2 cm width and 0,8 cm deep, hermetically closed with a cover. The platform was connected to a peristaltic pump to fed it with mineral medium (Mora et al 2018). The cover has a groove for microsensor insertion. Commercial UNISENSE amperometric H₂S microsensor was used in this study and measurements were taken by sensor introduction on immobilized sludge.

Monitoring was performed adding four increasing sulfate concentrations to mineral medium, generating different H₂S concentrations for microsensor detection.

3. Results

3.1. Kinetics

Batch assays with agar and alginate immobilization were performed. PVA and agar presented a high sulfate reduction rate, and alginate rate value was close to the observed on non-immobilized sludge. However, COD removal was not completely achieved in agar, PVA and alginate assays due to a deterioration of polymers by N₂ bubbling procedure which generated interferences in measurements (Figure 1).

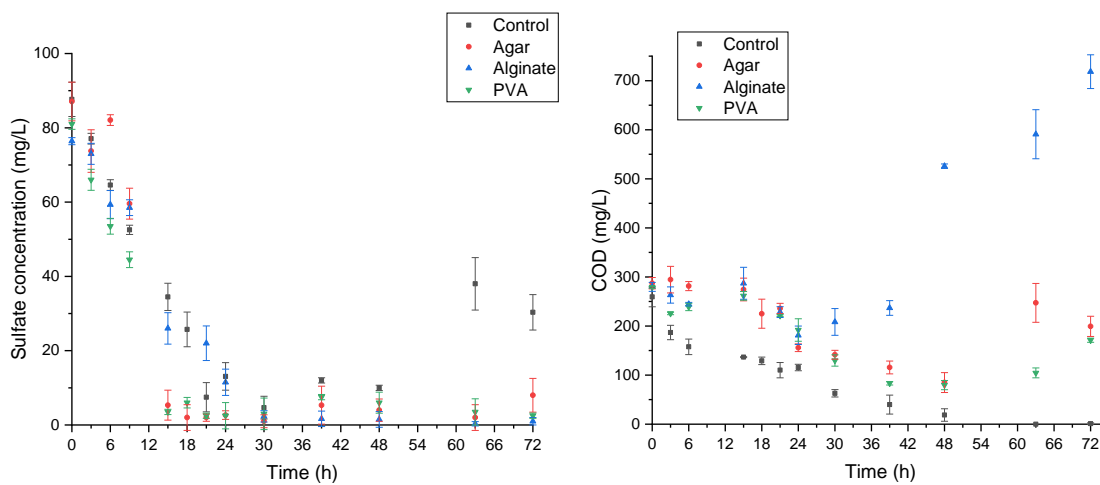


Figure 1: Sulfate and COD consumption kinetic of non-immobilized sludge (control) and immobilized sludge using agar, alginate and PVA.

Table 2: Sulfate consumption rates of immobilization materials.

	Agar	PVA	Alginate	Control
Sulfate consumption rate (mg/Lh)	5,0267 ±0,6	5,0158 ± 0,4	2,622±0,2	2,842±0,1
R ²	0,950	0,979	0,989	0,973

3.2. Long term assays

Long term performance of biomass immobilization was evaluated on an FPB for 1 month. Sludge immobilized using an agar and PVA matrix presented a start-up period of 12 days and, under stationary conditions, average sulfate removal were of 60% and 98% respectively (Figure 2). Besides, at day 15, COD removal of PVA matrix was higher than alginate immobilized sludge. Bioreactor with non-immobilized sludge was completely washed out at day 25, however, high COD removal was observed even when washed out due to proliferation of other microorganisms.

On the other hand, alginate immobilization showed a low mechanical resistance due the interaction between phosphate and calcium that weakened the alginate matrix. Biomass immobilized with alginate was washed out of the reactor after 96 h.

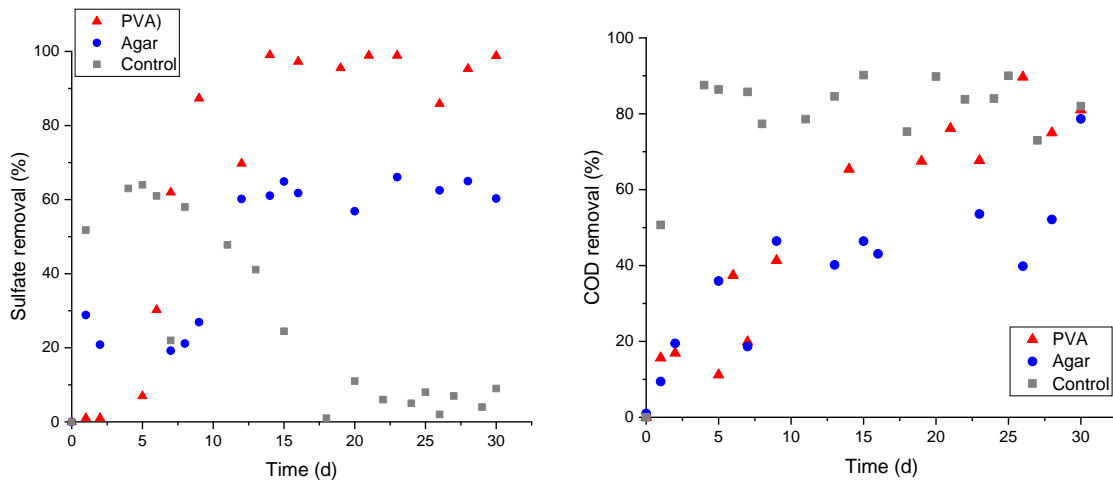


Figure 2: Sulfate and COD removal monitoring of non-immobilized sludge (control) and immobilized sludge using agar, alginate and PVA.

3.3. H₂S monitoring of immobilized sludge bioreactor

Monitoring was carried out for 72 hours and microsensor detected different H₂S concentrations. The increase of signal was not proportional to sulfate concentrations added due to the linear detection range of the microsensor was overpassed (0-300 μ M).

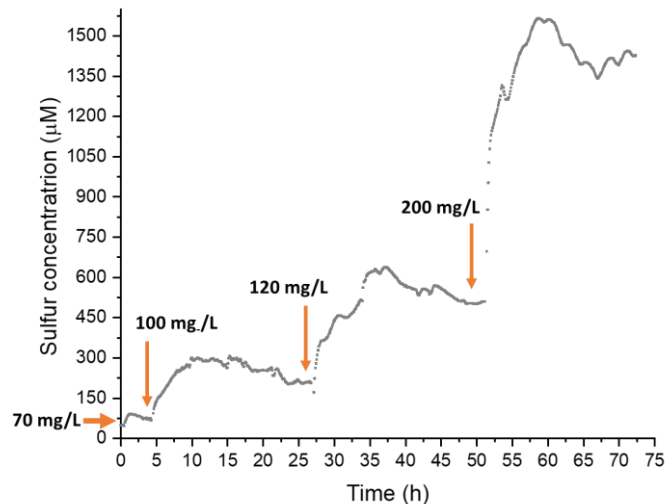


Figure 11: H₂S Monitoring of PVA immobilized sludge using an amperometric sensor.

4. Conclusions

Based on results, PVA is a suitable material for an immobilization of biomass sludge allowing measurement of H₂S through an amperometric microsensor. Also, has been demonstrated that PVA matrix enabled a higher mass transfer exchange between the sludge and mineral medium than agar and non-immobilized sludge, allowing sulfate reduction and COD removal. On the other hand, alginate cannot be used since it presented poor mechanical resistance.

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