A Study of the Operating Parameters of a Sulphate-Reducing Fixed-Bed Reactor for the Treatment of Metal-Bearing Wastewater

P. Kousi\textsuperscript{1,a}, E. Remoudaki\textsuperscript{1,b}, A. Hatzikioseyian\textsuperscript{1,c} and M. Tsezos\textsuperscript{1,d}

\textsuperscript{1}National Technical University of Athens, School of Mining and Metallurgical Engineering, Laboratory of Environmental Science and Engineering, Heroon Polytechniou 9, 15780 Athens, Greece.

\textsuperscript{a}pkousi@metal.ntua.gr \textsuperscript{b}remound@metal.ntua.gr \textsuperscript{c}artin@metal.ntua.gr \textsuperscript{d}tsezos@metal.ntua.gr

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Abstract. An upflow fixed-bed sulphate-reducing reactor has been set up and monitored for the treatment of metal-bearing wastewater. Zinc has been chosen as the target metal to be sequestered from influent water stream at initial concentrations ranging from 50 to 400 mg/l and initial pH values ranging from 3 to 5. Main operating parameters of the reactor, such as the composition and content of electron donor, electron acceptor, sulphate and metal removal capacity, have been monitored during ten months of continuous operation. The results obtained have shown that the reactor has a considerable capacity of completely reducing sulphates for initial concentrations up to 7,200 mg/l, completely removing soluble zinc for initial concentrations up to 400 mg/l and completely removing Total Organic Carbon (TOC), for initial concentrations up to 1,500 mg/l.

Introduction

Biological reactors based on Sulphate-Reducing Bacteria (SRB) have recently been developed in both pilot and full scale [1-5]. In these reactor schemes, Sulphate-Reducing Bacteria (SRB) oxidize simple organic compounds, such as lactic acid [6], under anaerobic conditions. The bacteria transform the sulphates, available by the wastewater, into hydrogen sulphide and bicarbonate ions are generated:

$$2\text{SO}_4^{2-} + 2 \text{CH}_3\text{CH(OH)COOH} \rightarrow 3\text{H}_2\text{S} + 6\text{HCO}_3^- \quad (1)$$

Hydrogen sulphide reacts with divalent soluble metals which are sequestered from wastewater as insoluble metal sulphides:

$$\text{H}_2\text{S} + \text{M}^{2+} \rightarrow \text{MS}^{(s)} + 2\text{H}^+ \quad (2)$$

where M stands for metals such as Zn, Fe, Cu, Ni, Pb and Cd.

Bicarbonate ions react with protons to form CO\textsubscript{2} and water; thus, removing acidity from solution as CO\textsubscript{2}:

$$\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2^{(g)} + \text{H}_2\text{O} \quad (3)$$

H\textsubscript{2}S and HCO\textsubscript{3}\textsuperscript{-} formed during sulphate reduction equilibrate into a mixture of H\textsubscript{2}S, HS\textsuperscript{-}, S\textsuperscript{2-}, CO\textsubscript{2}, HCO\textsubscript{3}\textsuperscript{-} and CO\textsubscript{2}\textsuperscript{2-}. This mixture buffers the solution pH typically around neutral and slightly alkaline values, [1]. The shift of the pH of the acidic solution may cause some metals to hydrolyze and precipitate as insoluble hydroxides or oxides.

From the above, two obvious advantages are the simultaneous sequestering of metals and sulphates. Metal sulphides are generally less soluble than their corresponding metal hydroxides; allowing quantitative metal precipitation [7, 8]. Metal sulphides are also more compact, have faster settling velocities and exhibit better thickening and dewatering characteristics than the corresponding hydroxide sludge [9]. Highly soluble oxyanions, such as chromate, selenate, molybdate and uranyl-carbonate complexes, can also be successfully sequestered from wastewater when treated in sulphate-reducing reactors thanks to: (a) the reducing, electron-rich environment of the reactor (reduction of the targeted element) and (b) the alkalinity generated by the bacterial
metabolism (precipitation of the targeted elements as hydroxides/oxides) [10]. Metals complexed with ammonia or cyanide are also more readily precipitated as sulphides than as hydroxides [11]. This study presents the results obtained from the continuous operation of a sulphate-reducing fixed-bed reactor for a period of ten months. The reactor has been set up and monitored in order to define main operating parameters.

Materials and methods

Sulphate-reducing fixed-bed reactor. The sulphate-reducing fixed-bed reactor, operating in upflow mode, is presented in Figure 1.

Figure 1. Sulphate-reducing fixed-bed reactor. Height: 1 m, diameter: 9.5 cm, bed height: 82 cm, head space (necessary for gas collection and removal): 18 cm.

The biofilm was established on porous sintered glass spheres of 0.6 cm diameter and 1,500 m²/l specific surface. This material has the advantage of a very large surface area, available for biofilm development.

Sludge from the anaerobic digestion tank of a wastewater treatment plant (Municipal Wastewater Treatment Plant, Metamorphosi, Athens) was used as inoculum for the development of a mixed culture of Sulphate-Reducing Bacteria.

The reactor was fed with a variation of Postgate's medium (DSMZ, Desulfovibrio medium, Medium 63) using lactate as electron donor.

The pH of the feed solutions was adjusted to 3-4 by addition of HCl (Merck, analytical grade). The reactor operated first for a period of about 35 days in batch mode (close loop) for biofilm establishment. Following the period of the establishment of the biofilm on the fixed bed of the reactor, the system was operated in continuous mode, fed with synthetic solutions containing the nutrient medium and varying zinc (50-400 mg/l, added as Merck ZnCl₂) and iron (100 mg/l, added as Merck FeSO₄·7H₂O) concentrations. Sulphates were added at the appropriate concentration as Na₂SO₄ and MgSO₄·7H₂O. The reactor operated continuously for 10 months at room temperature (mean temperature 25°C). In order to study the influence of initial organic carbon, sulphate and zinc concentrations on the reactor efficiency, a constant Hydraulic Residence Time (HRT) value of 9 hrs was chosen.

Liquid phase monitoring. During the operation of the reactor, sampling was systematically performed at the following points: inlet, outlet and 8 sampling ports along the column length. The liquid phase samples were vacuum filtered through 0.45 µm sterilized membranes before any chemical determination. The pH of the feed and the outlet solutions was systematically monitored.
The sulphate concentration was determined by turbidimetry at 450 nm after formation of BaSO4 (Hach, DR/2000, Method 8051). TOC was determined by colorimetry after persulphate oxidation of carbon to carbon dioxide and colour change of a pH indicator (Hach, DR/2500, Method 10129). Zinc and iron concentrations were determined by ICP (Leeman Labs, Direct Reading Echelle). All determinations were performed in duplicate. Analytical errors have been estimated to be lower than 5%.

Results and discussion

**pH variation.** Figure 2(a) presents the variation of pH monitored in the influent and the effluent during the operation of the reactor. The pH, initially adjusted at 3-5 in the feeding solution, always reaches a value of 6.0-8.8 as a result of the alkalinity generated during the SRB metabolism. Figure 2(b) shows that the influent flow is neutralized within the first 10 cm of the column length, indicating an intense microbial activity at the bottom of the column.

![Figure 2](image1.png)

**Figure 2.** (a) pH variation during the 10-month operation of the reactor and (b) typical pH profiles along the column length (HRT=9h).

**Sulphate reduction.** During ten months of continuous operation of the reactor, initial concentrations of sulphates ranged from 1,600-7,200 mg/l. Figure 3(a) shows that sulphates were reduced in most cases. From the data depicted on Figure 3, sulphate reduction rates have been calculated and varied from 4 to 20 g/l.d. Figure 3(b) presents profiles of sulphates reduction along the column of the reactor for different initial nutrient and sulphate concentrations.

![Figure 3](image2.png)

**Figure 3.** Sulphate reduction (a) during the 10-month operation of the reactor and (b) for different initial concentrations (HRT=9h).
From Figure 3, it is apparent that sulphates at initial concentrations up to 7,200 mg/l may be completely reduced at the first 50 cm of the bed length indicating the increased activity of the SRB culture in the reactor.

**Nutrient consumption.** The concentration of lactate was measured as total organic carbon concentration (TOC). Figure 4 presents characteristic TOC profiles obtained along the bed of the column for initial TOC concentrations ranging from 700 to 1,500 mg/l. A very satisfactory reproducibility of the results can be first observed from this figure. The profiles show that, for initial TOC concentrations up to 1,500 mg/l, TOC can be completely removed by the column at the first 60 cm of the bed.

**Metal removal.** The reactor operated for Zn initial concentrations ranging from 50 to 400 mg/l and Fe 100 mg/l. Both metals were precipitated quantitatively at any operating conditions during ten months of continuous operation of the reactor. SEM-EDX data obtained for solid samples confirm that amorphous phases of iron and zinc sulphides are predominant [12].

The influence of zinc initial concentration on the microbial population activity was also studied. Figure 5 presents sulphates concentration profile as a function of the initial zinc concentration. The results presented on Figure 5 demonstrate that the microbial activity is not significantly influenced by the presence of zinc for initial concentrations up to 400 mg/l.

![Figure 4. TOC removal along the column bed for two different initial TOC concentrations (HRT=9h).](image)

![Figure 5. Sulphate reduction profiles along the reactor column for various initial zinc concentrations (HRT=9h).](image)

**Conclusions**

The following conclusions can be drawn from the continuous monitoring of the sulphate-reducing reactor:

1. Complete reduction of sulphates for initial concentrations up to 7,200 mg/l,
2. Complete removal of zinc for initial concentrations up to 400 mg/l through precipitation mostly as zinc sulphides,
3. Maintenance of the SRB population for influent pH values as low as 3,
4. Maintenance of the SRB population for initial zinc concentration as high as 400 mg/l,
5. Complete consumption of TOC for initial concentrations up to 1,500 mg/l and
6. Due to the high porosity of the support material, there is a microbial population of high density able to ensure very high metal, sulphate, TOC removal capacity even at the first centimetres of the bed height.
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References