A study of the operating parameters of a sulphate-reducing fixed-bed reactor for the treatment of metal-bearing wastewater

P. Kousi, E. Remoudaki, A. Hatzikioseyian & M. Tsezos
National Technical University of Athens, School of Mining and Metallurgical Engineering, Laboratory of Environmental Science and Engineering
Heroung Politechniou 9, 15780 Athens, Greece
Tel.: +30-210-7722271, Fax: +30-210-7722173, e-mail: tsezos@metal.ntua.gr

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 concentrations ranging from 50 to 400 mg/l and initial pH values ranging from 3 to 4. 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 6,000 mg/l, completely removing soluble zinc for initial concentrations up to 400 mg/l and completely removing 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. In these reactor schemes, SRB oxidize simple organic compounds, such as lactate acid, under anaerobic conditions. The bacteria transform the sulphates, available by the wastewater, into hydrogen sulphide and bicarbonate ions are generated:

\[ 3SO_4^{2-} + 2CH(OH)COOH \rightarrow 3H_2S + 6HCO_3^- \]

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

\[ H_2S + M^{2+} \rightarrow MS_{(s)} + 2H^+ \]

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

Bicarbonate ions react with protons to form CO₂ and water; thus, removing acidity from solution as:

\[ HCO_3^- + H^+ \rightarrow CO_2 + H_2O \]

H₂S and HCO₃⁻ formed during sulphate reduction equilibrate into a mixture of H₂S, HS⁻, S₂⁻, CO₂ and CO₃²⁻. This mixture buffers the solution pH typically around neutral and slightly alkaline values.

Process advantages:
• Simultaneous sequestering of metals and sulphates.
• Metal sulphides are generally less soluble than their corresponding metal hydroxides; allowing quantitative metal precipitation.
• Metal sulphides are also more compact, have a high metal, sulphate, TOC removal capacity even at the first centimetres of the bed height.
• The pH of the feed solutions was adjusted to 3-4

Materials & Methods

Sulphate-reducing fixed-bed reactor
• Upflow reactor
• Biofilm established on porous sintered glass spheres
• Duration: 10 months at room temperature (mean 25°C)
• Feed: synthetic solutions containing the nutrient variation of Postgate’s medium (DSMZ, Delft University, Medium 63) using lactate as electron donor
• pH of the feed solutions was adjusted to 3-4

Liquid phase monitoring
• Systematic sampling at: inlet, outlet and 8 sampling ports along the column length.
• Samples vacuum filtered through 0.45 µm sterilized membranes before any chemical determination.

Systematic monitoring of:
• The pH of the feed and the outlet solutions
• Sulphate concentration (by turbidimetry at 450 nm after formation of BaSO₄)
• Total organic carbon (TOC) concentration (by Leco combustion analyzer after formation of CO₂)
• Carbon dioxide concentration (by gas chromatography after formation of CO₂)
• Zinc and iron concentrations (by ICP)

Scope
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.

Conclusions
• Complete reduction of sulphates for initial concentrations up to 7,200 mg/l.
• Complete removal of zinc for initial concentrations up to 400 mg/l.
• Maintenance of the SRB population for influent pH values as low as 3.
• Complete consumption of TOC for initial concentrations up to 1,500 mg/l.
• 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.

Acknowledgment
This work was carried out in the frame of BioMinE (European project contract NMP1-CT-500329-1). The authors acknowledge the financial support given to this project by the European Commission under the Sixth Framework Programme for Research and Development. We also wish to thank our various partners on the project for their contributions to the work reported in this paper.

Results & Discussion

pH variation
Effluent pH: 6.0-8.8 as a result of the alkalinity generated during the SRBs metabolism

Wastewater neutralization within the first 10 cm of the column length

Sulphate reduction
Complete reduction of sulphate up to 7,200 ppm

Nutrient consumption
Complete removal of TOC up to 1,500 ppm

Metal removal
Quantitative precipitation of Fe & Zn
Amorphous phases of FeS & ZnS on crystals