Treatment of Acid Mine Drainage with Sulphate-reducing Bacteria Using a Two-stage Bioremediation Process

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Abstract
Acid mine drainage (AMD) causes several environmental problems in many countries. The use of biological processes with sulphate-reducing bacteria (SRB) has great potential within environmental biotechnology. The aim of this study was to develop a bioremediation system, using a mixed culture of SRB, for the treatment of AMD from São Domingos mine. Sulphate and heavy metals (Fe, Cu and Zn) concentrations, pH and Eh were monitored during 243 days. The process that was developed consisted of two stages that proved highly efficient at AMD neutralization and the removal of sulphates and the heavy metals iron, copper and zinc .

Key words: Sulphate-reducing bacteria, bioremediation, acid mine drainage (AMD), heavy metals

Introduction
In Portugal, as a result of extensive sulphide mining activities that occurred until recent times, several abandoned mines have accumulated large volumes of AMD in open pits and streams, characterized by high concentrations of heavy metals and sulphates as well as low pH values. These characteristics of AMD affect severely the ecosystems and population health. The São Domingos mine, located in SE of Portugal, a region with Mediterranean conditions and consequently with scarce hydrologic resources, is an example of such a situation. Its AMD is characterized by pH around 2 and media concentrations around 3 g/L sulphates, 500 mg/L Fe, 75 mg/L Cu and 140 mg/L Zn (Costa and Duarte 2005). Thus, in order to reduce environmental problems associated and increase the availability of water for irrigation is essential to develop an AMD treatment.

Several conventional chemical and physical processes are available for AMD treatment but they have generally demonstrated low efficiency and high cost. The use of biological processes with sulphate-reducing bacteria (SRB) has great potential due to the capacity to simultaneously reduce sulphate and remove high amounts of heavy metals as insoluble metal sulphides, with low installation and operation costs (Costa and Duarte 2005). The capacity of SRB to generate H_2S which precipitates the metals as sulfides has been used in a variety of treatments of heavy metal-contaminated waters/drainage (Costa *et al*. 2008; Hulshoff *et al*. 2001). The use of mixed cultures of SRB, obtained from natural sources, has several advantages namely their great availability and environmental adaptation (Gibert *et al*. 2002).

The aim of this study was to develop a bioremediation system with two stages and using a mixed culture of SRB, for the treatment of AMD from São Domingos mine, in order to obtain water for irrigation purposes

Methods
The SRB inoculum used was previously selected (Martins *et al*., 2007) and was obtained from samples of sludge from Montenegro waste water treatment plant (South of Portugal). A synthetic AMD with similar concentrations of heavy metal and sulphate as well as pH from São Domingos mine drainage was used (Costa and Duarte, 2005). The bioremediation system consisted of two stages: a calcite tailing column and an anaerobic upflow packed bed reactor similar to that described in Costa et al. (2008). The experiment was performed at room temperature (±22ºC) in a continuous system, with a hydraulic retention time of 15 days, for about 243 days. The carbon and energy source used was lactate.

Periodically, samples of each of the two columns were collected and filtered through 10 µm paper filter. Redox potential(Eh), pH, sulphate and heavy metals (Fe, Cu and Zn) were analyzed. Redox potential and pH were measured using a pH/Eh Meter (GLP 21, Crison). Sulphate concentration was measured by a UV-VIS spectrophotometer (Hach-Lange DR2800) using the method of sulfaVer4 (Hach-Lange). After sample acidification, heavy metals were measured by flame atomic absorption spectroscopy (Flame-AAS, Shimadzu AA-680 model spectrometer).

Results and Discussion

Three days after the inoculation of the anaerobic upflow packed bed reactor, black precipitates were formed, gradually extending from the base to the top of the columns. This occurrence and the decrease of the redox potential are indicators of the growth and activity of SRB (Figure 1). The variations of pH and redox potential during the treatment process are presented in figure 1.

Figure 1 *Changes of pH in synthetic acid mine drainage (AMD) and in the two stages of the bioremediation system and redox potential (Eh) in the effluent from bioreactor, over an experimental time of 243 days.*

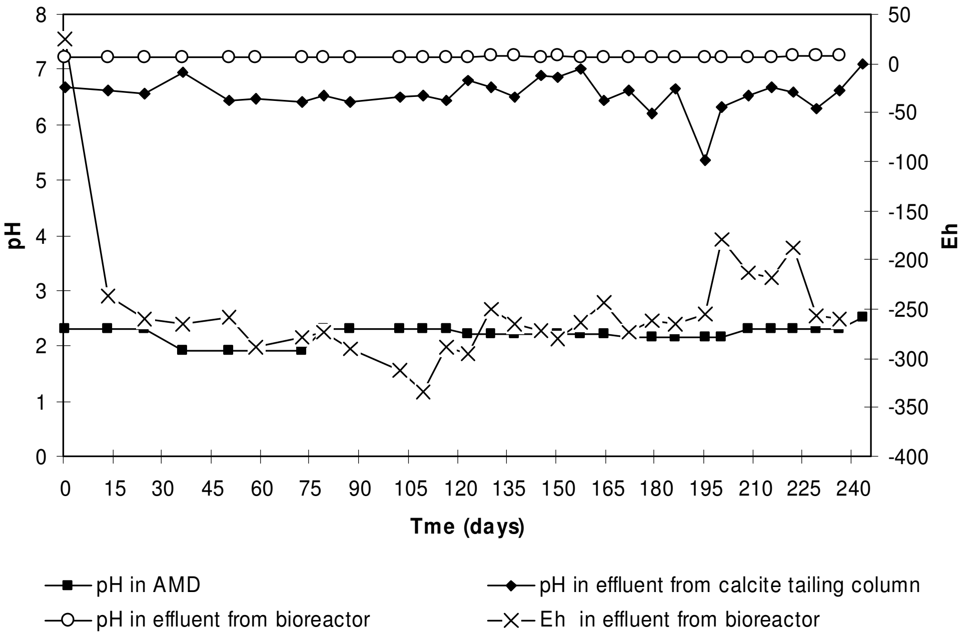
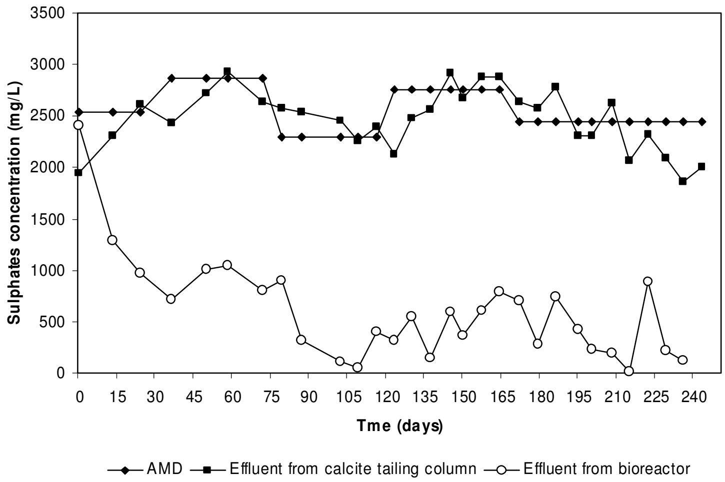
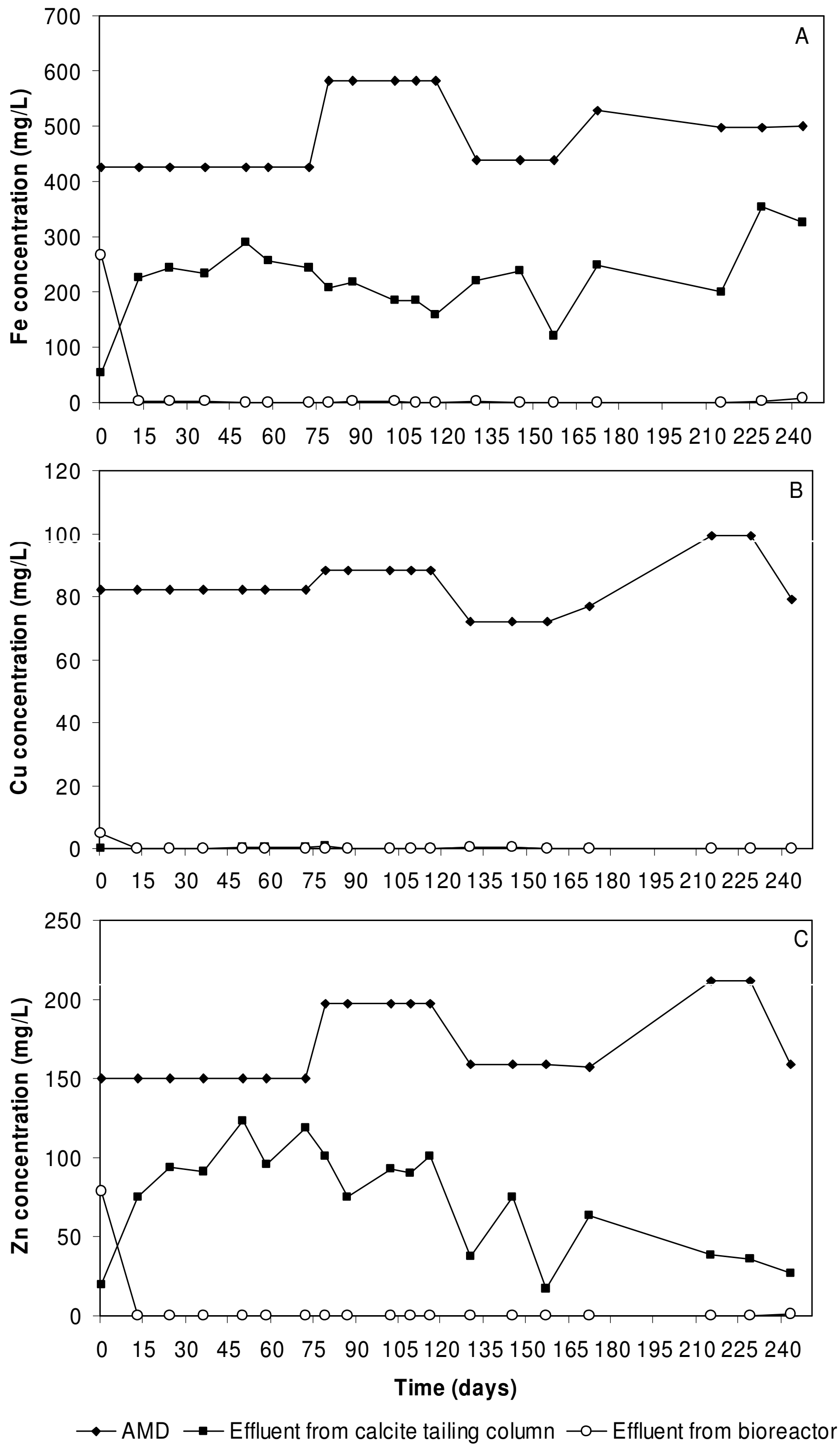


Figure 2 *Sulphate concentrations in synthetic acid mine drainage (AMD) and in the two stages of the bioremediation system, over an experimental time of 243 days.*



The neutralisation of the synthetic AMD occurred in the calcite tailing column, throughout the tested time (Figure 1). These pH values were within the range considered optimal for SRB activity (Cohen, 2006) and are in the agreement with the Portuguese legislation for irrigation waters (DL 236/98). The SRB present in the anaerobic bioreactor were capable of tolerating sulphate concentrations under continuous flow conditions. During the first 109 days of the treatment, the sulphate concentration decreased in the bioreactor, reaching values around 48 mg/L. After this period the sulphate removal was maintained around 75%. The activity of SRB was the key both for the sulphate removal by biological reduction and for metal removal.

Figure 3 *Changes in Fe (A), Cu (B) and Zn (C) concentration in synthetic acid mine drainage and in the two stages of the bioremediation system, during experimental time (243 days).*



Values of metals concentrations in the process are presented in Figure 3. In the calcite tailing column, partial removal of Fe and Zn was observed as well as complete removal of Cu. This fact is related with high adsorption capacity of the calcite material. The H_2S formed by SRB activity, in the anaerobic bioreactor, caused the precipitation of the remaining metals in the solution. The values of the three metals in the treated effluent were generally satisfactory considering the Portuguese legislation (DL 236/98). These concentrations are below the maximum recommended values for irrigation waters, which according to this legislation are: 2 mg/L for zinc, 0.2 mg/L for copper and 5 mg/L for iron. Thus, this process showed metal removal efficiencies higher than 99% (Figure 3).

Conclusions

The treatment of acid mine drainage with sulphate-reducing bacteria using a two-stage bioremediation process showed great capacity to remove high concentrations of sulphate, iron, copper and zinc. An increase of the pH values in the treated AMD was also observed due to the neutralization and increase in buffer capacity in the calcite tailing column. In the bioremediation system studied other lower cost carbon sources should be tested and natural AMD collected in the abandoned mine sites should also be used.

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