

HEAVY METAL REMOVAL FROM LIQUID EFFLUENTS USING AN ANAEROBIC MICROBIAL PROCESS

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ABSTRACT

This study aimed at investigating the possibility of using molasses as an organic substrate for sulphate reducing bacteria growth and to evaluate the removal efficiency of the main heavy metals present in the mining and metallurgical sulphates bearing wastewaters. The experiments were carried out in a continuous bench-scale bioreactor (13 litre upflow anaerobic sludge blanket reactor) operated with a hydraulic retention time of 18 hours. The bioreactor was inoculated with 7 litres of anaerobic sludge. An enrichment procedure for elevating the number of sulphate reducing bacteria was then started. Thus that, cadmium and zinc were further added to the synthetic effluent, whose removal as sulphide was evaluated. The used synthetic feeding solution represented drainage from a dam of the metallurgical industry with an added carbon source (molasses). The results obtained in the second step of this technical contribution study showed high metal removal efficiency (> 99%), and also indicated that those metals were not only removed as sulphide, since the alkalinity generated, as carbonate, was also responsible for their precipitation.

INTRODUCTION

In recent years, advances in knowledge about toxicity of heavy metals and their noxious effects on the environment have taken to the implementation of more rigid legal restrictions on the discharge of industrial effluents. However, taking into account the benefits that the heavy metals have produced for society, contributing to the development of goods which can bring about an improved quality of life for the population, the threat that they represent to the environment should be minimised through the search

for efficient, economic methods for their removal from effluents and discharges as a whole.

The main existing removal processes are precipitation, coagulation/flocculation, ionic transfer or separation by membranes. However, these processes are sometimes not feasible due to technical or economic problems. Moreover, the increasing awareness of the Brazilian population has made it imperative that existing environmental laws be complied with, which has led companies to search for new decontamination technologies. The use of biotechnological processes for treating heavy metals bearing effluents has gained increasing interest as an alternative ways, mainly because of their sensitivity in producing solutions, which can be discharged into the environment.

A highly promising biological process which is already employed in an industrial scale in Germany and Holland (Morper and Furst, 1991; Scheeren *et al.*; 1992) consists in removing heavy metals utilising the anaerobic production of sulphide ions by the sulphate reducing bacteria (SRB). Those bacteria utilise the sulphate ion as a final electron acceptor, generating CO₂, H₂O and high sulphide concentrations. This sulphide reacts with metals in solution, precipitating them in a highly insoluble form (sulphides) which can be recovered, and the sulphate concentration in the final effluent is also reduced (Hansen, 1994).

Although this process has already been employed, the problem of getting an organic substrate for the sulphate reducing bacteria (SRB), that be, both economically feasible and widely available has not yet been solved. Ethanol is used as a substrate in the industry (Scheeren *et al.*; 1992) but it is costly, and cannot be justified for many effluent treatments. Hence, the use of wastes containing organic substrates is seen as an excellent option for reducing the treatment cost, as in most cases the only major cost to be considered is the one of transportation. In this study, the waste evaluated was molasses, since it contains a high concentration of

organic matter and it is available at some locations in Brazil.

In this study, the main aims were:

- To assess the removal efficiency of the main heavy metals present in the mining and metallurgical sulphate bearing wastewaters, utilising molasses as the carbon source, and
- To check the occurrence of other ways to remove those metals not precipitated as sulphide.

EXPERIMENTAL

Experimental set-up

The experiments were carried out in a continuous bench-scale reactor (13 l), for a period of 348 days. A schematic view of the experimental set-up is shown in Figure 1. It is comprised of one influent tank (200 l) from where the solution is fed, through a peristaltic pump, into the upflow anaerobic sludge blanket reactor (UASB), and a gas collection system.

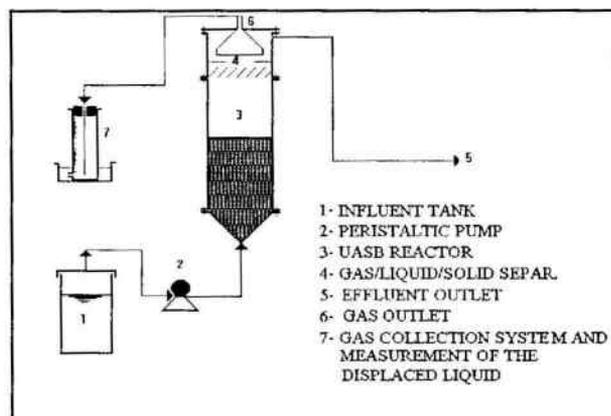


Figure 1 - Schematic diagram of laboratory UASB reaction system.

The upflow anaerobic sludge blanket process is characterised by a reactor containing no packing or any other type of biomass support material. The UASB reactor is basically made up of a vertical tank, in a prismatic form with a circular cross section, with a gas/solid separator located right on top of the reactor. The influent is fed in at the bottom of the reactor, in an upstream flow. Its even distribution through the sludge blanket is ensured by a perforated plate. The anaerobic bacteria present in the sludge provide the organic matter to stabilise. An important feature of this design is the gas/solid separator (GSS), which provides a quiescent zone on the upper part of the reactor, where suspended solids will settle and return to the sludge blanket. Any

gas being produced will flow through the GSS, to be trapped by a conical gas collector whose edges are immersed in the liquid above the GSS. The solution flowing through the GSS leaves the reactor through an outlet pipe at the top.

Experimental procedure

The bioreactor was inoculated with 7 litres of anaerobic sludge collected in the lower part of UASB reactor that is being used for treating the effluent from a yeast factory. An enrichment procedure for increasing the number of SRB was then started, lasting 224 days, time enough to be adapted to a distinct feeding solution composition, but these dates will not be presented in this report. After that, four experimental runs were accomplished with different organic contents (molasses). The flow rate and pH were monitored daily, ensuring the safe operational control of the experimental set-up.

The influent composition was defined so as to simulate the wastewater from drainage from a metallurgical industry dam, in which was added a carbon source (molasses). Thus, the composition of this synthetic effluent was around 80 mg/l zinc, 2 mg/l cadmium and 400 mg/l sulphate, which were added in the form of zinc sulphate, cadmium sulphate and sodium sulphate, respectively. No effort was made to deplete the O_2 content of the influent solution.

Influent and effluent sampling were undertaken three times a week for measuring chemical oxygen demand (COD), sulphate, sulphide and metals.

Analytical Methods

The sulphate and COD were determined according to APHA Standard Methods (Clesceri *et al.*, 1989). The dissolved sulphide was determined using Ag/Ag_2S electrode in non-filtered samples, and the soluble cadmium and zinc concentrations were determined by flame atomic absorption spectrometry (Varian Techtron Spectrometer, Model AA6).

RESULTS AND DISCUSSION

Removal of Organic Matter

The performance of this process, with regard to the removal of organic matter (molasses), was assessed through COD analyses of the reactor's influent and effluent, which results are shown in Figure 2.

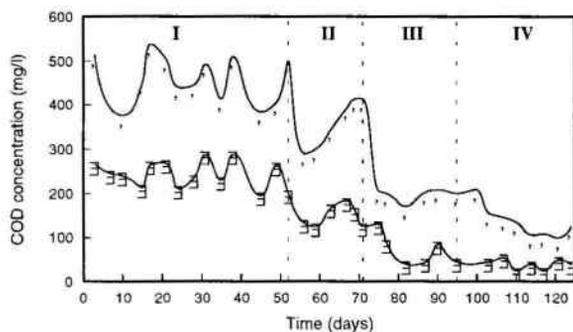


Figure 2 - COD influent (■) and effluent (○) concentration profiles against operation time.

It can be seen in Figure 2 that the concentration of organic matter in the influent decreased with time. Initially, it was oscillating around the 459 mg COD/l (run I), but dropped down to 135 mg COD/l after 95 days of operation (run IV). This reduction was necessary, since an excessive reduction in the sulphate by the SRB was produced because of the high level of availability of organic matter content in the reaction zone.

The COD oscillations seen in the concentration of organic matter during each run occurred as a result of the difficulty to prepare the diluted molasses solution.

Bacterial Reduction of Sulphate Ions

The reduction in the sulphate ions concentration is an indication that sulphide ions is being generated. Under anaerobic conditions, sulphate reducing bacteria (SRB) present in a sludge metabolise simple organic compounds produced during the decomposition of complex organic substrates, and reduce the sulphate ions present, producing H₂S (Postgate, 1984).

Sulphate reduction occurred during the whole period (data not presented), although the reduction efficiency decreased with time. In run I, the loading rate of sulphate reduced was extremely high, an average of 393.8 mg/l.d, generating an excessive production of sulphide ions. Therefore, the amount of organic matter made available was progressively restricted in the subsequent runs, as a means to diminish the production of sulphide ions. In the final run (run IV), the loading rate of sulphate ions reduced remained at around 92.2 mg/l.d.

Figure 3 presents the interdependence that exists between the organic matter consumed ($[\text{COD loading rate}]_{\text{inf.}} - [\text{COD loading rate}]_{\text{eff.}}$) and the amount of sulphate ions reduced by the SRB. This amount of sulphate ions was calculated as the difference between

the sulphate loading rate in the influent and that in the effluent of the UASB reactor ($[\text{Sulphate loading rate}]_{\text{inf.}} - [\text{Sulphate loading rate}]_{\text{eff.}}$).

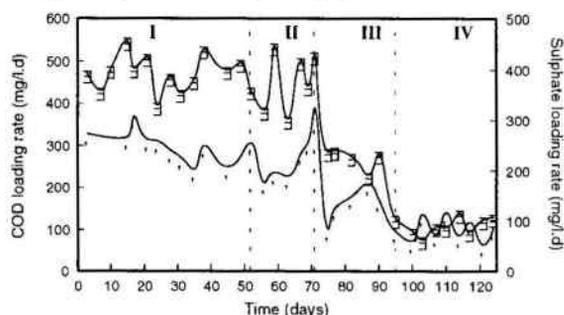


Figure 3 - Relation between the organic matter consumed, as COD loading rate (○), and the amount of sulphate ions reduced by the SRB, as sulphate loading rate (■), during the operation time.

It can be seen from the results shown in Figure 3 that as the amount of organic matter consumed decreases, the sulphate reduction likewise drops down, as the amount of sulphate reduced in runs III and IV was significantly lower. In those runs, the average values for reduced sulphate loading rate were 227.2 mg SO₄⁼/l.d and 92.2 mg SO₄⁼/l.d, respectively. It was estimated that it would be necessary to reduce around 200 mg/l.d of sulphate to produce sufficient sulphide for the metals present in the effluent to be treated. This reduction was not reached in run IV.

The Table 1 shows the results of the average reduced sulphate and sulphide-loading rate in the reactor's effluent.

Table 1 - Average reduced sulphate and sulphide loading rate in the four runs studied.

Run	Sulphate loading rate (mg/l.d)	Sulphide loading rate (mg/l.d)
I	393.8	41.0
II	380.5	36.4
III	227.2	20.5
IV	92.2	5.8

Although, the average amount of reduced sulphate in run IV is below the amount estimated as necessary to remove the metals present, there is still non-reacted sulphide in the reactor's effluent. The Brazilian Federal regulations state that it is prohibited to discharge effluents containing dissolved sulphide at levels higher than 1.0 mg/L, which makes it clear that the reactor's effluent would have to be further treated to remove the remaining sulphide. In industrial plants,

hydrogen peroxide (Granato, 1994) or biological process (Barnes *et alii*, 1992) are used. For low sulphide concentrations it seems that a chemical process is more suitable because of its simplicity and the small amount of reagent used. Another alternative to reduce the concentration of remaining sulphide, would be to further diminish the organic load fed into the reactor, provided this does not affect the metal removal.

Metal Removal

In this study, the removal of cadmium and zinc was assessed, since they are considered the main contaminating metals present in the drainage waters from the Brazilian metallurgical industry. In Figure 4, we can see the analytical results of cadmium (a) and of zinc (b) concentrations in the reactor's influent and effluent, as well as the discharge limits for cadmium (0.2 mg/l) and zinc (5 mg/l) established by Brazilian Federal regulations.

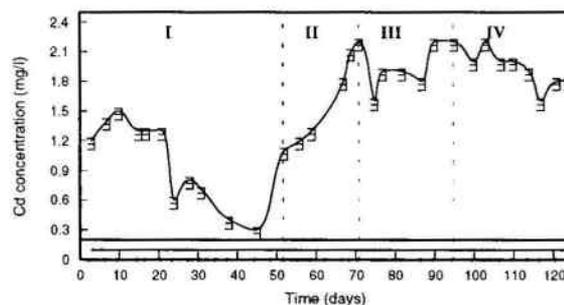
The results shown in Figure 4 indicate that the concentration of both zinc and cadmium in the reactor's effluent remained below the established discharge limits. However, in run IV, the concentration of reduced sulphate ions (Table 1) was not enough for metal removal to take place only as sulphide. In this case, there must have been some interference from other forms of removal.

It is known that during the metabolization of simple organic compounds ("CH₂O") by SRB, occurs a reduction in the level of sulphate ions present, generating H₂S and alkalinity (bicarbonate), as shown in equation 1.

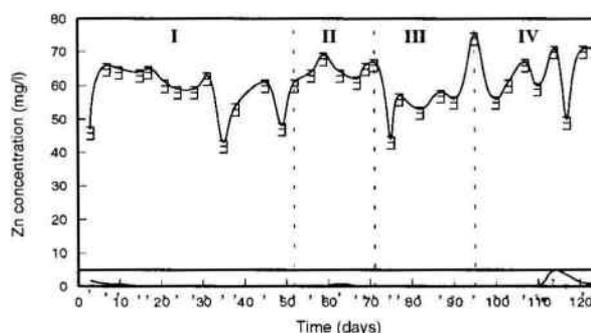


It is likely that this bicarbonate formed was in charge of the precipitating some of the metals removed from the solution, since the formation of a white precipitate was observed on the reactor wall.

In addition, the average pH in the reactor effluent (5.90) was significantly lower than that in the influent (6.83), indicating the probable consumption of carbonate ions to remove metal instead of neutralising the acidity generated during the precipitation of the metallic sulphides. However, this observation should be confirmed through some chemical analyses and observations of the sludge using a scanning electron microscope.



(a)



(b)

Figure 4 – Concentrations of cadmium (a) and zinc (b) in the reactor's influent (○) and effluent (■) with time, as well as the respective discharge restrictions set by Brazilian Federal regulations (4).

Regardless of the removal mechanism, the process in question was shown to be capable of removing the metals in solution utilising a small quantity of molasses as a carbon source for SRB. The amount used was just 11.5 ml of raw molasses (COD=1.170 g/l) for each 100 litres of effluent containing around 2.0 mg/l cadmium and 70 mg/l zinc.

CONCLUSIONS

The following conclusions can be drawn from the experiments:

- High metal removal efficiency was obtained using a small quantity of molasses as a carbon source for the SRB. Just 11.5 ml of raw molasses (COD=1,170 g/l) is sufficient to remove around 2.0 mg/l of cadmium and 70 mg/l of zinc from each 100 litres of effluent.
- The metal concentrations in the effluent were below the levels required by Brazilian legislation (0.2 mg/l for cadmium and 5.0 mg/l for zinc);

- The concentration of reduced sulphate ions were not enough for removing the metals only as sulphide, so others removed forms are occurring.

ACKNOWLEDGEMENTS

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