

Treatment of acid and sulphate-rich effluents in an integrated biological/chemical process

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Abstract

A novel chemical/biological process is described in which sulphate and sulphide are removed simultaneously during biological treatment. Partial sulphate removal is achieved during chemical pre-treatment. In the biological stage sulphate is reduced to sulphide in a complete-mixed reactor through addition of sucrose or ethanol as a carbon and energy source. Sulphide is oxidised by allowing oxygen to enter the system in a controlled way. The experimental investigation of the process showed that sulphate and sulphide could be removed simultaneously due to co-existence of sulphate-reducing bacteria and sulphur oxidising bacteria. The volumetric sulphate reduction rate in a complete-mixed reactor, with sucrose as an organic carbon and energy source, amounts to 12.4 g SO₄/(ℓ.d). The rate of biological sulphate removal was found to be directly related to the square root of sulphate, COD and VSS concentrations respectively, and inversely proportional to sulphide concentration. The practical value of simultaneous sulphate and sulphide removal is that only one stage is required for removal of both sulphate and sulphide; a conventional complete-mixed reactor can be used; and sulphate can be removed in a consistent way to below 200 mg/ℓ (as SO₄) due to the stability of the process.

By combining the biological stage with CaCO₃-neutralisation and/or lime pre-treatment, the chemical cost can be reduced. Sulphate, associated with the over-saturated fraction after treatment with CaCO₃ or lime, can be removed through gypsum crystallisation. In the integrated sulphate removal process (CaCO₃-neutralisation, lime treatment and biological stages), sulphate can be removed from 9 200 mg/ℓ (typical sulphate concentration of coal discard leachate) to 2410 mg/ℓ, 1 230 mg/ℓ and 205 mg/ℓ (as SO₄) in the various stages respectively. The chemical cost with the integrated process amounts to R2.94/m³, versus R12.44/m³ when all the sulphate is removed using the biological stage only. Similarly, the cost for treating magnesium sulphate-rich mine water amounts to R1.92/m³ for the integrated process, versus R3.11/m³ for biological treatment only.

Keywords: acid mine water; ethanol; kinetics; sulphate reduction; sulphide oxidation; sucrose

Introduction

Industrial effluents rich in sulphate, acid and metals are produced when sulphuric acid is used as a raw material, and when pyrites are oxidised due to exposure to the atmosphere, e.g. in the mining industry. Acidic industrial effluents require treatment prior to discharge into sewage networks or into public watercourses. In water-rich countries, the main causes of concern are the low pH and metal content of acidic effluents. Salinity is not a problem due to dilution with surplus capacity of surface water. In semi-arid countries like South Africa, the high salinity associated with acidic industrial effluents is an additional concern.

Biological sulphate removal can be used to treat industrial effluents to achieve, in addition to sulphate removal, metal removal and neutralisation. Sulphate can be removed as elemental sulphur via sulphide as an intermediate product when an energy source is provided. Desalination is achieved by effecting calcium carbonate crystallisation after sulphate removal. Metals are completely removed by precipitation as sulphides. Alkalinity is generated in quantities stoichiometrically equivalent to the amount of sulphate removed, which allows direct treatment of acid water.

The biological sulphate removal process has been developed over the past 15 years to the stage where it can compete successfully with other sulphate removal technologies for full-scale treatment of

mine and other industrial effluents. Maree and Strydom (1985) showed that sulphate could be removed in an anaerobic packed-bed reactor using sucrose, pulp mill effluent or molasses as a carbon and energy source. Metals like nickel, cadmium and lead were completely removed due to precipitation of metal sulphides. Maree and Hill (1989) showed that a three-stage process could be applied for sulphate removal, using molasses as the carbon and energy source in an anaerobic packed-bed reactor. Sulphide can be stripped with a mixture of CO₂/N₂ from the effluent of the anaerobic reactor in an H₂S-stripping stage, and residual COD and CaCO₃ can be removed in an aerobic final treatment stage. Maree et al. (1991) showed that when molasses is used as a carbon and energy source it could either be utilised in the fermented or unfermented form. When molasses is allowed to ferment, acetic acid is the main carbon and energy source for the sulphate-reducing bacteria. When molasses is kept sterile in the storage tank, sucrose is the main carbon and energy source with acetic acid as the metabolic end product.

With this information, it was concluded that by running two anaerobic sulphate removal reactors in series, sucrose could be fermented to lactate in the first reactor and, via acetate, to CO₂ in the second reactor. Du Preez et al. (1992) were the first to demonstrate that producer gas (mixture of H₂, CO and CO₂) can be used as a carbon and energy source for biological sulphate reduction. Both H₂ and CO were utilised as the carbon and energy source. Visser (1995) investigated the competition between sulphate-reducing bacteria (SRB) and methanogenic bacteria (MB) for acetate as the carbon and energy source in an up-flow anaerobic sludge blanket (UASB) reactor. He found that at pH values less

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