

Full Length Research Paper

# Optimal sulphuric acid production using *Acidithiobacillus caldus* (DSM 8584): Bioprocess design for application in ion-exchange

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An optimised bioprocess was designed for the optimal production of sulphuric acid for application in an isotope recovery ion-exchange process. Firstly, the production of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) was optimised in aerated batch bioreactors using *Acidithiobacillus caldus* (DSM 8584) using elemental sulphur, achieving  $\text{H}_2\text{SO}_4$  concentration of  $>0.4$  to  $\sim 0.5$  M (0.45 M average) with the following bioprocess parameters: product yield of 3.06 ( $Y_{p/s}$ ), oxygen uptake rate of 1.35 g/L.day (OUR), 52% sulphur conversion at a rate of 0.83 g/L.day ( $dS^\circ/dt$ ), achieving a sulphuric acid production rate of 2.76 g/L.day ( $dP/dt$ ), while the oxidation of elemental sulphur per dissolved oxygen consumed was 0.67 g  $S^\circ$ /g  $\text{O}_2$ . Secondly, after 80% (v/v) moisture loss from the recovered biological  $\text{H}_2\text{SO}_4$  titres, the acid solution was used for the recovery of nuclear grade lithium 7 ( $^7\text{Li}^+$ ) from a degraded resin, achieving  $>80\%$  recovery rate within two bed volumes (60 ml) at an averaged desorption rate ( $\bar{k}$ ) of  $0.1829 \text{ min}^{-1}$  and eluent rate of  $6.65 \text{ ml}\cdot\text{min}^{-1}$  in comparison to the  $\sim 60\%$   $^7\text{Li}^+$  recovery rate using a commercial grade mineral  $\text{H}_2\text{SO}_4$  using similar operational ion-exchange reactor parameters. The designed bioprocess proved to be an effective and environmentally friendly bioprocess for the recovery of valuable metals adsorbed onto ion-exchange resin.

**Key words:** *Acidithiobacillus caldus*, sulphuric acid, ion-exchange, desorption, lithium 7 isotope.

## INTRODUCTION

The use of micro-organisms in the bio-hydrometallurgy industry has attracted increasing attention because the processes being developed are environmentally friendly, require lower capital investment costs and are highly efficient compared to conventional methods (Liu, 2004). For example, *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* are considered to be effective in the bio-leaching of metal sulphides. Another sulphur oxidising bacterium, known as the *Acidithiobacillus caldus*, which has an optimum growth temperatures from 40 to 50°C, has been reported to dominate the sulphur-

oxidising bacterial population in both commercial bio-leaching and in bio-oxidation processes (Hallberg et al., 1996; Semenza et al., 2002). *A. caldus* is moderately thermophilic, unable to oxidise iron (II) and its characteristics closely resemble those of the mesophilic bacteria *A. thiooxidans* (Hallberg and Lindstrom, 1994; Hallberg et al., 1996; Rawlings et al., 1997). *A. caldus* is aerobic, Gram negative and is a chemoautotrophic micro-organism that grows on elemental sulphur as an energy source to produce sulphuric acid ( $\text{H}_2\text{SO}_4$ ) as an end-product. The elemental sulphur is biologically transformed by *A. caldus* in the presence of air, water and essential micro-nutrients to maintain desired cell growth and  $\text{H}_2\text{SO}_4$  production (Cerruti et al., 1998; Young et al., 2004; Liu, 2004). In order to meet the industrial

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requirements for a desorption process, a large quantity of biomass in the logarithmic growth phase is required to produce high concentrations of  $\text{H}_2\text{SO}_4$  (Liu, 2004). According to Butler (1975), the biomass and  $\text{H}_2\text{SO}_4$  production obtained by a convectional shaking flask using *A. thioxidans* on elemental sulphur proved to be 0.224 gDCW/L with 0.15 M of  $\text{H}_2\text{SO}_4$  being produced in 8 to 11 days. The bioreactor system was optimised by Liu (2004) who used response surface methodology (RSM) in terms of which cell and  $\text{H}_2\text{SO}_4$  concentrations of 0.7 gDCW/L and 0.38 M were achieved. This means that the design of a bioprocess requires that the production of biological  $\text{H}_2\text{SO}_4$  must be at an optimum and at a high concentration for use in any downstream processes. However, there is limited information on  $\text{H}_2\text{SO}_4$  production using elemental sulphur by *A. caldus* and the application of recovered acidic titres for application in ion-exchange processes.

This study focused on optimum  $\text{H}_2\text{SO}_4$  production by *A. caldus* (DSM 8584) using elemental sulphur. The biologically produced  $\text{H}_2\text{SO}_4$  was used for the recovery of  $^7\text{Li}^+$ , a valuable isotope, from a degraded lithiated ion-exchange resin which is used in the nuclear industry. The  $^7\text{Li}^+$  isotope recovered from the degraded resin may be re-used in the nuclear industry as a pH correcting agent for nuclear reactor coolant water. Furthermore, there is limited information about the recoverability of valuable isotopes for re-use from degraded resin, particularly using end-products of biotechnological processes, in particular acidic bio-products. The aim of this study was to report on the optimum biological production of  $\text{H}_2\text{SO}_4$  using elemental sulphur by *A. caldus* for use in the desorption of the  $^7\text{Li}^+$  isotope from a degraded lithiated mixed-bed ion-exchange resin. Furthermore, the bioprocess designed included the reduction of sulphurous colloids and *A. caldus* cells with an additional leachate removal process for the reduction of ionic constituents from both the degraded resin and the biological process, in such a way that it was feasible to re-use the  $^7\text{Li}^+$  recovered. Additionally, a kinetic model was used to determine desorption kinetic parameters and to simulate the desorption process taking into consideration design parameters such as bed porosity, resin capacity for the ion adsorbed on to the resin, eluent flow rate and ion-exchange reactor dimensions.

## MATERIALS AND METHODS

### Micro-organism selection and nutrient medium

*A. caldus* (DSM 8584), which had been isolated from mine water in continuous flow bio-oxidation tanks, was chosen as the strain for this study because it was found to dominate other sulphur oxidising bacterial populations in commercial bioleaching, thus rendering it suitable for large scale processes (Semenza et al., 2002). The culture strain, DSM 8584, used in this study, was obtained from the University of Cape Town (South Africa). An iron free medium, DSMZ 150 (without yeast extract), mixed with a filter sterilised (0.22  $\mu\text{m}$  filter) DSMZ 150a (trace element) solution was used to culture

the micro-organism. The DSMZ 150 used contained (g):  $(\text{NH}_4)_2\text{SO}_4$  (3.0);  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (0.50);  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (0.50); KCl (0.10); Ca  $(\text{NO}_3)_2$  (0.01) and 1000 ml of distilled water. The pH of the DSMZ 150 was adjusted to 2.5 using 6 M sulphuric acid. The trace element solution contained (mg):  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (11.0);  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.5);  $\text{H}_3\text{BO}_3$  (2.0);  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (2.0);  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (0.8);  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.6);  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (0.9) and 10.0 ml of distilled water. For every 1000 ml of the DSMZ 150 medium, 10 ml of the DSMZ 150a and 27.78 g of sulphur were added, to constitute the nutrient medium for sulphuric acid production.

### Inoculum preparation, bioreactor operation and acid recovery

The bacterial strain was grown in the medium as described in Micro-organism selection and nutrient medium for a period of 7 days – until the pH was  $<1$ . After this period, 50 ml of the culture was used as inoculum in a 2000 ml Erlenmeyer flask which contained 1800 ml of the nutrient medium. Erlenmeyer flasks ( $n = 5$ , total volume = 9000 ml) were incubated at a temperature of  $40^\circ\text{C}$  in a rotary shaker at 200 rpm. The flasks were aerated continuously using humidified air at 0.7 L/min. The pH and sulphuric acid production was monitored every eight days over a period of 16 days. The sulphuric acid was then recovered by vacuum filtration by means of tubular aluminium oxide membranes (OD = 0.010 m; ID = 0.007 m; L = 0.25 m, average pore size across wall thickness = 3  $\mu\text{m}$ , operating pH = 0 to 14, and burst pressure = 10 bar) using a vacuum pump operating at  $-10$  bar. The membranes were clamped at the bottom to create an ultra-filtration operational mode. The recovered sulphuric acid was concentrated by evaporation of 80% (v/v) of the water at a temperature of  $80^\circ\text{C}$ . The process is illustrated in Figure 1. The sulphuric acid was then further processed by filtering the acid recovered using a 0.22  $\mu\text{m}$  filter in order to remove traces of cells and sulphur colloids.

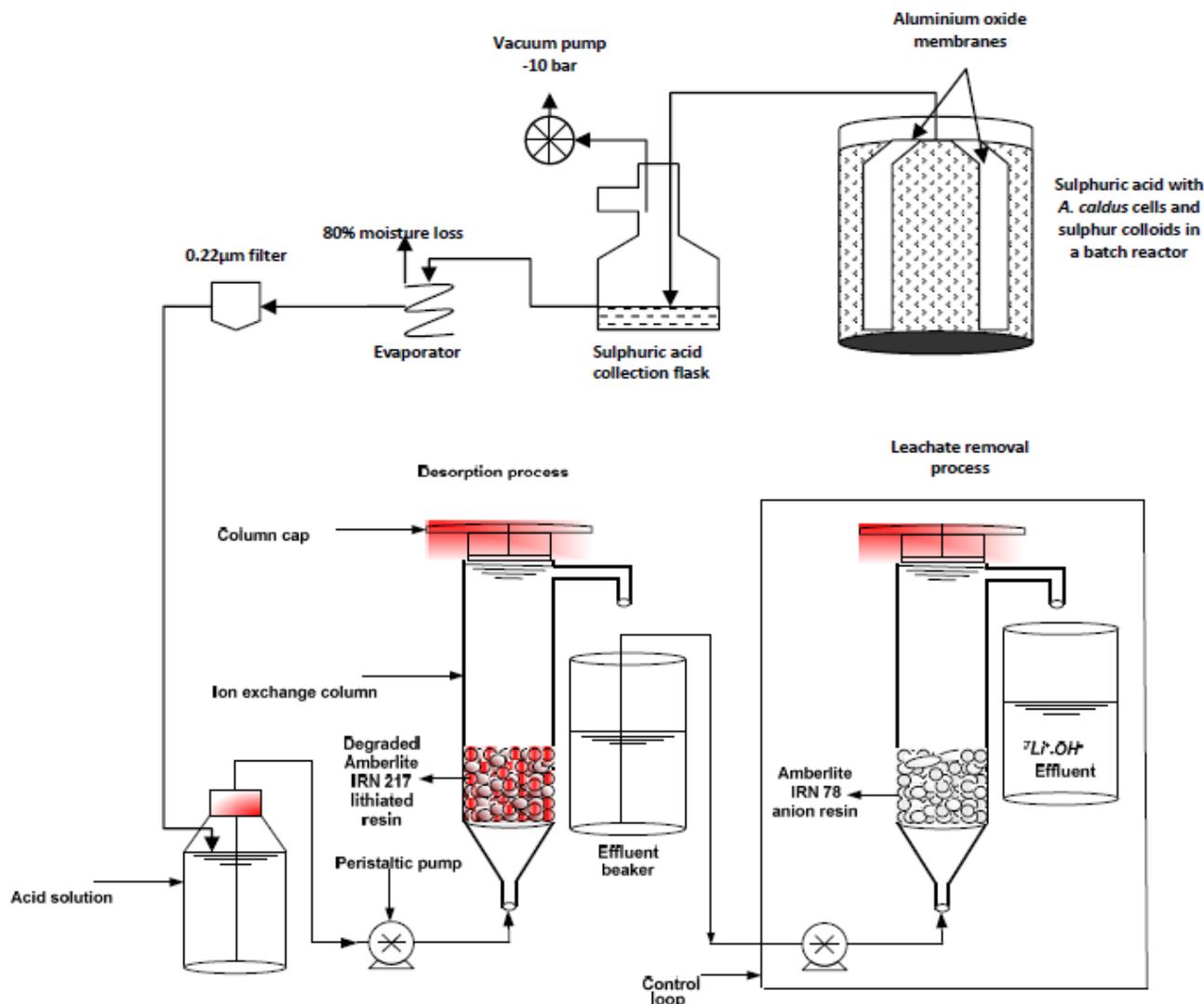
### Analysis of pH, sulphuric acid concentration and leachates

The pH was monitored using a Metrohm 744 pH meter. The sulphuric acid concentration was determined by titration with 0.175 M of sodium hydroxide solution with phenolphthalein as an acid base indicator (Cerruti et al., 1998). The concentration of  $^7\text{Li}^+$  and cation leachates recovered in the effluent solution was determined by a Varian Liberty II Radial ICP-MS (Geology Department, Stellenbosch University, South Africa). The  $\text{H}_2\text{SO}_4$  samples were diluted 20x before analysis. Matrix matched calibration standards were prepared for the  $\text{H}_2\text{SO}_4$  samples, and the accuracy of the calibration was verified with a quality control standard before analysis. The nitrates ( $\text{NO}_3\text{-N}$ ) were analysed by means of an auto-analyser using the cadmium reduction method (Mitsch et al., 2005) while the chlorides ( $\text{Cl}^-$ ) were analysed by titrating standardised silver nitrates solutions to the first potentiometric end-point which corresponded to the micromoles of chloride ions present in the eluant (Tang and Gordon, 1980). In addition, the fluorides were determined using a Colorimetric Spectrometer (Tokalioglu et al., 2001). The sulphates ( $\text{SO}_4^{2-}$ ) and phosphates ( $\text{PO}_4^{3-}$ ) were both determined using an ICP-MS while the carbonates ( $\text{CO}_3^{2-}$ ) were determined by titration with HCl acid.

### Lithium column elution apparatus and procedure

#### Desorption process

The continuous elution experiments were carried out in a glass ion-exchange column with an internal diameter of 25 mm and a length of 30 mm. The column was filled with 30 ml of degraded lithiated mixed-bed resin. The concentrated 1 M biologically produced



**Figure 1.** A schematic illustration of the production and recovery of biological  $\text{H}_2\text{SO}_4$  from a batch bioreactor and the column used for the elution of lithium isotope ( ${}^7\text{Li}^+$ ) from 30 ml degraded lithiated mixed-bed resin including a leachate removal process.

$\text{H}_2\text{SO}_4$  was passed upwards through the mixed-bed column at a constant flow rate of 6.65 ml/min using a Gilson peristaltic pump (Germany). This flow rate corresponds to 13 BVs/h. One BV may be defined as the volume of the elution solution which is equivalent to the volume of the resin in the column. The flow rate used enabled adequate sampling of the eluate for determination of the elution profile of the resin whilst, not fluidising the resin. This flow rate was slightly higher than the flow rate used by Lukey and van Deventer (2000) whereby the results of a study on the elution of copper and iron cyanide complexes from ion-exchange resins were reported. Several bed volumes (18BV) of acid solution were passed through the column for each experiment. Eluate samples were taken at each 2BV (60 ml). All piping and connections were made with silicone tubing. For the control experiments dilute solutions of a commercial grade sulphuric acid were used.

#### Mathematical model: Desorption kinetics

The mathematical model used in this study for desorption kinetics

was similar to that which was previously proposed to model the desorption of  ${}^7\text{Li}^+$  using technical grade in-organic acids, that is,  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  (Basitere et al., 2012), from an ion-exchange resin. The model used was modified from an ethyl acetate desorption model from activated carbon (Tan and Liou, 1988). The desorption kinetics model is as shown in Equation 1:

$$\frac{dS_e}{dt} = -\frac{(1-\varepsilon)}{\varepsilon} \bar{k} S_0 \left[ e^{-\bar{k} \left( t - \frac{zL}{u_z} \right)} - e^{-\bar{k}t} \right] \quad (1)$$

The desorption rate constant,  $\bar{k}$ , was evaluated by fitting equation 1 to the experimental data using an ODE (Polymath 5.1). This was done using Microsoft Excel 2000 Solver<sup>®</sup> to find values that minimised the absolute error between the experimental and the calculated data taking into consideration the minimum sum of square differences (SSD) and the regression coefficient ( $R^2$ ) between the experimental and modelled data. The porosity of the

degraded lithiated mixed-bed resin was determined by weighing 30 ml of the mixed-bed resin. The density of the resin was then determined using a Pycnometer (ACCUPYC 1330). The mass of the 30 ml resin was divided by the resin density measured to give the actual volume which the resin beads occupied. The pore volume was determined as the difference between the apparent resin volume (30 ml) and the volume obtained from the density calculation (actual resin volume). Thereafter, the fraction of the resin pore volume,  $\varepsilon$ , was determined as a ratio between the pore volume and the apparent resin volume. The cation part of the resin used had a  ${}^7\text{Li}^+$  capacity of 2.19 eq/L while the anion:cation ratio was 1:1.4 (Rohm and Haas, France). The maximum resin capacity for  ${}^7\text{Li}^+$  quantified for a 30 ml degraded lithiated resin, and  $S_0$ , was determined to be equivalent to 15330 mg/L.

### The leachate removal process

The anion leachates reduction column was carried out under the same conditions that were used during the  ${}^7\text{Li}^+$  elution stage. This anion reduction column was filled with 90 ml of Amberlite IRN 78 anion resin. The effluent from the elution stage was passed through the anion resin in order to remove the anion leachates. The effluent was then analysed for anion contaminants so as to evaluate whether there had been reduction in the anion contaminants. The level of contaminants was compared to the specification pertaining to the nuclear reactor coolant water. The desorption and leachates removal processes are illustrated in Figure 1.

## RESULTS AND DISCUSSION

### Optimum sulphuric acid production and bioprocess parameters

Figures 2A and B depict the pH and cumulative  $\text{H}_2\text{SO}_4$  produced using *A. caldus* aerated batch bioreactors. The  $\text{H}_2\text{SO}_4$  productivity of the *A. caldus* culture using elemental sulphur reached an averaged cumulative concentration of 0.45 M over a period of 16 days. As had been reported by Kempner (1996) in respect of  $\text{H}_2\text{SO}_4$  production using *A. thiooxidans*, the rapid drop in pH from an initial value of 2.5 to 0.47 over a period of 16 days proved that the medium had become progressively more acidic as the culture had aged. The  $\text{H}_2\text{SO}_4$  productivity clearly depends on the type of bioreactor used, the conditions in the bioreactor, the sulphur surface area, the population of cells, the uniform contact between the liquid-solid-gas phase and the availability of dissolved oxygen (Cerruti et al., 1998). The advantage of the continuous aeration in the batch reactor is that the shear forces break down unstable particles, thus creating finer particles with a higher surface area and enable further sulphur oxidation as a result of the continuous supply of oxygen (Janssen et al., 1994). The  $\text{H}_2\text{SO}_4$  produced by these batch bioreactors was lower than the  $\text{H}_2\text{SO}_4$  produced in the experiments carried out by Liu (2004). This increase was in accordance with the application of response surface methodology (RSM) findings, whereby the simulated  $\text{H}_2\text{SO}_4$  concentration of 0.38 M was achieved during the optimal growth of *A. thiooxidans*. In this case, the increase in  $\text{H}_2\text{SO}_4$  concentration was

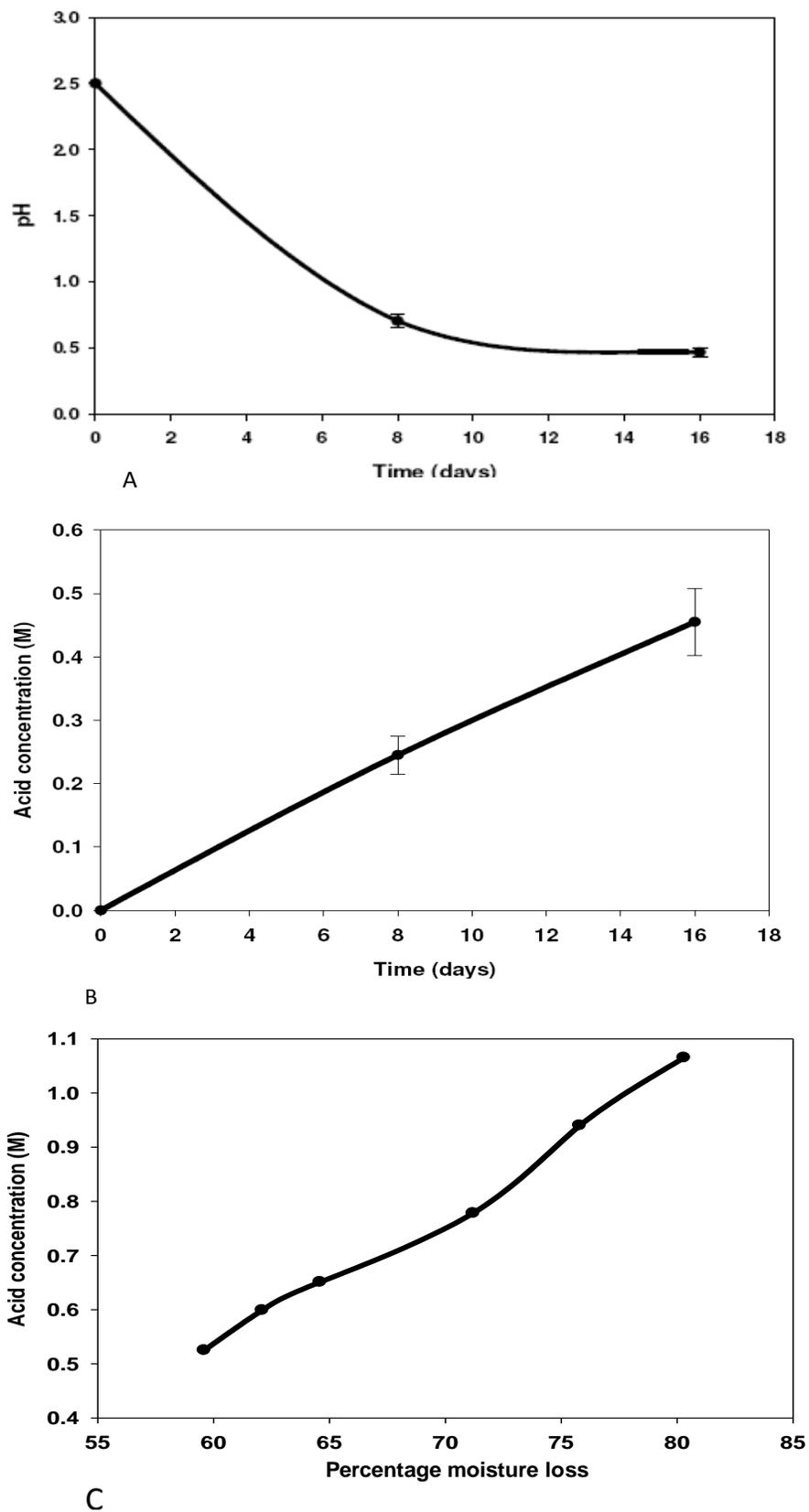
directly proportional to the sulphur concentration used and was higher than that obtained using conventional reactors and the growth medium for *A. thiooxidans*. By using *A. caldus* and optimising the reactor before use, the  $\text{H}_2\text{SO}_4$  produced in this study was 18% higher on average, with a maximum of 32%  $\text{H}_2\text{SO}_4$  production, compared to that reported by Liu (2004) using RSM.

In this study, the  $\text{H}_2\text{SO}_4$  solution recovered was concentrated using an evaporator, which resulted in the acid strength increasing to approximately 1 M acid by evaporating 80% (v/v) moisture. The rate of acid concentration increments was 0.025 M  $\text{H}_2\text{SO}_4$  per percentage moisture loss (Figure 2C). The concentrated  $\text{H}_2\text{SO}_4$  was used to recover the  ${}^7\text{Li}^+$  isotope from the degraded mixed-bed resin. The biologically produced  $\text{H}_2\text{SO}_4$  was compared to a dilute commercial grade mineral  $\text{H}_2\text{SO}_4$  solution by desorbing the  ${}^7\text{Li}^+$  isotope from the degraded lithiated mixed-bed resin.

In general terms, there are several mechanisms which describe the conversion of sulphurous substrates by sulphur oxidising acidiphilic bacteria such as *A. caldus*, *A. ferroxidans* and *A. thiooxidans*. In this study, the stoichiometrical relationship which sufficiently described the oxidation of sulphur by *A. caldus* (DSM 8584) was surmised as:  $2\text{S}^0 + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4$ . Using the suggested stoichiometric relationship, the following was deduced: the averaged oxidation of elemental sulphur per dissolved oxygen consumed calculated stoichiometrically on the basis of biological sulphuric acid production from sulphur by *A. caldus*, was determined to be 0.67 g  $\text{S}^0/\text{g O}_2$ , a result similar to that obtained by Hallberg et al. (1996), whereby elemental sulphur was dissolved in acetone and oxidised at 45°C achieving an oxidation rate of 0.71 g  $\text{S}^0/\text{g O}_2$  using *A. caldus* (DSM 8584). Furthermore, other bioprocess parameters quantified were (Table 1): 1) the product yield based on substrate consumption ( $Y_{p/s}$ ) which was 3.06; oxygen utilisation rate (OUR) of 1.35 g/L.day; 52% sulphur conversion after 16 days of bioreactor operation which was indicative of a sulphur conversion rate of 0.83 g/L.day and a sulphuric acid production rate ( $dP/dt$ ) of 2.76 g/L.day. As recently mentioned by Shiers et al. (2011), it is problematic to evaluate biomass yield of *Acidithiobacillus* bacteria on elemental sulphur oxidation due to the attachment of the cells to the surface of sulphur. Since the product yield based on substrate consumption,  $Y_{p/s}$ , is a based on the product of both the biomass yield based on substrate consumption ( $Y_{x/s}$ ) and the product yield based on biomass generated ( $Y_{p/x}$ ), that is,  $Y_{p/s} = Y_{x/s} * Y_{p/x}$  (Shuler and Kargi, 2002; Doran, 1995), a correlation is proposed to estimate the biomass yield ( $Y_{x/s}$ ) as shown in equation 2, taking into consideration,  $Y_{p/s}$  obtained in this study.

$$3.06\alpha = Y_{x/s} \quad (2)$$

Whereby  $\alpha$  is the inverse of the product yield based on biomass generated, that is,  $\alpha = (Y_{p/x})^{-1}$ . For this to be



**Figure 2.** (A) pH evolution during oxidation of elemental sulphur. (B) Cumulative production of  $H_2SO_4$  in an aerated batch bioreactor with *A. caldus* immobilised on elemental sulphur. (C) Acid concentration increase with the percentage of moisture loss.

valid, it was assumed that the oxidation of sulphur is directly proportional to the quantity of *A. caldus* cells attached to the elemental sulphur as it may select optimal attachment on the sulphur surface for chemoautotrophic growth as suggested by Edwards et al. (2000). In this study, a high quantity of biomass was observed to be attached to the mineral surface than that available in suspension.

### Resin degradation

Nuclear grade lithiated resin stored under fluctuating temperature conditions results in the degradation of the anion part of the resin, resulting in an inefficient ion-exchange process and the release of undesirable leachates. The degraded lithiated mixed-bed resin used in this study was determined to be unsuitable for use in a pressurised water reactor (PWR) process in the nuclear industry. Overall, the fluctuating storage temperature conditions, affects the shelf-life of the ion-exchange resin (Harland, 1994). It was observed that resin stored over a long period of time, under varying temperature conditions, results in the moisture content inside the resin escaping and in certain instances leading to the resin polymer stretching due to freezing (Mamo et al., 2004). This causes the resin to break-down and release organically bound impurities due to broken polymer bonds. The manufacturer of the nuclear grade resin, Rohn and Haas (France), indicated that the minimum shelf-life of the anion part of the degraded lithiated mixed-bed resin is 2 years and cation part resin is 5 years. However, the resin can be stored longer than the recommended shelf-life under good storage temperature conditions and can be analysed for potential leachates before use. Degradation of the hydroxide form of a strong base anion resin can be explained by the Hoffman degradation mechanisms (Harland, 1994). The predominant route of degradation is due to the loss of the functional group on the resin, resulting in the liberation of leachates and free amine. In this study we attempt to recover  ${}^7\text{Li}^+$  from a degraded lithiated Amberlite resin using a biologically produced acid. The technique reported here can be used for large quantities of degraded resin or resin stored passed its shelf-life for the recovery of valuable elements.

### Desorption of the ${}^7\text{Li}^+$ isotope from the degraded lithiated resin

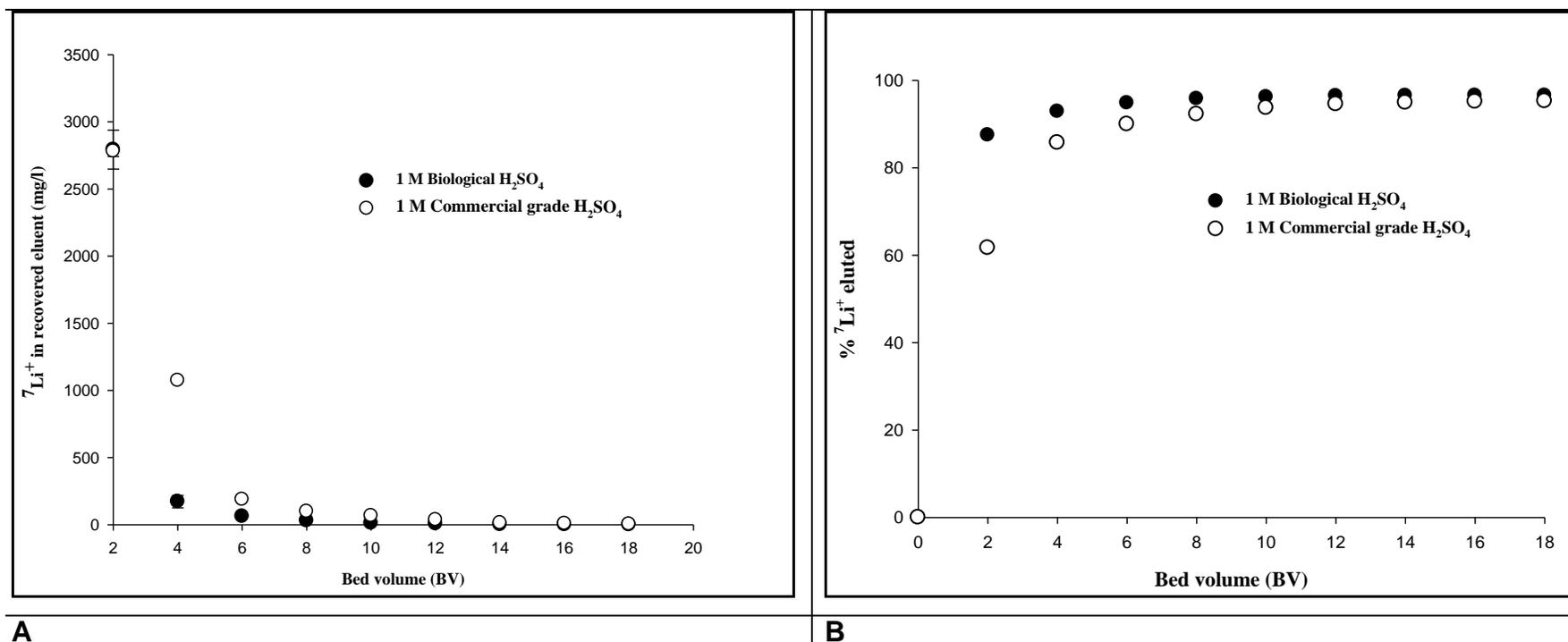
Figure 3A and B depicts the desorption of the  ${}^7\text{Li}^+$  isotope from a degraded lithiated mixed-bed resin in a continuous ion-exchange column, using 1 M biologically produced  $\text{H}_2\text{SO}_4$  as compared with 1 M commercial grade  $\text{H}_2\text{SO}_4$ . A desorption rate of >80% was observed using biologically produced  $\text{H}_2\text{SO}_4$  at the initial stages (2BVs). This was higher than the 61% achieved by commercial

grade mineral acid at the same stage. It was hypothesised that the presence of other cations such as sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) in the influent contributed to the observed phenomena. These cations also have an affinity to exchange with the  ${}^7\text{Li}^+$  on the cation part of the mixed-bed resin as compared with the commercial grade acid used (Figure 4) in which some of trace ions concentration are minimal. The overall desorption rate was 95% for both the biologically produced  $\text{H}_2\text{SO}_4$  and the commercial grade mineral  $\text{H}_2\text{SO}_4$  after passing 18BV. The biologically produced  $\text{H}_2\text{SO}_4$  proved to be as efficient as the commercial grade mineral  $\text{H}_2\text{SO}_4$  in recovering the  ${}^7\text{Li}^+$  isotope from the degraded Amberlite resin. It may, thus, be concluded that biologically produced  $\text{H}_2\text{SO}_4$  may also be used in the desorption of other metal ions adsorbed on ion-exchange resin using an acid production process, which is more environmentally friendly compared to other conventional methods.

Figure 5 illustrates the mathematical model fit between experimental and simulated data of the desorbed  ${}^7\text{Li}^+$  isotope using biological  $\text{H}_2\text{SO}_4$ . The model used took into consideration reactor sizing and other operational parameters. The comparison between the simulated and the experimental data was sufficient with a correlation coefficient ( $R^2$ ) of 0.982. The overall desorption rate ( $\bar{k}$ ) was determined by minimising the absolute error between the experimental and calculated data and was found to be  $0.1829 \text{ min}^{-1}$ . The ( $\bar{k}$ ) value for biological systems was higher as compared to the commercial grade  $\text{H}_2\text{SO}_4$ , showing there was higher ion-exchange kinetics using biological  $\text{H}_2\text{SO}_4$  as compared to commercial grade  $\text{H}_2\text{SO}_4$ . Furthermore, it was also observed that between 0 to 18 min, biological  $\text{H}_2\text{SO}_4$  desorption rate was higher as compared to commercial grade  $\text{H}_2\text{SO}_4$ . This suggests that by reducing sampling intervals, the absolute error between the experimental and simulated data can be reduced to a minimum, thus improving the analysis of the kinetics involved.

### Leachates in the recovered effluent

Table 2 and Figure 4 indicates the level of cation and anion leachates in the  ${}^7\text{Li}^+$  isotope effluent after passing biologically produced  $\text{H}_2\text{SO}_4$  as compared to when the commercial grade  $\text{H}_2\text{SO}_4$  was used. The level of cations did not exceed 300 mg/L (potassium being the highest) in the effluent, although there were trace metals such as sodium (Na), potassium (K), manganese (Mn) and zinc (Zn); trace elements in the nutrient medium used to produce  $\text{H}_2\text{SO}_4$  biologically, with observed traces of lead (Pb) from either the sulphur used or the degraded resin. Additionally, a large quantity of anion leachates was found in the effluent. This was, in turn, attributed to the leachates from the eluant solution of both the biological



**Figure 3.** (A) Lithium 7 isotope desorption and (B) percent <sup>7</sup>Li<sup>+</sup> isotope desorption using biologically produced H<sub>2</sub>SO<sub>4</sub> by *A. caldus* cells as compared with mineral sulphuric acid.

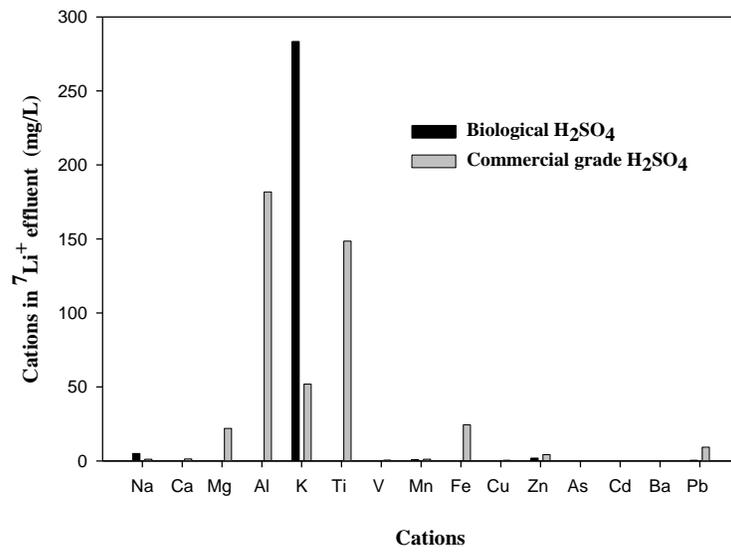
and commercial grade H<sub>2</sub>SO<sub>4</sub> used. Furthermore, as the degraded mixed-bed resin had been degraded, the release of anion leachates further contributed to the higher quantity of anions in the <sup>7</sup>Li<sup>+</sup> isotope effluent. The Amberlite IRN 78 proved to be capable (> 99%) of reducing the anion leachates from the <sup>7</sup>Li<sup>+</sup> isotope effluent using both biologically produced H<sub>2</sub>SO<sub>4</sub> and commercial grade H<sub>2</sub>SO<sub>4</sub> (Table 2).

## Conclusions

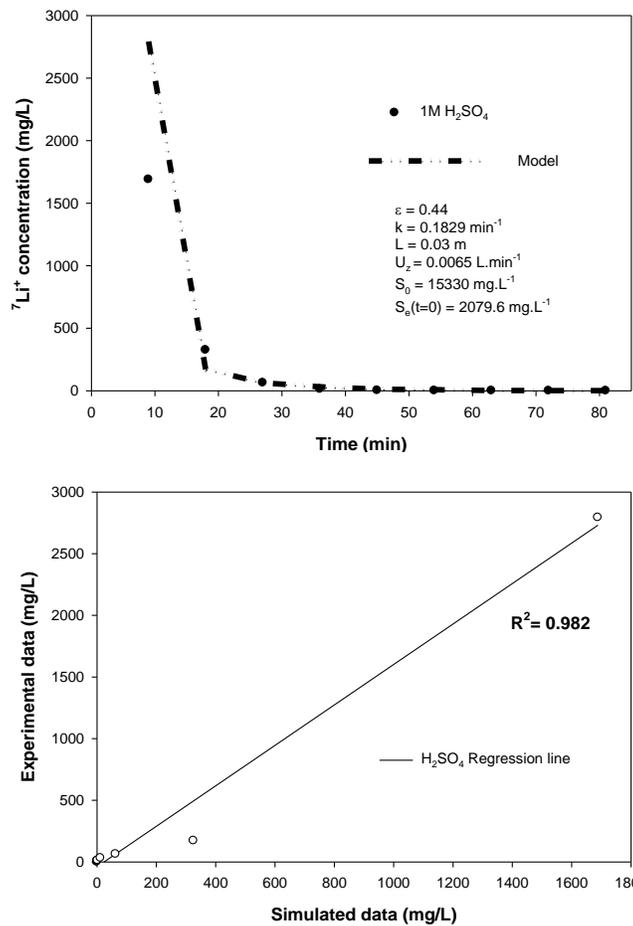
Most of the published literature reviewed on

desorption processes use commercially grade mineral acids, HCl or H<sub>2</sub>SO<sub>4</sub>, to recover minerals from ion-exchange resin. This also includes the regeneration of different polystyrene-based resin. This study focused on recovery of <sup>7</sup>Li<sup>+</sup> isotope from a degraded Amberlite resin, which is used in the nuclear power generation industry. The study explored the use of a biologically produced from optimised bioreactors H<sub>2</sub>SO<sub>4</sub> to recover the valuable isotope from a degraded unusable resin. The implications of the research findings are that biological produced H<sub>2</sub>SO<sub>4</sub> can be used in mineral recovery from industrial resin and to regenerate such resin as it was proven that the use of

biologically produced H<sub>2</sub>SO<sub>4</sub> performed similarly to that of commercially grade mineral acids. The desorption process was also modelled using a mathematical model developed to simulate the desorption kinetics of the <sup>7</sup>Li<sup>+</sup> isotope. The model used can be modified to take into consideration the desorption kinetics of the process being modelled. These conclusions are supported by the following findings: an elution efficiency of > 80% was achieved at the initial stage of 2BV. This was higher than the 60% efficiency rate of mineral H<sub>2</sub>SO<sub>4</sub> at the same stage. The overall elution efficiency of > 90% was achieved after passing 18BV's; a result similar to that achieve



**Figure 4.** Cation leachates in the <sup>7</sup>Li<sup>+</sup> isotope effluent from the desorption process.



**Figure 5.** Simulated and experimental desorption curve for lithium isotope using 1M biological H<sub>2</sub>SO<sub>4</sub> and the correlation between experimental and simulated data.

**Table 1.** Optimum bioprocess parameters for production of sulphuric acid by *A. caldus* (DSM 8584).

Parameter	Value (units)
Product yield based on sulphur consumption, $Y_{p/s}$	3.06
Oxygen uptake rate (utilisation rate), $OUR$	1.35 g/L.day
Sulphur conversion after 16 days (fraction)	0.52
Substrate conversion rate (sulphur utilisation rate), $dS^o/dt$	0.83 g/L.day
Oxidation of sulphur per dissolved oxygen consumed	0.67 g S <sup>o</sup> /g O <sub>2</sub>
Sulphuric acid production rate, $dP/dt$	2.76 g/L.day

**Table 2.** Averaged anion leachates in the <sup>7</sup>Li<sup>+</sup> effluent pre- and post-leachates removal process using Amberlite IRN 78 anion resin.

Anion species <sup>a</sup>	1 M biological H <sub>2</sub> SO <sub>4</sub>			1 M commercial grade H <sub>2</sub> SO <sub>4</sub>			Nuclear reactor coolant water specifications (µg/L)
	Concentration <sup>b</sup> (mg/L)	Purification <sup>c</sup> (mg/L)	Reduction <sup>d</sup> (%)	Concentration <sup>b</sup> (mg/L)	Purification <sup>c</sup> (mg/L)	Reduction <sup>d</sup> (%)	
Cl <sup>-</sup>	13393.11	88.11	99	36460.99	123.36	99.66	<50
SO <sub>4</sub> <sup>2-</sup>	51478.18	998.65	98	48277.26	464.33	99.04	<50
CO <sub>3</sub> <sup>2-</sup>	nd	nd	-	Nd	nd	-	nd
NO <sub>3</sub> <sup>-</sup>	0.01	nd	100	27.98	nd	100	nd
F <sup>-</sup>	18.50	0.1	99	Nd	nd	-	<50
PO <sub>4</sub> <sup>2-</sup>	557.96	19.55	96	Nd	nd	nd	nd

nd, not detected. <sup>a</sup>Anion species in the recovered <sup>7</sup>Li<sup>+</sup> eluent from the desorption process; <sup>b</sup>anion concentration from the desorption process using biological and commercial grade H<sub>2</sub>SO<sub>4</sub>; <sup>c</sup>anion concentration after passing through Amberlite IRN 78 Anion resin; <sup>d</sup>percentage reduction of anion leachates by Amberlite IRN 78 resin.

by commercial grade mineral sulphuric acid. The biologically produced H<sub>2</sub>SO<sub>4</sub> revealed the same ability to extract the <sup>7</sup>Li<sup>+</sup> isotope as compared to the widespread conventional method using commercial grade H<sub>2</sub>SO<sub>4</sub>. The decontamination process showed a potential to reduce the leachates level, however the process needs to be optimised to be able to reduce the level of anion and cation leachates required by the nuclear industry.

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**Nomenclature:**  $\bar{k}$ , Desorption rate constant (min<sup>-1</sup>);  $L$ , ion-exchange column length (m);  $OUR$ , oxygen uptake rate (g/L.day);  $dP/dt$ , sulphuric acid production rate (g/L.day);  $S_e$ , amount of lithium in the resin at exit port

(mg/L);  $S$ , concentration of lithium in the resin (mg/L),  $S_o$ , <sup>7</sup>Li<sup>+</sup> capacity on a 30 ml degraded lithiated resin (mg/L);  $dS^o/dt$ , sulphur utilisation rate (g/L.day);  $u_z$ , axial eluent flow rate at the entry (L/min);  $t$ , time (min);  $Y_{p/s}$ , product yield based on substrate consumption;  $Y_{x/s}$ , biomass yield based on substrate consumption;  $Y_{p/x}$ , product yield based on biomass generation;  $\epsilon$ , porosity;  $\alpha$ , Inverse of the product yield based on biomass generated.

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