Bio-desorption of lithium isotope ($^{7}Li^{+}$) from a degraded lithiated mixed-bed ion-exchange resin using *Acidithiobacillus caldus*

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Abstract

The production of sulphuric acid was investigated in optimised aerated batch bioreactors, with *Acidithiobacillus caldus* (DSM 8584) using elemental sulphur as the source of energy. In these aerated batch bioreactors, sulphuric acid production of 0.4M was achieved over a period of 16 days. The sulphuric acid was concentrated to ~1M by evaporating 80% (v/v) of moisture. The concentrated sulphuric acid was passed through a continuous ion-exchange packed-bed column containing a degraded lithiated mixed-bed resin to elute the Lithium 7 isotope ($^{7}Li^{+}$) on the cation part of the mixed-bed resin. Desorption rates >90% were achieved within 18 bed volume (BV) using the biologically produced sulphuric acid. These results showed similar desorption rates of $^{7}Li^{+}$ to that of 1M of commercial graded mineral sulphuric acid. The use of the biological produced sulphuric acid showed an economical and effective method which could be considered to recover valuable metals adsorbed on ion-exchange resin.

Keywords: *Acidithiobacillus caldus;* Bio-desorption; Lithium isotope; Ion-exchange

1. Introduction

The use of micro-organisms in the bio-hydrometallurgy industry has attracted increasing attention because the process is environmentally friendly, requires low capital cost and has high efficiency compared to convectional methods (Liu *et al.*, 2004). *Acidithiobacillus ferroxidans* (*A. ferroxidans)* and *Acidithiobacillus thioxidans* (*A. thioxidans*) are considered to be effective in the bacterial bio-dissolution of metal sulphides (bioleaching). However, another sulphur oxidising bacterium known as the *Acidithiobacillus caldus (A. caldus*), with an optimum growth of temperature 40 to 50^{o}C, has been reported to dominate sulphur-oxidizing bacterial populations in commercial bioleaching and bioxidation plants (Kevin *et al.*, 1994; Semenza *et al.*, 2002). *A. caldus* is moderately thermophilic, unable to oxidise Iron(II) and its characteristics are close to the mesophilic bacteria *A. thioxidans* (Hallberg & 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 as the 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 sulphuric acid production (Cerruti *et al.*, 1998; Young *et al.*, 2004; Liu *et al.*, 2004).

Amberlite IRN 217 lithiated mixed-bed resins are used in the Reactor Chemical and Volume control (RCV) of the Pressurised Water Reactor (PWR) in the nuclear industry to reduce radioactive isotopes formed during nuclear fission in the nuclear reactor. The radioactive isotopes such as Cesium and Cobalt, as well as Sulphates and Chlorides, cause corrosion in the nuclear reactor. The ionic form of the cation resin is in $^{7}Li^{+}$ form to prevent removal of $^{7}Li^{+}$

47 which is used as an additive to control pH in the reactor coolant water while the anion resin is
48 conditioned to operate in Borate form to prevent removal of Boron from the reactor coolant
49 water. The cation resin of the mixed-bed resin removes all cationic radioactive isotopes and
50 impurities, while the anion resin removes all anionic impurities. The lithiated mixed-bed resin
51 is costly due to the valuable $^{7}Li^{+}$ isotope used and the recovery of the isotope from the
52 degraded lithiated resin is of importance in that it can be re-used in the nuclear reactor.
53
54 This study focused on the sulphuric acid production *by A. caldus* using elemental sulphur. The
55 biologically produced sulphuric acid was used to desorpt lithium 7 ($^{7}Li^{+}$), a high value isotope,
56 from a degraded Amberlite lithiated ion-exchange resin used in the nuclear industry. To meet
57 industrial requirements for a desorption process, a large quantity of biomass in logarithmic
58 growth phase is required to produce a high concentration of sulphuric acid (Liu *et al.*, 2004).
59 The cell and sulphuric acid production obtained by convectional shaking flask using *A.*
60 *thioxidans* on elemental sulphur were reported by Butler (1975) to be 0.224g cell/L while
61 0.15M of sulphuric acid was produced in 8 to 11 days. The bioreactor system was optimised by
62 Liu (2003) using response surface methodology, whereby cell and sulphuric acid concentration
63 of 0.7 gcell/L and 0.38M were achieved. However, there is limited information on sulphuric
64 acid production using elemental sulphur by *A. caldus*. The aim of this study was to report on
65 biological sulphuric acid production using elemental sulphur by *A. caldus* in optimised
66 continuous aerated batch bioreactors. Furthermore, the acid produced was used in the
67 desorption of $^{7}Li^{+}$ isotope from a degraded lithiated mixed-bed ion-exchange resin. A
68 decontamination process was used to reduce the identified leachates such that the $^{7}Li^{+}$
69 containing solution can be recovered for re-use in the nuclear reactor.

2. Materials and methods

2.1. Micro-organism selection and nutrient medium

A. caldus (DSM 8584) was isolated from mine water in a continuous flow Bio-oxidation tanks were chosen as the strain for this study because it was found to dominate other sulphur oxidising bacterial populations in commercial bioleaching, making 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 µm filter) DSMZ 150a (trace element) solution was used to culture the micro-organism. The DSMZ 150 used contained (g): $(NH_4)_2SO_4$ (3.0); $K_2HPO_4.3H_2O$ (0.50); $MgSO_4.7H_2O$ (0.50); KCl (0.10); $Ca(NO_3)_2$ (0.01) and 1000 ml of distilled water. The pH of the DSMZ 150 was adjusted to 2.5, using 6M sulphuric acid. The trace element solution contained (mg): $FeCl_3.6H_2O$ (11.0); $CuSO_4.5H_2O$ (0.5); H_3BO_3 (2.0); $MnSO_4.H_2O$ (2.0); $Na_2MoO_4.2H_2O$ (0.8); $CoCl_2.6H_2O$ (0.6); $ZnSO_4.7H_2O$ (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 was used.

2.2 Inoculum preparation, bioreactor operation and acid recovery

The bacterial strain was grown in the medium as described in section 2.1 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 containing 1800 ml nutrient medium. Five flasks (total volume = 9000 ml) were incubated at a temperature of 40^{o}C in a rotary shaker at 200rpm. The flasks were aerated continuously at 0.9 L/min. The pH and sulphuric acid production was monitored every 8 days over a period of 16 days. The sulphuric acid was recovered by vacuum filtration using pure

Aluminium oxide membranes (OD = 0.010 m; ID = 0.007 m; L = 0.25 m; average pore size across wall thickness = 3 µm; operating pH = 0 – 14; burst pressure = 10 bar) using a vacuum pump operating at -10 bar and the membrane was clamped at the bottom to create an ultra-filtration operation mode. Furthermore, the sulphuric acid was further processed by filtering the acid recovered using a 0.22 µm filter to remove cells and sulphur colloids. The sulphuric acid was concentrated by evaporation 80% (v/v) of water at a temperature of 80^{o}C. The process is illustrated in Figure 1.

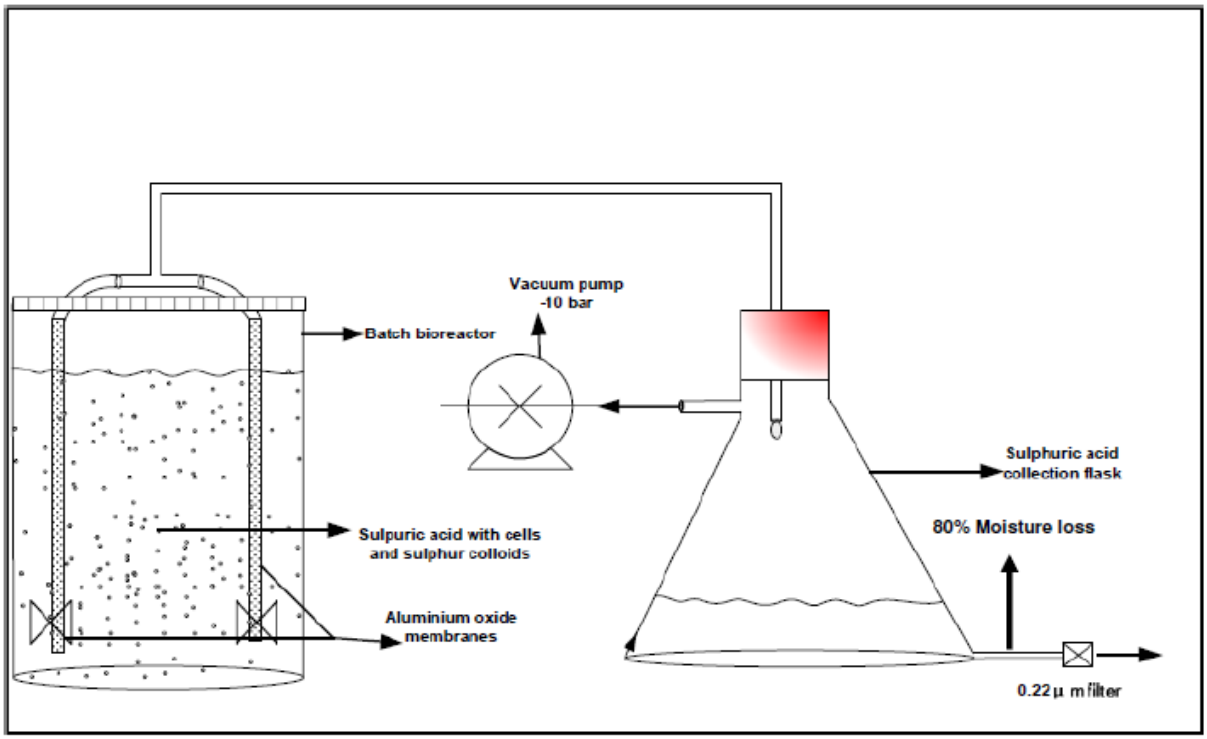

Figure 1: The recovery of sulphuric acid from the batch bioreactor

2.3 Analysis of pH, sulphuric acid concentration and metal ions

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 $^{7}Li^{+}$ and cation leachates recovered in the effluent solution was determined by a Varian Liberty II Radial ICP-AES instrument (Stellenbosch University, Geology Department, South Africa). H_2SO_4 samples were diluted 20x before analysis. Matrix matched calibration standards were prepared for H_2SO_4 samples, and the accuracy of calibration was verified with a quality control standard before analysing. Nitrates (NO_3-N) were analysed using an auto-analyser using the Cadmium reduction method (Mitsch *et al.*, 2005) while the Chlorides (Cl^-) were analysed by titrating standardised silver Nitrates solutions to the first potentiometric end-point, which corresponded to the micromoles of Chlorides ions present in the eluant (Tang & Gordon, 1980). Furthermore, Fluorides were determined using a Colometric Spectrometer (Tokalioglu *et al.*, 2001). The Sulphates (SO_4^{2-}) and Phosphates (PO_4^{2-}) were both determined using an Inductively Coupled Plasma Spectrometer (ICP-MS) while Carbonates (CO_3^{2-}) were determined by titration with HCl acid.

2.4 Lithium column elution apparatus and procedure

2.4.1 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 300 mm. The column was filled with 30 ml of degraded Amberlite IRN 217 lithiated mixed-bed resin. The cation part of the resin used had a lithium capacity of 2.03 eq/L and mixed-bed ratio was 1:1.4 (anion: cation). The concentrated 1M biologically produced H_2SO_4 acid concentration 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 BV/hr. One BV was defined as the volume of the elution solution which is equivalent to the volume of the resin in a column. The flow rates used enabled adequate

131 sampling of the eluate for determination of the elution profile of the resin while not fluidising the
132 resin. This was slightly higher than the flow rate used by Lukey (2000) in the elution of Copper
133 and Iron cyanide complexes from ion-exchange resins. Several bed volumes (18BV) of acid
134 solution were passed through the column for each experiment. After the experiment, the resins
135 were rinsed with distilled water to remove acid left on the resin. Eluate samples were taken at
136 each 2BV (60 ml). The flow rate remained constant throughout the experiment. All piping and
137 connections were made with silicone tubing. For control experiments, a dilute solution of a
138 commercial grade sulphuric acid was used.
139
140 **2.4.2 The anion purification process**
141 The anion reduction column was carried out under the same conditions as the elution stage. The
142 anion reduction column was filled with 90 ml of Amberlite IRN 78 anion resin which was triple
143 that of the degraded Amberlite IRN 217 lithiated mixed-bed in the elution stage. The effluent
144 from the elution stage was passed through the anion resin to remove anion leachates. The
145 effluent was analysed for anion contaminants to evaluate if there was reduction of anion
146 contaminants. The level of contaminants was compared to the specification required in reactor
147 coolant water of the pressurised water reactor (PWR). The desorption and leachates removal
148 processes are illustrated in Figure 2.
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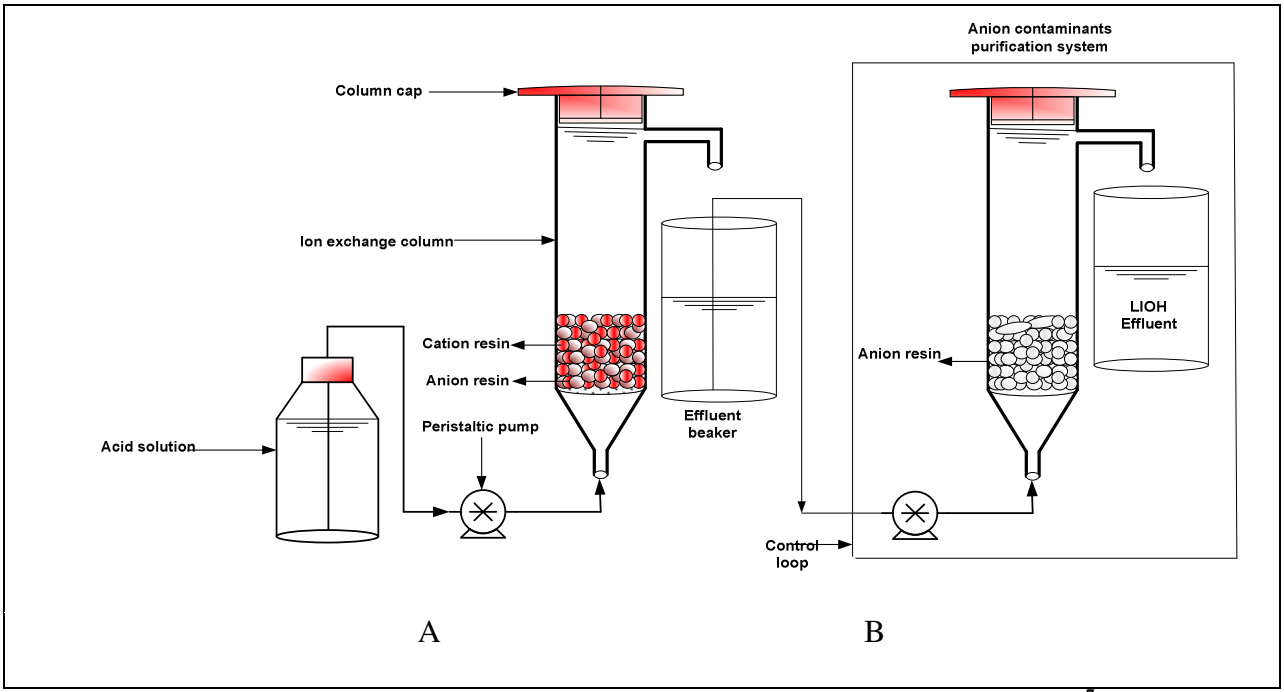


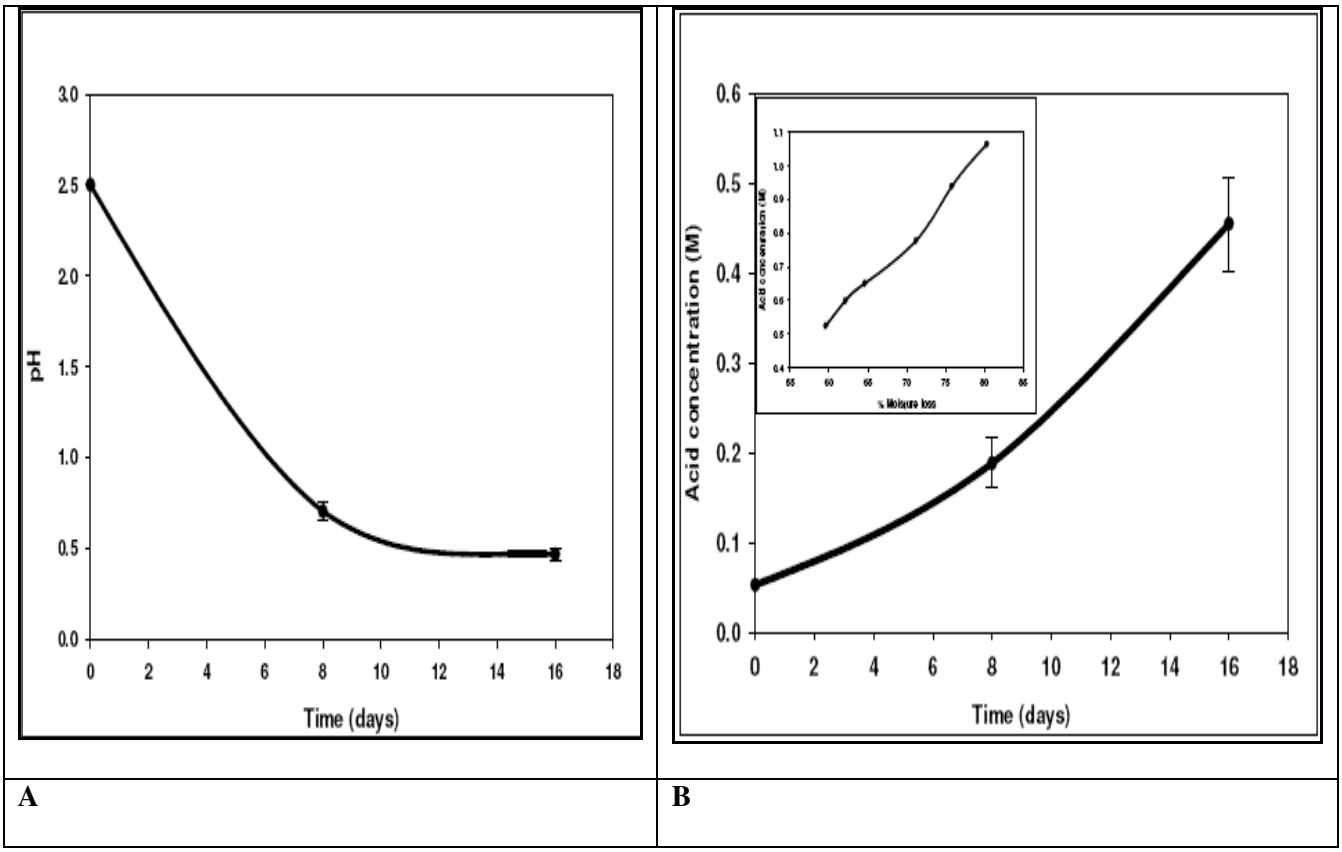
Figure 2: [A] Schematic illustration of the column used for the desorption of lithium isotope ($^{7}Li^{+}$) from 30ml Amberlite 217 lithiated mixed-bed resin using biological y produced sulphuric acid and [B] the anion leachates removal process.

4. Results and discussion

4.1 Sulphuric acid production

Figures 3A and 3B indicate the pH and the cumulative production of sulphuric acid obtained in the *A. caldus* aerated batch bioreactor. The sulphuric acid productivity by culture *A. caldus* on elemental sulphur reached an average cumulative rate of 0.4M over a period of 16 days. The rapid drop in pH from an initial value of 2.5 to 0.47 over a period of 16 days, showed that the medium became progressively acidic as the culture aged, as reported by Kempner (1996) for sulphuric acid production using *A. thioxidans*. The sulphuric acid productivity depended on the type of bioreactor and conditions in the bioreactor used; the sulphur surface area; the population of the immobilised cells; the uniform contact between liquid-solid-gas phase and the availability of dissolved oxygen (Cerruti *et al.*, 1998). The advantage of continuous aeration in the batch

reactor is such that the shear forces which breaks down unstable particles, creating finer particles with a higher surface area, enables further sulphur oxidation due to continuous supply of oxygen (Janssen *et al.*, 1994). The sulphuric acid produced by these batch bioreactors was approximately 2.7-fold greater than sulphuric acid produced by Liu (2003). This amount was in agreement with the simulated sulphuric acid concentration of 0.38M by Liu (2003) on the optimal production of sulphuric acid by *A. thioxidans* using a response surface methodology whereby an increase of sulphuric acid concentration was directly proportional to the sulphur concentration used.



A **B**

Figure 3: [A] pH evolution during oxidation of elemental sulphur, [B] cumulative production of sulphuric acid in an aerated batch bioreactor with *A. caldus* immobilised on elemental Sulphur with an embedded graph showing the acid concentration increase with the percent of moisture loss.

The acid was concentrated using an evaporation technique, such that the acid strength was increased to approximately 1M acid by evaporating 80% (v/v) water. The rate of acid concentration increments was 0.025M H_2SO_4 per % moisture loss (See embedded graph in Figure 3A). The concentrated sulphuric acid was used to recover $^{7}Li^{+}$ isotope from degraded mixed-bed resin. The biologically produced sulphuric acid was compared to a dilute commercial grade mineral sulphuric acid solution by desorpting the $^{7}Li^{+}$ isotope from degraded Amberlite IRN 217 lithiated mixed-bed resin as shown in Figure 4.

4.2 Bio-desorption of $^{7}Li^{+}$ isotope from degraded mixed-bed resin

Figure 4 represents the desorption of $^{7}Li^{+}$ isotope from a degraded Amberlite IRN 217 lithiated mixed-bed resin in a continuous ion-exchange column using 1M biologically produced sulphuric acid in comparison with mineral sulphuric acid. Desorption rate >80% was observed for the biologically produced sulphuric acid at the initial stages (2BV's), which was higher than the 61% achieved by commercial grade mineral acid at the same stage. The results showed that the biologically produced sulphuric acid showed high desorption kinetics in the initial stages of the desorption process compared to the commercial grade sulphuric acid. This was due to the presence of other cations such as Sodium (Na^{+}), Magnesium (Mg^{2+}), Potassium (K^{+}) and Calcium (Ca^{2+}) in the influent which also have an affinity to exchange with the $^{7}Li^{+}$ on the cation part of the mixed-bed resin when compared to the commercial grade acid used (see Figure 6). The overall desorption rate was 95% for both biologically produced sulphuric acid and commercial grade mineral sulphuric acid after passing 18BV, a result similar to that achieved when HCl was used. The biologically produced sulphuric acid has shown an equivalent efficiency in desorpting $^{7}Li^{+}$ isotope from the degraded Amberlite resin as the commercial grade

mineral sulphuric acid. This showed that biological production of sulphuric acid can also be used in the desorption of other metal ions adsorbed on ion-exchange resin using a process which is economically beneficial and environmentally friendly compared to other conventional methods.

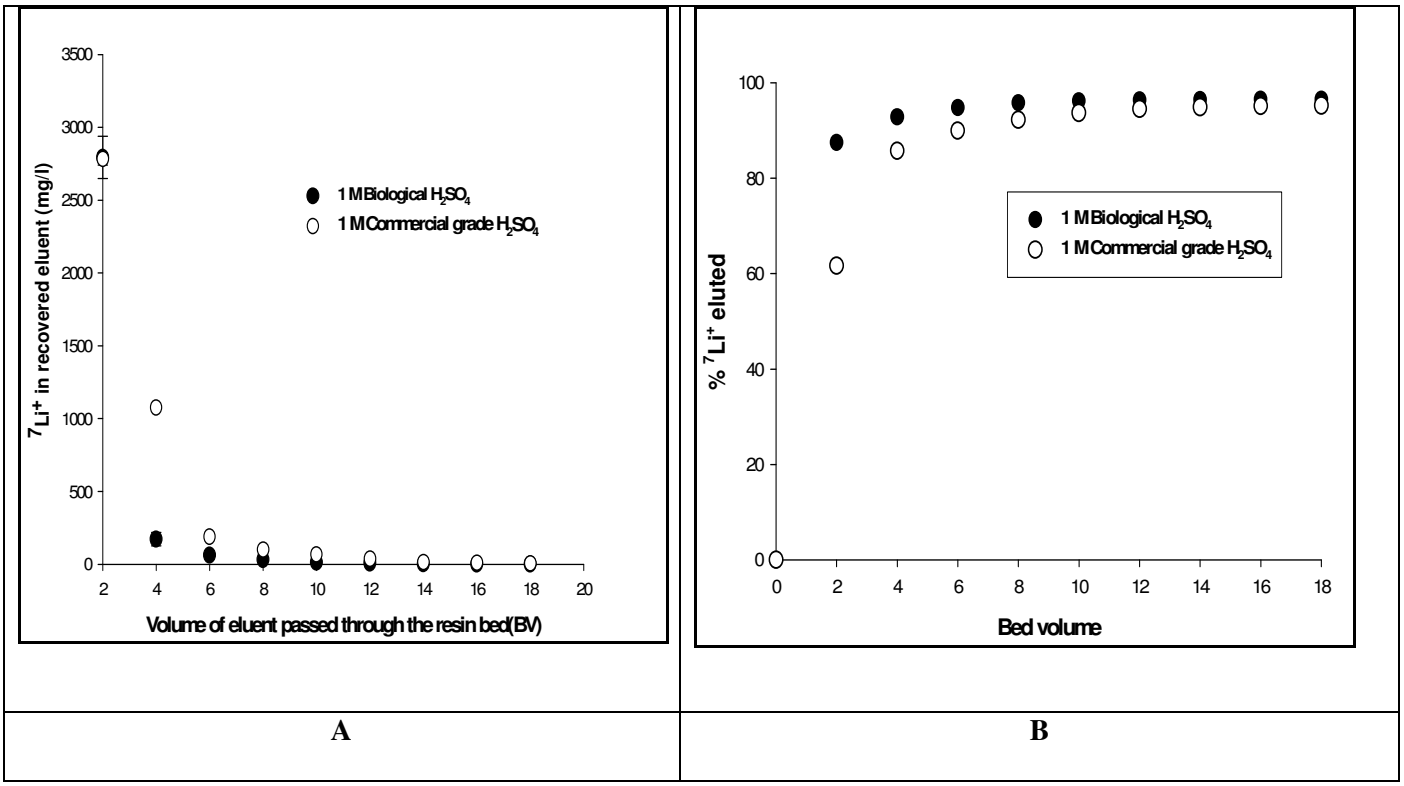


Figure 4: Lithium 7 isotope desorption using biologically produced sulphuric acid by *A. caldus* cells in comparison to mineral sulphuric acid.

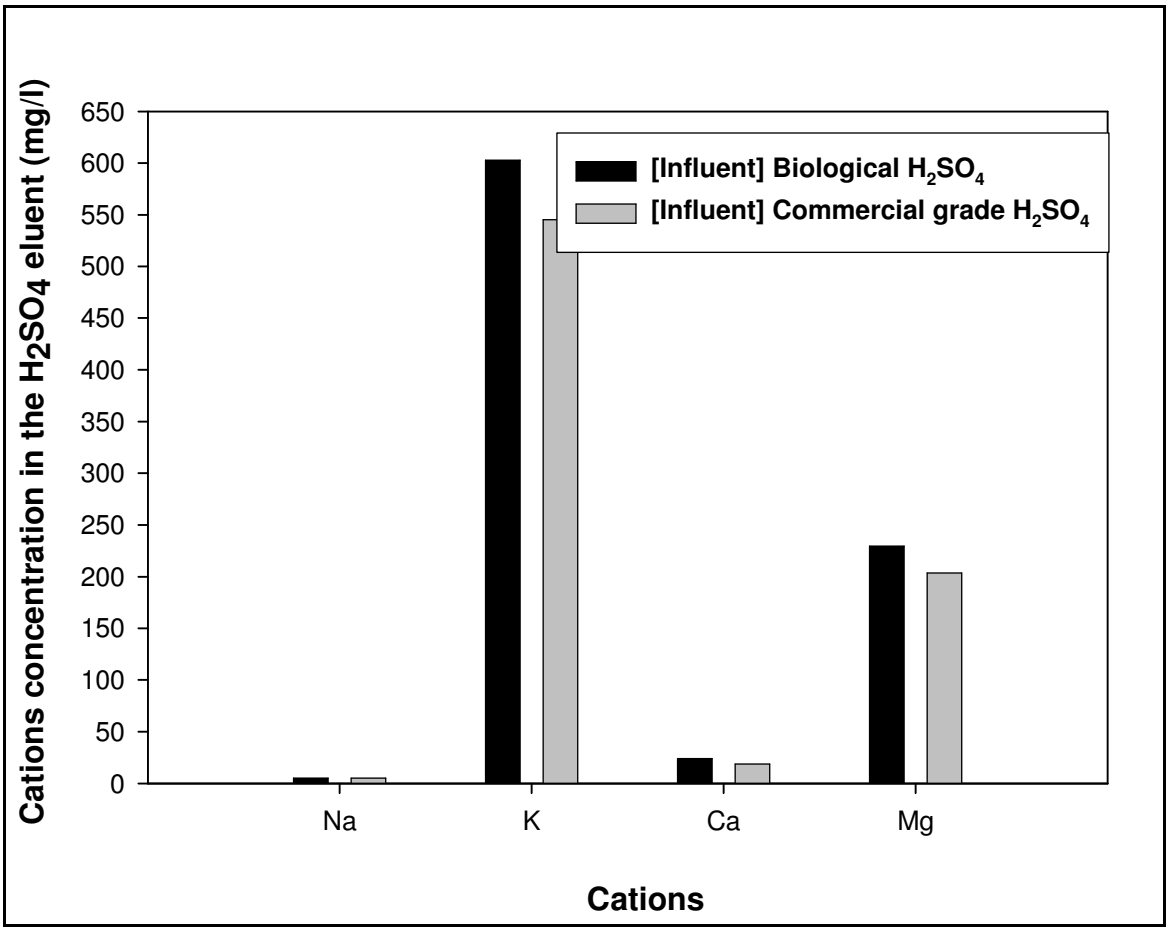


Figure 5: Cations in the biological and commercial grade H_2SO_4 influent

Table 1, illustrates the comparison of desorption kinetic parameter between the biological H_2SO_4 and commercial grade H_2SO_4. The desorption rate constant (k) for the biological H_2SO_4 was 0.0637 at $t \leq 27$ min, which was higher than the commercial grade H_2SO_4 of 0.0497. This shows that at $t \leq 27$ min, the biological H_2SO_4 desorpt a higher concentration of $^7Li^+$ isotope as shown in Figure 6. The desorption rate of biological H_2SO_4 decreases at $t > 27$ min as compared to the commercial grade due to the amount of the $^7Li^+$ isotope desorpted at the initial $t \leq 27$ min. The overall correlation coefficient (R^2) comparison between simulated and experimental data for biological desorption was 0.88 and for commercial grade desorption was 0.97. The commercial grade desorption simulated data fit to experimental data was more sufficient with a correlation

coefficient (R^2) of 0.97 as compared to biological desorption data with correlation coefficient of 0.88.

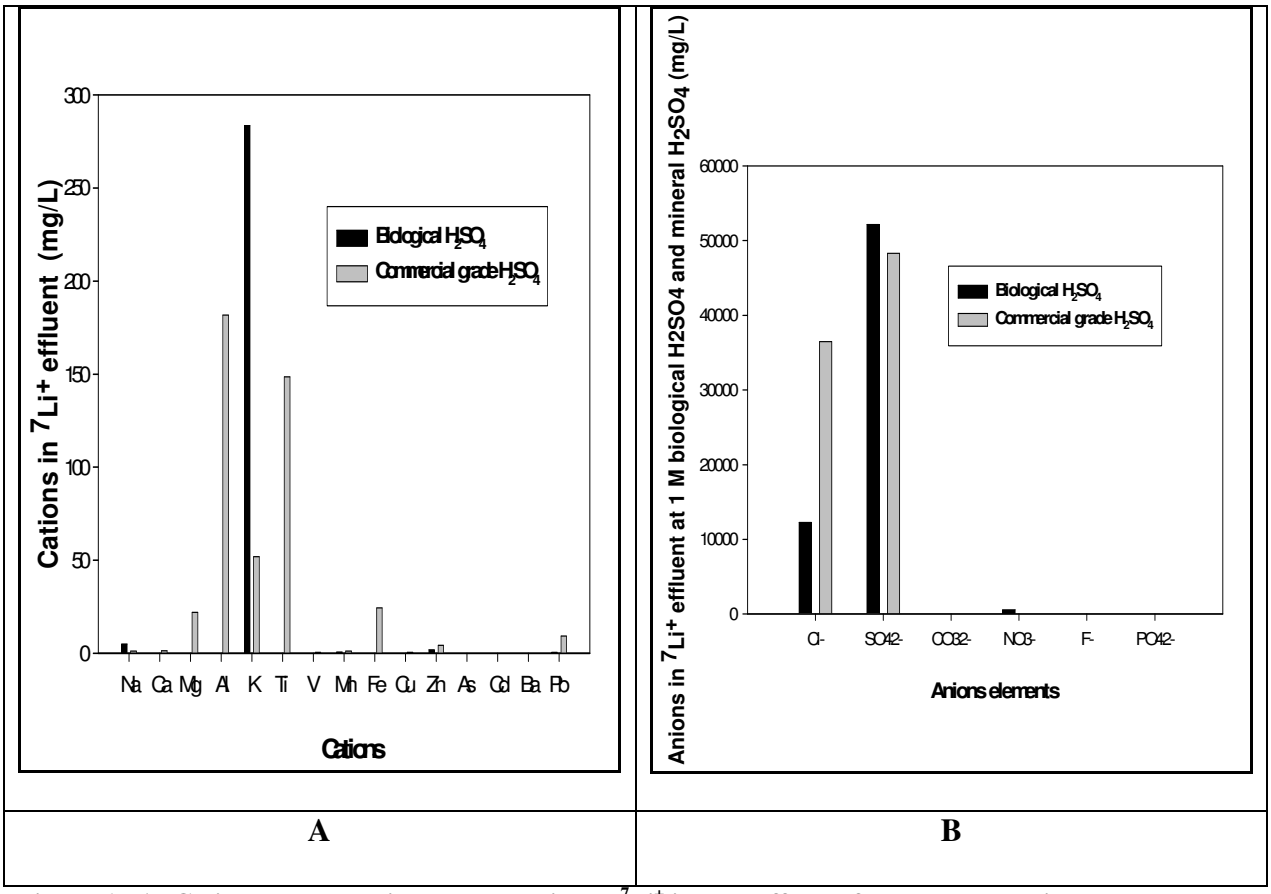
Table 1: Comparison of kinetic parameter between Biological and Commercial grade H_2SO_4

Kinetic Parameters	Biological H_2SO_4	Commercial grade H_2SO_4
Desorption rate constant (min^{-1}) (0 – 27 ≤ t > 27)	0.0637 - 0.0035	0.0497 - 0.0598
Correlation Coefficient (R^2)	0.88	0.97

R^2 - determined to compare simulated values to experimental values

4.3 The amount of leachates in the recovered effluent

Figure 6 indicates the level of cations and anions leachates in the $^7Li^+$ isotope effluent after passing biologically produced sulphuric acid in comparison to the commercial grade mineral sulphuric acid. The level of cations did not exceed 200 mg/L with a high quantity of Zinc (Zn), Calcium (Ca) and Magnesium (Mg) observed in the biologically produced sulphuric acid. The high quantity of these metallic ions was attributed to the trace elements used for cellular growth in the media used during sulphuric acid production by *A. caldus*. A large quantity (approximately 50000 mg/L) of anion leachates were found in the effluent. The large quantity of these anions was attributed to the leachates from the eluant solution of both biological and commercial grade sulphuric acids used. Furthermore, as the Amberlite IRN 217 mixed-bed resin was degraded, the release of anion leachates further contributed to the high quantity of anion in the $^7Li^+$ isotope effluent.



241 **Figure 6: [A] Cations and [B] anions leachates in the $^{7}Li^{+}$ isotope effluent from the desorption process.**

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243 The Amberlite IRN 78 showed a higher capability (>90%) of reducing the anion leachates from
244 the $^{7}Li^{+}$ isotope effluent using both biologically produced H_2SO_4 and commercial grade H_2SO_4
245 as illustrated in Table 2.

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253 **Table 2: Averaged anion removal from the $^{7}Li^{+}$ effluent using Amberlite IRN 78 anion resin**

Anion species[a]	1M biological H_2SO_4			1M commercial grade H_2SO_4			Reactor coolant spec. (μg/L)
	Concentration[b] (mg/L)	Purification[c] (mg/L)	Reduction[d] (%)	Concentration[b] (mg/L)	Purification[c] (mg/L)	Reduction[d] (%)	
Cl^-	13393.11	88.11	99.	36460.99	123.36	99.66	<50
SO_4^{2-}	51478.18	998.65	98	48277.26	464.33	99.038	<50
CO_3^{2-}	nd	nd	-	nd	nd	-	nd
NO_3^-	0.01	nd	100	27.98	nd	100	nd
F^-	18.50	0.1	99	nd	nd	-	<50
PO_4^{2-}	557.96	19.55	96	nd	nd	nd	nd

254 *nd- not detected*

255 *[a]Anion species in the recovered $^{7}Li^{+}$ eluent*

256 *[b]Anion concentration in HCl/H_2SO_4 eluent*

257 *[c]Anion concentration after passing through Amberlite IRN 78 anion resin*

258 *[d]Percentage reduction of anion leachates by Amberlite IRN 78 resin*

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260 **5. Conclusion**

261 This study showed the possibility of producing an acid concentration of 0.4M using *A. caldus*
262 immobilised on elemental sulphur. The application of the biologically produced sulphuric acid to
263 desorpt $^{7}Li^{+}$ isotope from degraded Amberlite mixed-bed was efficient. An elution efficiency
264 >80% was achieved at the initial stage of 2BV and this was higher than the 60% efficiency rate
265 from mineral sulphuric acid at the same stage. The overall elution efficiency of greater than 90%
266 was achieved after passing 18BV's, a result similar to that achieved by commercial grade
267 mineral sulphuric acid. The biologically produced sulphuric acid has showed the same ability to
268 extract the $^{7}Li^{+}$ isotope when compared to the commonly used convectional method of

commercial grade sulphuric acid. The leachates decontamination process can be used to reduce the leachates to an adequate level for re-use.

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