CRANFIELD UNIVERSITY

Katherine Gobey

The recovery of high value metals from spent lithium-ion batteries.

SCHOOL OF AEROSPACE TRANSPORT AND MANUFACTURING
MRes in Manufacturing

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Academic Year: 2017 - 2018

Supervisor: Dr Qi Zhang
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ABSTRACT

Much of the modern technological world in which we live is dependent on reliable energy storage in the form of batteries, from small goods such as mobile phones, to backup power systems, and everything in between.

Battery use is expected to increase considerably in the near future, and as such so will battery waste, resulting in a need for efficient, economical, and environmentally friendly processing and recycling of waste batteries and their components.

This project set out to investigate a new potential method of separation of cobalt and lithium from Lithium-Ion Batteries (LIB), using sodium alginate, an anionic polysaccharide already widely harvested from multiple species of seaweed, that forms an insoluble cross link polymer with divalent cation Co^{2+}, thus allowing cobalt to be easily extracted and separated from the lithium in the solution.

It was found that, following creation of a cobalt ion solution using water, nitric acid, and reductant hydrogen peroxide, sodium alginate solution readily formed insoluble cobalt alginate, which can then be easily removed from the solution, allowing separation of lithium and cobalt in a simple step.

With fresh sodium alginate beads added in multiple runs of 2 hours up to 93.4% of cobalt by mass was removed from the solution. Alginate added and left for up to 72 hours produced lower yields of up to 79.82% removal.

Keywords:

Cobalt, recycling, reclamation, sodium alginate.

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LIB	Lithium Ion Battery
LCO	Lithium Cobalt Oxide
SEM	Scanning Electron Microscope
EDS	Energy Dispersive X-Ray Spectroscopy

1 INTRODUCTION

1.1 Background

Since the discovery and harnessing of electricity many centuries ago, there presented the challenge of storage. Benjamin Franklin, famous for his experiment flying a kite during a lightning storm, is credited with the first recorded use of the word battery, which he employed to describe a set of capacitors charged using a static generator then discharged via an electrode [1]. Since then, batteries have gone from a niche and novel object to a vital part of modern technological life.

Usage of batteries is expected to increase further for many years to come with a rise in demand from multiple diverse sectors. Energy storage is vital not only in smaller consumer goods, but also as we shun combustion engines in favour of electric or hybrid vehicles and power generation moves from fossil fuels to renewable yet intermittent energy sources such as solar and wind. As battery usage increases, so too does associated waste, with an estimated 0.33-0.4 million metric ton of spent Lithium Ion batteries (LIB) entering the waste stream between 2015 and 2040 [2]. This presents a significant issue, as incorrect disposal of LIBs can cause environmental damage, as well as wasting valuable and finite resources such as cobalt and lithium.

1.2 Incentive

A number of governments have introduced partial or total bans on landfill disposal of LIBs, for example at US national level LIBs are not regulated by the Resource Conservation Recovery Act (RCRA), however two states, California and New York, have passed legislation banning their disposal at landfill [3]. Additionally, in the EU LIBs are classified as Absolute Non Hazardous (ANH) waste [4], and the 2006 Battery Directive works to eliminate the disposal and incineration of batteries regardless of their hazard status. The Directive also had set stringent targets for recycling of spent batteries, with collection targets of 25% for 2012 and

45% for 2016 [5], and that such collected batteries undergo appropriate treatment or recycling. Importantly, it set minimum efficiency levels of recycling techniques used, with LIB recycling reclaiming 50% of the batteries by average weight[6], meaning that effective recycling techniques must be developed and adopted to ensure compliance to the Directive, and ensuring that recycling processes are worthwhile and not applied minimally to adhere to legislation.

In addition to legal obligations, there are also economic and political benefits to efficient recycling of batteries. Batteries contain valuable finite resources, in particular the metals in anodes and cathodes.

1.2.1 Cobalt

A significant proportion of the world's yearly cobalt extraction comes from the Democratic Republic of the Congo, with the Katanga Province to the south containing an estimated 34% of the world's cobalt reserves[7], with ongoing mine expansions expected to increase that share up to 73%. Much of this is mined in unsafe conditions, with little regard paid to worker safety or environmental protection, with child labour, injury, and even death common occurrences [8]. And whilst its civil war (which itself was partly provoked, and funded, by trade in conflict minerals) ended in a peace treaty in 2002, eruptions of violence are still frequent and mines are valuable territory for clashing groups, resulting in interruptions in supply and volatile prices [9], with prices for cobalt at the London Metal Exchange more than doubling from $24095 to $59000 per metric ton in the 12 month period from September 2016 to 2017 [10], and the cost expected to rise further with increased demand. As a typical EV battery can contain a significant quantity of cobalt, 14kg in the case of the Tesla Model S [11], this presents considerate concern.

1.2.2 Lithium

Similar to cobalt, lithium has an often troublesome supply. Whilst there are considerable reserves of lithium in ores, mining these has become relatively uncommon owing to the much cheaper process of extraction from water, with an estimated 66% of the world's lithium reserves found in brines [12]. 80% of the total world reserves of lithium exist in Bolivia, Chile, and Argentina [12], where lithium is typically obtained after evaporation of water in the sun, which whilst requiring little, if any, additional energy input, is a slow process.

Whilst previously the largest use of lithium was in the glass and ceramics industry (35% in 2015) [13], an increase in battery demand has resulted in the LIB industry's consumption overtaking lithium's traditional usage, and with exponentially increasing demand come rises in price, with lithium carbonate prices increasing by 50% between 2014 and 2016 [14] and further increases predicted.

1.3 Battery Design

Batteries in their most basic form consist of an anode, a cathode, and an electrolyte, all enclosed in a casing. There are many different compositions and types of battery, however we will focus on the most common type, the lithium ion battery (LIB).

1.3.1 Anode

LIBs commonly utilise graphite as the anode material, consisting of layers of hexagonally bonded carbon sheets, in-between which Li^+ ions are held in a process known as intercalation [15]. Graphite as an anode has relatively low capacity, 372 milliamp hours per gram ($mAhg^{-1}$) [15], however owing to its low expansion during intercalation it exhibits excellent maintenance of its charge capacity over many charge-discharge cycles, and as such has become the most common anode choice.

Other anode materials utilise the ability of Lithium ions to form alloys. Metals such as tin, aluminium, and antimony offer capacities much higher than graphite (994 $mAhg^{-1}$ $Li_{22}Sn_5$, 993 $mAhg^{-1}$ LiAl, and 536 $mAhg^{-1}$ Li_3Sb respectively) [16][17] and theoretical capacities of up to $4200mAhg^{-1}$ are possible with silicon alloys such as $Li_{22}Si_5$ [18]. The high capacities of these materials are at the cost of total battery life, as anodes composed of alloying metals undergo considerable expansion during intercalation, often several times original volume [19], resulting in damage to the anode itself as well as potential damage to the solid electrolyte interphase (SEI) protective layer that acts to prevent physical contact between Li and the solvent [20].

1.3.2 Cathode

During intercalation of the cathode, the material acts as a host to guest ions, which in the case of LIBs are Li^+ ions.

Lithium secondary batteries were first commercialised in 1991 by SONY, who also popularised the term LIB [21], and their basic composition has remained mostly unchanged since.

SONY's first LIBs utilised Lithium Cobalt Oxide, $LiCoO_2$ (LCO), which had been investigated and proposed as a cathode material by Goodenough in 1980 [22], and remains the most widely utilised cathode material with 36% market share [23], which is testament to its beneficial attributes. In LCO Cobalt and Lithium are held in octahedral sites in alternating layers [19], during discharge, Li^+ ions travel from the negative graphite electrode to CoO_2 layers, via an electrolyte. On charging this process is reversed.

$LiCoO_2$ is the preferred material owing to a number of beneficial properties, such as its relatively high theoretical specific capacity and volumetric capacity (274 $mAhg^{-1}$ and 1363 $mAhcm^{-3}$ respectively) [19]. It also has high discharge voltage of 4.2V [24], as well as low self-discharge, and reliable cycling performance.

Despite its wide use, LCO is not without its disadvantages. A major drawback is its higher cost, as whilst once an economic option, aforementioned price increases in cobalt had drastically increased the costs of LCO production. Additionally, LCO has lower thermal stability and risks thermal runaway when overcharged or exposed to high temperatures. Thermal runaway is a risk with all LIBs, however LCO often reaches higher temperatures and releases more gas than other cathode materials [25], which risks damage to nearby components or injury to users.

1.3.3 Electrolyte

The role of the electrolyte in a battery is to facilitate flow of ions between the anode and cathode, thus providing current.

Essentially, electrolytes consist of a lithium salt held within a solvent. There are two main types of electrolyte utilised in LIBs: liquid electrolytes and gel electrolytes. Liquid electrolytes are solutions of lithium salts in organic solvents. Gel electrolytes are ionically conducive materials wherein the salt and solvent are dissolved or mixed with a polymer of high molecular weight [26]. An advantage of gel solvents is that the battery does not have to be encased in a rigid metal case, meaning flexible batteries can be produced that can fit around components, making them preferable in consumer electronics applications such as mobile phones where compact design is desirable.

1.3.3.1 Solvents

Carbonates are the most frequently utilised solvents in liquid electrolytes owing in part to their stability and safety, with common types include ethylene carbonate (EC), polypropylene carbonate (PC) and dimethyl carbonate (DMC) amongst others. Generally multiple carbonates are used in an electrolyte solvent to benefit from the range of properties and thus improve performance [26].

1.3.3.2 Salts

Choice of salt can impact upon performance of the battery; the most commonly used salt in LIBs is Lithium hexafluorophosphate ($LiPF_6$) owing to its high conductivity, however $LiPF_6$ produces hydrofluoric acid (HF) on contact with water and therefore must be handled in a dry environment, which has implications for end of life processing.

1.3.3.3 Additives

Other substances are added to the electrolyte to control and enhance performance. For example vinylene carbonate (VC) is frequently used due to its preferential reduction at the anode, resulting in faster formation of the SEI and higher reversible capacity [27].

Additives typically constitute less than 10% of the electrolyte at manufacture but can be almost totally consumed by formation of the SEI.

1.4 Principle of operation

Batteries operate by converting chemical energy to electrical energy. In primary batteries such as zinc-carbon cells and alkaline batteries this is achievable immediately after manufacture, whereby an electrochemical reaction occurs and produces current in the battery. This reaction continues until the chemicals in the battery have been used up and the battery ceases to produce current. In primary cells this is an irreversible process and the batteries cannot be recharged and must be disposed of after use. For this reason, primary cells are known as an uneconomical and environmentally destructive technology and market share is declining in favour of secondary cells, which must be charged before use by applying an external voltage but can be recharged and used multiple times.

In the case of an LCO battery, lithium ions move between a graphite anode and a cobalt oxide cathode, where the following reactions occur:

At the anode:

$$6\mathrm{C} + x\mathrm{Li} + xe^{-} \leftrightarrow \mathrm{C}_6\mathrm{Li}_x \tag{1-1}$$

At the cathode:

$$\mathrm{LiCoO}_2 \leftrightarrow \mathrm{Li}_{(1-x)}\mathrm{CoO}_2 + x\mathrm{Li}^{+} + xe^{-} \tag{1-2}$$

Where the forward reaction is during charge and the reverse reaction during discharge [28].

This results in the overall process:

$$\mathrm{LiCoO_2} + 6\mathrm{C} \leftrightarrow \mathrm{Li}_{(1-x)}\mathrm{CoO_2} + \mathrm{C_6Li}_x \tag{1-3}$$

1.5 Methods of Recycling

Presently there are two main methods of processing of spent batteries: pyrometallurgical and hydrometallurgical, which both have their own inadequacies and present further challenges.

Both methods share initial stages of processing: first, the battery must be discharged. This can be done either by submerging the battery in a brine solution, where care must be taken to disperse oxygen produced to avoid explosion, or discharge can be achieved using a resister, where temperature must be kept below 90ºC to prevent fire. Then the outer casing may be removed via cutting or unscrewing, when plastic, steel, and iron can be obtained. Some processes also require the material to be crushed or ground to produce a dust.

Considerable research is being conducted into alternative methods of recycling to pyrometallurgical and hydrometallurgical techniques, hoping to improve upon their negative environmental impact.

1.5.1 Pyrometallurgical

Methods of processing that utilise thermal energy incur chemical change are known as pyrometallurgical, from the Greek πυρ (pyr), for fire.

Commercial pyrometallurgical processes often make use of the organic compounds present within the batteries, such as graphite electrodes, as a source of carbon for the thermal reduction [29]. This typically results in an alloy containing copper, cobalt, nickel, and iron in varying proportions. This alloy can then be subject to further processing to separate the metals. In addition to the alloy, a slag of manganese, aluminium, and lithium is produced [30].

Pyrometallurgical processes benefit from being relatively simple and easy to scale up to a commercial level, however it can be inefficient owing to the energy required to reach an adequate temperature to induce chemical reactions, and additionally the process produces waste gasses such as carbon dioxide, carbon monoxide, sulphur dioxide, and volatile organic compounds that require significant processing before they are allowed to enter the environment [31]. Pyrometallurgical processes result in a slag and/or alloy that must be further processed, generally via hydrometallurgical methods, in order to recover the desired metals in usable forms.

1.5.2 Hydrometallurgical

Contrary to pyrometallurgy, hydrometallurgy utilises aqueous chemistry to extract metals. For the reclamation of metals such as Li from LIBs this usually involves use of a strong acid such as sulphuric acid (H_2SO_4) to create a solution, followed by chemical precipitation and filtering [28].

When LCO is recycled using H_2SO_4 the following reaction occurs:

$$2\mathrm{LiCoO_2} + 3\mathrm{H_2SO_4} \rightarrow 2\mathrm{CoSO_4} + \mathrm{Li_2SO_4} + 0.5\mathrm{O_2} + 3\mathrm{H_2O} \quad \textbf{(1-4)}$$

A similar reaction occurs with the use of hydrochloric acid (HCl) however this reaction produces dangerous chlorine gas and therefore is less preferred[32].

Conditions must be controlled to ensure optimum rate of reaction and reclamation of Cobalt and Lithium. Studies have been conducted to investigate the effect pH, temperature, and solid-to-liquid (S/L) ratio have on the process, where one study found that at 90ºC with an acid concentration of 4 M 95% of cobalt was leached within 4 hours [33]. This cobalt is then extracted using chemical deposition, leaving a solution containing lithium and copper which can be further processed.

The principal drawbacks to the hydrometallurgical process include dangers to workers from strong acids, and environmental concerns from process waste. Additionally, the resultant ion solution must undergo extensive processing to separate its constituents into more usable forms.

1.5.3 Bioleaching

A promising technique uses bioleaching to extract the valuable metals. Bioleaching techniques use acidophilic bacteria such as acidithiobacillus feroooxidans, which takes elemental sulphur and ferrous ions an energy sources to produce sulphuric acid and ferric ion leachants. Lithium is extracted using the sulphuric acid, with bioleaching of cobalt occurring by reduction of insoluble Co^{3+} into soluble Co^{2+} using Fe^{2+},which can then be released by acid dissolution [34].

This method involves first milling the cathode and anode materials into a fine dust and sieving this through a mesh to obtain a powder [34] that can then be used for the bioleaching. Analysis of the powder by x-ray diffraction can be used to ascertain the initial composition of the waste, and the final leached residues can similarly be analysed using energy-dispersive X-ray spectroscopy (EDX) or X-ray photoelectron spectroscopy (XPS), to determine the effectiveness of the process [34].

Correct conditions are imperative to the process, for example the liquid to solid ratio must be kept high as cobalt and lithium can be toxic to the bacteria. Experiments have also shown that the initial pH of the mixture can effect bacterial growth and therefore rate of leaching, with a lower starting pH producing more preferable results, although the final pH of the solution remains independent of the initial pH owing to the acid producing nature of the bacteria [35].

So far, bioleaching is not in use at commercial or industrial scales. This is due mostly to its time-consuming nature, with current techniques requiring days or even weeks to obtain worthwhile amounts of Li and Co. Further research is needed to better understand and harness the processes involved.

2 Proposed Recycling

2.1 Sodium Alginate

Sodium alginate is the sodium salt of alginic acid, a polysacharride already widely harvested from multiple species of brown algae from the class Phaeophyceae, and is a safe, cheap, and renewable resource.

It exists as a linear copolymer when in a solution of water, which then forms a cross linked polymer when exposed to divalent cations. The insoluble nature of this cross-link polymer has led to sodium alginate to be employed in a wide variety of applications. It is currently used in novel gastronomy, where its spherification properties are utilised to make mock caviar, raindrop cakes, and to thicken sauces, often as a vegetarian alternative to animal derived hydrocolloids such as gelatine. It is also used in over the counter heartburn medicine, where it reacts with gastric acid to produce a physical barrier separating the oesophagus from stomach acid [36].

It is proposed that sodium alginate will form an insoluble cross-linked polymer in the presence of cobalt ions found within the LCO, thus allowing the cobalt to be easily separated from the lithium remaining in the solution in one easy step.

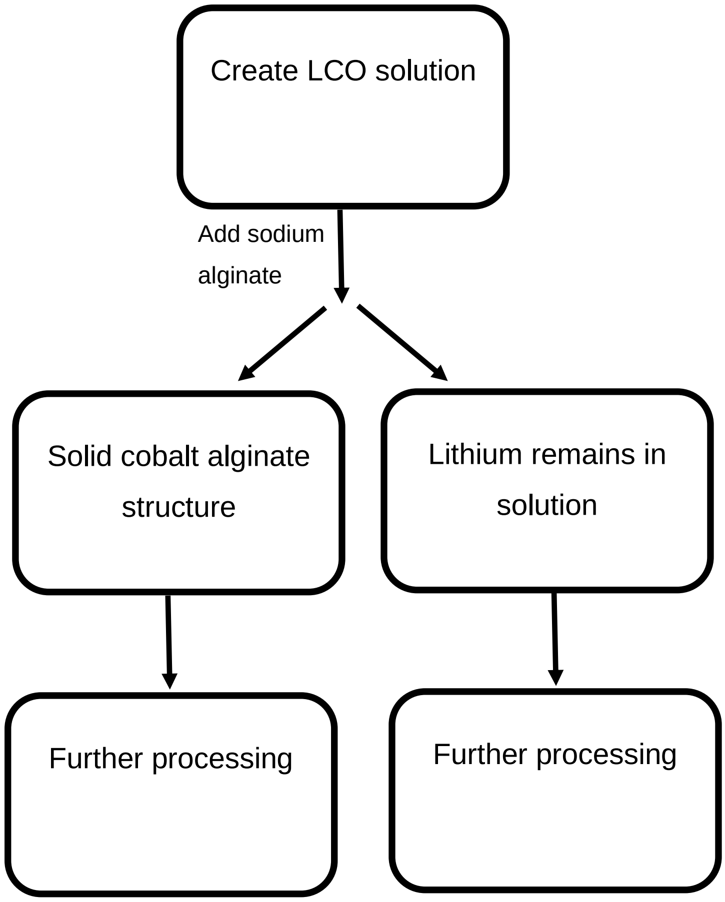

Figure 2-1 Proposed method of cobalt separation

2.1.1 Previous use of sodium alginate

Potential use of sodium alginate for cobalt ion removal has been explored previously, using various methods and for various purposes.

Many trialled methods have involved first creating calcium alginate, with removal of cobalt occurring as it swaps out the calcium ions in the structure. One such study first formed alginate beads by dropping sodium alginate into a calcium chloride solution [37]. The formed beads are then added to a cobalt containing solution and allowed time for adsorption. FTIR analysis of the beads before and after exposure to the cobalt solution had confirmed that adsorption of cobalt had occurred.   The beads were then washed with Hydrochloric Acid to desorb cobalt ions so that they could be reused.

Other methods have attempted to add sodium alginate directly to the cobalt solution, skipping out the calcium alginate step. One study applied a thin layer of sodium alginate to the internal walls of a tube, which was allowed to dry before a cobalt chloride solution was added. A second method consisted of dropping sodium alginate directly into the solution, wherein solid beads were formed as cobalt diffused across. Subsequent changes in cobalt concentration were measured via titration using EDTA as the titrant, confirming removal of cobalt ions from the solution using both methods [38] .

Alginate beads may also be reused following washing with hydrochloric acid to desorb cobalt ions [37].

Both studies confirmed that alginate can be used to successfully extract cobalt from a solution, however no research has been conducted on its potential use in reclaiming cobalt from battery component LCO.

3 Methods

3.1 Materials

Sodium alginate and $LiCoO_2$ were obtained from Sigma Aldrich. 70% HNO_3 and 30% H_2O_2 were acquired from Fisher Chemical. All materials used were laboratory reagent grade.

3.2 Procedure

A number of procedures were attempted before successful methods were established.

Experiments were conducted in a laboratory of uncontrolled room temperature between 20ºC and 30ºC . No attempt was made to monitor or control pH.

3.2.1 Method one

Initially it was hoped that LCO may react with sodium alginate in an aqueous solution.

A quantity of LCO was weighed and added to a round bottomed flask along with 100ml deionised water and sodium alginate. This was then heated for 30 minutes at set temperatures between 30ºC and 90ºC and stirred. This set up is detailed in Figure 3-1 Set up of procedure for creating cobalt solution.

Batch	LCO (g)	Alginate (g)	Temperature (ºC)
B1	0.2494	1.0039	30
B2	1.0052	3.0071	30
B3	1.0013	3.0021	30
B4	1.0017	3.0005	30
B5	1.0001	2.9990	50
B6	0.9996	3.0002	70
B7	0.9998	3.0009	80
B8	0.9993	3.0004	90

Table 3-1 Details of batches produced using Method One

The resulting gel mixture was subject to separation of parts using centrifuge for 15 minutes at 4000 rpm, with the acquired solid tested using XRD against known LCO powder, which confirmed that no reaction had occurred.

3.2.2 Method two

Once it was known that the LCO must be split into ions in order to react with the alginate, solutions were made of varying proportions of deionised water, nitric acid, and hydrogen peroxide.

A solution of cobalt ions was prepared by mixing 70 ml deionised water with 15 ml HNO_3 and then 15 ml H_2O_2, to which was added the LCO of different masses. This combination of materials was chosen as they have been shown in the literature to successfully split LCO for another application [39], however the ratios used were changed slightly to ensure full splitting of the LCO powder. This mixture was placed in a round bottomed flask and heated to 80ºC with the use of an oil bath with a magnetic stirrer at 400 rpm for one hour. A condenser was used to prevent escape of water from the solution.

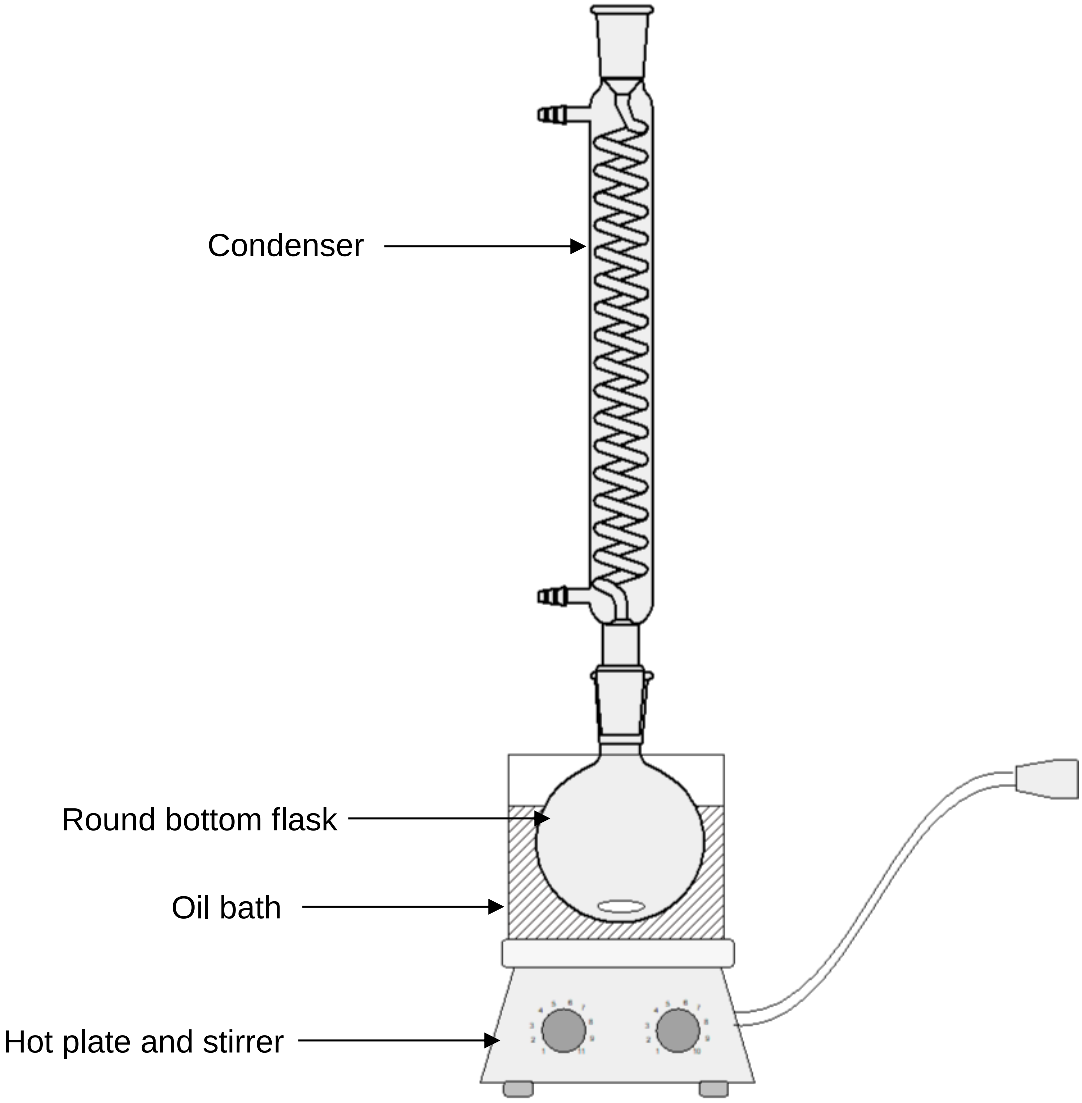

Figure 3-1 Set up of procedure for creating cobalt solution

Batch	LCO (g)
B9	0.0024
B10	0.0029
B11	0.0100
B12	0.0208
B13	0.0498
B14	0.1001
B15	0.2004
B16	0.3006
B17	0.2994
B18	0.3000

Table 3-2 Lithium Cobalt Oxide content added to each batch for production of the cobalt solution.

During production of the cobalt solution, a sodium alginate solution is prepared, with approximately 5 g of sodium alginate powder added to 200 ml deionised water and gently heated to approximately 40ºC and stirred for 30 minutes until the powder is completely dissolved. Exact quantities are detailed in Table 3-3 **Sodium alginate added to each batch for production of alginate solution.** To facilitate faster production of the solution, alginate powder was added gradually to the water during stirring, to prevent large lumps from forming that were difficult to mix into the solution. Once dissolved, the solution was left to cool and to allow air bubbles to rise and escape.

Batch	Sodium Alginate (g)
A1	4.9995
A2	5.0022
A3	4.9985
A4	5.0006
A5	5.0003
A6	5.0010
A7	4.9992
A8	5.0006
A9	5.0008
A10	4.9996
A11	5.0006
A12	5.0011
A13	5.0004
A14	4.9997

Table 3-3 Sodium alginate added to each batch for production of alginate solution.

After both solutions are prepared and allowed to cool sufficiently, the cobalt solution is transferred to a bottle and a 10 ml sample taken. The sample is then place into a separate beaker with 100 ml of the sodium alginate solution. A solid gelation product is formed immediately, however the solution mixture is left overnight to allow the cobalt ions to diffuse across the solid barrier.

After being left to diffuse, excess liquid is drained from the beaker before the gel is subject to rinsing with deionised water and filtering three times in order to remove ions trapped in the solid but not physically bonded to the alginate structure.

After the third wash, the gel is dried in the oven overnight at 90ºC. The dried gel is then loosely crushed using a pestle and mortar.

The first successful batch was then tested using SEM EDS to ascertain whether the method had successfully separated the cobalt.

Once it was established that cobalt could be successfully separated using this technique, the SEM stage was skipped and the dried powder weighed, and burned in the furnace at 600ºC for two hours, with a temperature increase of 1ºC per minute and a decrease of 5ºC per minute.

The resultant powder is again weighed, then tested using XRD to establish its composition.

3.2.3 Method three

For the final method, as detailed in Figure 3-2 Flow chart detailing procedure of Method Three, the batches of known cobalt concentration made up for previous methods were tested in the UV-Vis spectrophotometer, to establish a concentration curve for cobalt ions in the solution.

The batches were then split into 50 ml samples, into which a set amount of sodium alginate gel at known concentration was dropped via pipette, forming cobalt alginate beads. Addition of alginate in the form of beads was chosen as it has been shown to have successfully utilised in cobalt ion removal from a solution in studied literature [37]. This was then left for two hours at room temperature to allow the cobalt to diffuse across the bead, before the beads were removed via a ceramic filter funnel. A sample was then taken from the remaining solution which was then tested in the UV-Vis to determine absorbance, from which the concentration and thus the amount of cobalt removed could be calculated. This sample was returned to the solution when volume was measured using a cylinder, and the process repeated.

For the first attempt, 2 ml of alginate solution A11 was pipetted into B15 and B16 and left for two hours, after which the beads were removed and a sample from the remaining solution from each for testing in the UV Vis. Testing showed no change in absorbance, and so whilst the beads did remove some cobalt (as evidenced by their hardening and pink colour), the change in concentration in the solution was below the level that can be detected with the UV-Vis

Spectrophotometer, and thus it was determined that 2 ml sodium alginate per 50ml cobalt solution was inadequate for effective removal of cobalt ions. It was decided then that subsequent trials would use 5 ml sodium alginate solution for each attempt. This proved to be more successful, with measurable decreases in absorbance with each run. It should be noted also that there was a decrease of approximately 2-4 ml of cobalt solution with each attempt, which can be attributed to losses during filtering of the beads and transfer of the solution between glassware.

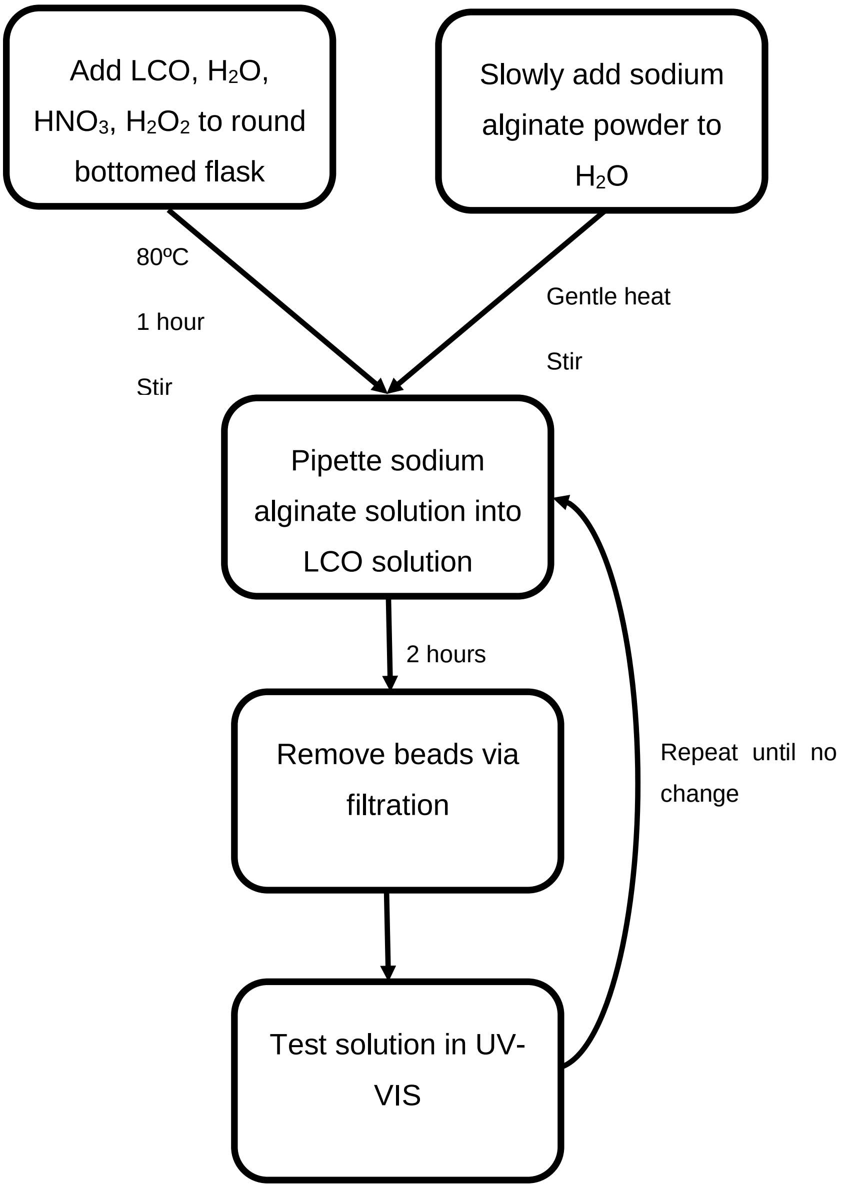

Figure 3-2 Flow chart detailing procedure of Method Three

3.2.4 Method four

For the final method, shown in figure Figure 3-4 Flow chart detailing procedure of Method Four, the volume of alginate added to the solution was changed.

A 100 ml cobalt solution was created as in Method Two and Method Three and displayed in **Error! Reference source not found.**, which was then tested for absorbance (and thus concentration) in the UV-Vis spectrophotometer. It was then split into 5 samples of 20 ml in 50 ml glass beakers. Into each solution containing beaker sodium alginate was added in varying quantities, from 2 ml to 10 ml in 2 ml steps, using a pipette as before to produce alginate beads. The beakers were then covered to prevent escape of water through evaporation and left for two hours, allowing cobalt to diffuse across the alginate beads. Other than a brief swilling after addition of the beads to ensure their even distribution, no stirring, shaking, or other forms of agitation were employed.

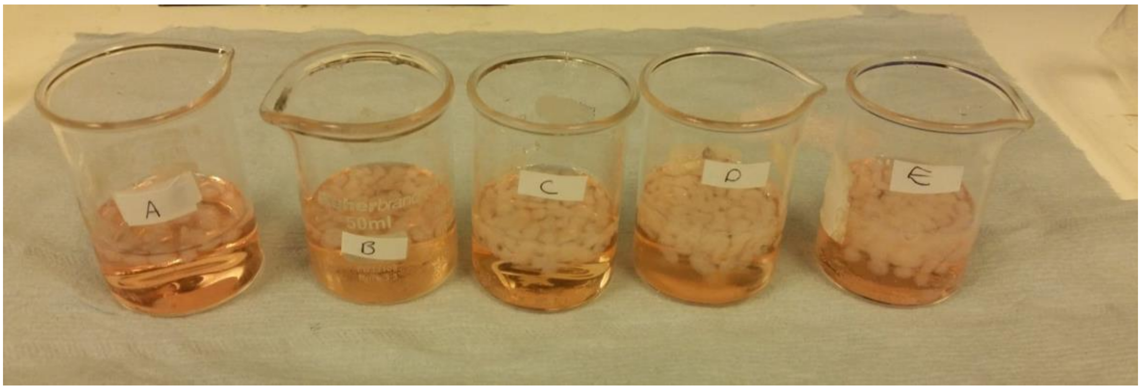

Figure 3-3 A set of samples of B16 immediately following addition of alginate beads.

After two hours, samples of the solution were taken and again tested in the UV-Vis Spectrophotometer to measure absorbance, from which concentration and quantity of cobalt removed could be established.

The samples were returned to the solution and left for a total of 24 hours (including the 2 hours already passed) and tested again. This was repeated at 48 hours.

This procedure was repeated with different volumes of sodium alginate solution added.

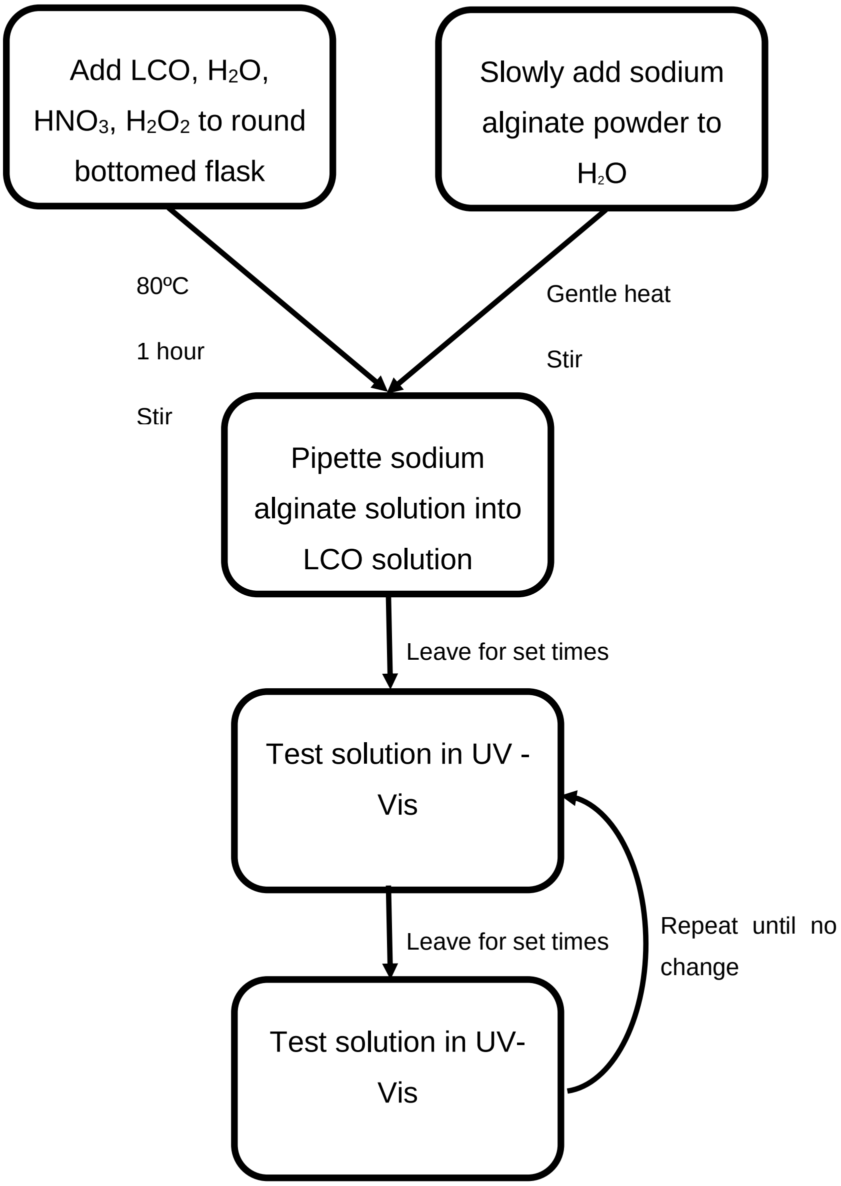

Figure 3-4 Flow chart detailing procedure of Method Four

3.3 Analysis

3.3.1 UV-Vis Spectrophotometry

The amount of cobalt in each solution was calculated from the absorbance, as measured by the UV-Vis Spectrophotometer, here the Beckman Coulter DU 730 model was used.

UV-Vis Spectroscopy works on the principle that light is absorbed by excitation of electrons between defined bands of energy. As a result of the quantised nature of these energy levels, only light with specific energy (and thus wavelength) will be absorbed. The UV-Vis spectrophotometer shines light of varying wavelengths through a cuvette containing the sample and measures this unitless absorbance, A, using the Beer-Lambert Law:

$$A = log_{10}\frac{I_0}{I} \tag{3-1}$$

Where I_0 is the known intensity of the incident light and I is the transmitted intensity as measured by the detector.

At the range of the UV-Vis spectrophotometer used (200-700 nm), photons are only absorbed by non-binding orbitals and conjugated π bonds. Consequently, in our solution, as there are no organic molecules producing peaks corresponding to bonds and the lithium does not produce an absorbance peak, the single peak seen can be attributed to the presence of cobalt (II) ions.

3.3.2 SEM EDS

Elemental analysis was conducted using the EDS (Energy dispersive X-Ray Spectroscopy) feature of the SEM (Scanning electron microscope).

The SEM works by firing a focused highly concentrated beam of electrons onto the surface of the sample which stimulates emission of backscattered electrons and secondary electrons. These are then measured using detectors and detailed images with a large depth of field can be obtained.

The beam of electrons also results in emission of characteristic x-rays, which occur when an electron is ejected from an inner shell of the atom, resulting in a higher energy electron dropping into the created hole and losing energy in the form of an x-ray. The emitted x-rays are quantised due to the discrete energy shells, and therefore can be used for elemental analysis.

3.3.3 X-Ray Diffraction (XRD)

XRD techniques were used to determine the crystalline structure of obtained powders. During XRD analysis X-Rays are directed onto the sample at a range of incident angles which then produce the detected secondary rays through elastic scattering on the electrons. Electrons in the crystal act as a diffraction grating, and thus knowing the incident angle (θ) and the wavelength of the radiation (λ), Bragg's Law can be applied to the secondary rays to determine d, the spacing between diffraction gratings (electrons in the crystal):

$$n\lambda = dsin\theta \tag{3-2}$$

Where n is the order of diffraction, set to 1 for XRD.

Collected data can then be referenced against other samples or databases of known samples to determine possible compositions.

4 Results

4.1 Method One

During the first method no reaction occurred. After heating and stirring there were no visible changes to the solution, and after centrifuging distinct layers of black powder, transparent alginate and water were observed.

This powder was confirmed as unreacted LCO by testing the powder obtained using XRD against known LCO from the software database.

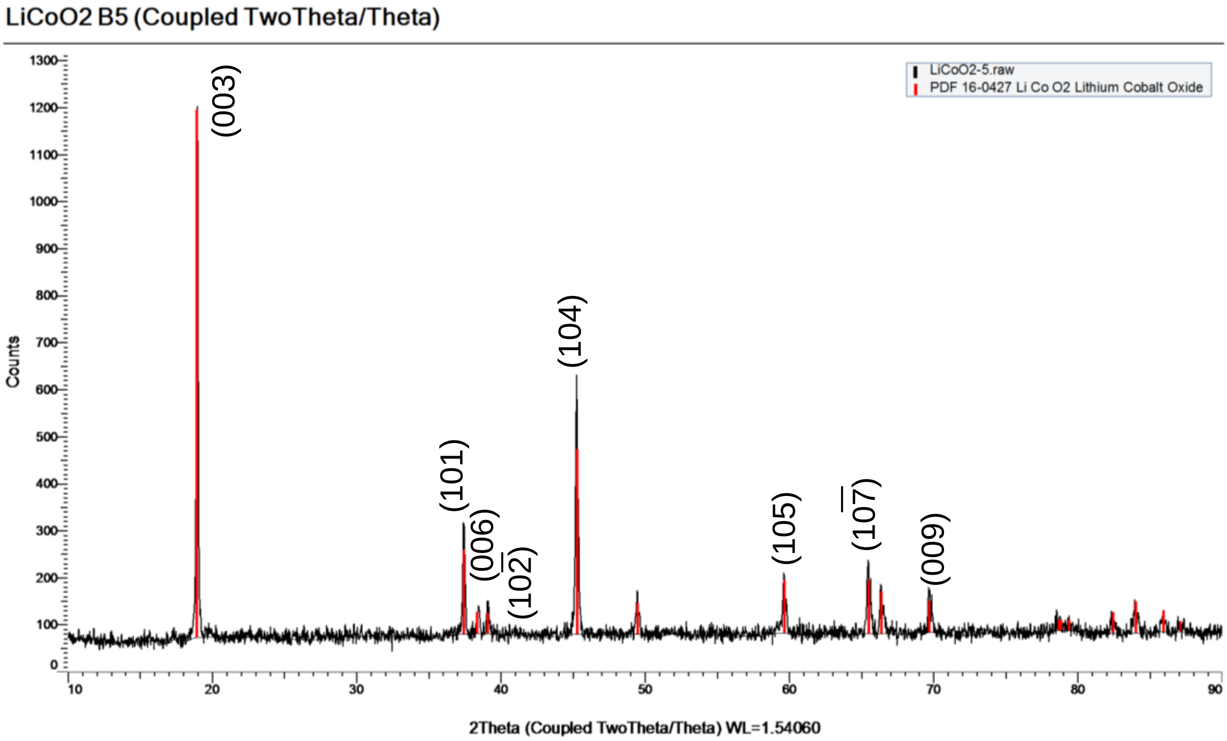

Figure 4-1 Results obtained from XRD analysis of powder obtained using method one (black) compared against known $LiCoO_2$ (red) with Miller indices labelled for the significant peaks.

4.2 Method Two

Method two successfully reacted sodium alginate with cobalt, to produce cobalt alginate solid. This was evidenced observationally, with a solid immediately formed upon mixing of the two, which then gradually becomes a milky opaque. Once dried, the solid is visibly pink in appearance, further suggesting presence of cobalt, however the distribution of pink within the solid was not uniform, with some parts much darker than others, suggesting uptake of cobalt across the solid was not even. Presence of cobalt was confirmed by testing the dried solid in the SEM using EDS as shown below.

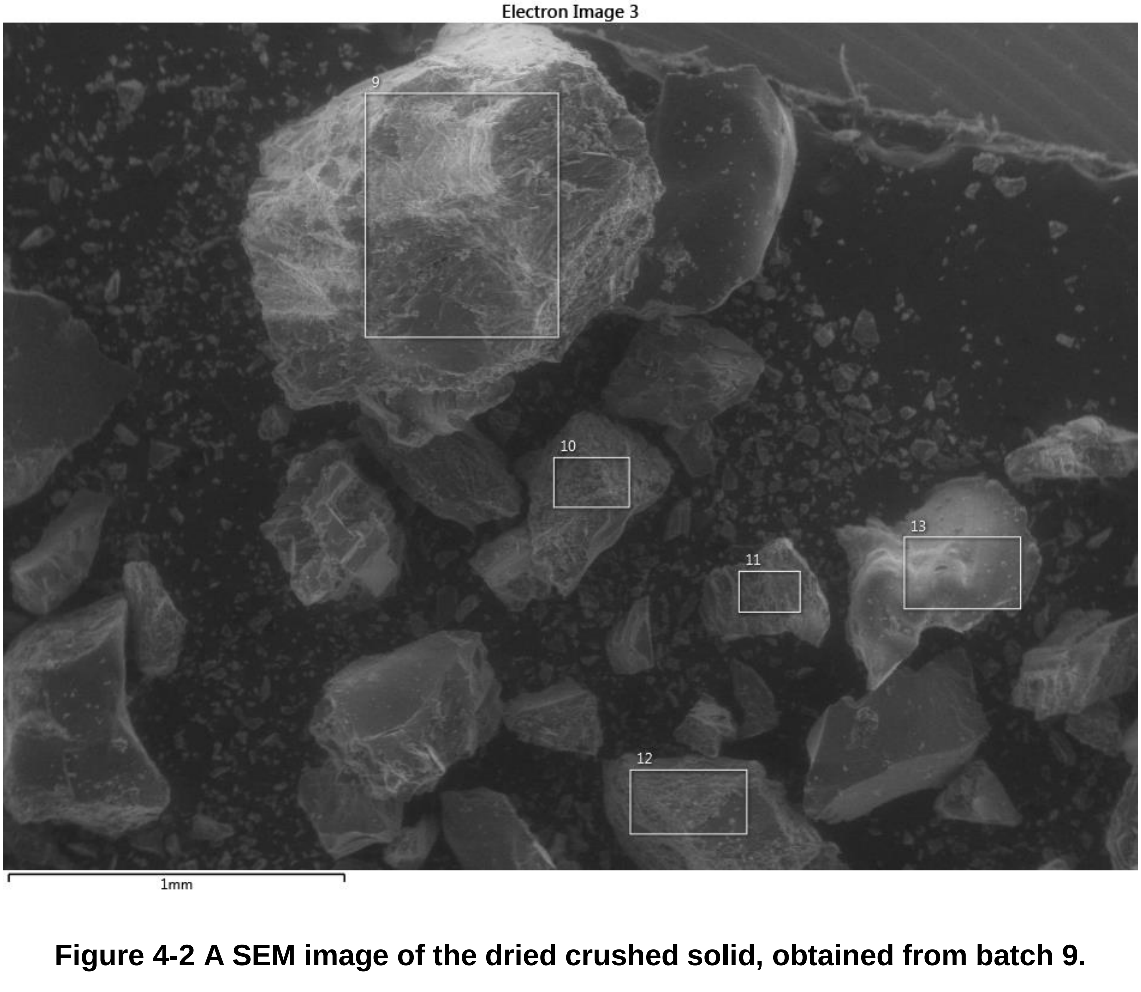

Figure 4-2 A SEM image of the dried crushed solid, obtained from batch 9.

Weight %	Carbon	Oxygen	Sodium	Cobalt
Area 9	36.19	53.84	7.65	0
Area 10	35.52	57.49	5.5	0.03
Area 11	44.28	51.07	3.9	0.16
Area 12	37.96	57.46	4.19	0
Area 13	23.41	54.69	10.33	0
Average	35.472	54.91	6.314	0.038

Table 4-1 Corresponding EDS analysis of areas in SEM image.

Whilst this method produced verified cobalt alginate, the form produced meant accurate analysis was difficult: The alginate solid formed as large lumps meaning washing was difficult, and the high ratio of alginate to cobalt solution used meant that the concentration of cobalt in the final solid was very low and not evenly distributed as evidenced in the SEM EDS data. The low concentration of cobalt also meant that, after burning in the furnace, very little cobalt compound was produced, to the extent that XRD analysis of the resultant powder was inconclusive.

4.3 Method Three

For this section, a run is defined as being each addition of 5ml sodium alginate solution (as beads) to the cobalt solution, left for two hours, with the beads then being removed.

Method three produced promising results. The first indications that cobalt had been successfully taken up in the alginate solid were visible observations, for example initially the beads float at the top of the solution, however during the two hours diffusion time their density increases as cobalt is taken up in the cross-link polymer, until the density of the bead is greater than the density of the solution, and the beads fall to the bottom of the beaker.

Another visual indicator that cobalt was removed from the solution is that of colour change. Cobalt ions give the solution an obvious pink appearance. Samples taken before and after the runs show a significant decrease in colour, and conversely alginate beads are a semi opaque white when first formed, however become noticeably pink after each run. The colour change in the solution can be seen in the image below.

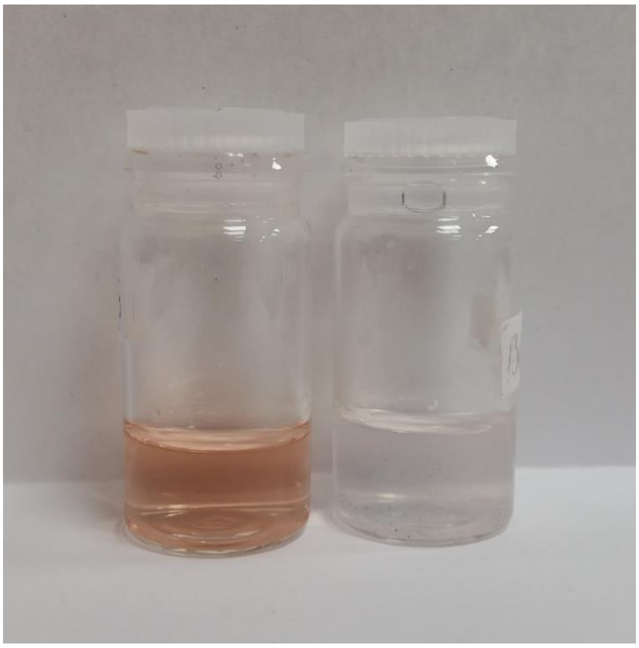

Figure 4-3 Samples taken from B16 before (left) and after (right) 17 runs.

Quantitative analysis using the UV-Vis Spectrophotometer was employed to confirm cobalt removal, however accurate analysis at lower concentrations was not possible due to the relatively large error of the spectrophotometer being used (±0.005) [40]. This was particularly evident for B13, as the initial absorbance and following changes in absorbance were too small to be accurately measured. Subsequently, data obtained from this batch was not considered for final analysis.

For batches of higher initial concentration, a decrease in absorbance was observed for each run of alginate added to the solution. Occasionally an increase in concentration was detected, however this can be attributed to the aforementioned accuracy of the spectrophotometer.

Firstly a concentration curve was obtained by taking samples of cobalt solution of known concentration and measuring their absorbance at the cobalt peak, which occurred between 509 nm and 510 nm (the spectrophotometer used has an accuracy of ±1 nm) [40].

Concentration was calculated from the known mass of LCO added using the following formula

$$Molar\ concentration\ (M) = \frac{mass\ (g)}{molar\ mass\ (gmol^{-1})} \div volume\ (l) \tag{4-1}$$

Using B11 as an example, where 0.01g of LCO was added to a 100 ml solution, and taking the molar mass of LCO as 97.87 $gmol^{-1}$ [41]

$$Molar\ concentration\ (M) = \frac{0.01}{97.87} \div 0.1 \tag{4-2}$$

$$Molar\ concentration = 0.00120\ M \text{ to three significant figures} \tag{4-3}$$

As there is one atom of cobalt per molecule of LCO ($LiCoO_2$), we can establish that one mole of LCO will contain one mole of cobalt ions.

This data was then displayed as a graph, with a linear plot added with the intercept set at x=0.

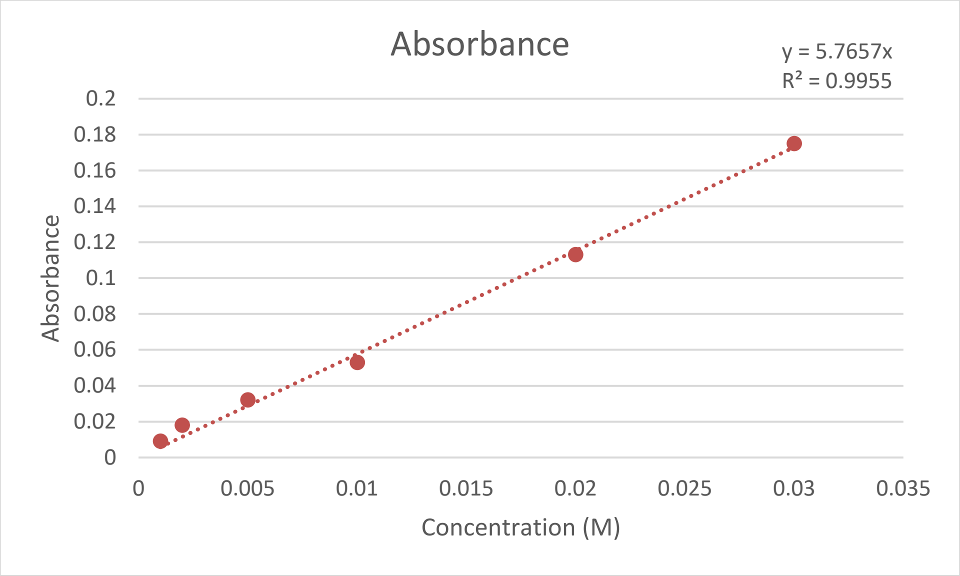

Figure 4-4 A Calibration Curve of cobalt ions in a solution

From this, we can then use the measured absorbance (a unitless value) to calculate the concentration of cobalt ions in a solution of unknown concentration using the following relationship.

$$Molar\ concentration\ (M) = \frac{Absorbance}{5.7657(M^{-1})} \tag{4-4}$$

The mass of cobalt can then be calculated using a rearranged form of equation (4-1).

$$mass\ (g) = molar\ mass\ (gmol^{-1}) \times\ concentration\ (M) \times volume\ (l) \tag{4-5}$$

This time using the molar mass of cobalt, 58.933 $gmol^{-1}$.

Applying these equations to absorbance data obtained, data obtained from the UV-Vis Spectrophotometer was processed and displayed as below.

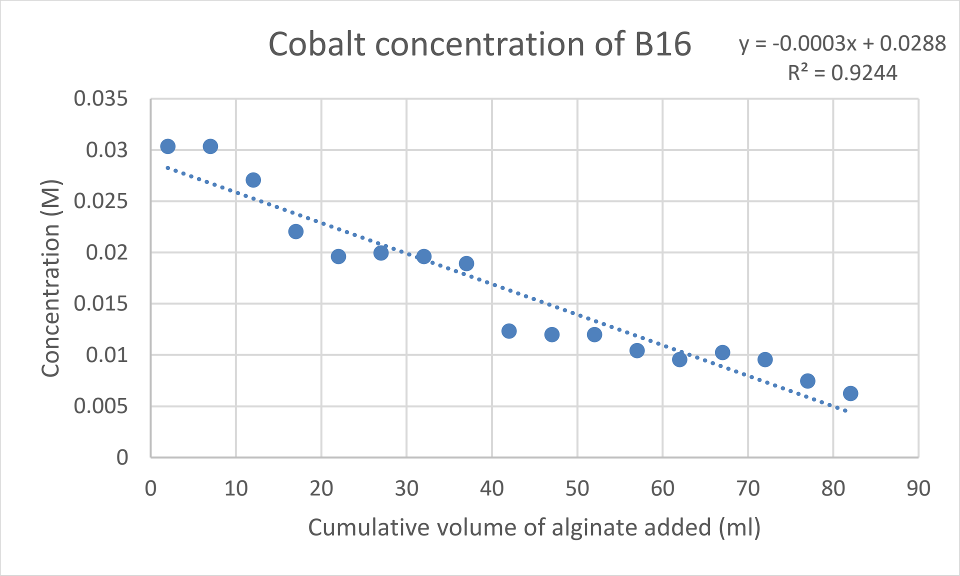

Figure 4-5 Concentration of cobalt in B16 with the cumulative volume of alginate added at each run

The graph shows that cobalt is indeed removed from the solution during each run as there is decrease in concentration each time. The initial concentration as predicted by the linear fit of 0.0297 M is only 3.4% lower than the initial concentration of 0.0307 M as calculated from (4-1), suggesting an accurate linear fit to the data.

An interesting phenomenon displayed in this data is the apparent existence of steps in the declining concentration. The most likely explanation for this is the error introduced in the measuring equipment, in particular the UV-Vis spectrophotometer. As samples were processed and measured in batches, each use of the machine, although blanked with the same sample each time, likely introduced an error unique to that testing session, and hence batches tested different sessions exist in different steps. More work would be needed to be conducted to verify this.

From the concentration, the mass removed could be calculated. As there were losses of a few ml between runs, the mass lost in this solution was taken into consideration in the calculations, and only the mass lost through reaction with the alginate is displayed.

Plotting the cumulative mass of cobalt removed, the following graph was obtained.

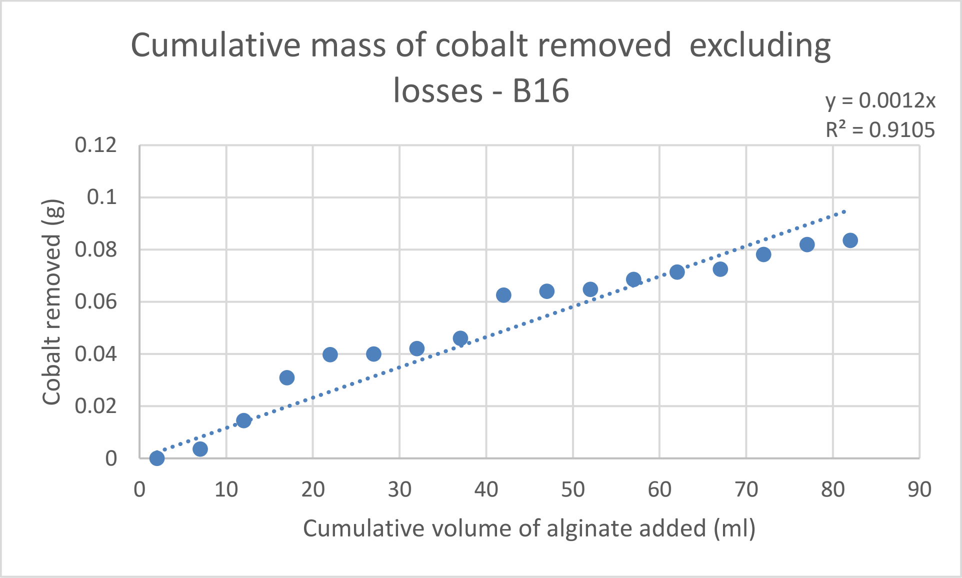

Figure 4-6 Cumulative mass of cobalt removed with each run.

Uptake of cobalt into the beads was again confirmed using EDS on the SEM, with beads taken from the second run of B16, rinsed three times, and dried.

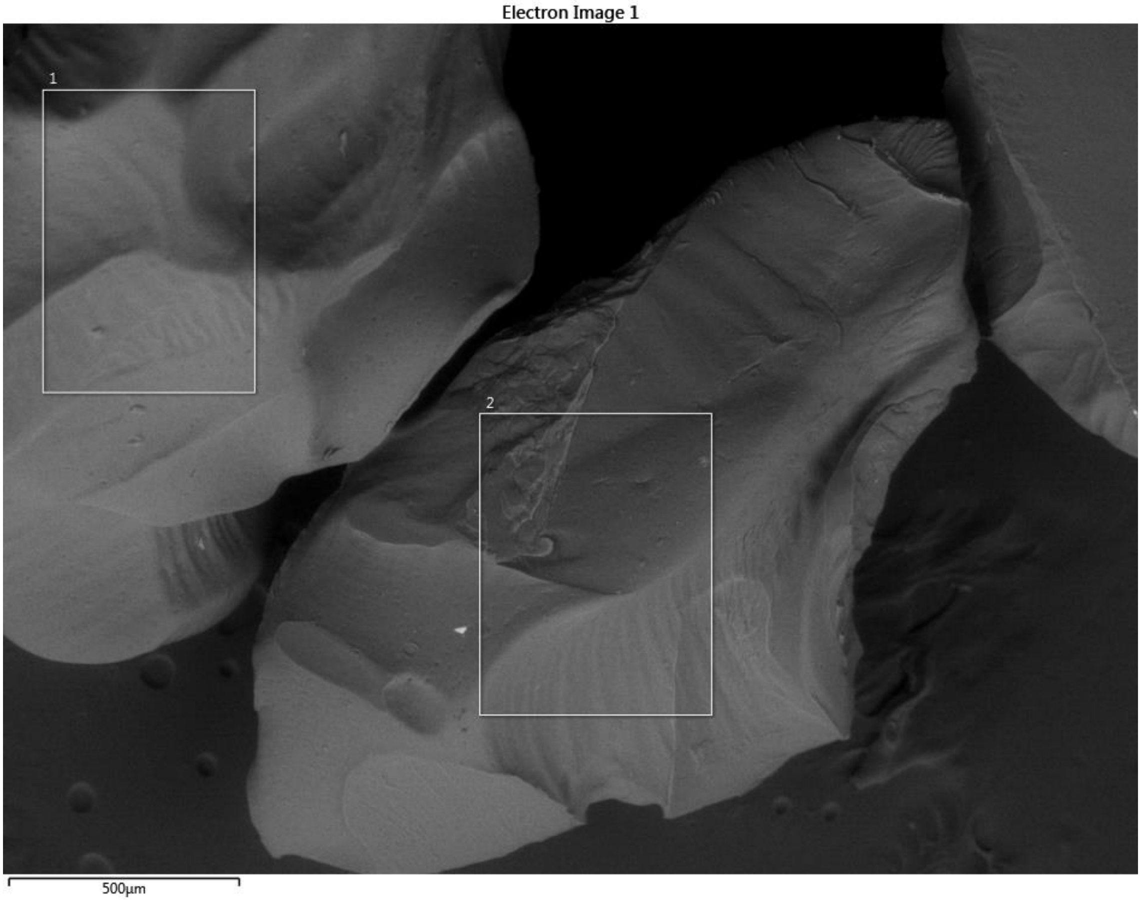

Figure 4-7 SEM image of a dried alginate bead

Weight %	Carbon	Oxygen	Sodium	Cobalt
Area 1	39.42	57.05	1.08	2.44
Area 2	39.90	56.28	0.94	2.89
Average	39.66	56.665	1.01	2.665

Table 4-2 Corresponding EDS analysis of areas in SEM image.

Figure 4-8 Dried cobalt alginate beads taken from the fifteenth run of B16 (left) and the first and second run of B16 (right), in which the different uptakes of cobalt can be observed from the change of colour.

EDS analysis confirmed notable uptake of cobalt in the beads, with significantly more cobalt than sodium detected, suggesting that the cross-linked polymer was formed with the swapping of one cobalt ion per two sodium ions as predicted. Lithium was not detected in non-negligible amounts, confirming that the beads were adequately washed of the solution and thus cobalt detected is that which reacted with the alginate.

For B16, after 17 runs 93.4% of cobalt had been removed from the solution, for B15, which had a lower initial concentration of cobalt ions, 92.2% was removed after the same number of runs. This excludes cobalt lost between runs.

After 17 runs there was no significant peak shown in the UV-Vis data, due to the lower accuracy of the UV-Vis spectrophotometer at such low concentrations, therefore it was not possible to gather further data.

4.4 Method Four

The final method produced results from which we can establish the effect the ratio of sodium alginate to cobalt solution has on cobalt adsorption.

There was strong positive correlation between the ratio of alginate added and the amount of cobalt removed.

To process the data, mass of the cobalt in the sample and mass removed were calculated as above, and plotted as a percentage, as shown for B17 below:

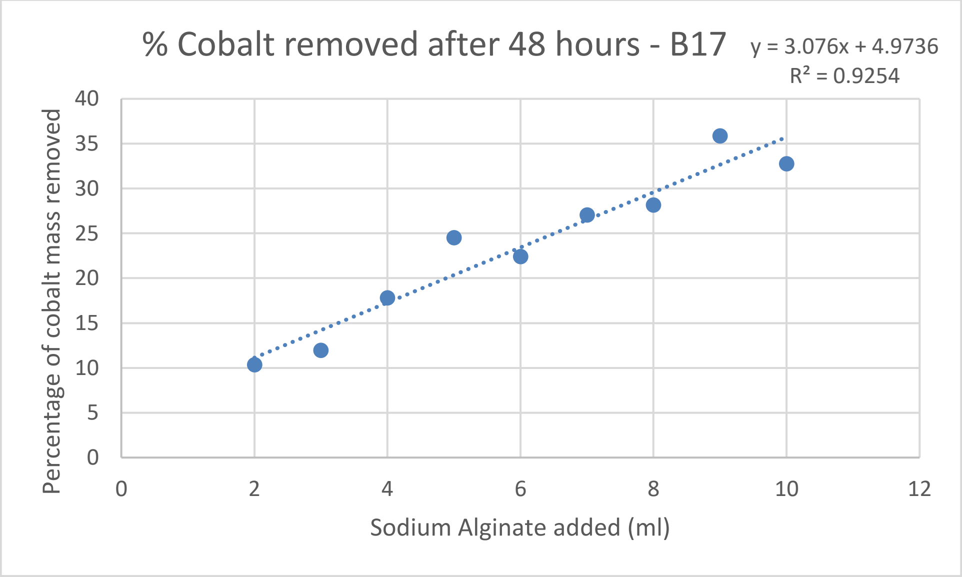

Figure 4-9 Percentage of cobalt removed from B17 samples after 48 hours

Fitting a linear relationship to the data, the relationship between alginate added and percentage removed was established:

$$cobalt\ removed(\%) = 3.4642(ml^{-1})\ \times alginate\ added\ (ml) \qquad \textbf{(4-6)}$$

It is important to note that this relationship stands only for the conditions of this method: an initial concentration of cobalt of 0.03 M and a sodium alginate concentration of 0.116 M.

From this, the total alginate added to achieve 100% cobalt removal can be predicted, which for this sample would be 28.866 ml (to three significant figures) alginate solution per 20ml sample.

It is perhaps more useful to consider the alginate added to cobalt solution in terms of the volume ratio, such that it can be applied to solutions of different volumes.

For B17, the volume ratio of sodium alginate to cobalt needed to achieve complete removal of cobalt would be 1.44:1 (to three significant figures).

The same analysis is applied to a second batch (B18) of initial cobalt concentration 0.02 M, however twice the data points were taken (0 to 20 ml in increases of 2 ml), producing the below graph, showing a similar yet slightly different linear relationship.

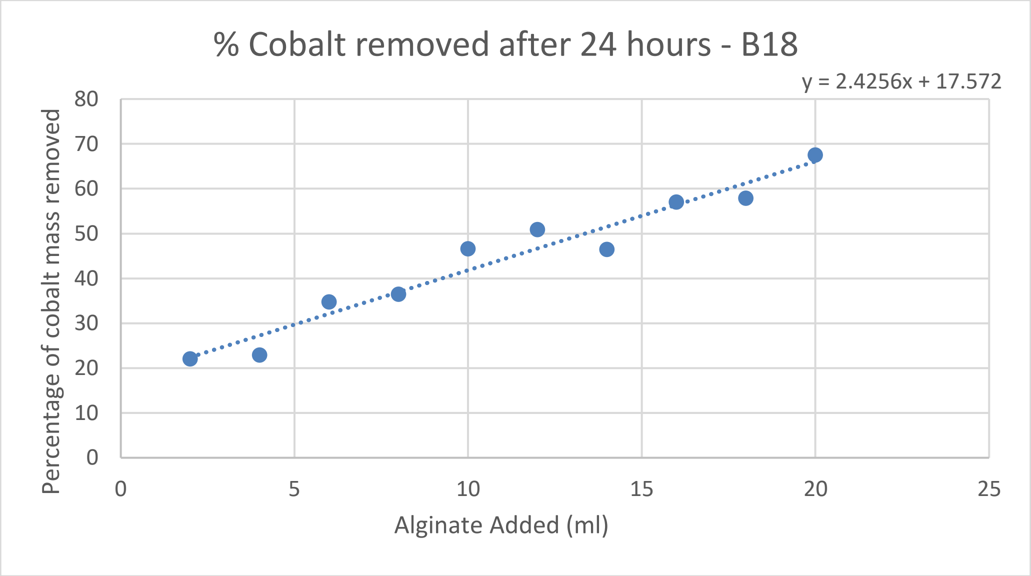

Figure 4-10 Percentage of cobalt removed from B18 samples after 24 hours

An interesting observation is that applying a linear relationship, the fit would not pass through the origin as we would expect. There are a number of possible explanations for this. One study found that uptake cobalt uptake in an alginate occurred at two rates, a faster rate when cobalt was reacting with the initially formed outer membrane of the bead, and a slower rate once this wall was formed and cobalt had to diffuse across to react with alginate in the middle of the bead [38]. Another possibility is that, as there was no stirring or agitation of the solution during the runs, those with fewer alginate beads allowed for faster uptake of cobalt as there was less crowding and cobalt ions in the solution could more readily come into contact and thus react with the alginate.

It was not possible to investigate this further owing to the accuracy of the UV-Vis Spectrophotometer used; more sensitive testing equipment or alternative analysis methods would be necessary to study this relationship.

Taking the linear relationship for B18 and applying the same analysis above to predict the alginate needed for 100% removal of cobalt ions, we arrive at a volume ratio of 1.69:1, or 33.982ml alginate solution per 20ml cobalt solution.

Using the prediction for B18, further runs were conducted to investigate maximum yield of cobalt from the solutions. As the volume of alginate solution was greater than the volume of cobalt solution, runs were conducted in two parts.

As initially the linear relationship was forced through the origin, the first prediction resulted in a volume of alginate added as 27.168 ml, therefore an initial trial of 28 ml was chosen. This was taken from the first run B18d, 18 ml alginate in 20 ml cobalt solution, with the alginate beads removed after 48 hours and a second run of 10 ml alginate added.

			Absorbance	Cobalt mass removed
Total alginate	Alginate per run	Initial	0.114	
28 ml	+18 ml	After 24 hours	0.051	55.26%
		After 48 hours	0.048	57.89%
	+10 ml	After 72 hours	0.029	74.56%

Table 4-3 Volumes for B18 yield test with 28ml alginate solution

After this showed incomplete removal of cobalt ions and the linear relationship re-evaluated and adjusted, the figure of 33.982 ml was calculated, and so another trial using total 34 ml alginate was conducted, again in two stages.

			Absorbance	Cobalt mass removed
Total alginate	Alginate per run	Initial	0.114	
34 ml	+16 ml	After 24 hours	0.051	55.26%
		After 48 hours	0.049	57.02%
	+18 ml	After 24 hours	0.029	74.56%
		After 48 hours	0.023	79.82%

Table 4-4 Volumes for B18 yield test with 34ml alginate solution

Despite calculations predicting total removal of cobalt from the solution with this volume of alginate, there was only 79.82% removed.

This discrepancy could be due to a number of factors. One possible explanation is that as there was no stirring or agitation of the beads in the solution and cobalt can only react with the alginate on contact, with the remaining 20.18% which was not taken up by the alginate beads simply because it did not come into contact with them and thus did not have the opportunity to do so.

Another possibility may be that cobalt ions did not readily pass across the cross-linked alginate to swap out with the sodium attached to the alginate in the centre of the bead, meaning total cobalt saturation of the alginate was not possible. Applying heat to the solutions during runs may alleviate this.

4.5 Experimental conclusions

The variations in experimental methods conducted gives useful insight into the reaction of the alginate with the LCO.

Data obtained has shown that the primary hypothesis of the project, that sodium alginate may be used to separate cobalt from lithium obtained from LCO, is true. There is also limited data that may explain the effect of some variables, such as the ratio of alginate beads to cobalt solution, has on the rate and overall efficiency of cobalt uptake.

Method One indicated that alginate does not readily react with LCO, and whilst it was important to discover this, in future this method could be discounted.

Method Two showed that alginate does indeed form a solid when contact is made with cobalt ions, and that this is a plausible method to separate cobalt and lithium ions from a solution. Although it provided this useful discovery, processing of the samples produced was difficult and time consuming, and thus not likely to be successfully employed large scale, so this method too may be discounted from future study.

Methods Three and Four provided the most useful data, and so future study may focus on the techniques used for these. Addition of alginate to the solution in the form of beads proved the most efficient method and also allowed for easier processing of the sample and collection of data. Addition of fresh beads for each “run” as in Method Three allows for rapid uptake of cobalt during initial formation of the beads, however removal of the beads each time introduced significant losses of solution and thus there was potential loss of cobalt ions not taken up in the alginate balls.

There is still, however, considerable opportunity for improvement of the methods. Honing methods for example by control of variables such as stirring and heating may drastically increase cobalt uptake, reducing time spent on each set of data and thus allowing for a higher quantity of data to be obtained.

There is also much scope to reduce uncertainty in the data obtained. The majority of the uncertainties arise from human use and interpretation of equipment, such as observational error in measuring volumes of liquid in measuring cylinders. Additionally, there existed environmental sources of error, for example fluctuations in ambient temperature in the laboratory, the potential unrecorded introduction of agitation from other equipment or laboratory users, and unintentional contamination of equipment or chemical supplies. A more tightly controlled laboratory environment would help in obtaining more accurate data.

Additionally, improved methods of data collection may result in attainment of more accurate data, for example, the UV-Vis spectrometer used had limited accuracy at lower concentrations which hindered the range of results that could be obtained. A higher accuracy unit, or alternative method of determining cobalt concentration, could prove beneficial.

5 Conclusion

Efficient recycling and reclamation of cobalt from spent lithium ion batteries is of significant and increasing importance, and current methods of recycling have many inadequacies and are not appropriate long term for the predicted increase in LIBs entering the waste stream. Consequently, research resulting in improvements or alternatives to these processes is vital.

Research undertaken for this project has produced useful results in a number of areas. It has confirmed that sodium alginate can be used to separate cobalt from lithium in a solution and provides additional knowledge on factors affecting this process.

Main objectives of the project were firstly to determine if sodium alginate could be used to separate lithium and cobalt from lithium cobalt oxide, and if so, to establish the effect of potential variables on the speed or efficiency of the process.

Method 1 showed that LCO does not readily react with sodium alginate, instead it must be split into ionic components in order to facilitate the reaction of cobalt with alginate.

Results obtained from methods 2, 3, and 4, confirm that sodium alginate can be used to effectively separate cobalt from lithium from an obtained LCO powder when split into ions in a solution. The variation in the methods and subsequently the results obtained also demonstrated the necessity to test a variety of methods to determine those of higher efficiency, and which methods may potentially be applied in large scale commercial battery recycling facilities.

It has been discovered that the form of alginate added to the solution is an important variable. Method Three and Four demonstrated that addition of alginate via pipetting to form solid beads of small diameter is an efficient method of cobalt uptake owing to the higher surface area to volume ratio. Beads were also easier to remove from the solution when compared to the alginate “worms” produced when the alginate solution was poured into the cobalt solution as in Method Two, which makes it a more promising proposal for scaling up.

When added at a low alginate to cobalt ratio in short runs, as in Method Three, cobalt yields of up to 93.4% were possible. Higher ratios seemed to inhibit adsorption, with maximum yields of 79.82% recorded. Such high rates of cobalt recovery prove extremely promising in the potential use of sodium alginate in the LIB recycling process, and has the potential to be a genuine contender to currently applied techniques.

It has been proven that sodium alginate can be used to separate cobalt from lithium, and thus there is promise that it could be used to successfully reclaim cobalt from LIBs during recycling process in an economical, safe, and scaleable manner, with potential for its use in large scale recycling operations.

6 Further work

Further work into the viability of alginate may focus on two areas: improving and refining the process of alginate and cobalt ion interaction, and its potential application into large scale recycling.

In order to improve the reaction process, variables that warrant further investigation include:

- pH

  Acidity of the solution may affect speed and / or efficiency of cobalt ion uptake

- Stirring / agitation

  Application of a form of stirring or agitation may increase speed and efficiency of uptake as cobalt ions are more likely to make contact with the beads and thus bond with the alginate.

- Heat

  Heat may increase speed and efficiency of cobalt ion uptake as ions with greater energy may be more likely to penetrate the solid bead wall to bond with the bead interior.

- Bead size

  A smaller bead size, resulting in a larger surface area to volume ratio, may allow for faster uptake of cobalt as more cobalt ions would be taken up during the initial formation of the bead outer wall as opposed to the slower rate of uptake of ions diffusing across the solid into the bead interior.

- Concentration
  - Alginate
  - Cobalt ions

  Concentration, and thus viscosity, of the alginate solution may affect uptake of cobalt ions, with lower concentrations allowing for faster diffusion, and more viscous solutions requiring cobalt ions to have more energy to diffuse through and react with the polymer.

In order for alginate to be utilised in the reclamation of cobalt, it is not enough for it to only be able to separate out the cobalt. There must be efficient methods of further processing of the cobalt alginate structure to obtain the cobalt in a usable form. Potential methods for this may include burning of the cobalt alginate at sufficiently high temperatures such that organics are burnt off leaving a cobalt compound, or washing the cobalt from the alginate using a solvent such as hydrochloric acid.

Ultimately, research would be needed for application of alginate into real world recycling, including supporting processes, equipment, safety considerations, and financial viability, to understand its potential role in current and future recycling processes.

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APPENDICES

A.1 Method Three data

A.1.1 Batch 16

Initial Absorbance 0.175

Run	Alginate added (ml)	Absorbance
1	2	0.175
2	5	0.156
3	5	0.127
4	5	0.113
5	5	0.115
6	5	0.113
7	5	0.109
8	5	0.071
9	5	0.069
10	5	0.069
11	5	0.060
12	5	0.055
13	5	0.059
14	5	0.055
15	5	0.043
16	5	0.036

A.2 Method Four data

A.2.1 Batch 17

Alginate added (ml)	Initial Absorbance	Absorbance after 48 hours
2	0.174	0.156
3	0.159	0.140
4	0.174	0.143
5	0.159	0.120
6	0.174	0.135
7	0.159	0.116
8	0.174	0.125
9	0.159	0.102
10	0.174	0.117

A.2.2 Batch 18

Alginate added (ml)	Initial Absorbance	Absorbance after 24 hours	Absorbance after 48 hours
2	0.118	0.098	0.092
4	0.118	0.097	0.091
6	0.118	0.082	0.077
8	0.118	0.084	0.075
10	0.118	0.071	0.063
12	0.114	0.058	0.056
14	0.114	0.062	0.061
16	0.114	0.051	0.049
18	0.114	0.051	0.048
20	0.114	0.041	0.037