CHROMIUM RECOVERY FROM TANNERY WASTEWATER USING MOLECULARY IMPRINTED POLYMERS

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ABSTRACT

Tanning with chromium is a commonly used process to produce leather. A liquid waste stream of the process is tanning liquor, which can contain 4000-6500 ppm chromium. The chromium is a hazardous waste product which must be removed from the tanning liquor before the tanning liquor can be treated and discharged. The current method for chromium removal involves pH adjustment, precipitation and filtration before disposal of the solid chromium to hazardous waste land fill. In some countries, the waste tanning liquor is discharged directly into rivers and streams which can lead to pollution, disease and sickness. The disposed chromium represents a loss of valuable material and is also a non-sustainable practice. Thus, many previous studies have been completed which attempted to recover and reuse the chromium from tanning liquor. However, these studies had limited success due to other contaminants being present in the recovered chromium causing a reduction in tanned hide quality.

A molecularly imprinted polymer (MIP) has been developed which can selectively capture chromium from the tanning liquor. This study found the MIP could recover chromium from tanning liquor. A pilot plant capable of processing up to 100-250 L/hour of tanning liquor ran for three weeks at a local tannery and recovered enough chromium for multiple hide tanning trials. The chromium level in the treated tanning liquor was reduced by 85-90%. Hides tanned with the recovered chromium were analyzed and showed similar quality to hides tanned with virgin chromium. An industrial scale system capable of processing up to 5000 L/hour of tanning liquor with 5000 ppm chromium was designed and its capital cost to build using local fabrication and process control contractors was estimated to be NZ$600,000. The system operating full time at its maximum capacity had a payback period of 2.11 years.

KEYWORDS

Chromium, Tannery, Heavy Metals, Industrial Wastewater, Product Development

PRESENTER PROFILE

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1 INTRODUCTION

Chromium is a prominent component of the tanning process. Approximately 20-30% of the chromium entering the tanning process is not incorporated into the hides and requires treatment and disposal (Ludvik, 2000a, Esmaeili et al., 2005). The current method for chromium removal involves pH adjustment, precipitation and filtration to lower the moisture content before disposal of the solid chromium to hazardous waste land fill (Ludvik, 2000b, Belay, 2010). This unutilized chromium represents a substantial economic loss of a valuable material. In addition, fees must be paid for it to be disposed of in hazardous material landfill. Negative environmental effects can be experienced from waste chromium, and environmental regulations regarding it are increasing (Minas, 2011, UNIDO, 2011, Rajamani et al., 2002, Karale et al., 2007). It is a finite resource and disposal costs are also likely to increase matching new environmental regulations. Increased consumer awareness has also lead to an increased demand for leather produced using sustainable practices. These reasons make the idea of capturing and reusing the chromium from tanning liquor appealing.

Tanning liquor contains components such as salts, fats, metals (iron, copper, manganese), formaldehyde, lime and sulphides (EHS, 2007, Rajamani). Several methods have been trialed over the last 60 years for reusing and recovering the chromium from tanning liquor. These include direct recycling of the tanning liquor, chromium precipitation and filtration, or ion exchange (Rajamani, Yassen et al., 2015, Li et al., Panswad et al., 2001, Chang, 2001, Belay, 2010, ShoeBAT, 2014). However, there were concerns with variability in recovered chromium quality, poor tanned hide quality, iron build up (causing hide staining) and ability of the processes to deal with large volumes of the tanning liquor efficiently. One study claimed to have produced tanned hides using various combinations of recovered chromium and virgin chromium, however the tanned hides showed evidence of staining (Kanagaraj et al., 2008). Other studies have not provided data on the quality of the hides produced using the recovered chromium or the economic viability.

MIPs are polymers which have been synthesized in the presence of a template molecule. The template molecule is then removed from the polymer in a series of cleaning steps. This produces a polymer with complementary binding sites for the template molecule allowing selective recovery. MIPs can be used as free flowing powders, embedded onto fibers or coated onto structural scaffolds such as beads. These materials can be used to treat industrial waste waters by binding and removing the contaminating compound from the waste water (Huang et al., 2015).

A MIP was developed to selectively capture chromium from tanning liquor. The MIP was coated onto beads so it could be used to bind chromium from tanning liquor in a packed recovery column. The bound chromium is released using a weak solution of sodium hydroxide to weaken the interactions between the chromium and the polymer. The recovered solution of chromium is called the eluent. The polymer is then regenerated using a weak solution of formic acid, this solution is called the regenerant. This method provides an advantage over other methods as it can produce a purer solution of chromium with less contaminants which could reduce tanned hide quality.

This paper outlines the recovery of chromium from tanning liquor using the chromium imprinted MIP. It will cover bead properties, results in tanning liquor at pilot scale, quality of hides tanned with the recovered chromium and economic analysis of implementing an industrial scale system in different size tanneries.

2 CHROMIUM RECOVERY

2.1 BEAD PROPERTIES

The chromium imprinted polymer was produced using precipitation polymerization in a glass reactor. The imprinted bead was analyzed using a Hitachi Scanning Electron Microscope (SEM), Malvern Mastersizer and a Quantachrome Instrument Surface Area and Pore Size Analyzer. The pressure drop in the 7 litre packed column was determined by pumping water through the column at different flow rates and recording the pressure on the pressure transmitter.

Figure 1: SEM of blank bead before imprinting.

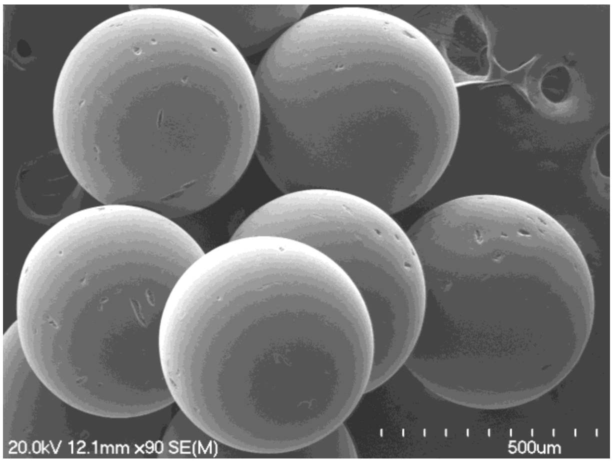
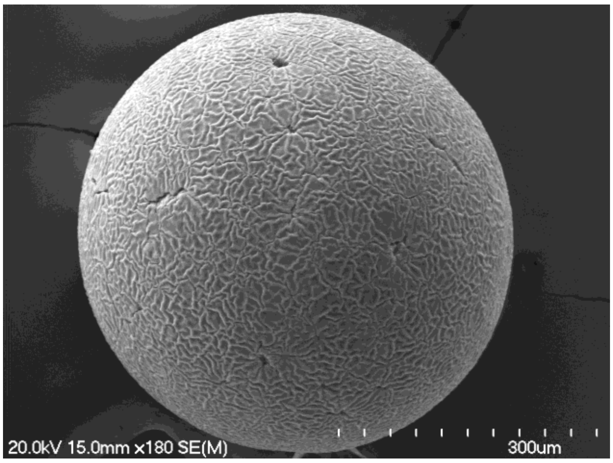
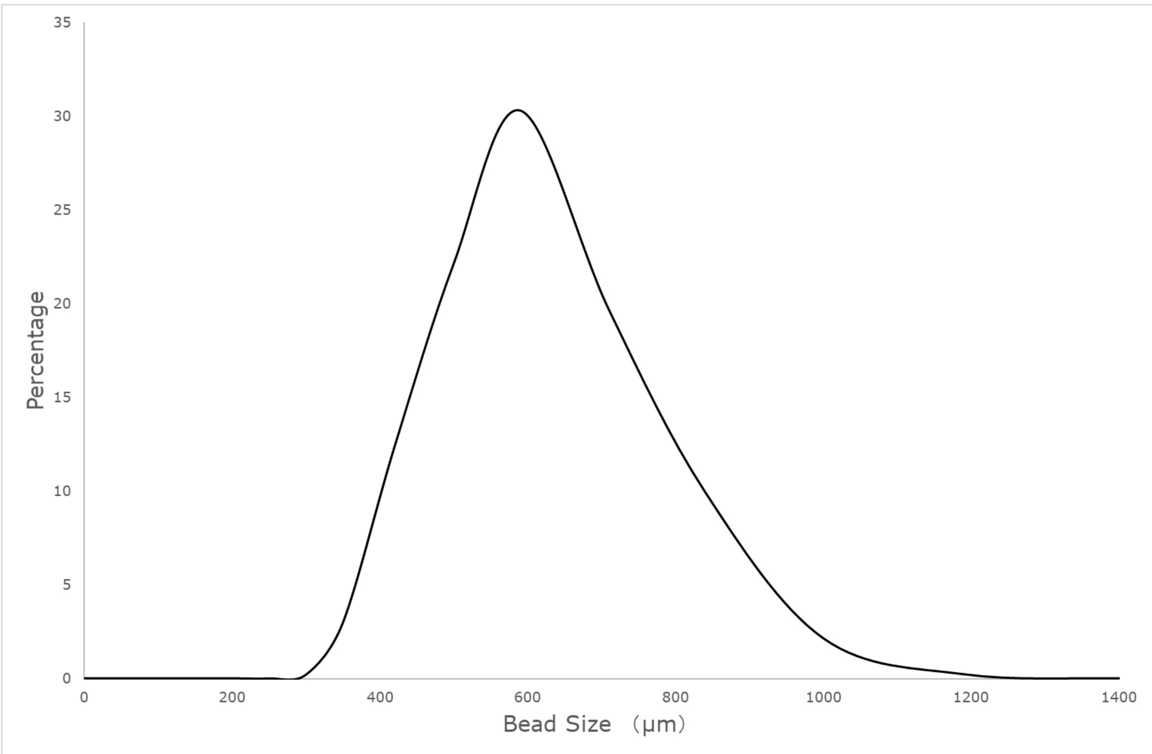


Figure 2: SEM of bead after imprinting.



The surface area of the imprinted bead was 57 m^2/g. The average pore diameter was 6.4 nm. The bead size distribution curve is shown below in Figure 3. The measured pressure drop through the packed column at different linear flow velocities is shown in Figure 4. The measured pressure drop and bead size can be used to estimate the pressure drop in larger columns at different linear flow velocities using Equation 1 (DOW, 2017).

Figure 3: Size distribution of imprinted beads.



Equation 1: Pressure drop in a packed column (DOW, 2017).

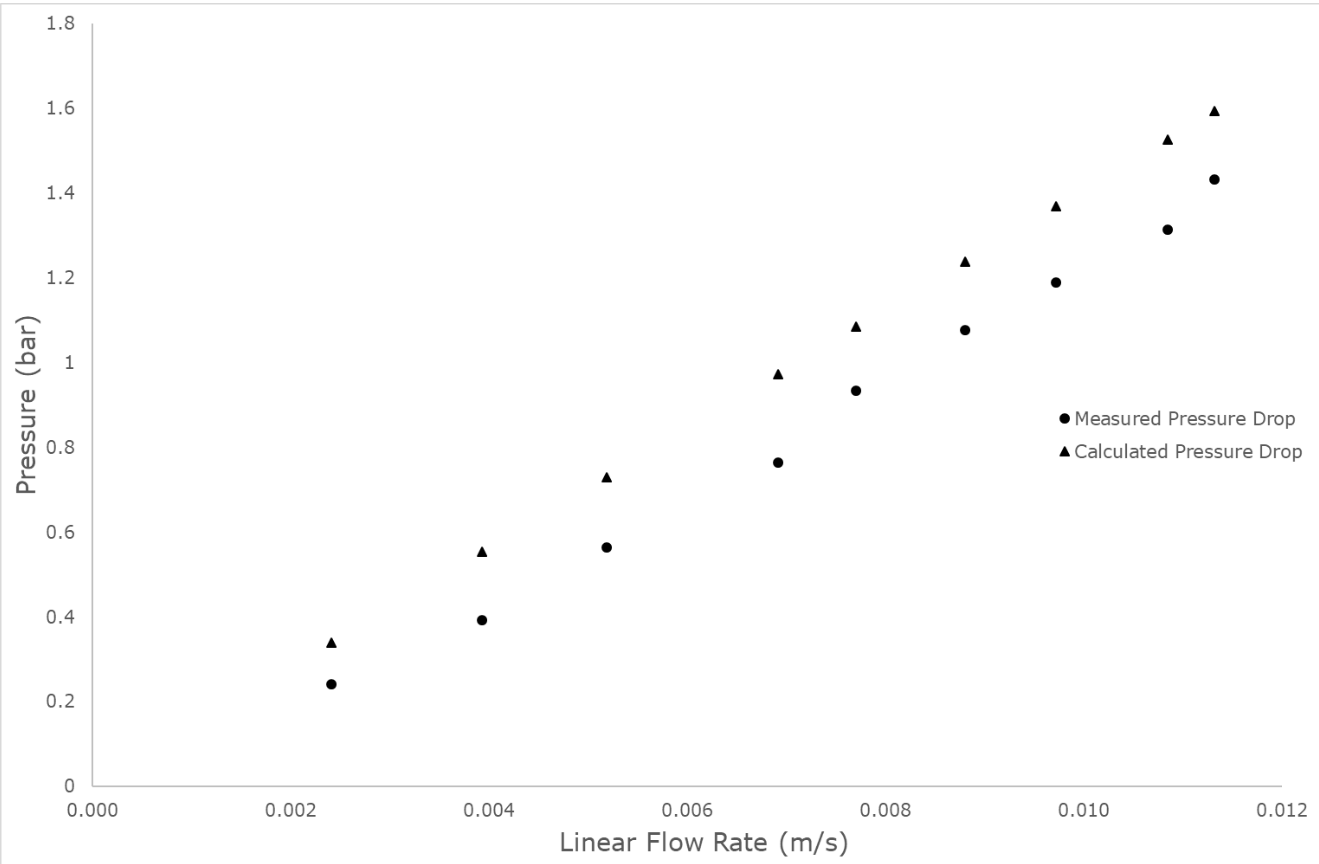
$$\frac{\Delta P}{L} = \frac{173 \times \mu \times V_o \times A_f}{Dp^2}$$

Where ΔP is the pressure drop (kPa), L is the column length (1 m), μ is the viscosity of water (1.002 Pa.s), V_o is the linear flow velocity (m/s), Dp is the bead diameter (600 μm) and A_f is the flow coefficient.

The flow coefficient was calculated using the measured pressure drop at different linear flow velocities and measured physical dimensions. Equation 1 was then applied to estimate the pressure drop through the column at the different linear flow velocities. The estimated pressure drop was compared to the actual pressure drop. The estimated values were higher than the measured values. This could have been caused by using a constant bead diameter of 600 μm in the calculations, whereas the actual bead diameters varied from 300 to 1200 μm which would have lead to tighter column packing and a higher pressure drop.

The data showed the pressure drop which would be expected when operating the recovery columns at different flow rates. The expected pressure drop when operating with tanning liquor would be slighlty higher due to other components in the tanning liquor causing a higher viscosity than water. However, a substanitally higher pressure drop during operation could indicate a fouled column, blocked feed/exit nozzles or broken beads.

Figure 4: Measured pressure drop and calculated pressure drop at different linear flow velocities.

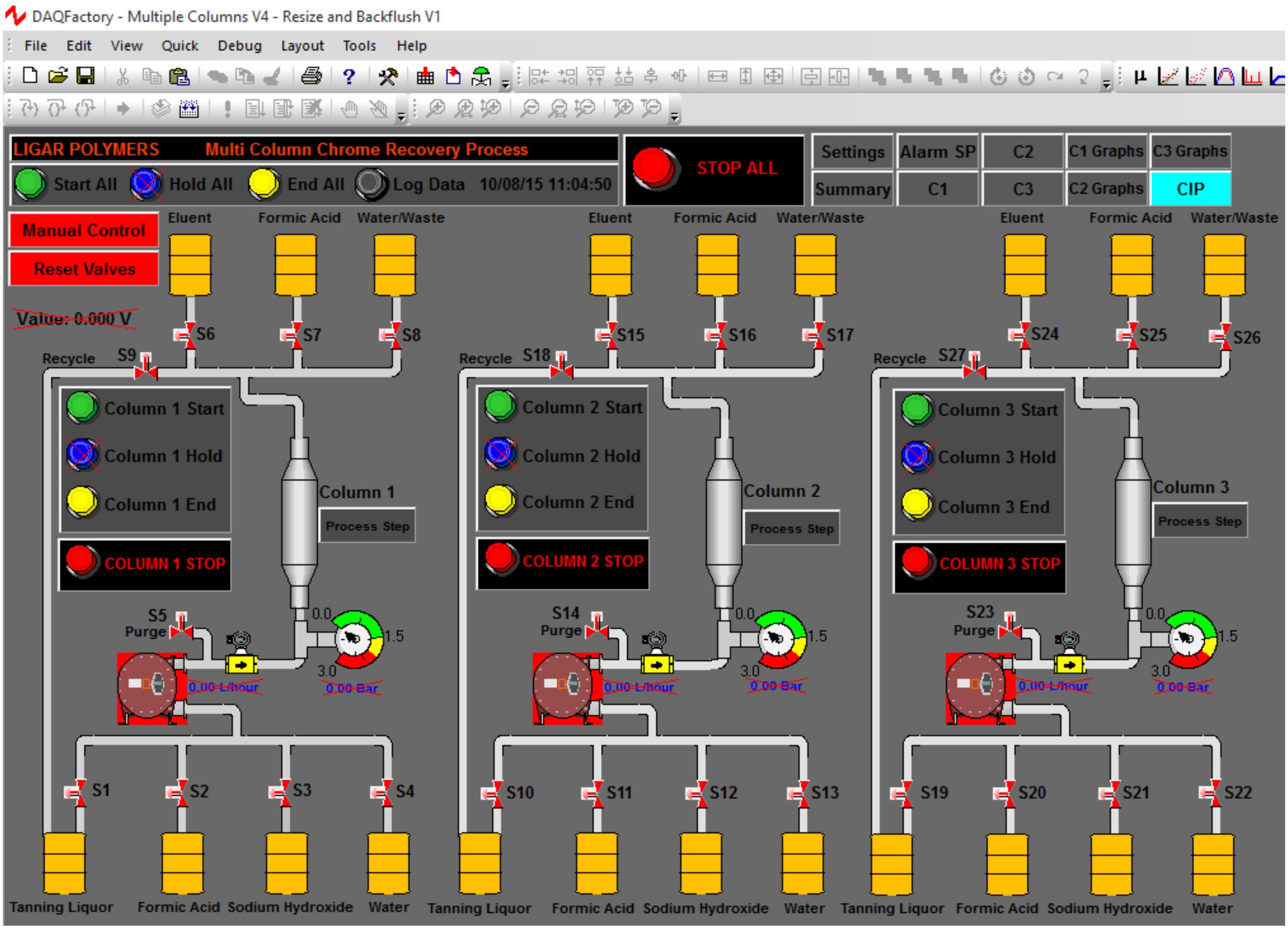


2.2 PILOT TRIAL

A pilot plant was constructed using three 7 litre polymethyl methacrylate columns, PVC hosing, peristaltic pumps, pneumatically operated valves and pressure sensors. Human Machine Interface (HMI) screens were generated (Figure 5) and the process was automated using DAQFactory software installed on a Panasonic Toughbook®.

There were three main stages to the chromium recovery process. These were chromium binding from tanning liquor onto the beads, elution of chromium from the beads and regeneration of the beads. At the completion of the regeneration stage, the chromium binding stage was started again. Each column was at a different stage of the recovery process and was operated independently of the other columns.

Figure 5: HMI screen produced using DaqFactory software.



The pilot plant was transported to a tanning facility and set up next to the existing tanning liquor treatment facility (Figure 6). Tanning liquor was supplied regularly from the tannery. The chromium concentration in the supplied tanning liquor varied throughout the trial but was usually within 4000-5000 ppm. An improvised pre-filter was used to remove suspended solids and no pre-treatment was utilized to remove fats or grease prior to using the imprinted beads to recover the chromium. Eluent and regenerant solutions where prepared as required using sodium hydroxide pellets and concentrated formic acid diluted to the required concentrations using water from a wash down hose.

Figure 6: Pilot plant in operation at a local tannery.

Samples of the tanning liquor, treated tanning liquor, eluent and regenerant were obtained at various intervals while the plant was operating (Figure 7). The chromium and iron concentration of the samples were determined using atomic adsorption spectroscopy. The amount processed in a day ranged from 400-2500 litres. In total, 9300 litres of tanning liquor was processed during the pilot trial. Figure 8 is an example of the chromium distribution in the treated tanning liquor, eluent and regenerant during a typical day of running the pilot plant. Approximately 85% of the chromium was recovered in the eluent, approximately 10% of the chromium remained in the regenerant and less than 5% in the treated tanning liquor. Iron levels in the recovered eluent were below detectable limits.

Figure 7: Treated tanning liquor (left), eluent (middle) and regenerant (right).

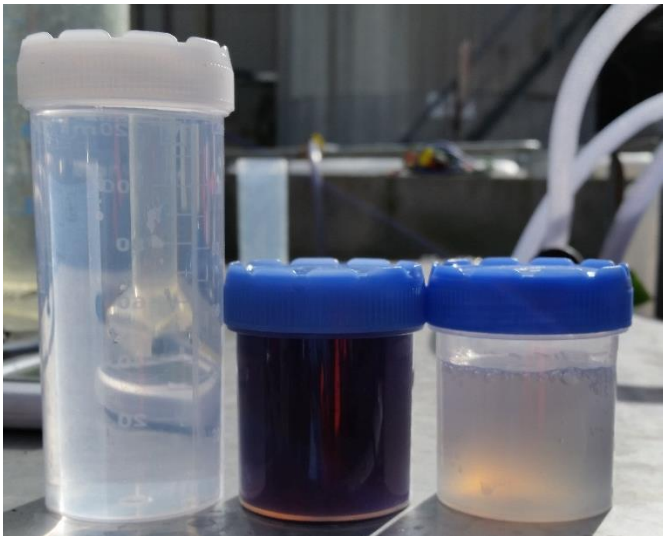
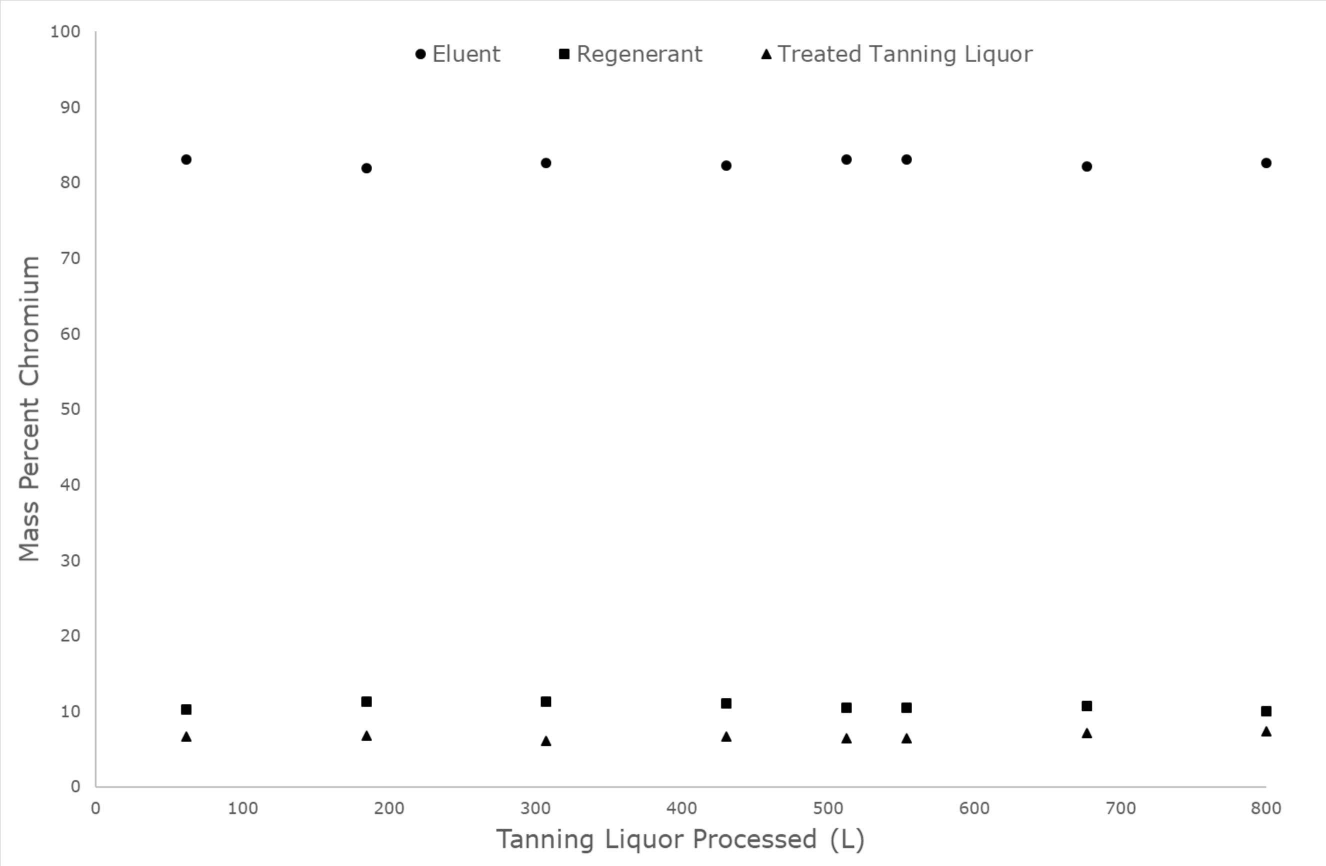


Figure 8: Chromium distribution during pilot plant operation.



At the completion of the pilot trial a sample of the imprinted beads was taken to be analysed on the SEM. This revealed that the surface of the beads had become fouled (Figure 10). This fouling was most probably caused by fats or small hide particles. This outlined the importance of effectively removing fats and hide particles from the tanning liquor before it contacts the imprinted beads. Most importantly it showed that the imprinted beads appeared to still be intact.

Figure 9: SEM of bead after imprinting.

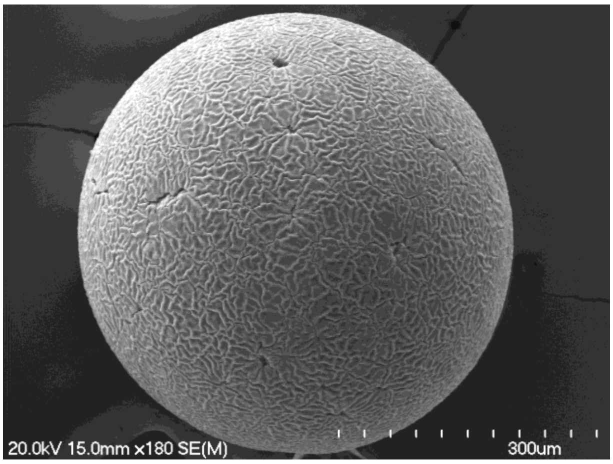
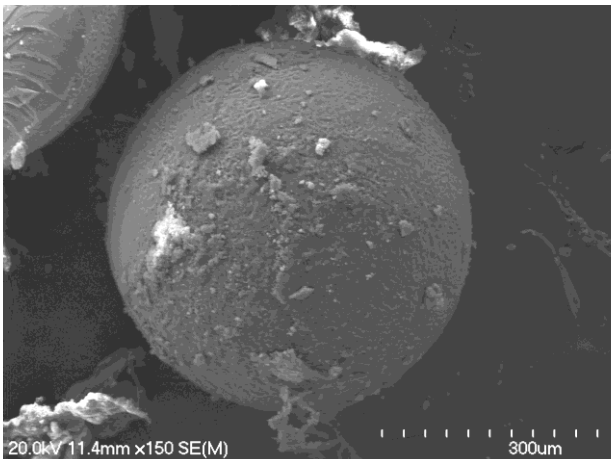


Figure 10: SEM of imprinted bead after use.



2.3 TANNING TRIAL

The recovered chromium was used in tanning trials completed by a local tannery. The tanning was completed in a pilot tanning drum with three 25 kg bovine hides per trial. The tanned hides were inspected visually by tannery staff and sent for analysis at New Zealand Leather and Shoe Research Association (LASRA). The results are presented in Table 1.

Table 1: Property of bovine hides tanned with recovered chromium.

	Acceptable Range	**100% Virgin Chrome**	**80% Virgin Chrome 20% Rec. Chrome**	**100% Rec. Chrome**
Visual Inspection	NA	Acceptable	Acceptable	Acceptable
Shrinkage Temperature (°C)	≥ 100.00	106.00	105.75	93.50
Full Thickness Chrome (% as Cr2O3)	3.50 – 4.00	3.40	4.35	2.55
Grease (%w/w)	1.00 - 1.50	Not Tested	1.40	2.60

The hides tanned with 20% recovered chromium/80% virgin chromium were visually acceptable with no obvious quality differences (e.g. staining, chromium penetration) when compared to hides tanned with 100% virgin chromium. LASRA analysis confirmed visual observations with the shrinkage temperature, full thickness chromium percentage and grease content within the acceptable ranges.

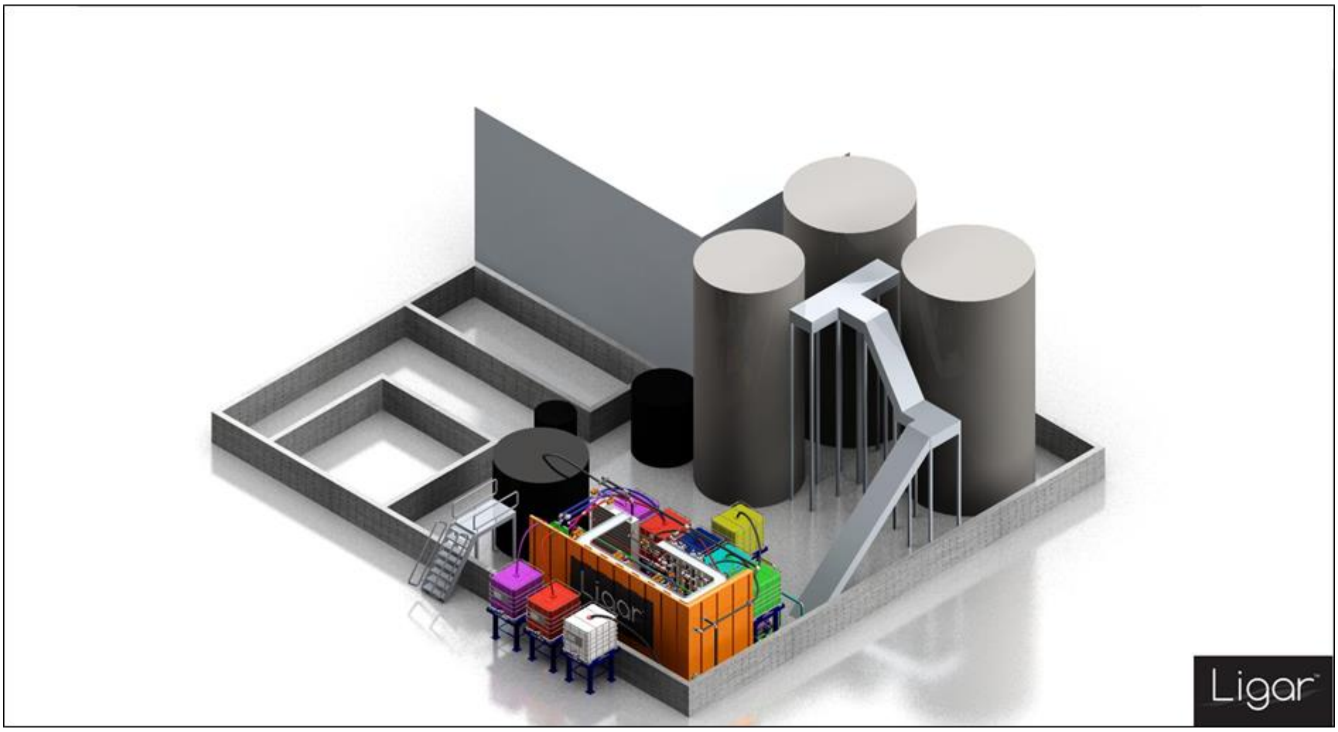
When inspected visually there were no obvious quality differences between hides tanned with 100% recovered chromium and 100% virgin chromium. However, the results obtained from LASRA revealed that the hides tanned with 100% recovered chromium had a shrinkage temperature and full thickness chromium percentage slightly lower than the acceptable range. The grease content was higher than the acceptable range, however this result was most likely related to the lack of pre-treatment of the tanning liquor before chromium recovery rather than imprinted bead performance. Despite these results, this outcome was the first time that hides had been able to be tanned with 100% recovered chromium with adequate chromium penetration and no visual differences in quality able to be detected.

It would be beneficial to complete further tanning trials with 40, 60 and 80% recovered chromium. Also, it would be interesting to see if better tanning liquor pretreatment to removes fats prior to chromium recovery using imprinted beads could improve the quality of the recovered chromium to a level where 100% recovered chromium could be used to obtain tanned hides with shrinkage temperature, full thickness chromium percentage and grease content of acceptable values.

2.4 ECONOMIC ANALYSIS

An industrial scale plant was designed and its cost was estimated working with local fabrication and instrumentation contractors. It was designed to be installed and commissioned quickly with minimal interruption to normal tannery operations.

Figure 11: Computer aided visualization of an industrial scale chromium recovery plant installed next to a pre-existing tanning liquor treatment facility.



The plant can process 5000 litres of tanning liquor per hour and it was estimated that the plant would cost NZ$600,000 to build. The payback period was calculated for different daily chromium recovery rates assuming the chromium concentration of tanning liquor was 5000 ppm and the cost of chromium sulphate was NZ$1.85 per kg. The annual maintenance costs were estimated to be 4% of the capital cost as recommended for a basic chemical process (Sari, 2014). Average disposal costs for hazardous land fill was estimated to be NZ$125 per ton. Savings in chemicals that are used in the existing chromium removal process before tanning liquor discharge was not included as this will vary between tanneries and location. The cost of operating labor was not included as this figure is dependent on the location of the plant. Energy cost requirements were also excluded as this would be dependent on how many hours the plant was operated for and its location.

Table 2: Payback period for different chromium recovery rates.

Chromium Recovery (kg/day)	100	200	300	400	500	600
Payback with Disposal Cost Savings (years)	21.89	7.61	4.61	3.30	2.57	2.11
Payback without Disposal Cost Savings (years)	31.58	9.68	5.71	4.05	3.14	2.56

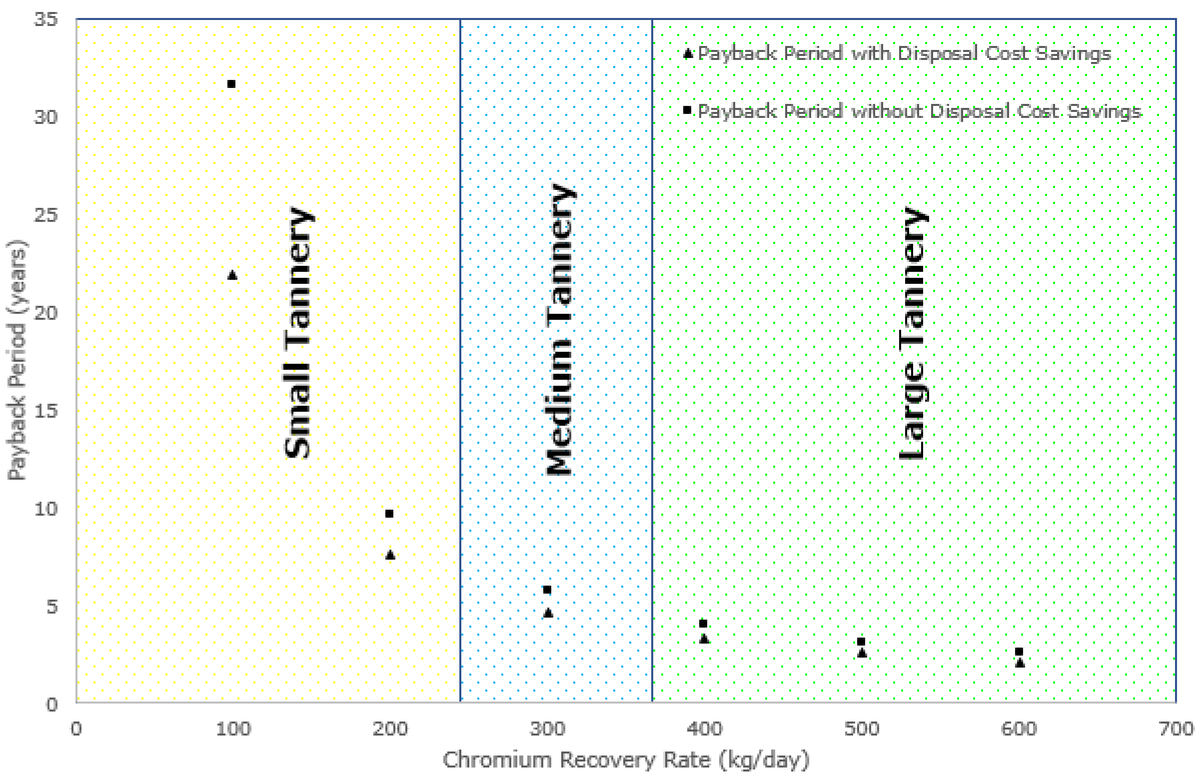
The payback period for the plant was heavily dependent on the chromium recovery rate. It is worth noting that the cost of chromium used in these calculations is near the lower end of its historical value. If the cost of chromium were to increase then the payback period for the plant would become more attractive. At chromium's current value the plant and payback period does not become attractive until 300-400 kg of chromium is recovered per day if savings in avoided solid waste disposal are considered. If no solids waste disposal savings are considered then 400-500 kg of chromium must be recovered per day before the plant paybacks in an acceptable period.

Collected tannery capacity data indicated that a small sized tannery will be able to recover 125-250 kg per day. This indicates that at the current value of chromium, the plant would not be viable for small tanneries. In locations such as India where multiple small tanneries operate independent of each other in a common industrial zone, a centralized chromium recovery plant may be a suitable option to treat tanning liquors collected from many small tanneries.

New Zealand tanneries are considered middle range in size when compared internationally. For medium sized tanneries recovering up to 300 kg of chromium per day the economic case for the plant becomes borderline. Other factors such as increased tannery sustainability, leading innovation and increased marketability may help to drive the decision in favor of installing the chromium recovery plant.

Countries such as China and Brazil operate large tanneries. The plant is economically attractive for large tanneries which can recover over 300 kg of chromium per day. If the plant is used to its full capacity to recover 600 kg of chromium per day, then the payback period is 2.11 years if savings in disposal costs are considered or 2.56 years if savings in disposal costs are not considered Figure 12.

Figure 12: Payback period for different sized tanneries.



It is important to note that due to variations in how tanneries are operated, chemical costs, disposal practices and disposal costs only a basic economic analysis was completed in this paper and the payback periods calculated for different chromium recovery rates should only be used as a starting point. For more detailed results, an in depth economic analysis should be completed for individual tanneries where the plant is to be installed.

3 CONCLUSIONS

An imprinted polymer bead was produced which could bind chromium from tanning liquor. The surface area and average pore diameter of the imprinted bead was 57 m^2/g and 6.4 nm respectively. The imprinted bead was used in a pilot plant and recovered 85% of the chromium in tanning liquor. Hides were tanned with 100% recovered chromium and 20% recovered/80% virgin chromium. The tanned hides were visually similar to hides tanned with 100% virgin chromium. However, shrinkage temperature, chromium percentage and grease content analysis revealed only the hides tanned with 20% recovered chromium/80% virgin chromium were of acceptable quality. An economic analysis revealed that a chromium recovery plant using imprinted polymers would be economically viable for medium to large sized tanneries. An alternative option could be to collect tanning liquor from multiple tanneries and recover the chromium in a centralized processing plant. This technology can help to improve the tanning industry's operating efficiency and sustainability by recovering chromium of a suitable quality for it to be reused in the tanning process. This will result in less chromium entering waterways, helping to prevent contamination and disease.

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