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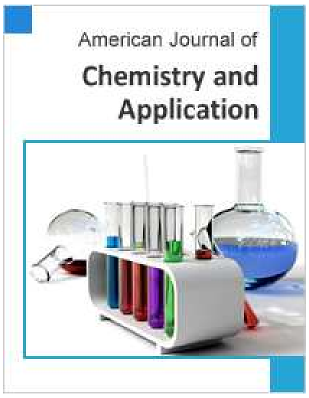

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Effect of Alkali and Acid Concentration in Extraction of Chromium III from Tannery Solid Waste

Putshaka J. D.[1], Yakubu A.[1], Aliyu Jauro[2], Harami H. M.[2], Kolo M.[2]

[1]Department of Research and Development, Nigeria Institute of Leather and Science Technology, Zaria, Kaduna State - Nigeria
[2]Department of Chemistry, Abubakar Tafawa Balewa University, Bauchi State -Nigeria

Email address
jputshaka@yahoo.co.uk (Putshaka J. D.)

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Abstract

Samples of solid waste from the tanning industry in the form of buffing and shaving wastes were subjected to series of treatment in an attempt to extract chromium III from them. Results obtained from analysis of samples containing this metal show that leather buffing waste contained more moisture and volatile matter than that in leather shaving waste, while the latter contained more ash and chromium than the former. An upward trend in extractable chromium concentration in both leather shaving waste and leather buffing waste was observed with increase in the amount of alkali (sodium carbonate) Spectroscopic analysis of both samples after pretreatment with different concentrations sodium carbonate also indicate that the concentration of chromium in leather shaving was higher than that in its counterpart. The percentage recovery of chromium from both samples was determined with considerations given to parameters to examine the effect of acid concentration, and contact time. In most cases, the percentage recovery of chromium was observed to be higher for samples from leather buffing waste than that in leather shaving waste although the recorded amount of chromium in the latter was higher. It was discovered from this study that although more chromium was found in leather shaving waste than leather buffing waste, the percentage recovery of the metal from leather buffing waste was higher considering the parameters used in this study. Optimum recovery of chromium from both samples was however achieved when they were treated with 25% solution of sodium carbonate, carbonized at 600°C, acidified with 1.0M sulphuric acid, contacted with steam at temperature of 100°C in the reactor for a maximum period of 40minutes. With these results, further study can be carried out to recycle and ascertain the efficiency of chromium extracted in leather tanning process.

1. Introduction

Chromium occupies an unrivalled position in the tanning Industry since its introduction in 1984 by A. Schultz (Gangopadhyah et al 2000). Currently about 80-90% of global leather production is tanned with safe chromium III salts (BLC 2010, Covington, 2009, Sunder et al 2002). Tanning using chromium salts confer exceptional and unsurpassed properties such as good mechanical resistance, hydrothermal resistance and softness to the leather (Chargne et al, 1996; Belay, 2010, Gangopadyhah 1996)

After chrome tanning and during mechanical operations such as shaving and buffing substantial part of the chromium salt used in tanning process is also lost and carried away with solid waste such as shavings buffing dust and trimmings. In United States, almost 56,000 metric tons of chromium-containing solid wastes are generated by the leather industry each year, and approximately ten times this amount is generated worldwide (Taylor et al., 1994) A typical tannery processing 2000 to 3000 tonnes of hides per day will lose about 2500 pounds (1134kg) of chromium as Cr_2O_3 daily. While about 50 to 60% of this quantity is lost in tannery waste water 40 to 50% of it is lost in solid leather waste generated during mechanical operations. These leather wastes in the form of shavings and buffing dust are usually generated by the leather industry and are dumped in landfills constituting environmental nuisance and potential source of soil, and water pollution. Tannery solid wastes (trimmings, shavings and buffing dust) are considered potentially hazardous wastes. These wastes, when disposed of in landfills, can cause leachate problems for extended periods of time since their degradation is very slow (Muralidhara and Maggins, 2007) Chromium leaching in soil has been discovered to be very sensitive to pH to pH values within the range of 4 – 12 Under this condition the leachate containing this heavy metal from these wastes especially in its hexavalent state may constitute serious danger to human health and the entire ecosystem.

Hexavalent chromium is toxic and carcinogenic, even a concentration that is as low as 10mg/l can cause nausea and vomiting and higher concentrations can be fatal (Adamson, 1976). Contact with hexavalent chromium can cause skin irritation and problems associated with the respiratory tract. (Bharti et al, 1966)

Various laboratory and industrial trials have demonstrated that chromium containing leather waste may be thermally treated to produce an ash containing approximately 50% chrome oxide, which is similar in nature to the mineral ore feedstock, sodium chromite, used by the chromium chemicals manufacturing industry. In recent years considerable attention has been given to incineration (Louhab and Akssas., 2006), Sethuraman et al (2013) studied the effect of double pyrolysis of tanned leather solid waste for safe disposal and product recovery including chromium. Various methods of treating and recovering chromium from tannery wastes have been reported: The recovery of chromium from tannery solid wastes was reported by Jones (1975), whereby a process was developed for incinerating tannery solid wastes containing organic materials and chromium. Macchi et al., (1991) carried out a bench study on chromium recovery from tannery sludge, Chua and liu (1996) reported the release behavior of chromium from tannery sludge, while Shen et al (2001) extracted chromium III from tannery sludge by mineral acids.

Several other publications that reported on the removal or extraction of chromium from tannery wastes include; Zena et al (2010) who carried out Statically study for effect of some coefficients on chromium removal in leather waste, Barbara (2013), reported on kinetic modeling of chromium (III) extraction with aliquat 336 from alkaline aqueous solutions containing chlorides, Salma et al (2013) who extracted of chromium VI from chrome shavings, Zhen-Ren et al (2006)enhanced chromium recovery from tanning wastewater, Mehmet Erdem (2006) and Kanagaraj et al, (2008), reported the recovery of chromium from chrome shaving generated in tanning process and chrome tanning waste water respectively. Cabeza, (1998) carried out pilot scale studies on chrome shavings: Isolation of potentially valuable protein products and chromium.

Conventionally, chromium can be extracted from tannery solid waste or chromite deposit after fusion with sodium carbonate where it is converted to chromium VI according to the following equation:

$$2Cr(OH)SO_4 + 2Na_2CO_3 + H_2O$$

$$= Na_2Cr_2O_7 + 2Na_2SO_4 + 2CO_2 + 2H_2O$$

After alkaline fusion the hexavalent chromium which is a strong oxidizing agent is then reduced to chromium III by treatment in acid condition (Holleman, et al., 1985; Covington, 2009) according to the equation:

$$Cr_2O_7^{2-} + 14\ H_3O^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 21\ H_2O$$

This study outlines the effect of varied concentrations of alkali and acid in the process of extracting chromium from tannery solid wastes

2. Methodology

2.1. Sample Collection and Preparation

Sample of leather waste in the form of shavings and buffing dust was collected from tanneries located in Challawa industrial estate in Kano – Nigeria.

Samples were pretreated by drying and sieving through a mesh. Each sample was air-dried, for 5 hours at ambient temperature, followed by drying in an oven for a period of 3 hours at 100°C. The drying process helps to effect dehydration or desorption of physically adsorbed moisture present in the samples. After drying, each sample was pulverized and sieved through a mesh size of 0.75 mm aperture and kept in sample containers ready for carbonization.

2.2. Proximate Analysis and Determination of pH and Initial Chromium in Untreated Samples

For both samples of leather wastes; moisture, ash, volatile matter, pH and initial chromium content were determined in accordance with the official test methods prescribed by the American Society of Testing and Materials ASTMD (2010a), ASTMD (2010b) and ASTMD (2010c)

Moisture content was determined by heating each sample at 105°C for a period of 12 hours while ash and volatile matter were determined by heating the dried samples at temperature of 600°C for two hours. Initial chromium concentration in both samples was determined by atomic absorption spectrophotometer (Model 3300: Norwalk CT) after each sample was digested with nitric acid using method adopted by Zheljazkov and Nielson (1996) but with some modifications as described below:

One gram of each sample was placed in a 250ml digestion tube and 10 ml of concentrated HNO_3 was added, the sample was allowed to stand for 18hours at ambient temperature, the sample was then heated almost to dryness (to about 1ml), and 25ml of distilled water was added after which the solution was boiled for 1minute.

The interior wall of the tube was swirled throughout the digestion to keep wall clean and prevent loss of sample. The solution was then filtered with whatman No 42 filter paper and the chromium concentration in each sample determined using atomic adsorption spectrophotometer (A.A.S) and recorded

The pH of each sample of leather waste was determined using a portable pH meter by taking the pH of 100cm^3 filtered aliquot of 20g of each sample after soaking in 200cm^3 hot distilled water and cooling for six hours

2.3. Alkaline Treatment of Samples

Fifty grammes each of dry, pulverized sample of buffing dust was pretreated with of 5, 10, 15, 20, and 25% solution of sodium carbonate and allowed to dry at room temperature for twelve hours. The samples were thereafter pulverized. Samples of leather shavings were subjected to similar treatment after sized reduction in a milling machine

2.4. Carbonization of Alkaline Treated Samples

The dried alkaline treated samples of both leather buffing and shavings wastes were carbonized at 600°C in a muffle furnace for a period of thirty minutes, after which they were quenched with distilled water, dried in an oven at 100°C and kept in a dessicator until required.

The samples were coded according to the temperature at which they were carbonized as follows:

ALB_5, ALB_{10}, ALB_{15}, ALB_{20}, and ALB_{25}: For alkaline treated leather buffing Waste treated with 5, 10, 15, 20, and 25% sodium carbonate respectively

ALS_5, ALS_{10}, ALS_{15}, ALS_{20},and ALS_{25}: For alkaline treated leather shaving waste treated with 5, 10, 15, 20, and 25% sodium carbonate respectively

2.5. Determination of Chromium Concentration in Carbonized Samples Treated withAlkali at Varied Concentrations

Chromium concentration in each ash sample was determined by using atomic absorption spectroscopy using similar procedure to that of the untreated samples

2.6. Acidification/Reduction of Chromium in Carbonized Ash Samples

50 grammes (50g) each of chromium containing carbonized ash sample was impregnated with 100cm^3 of concentrated solution of sulphuric acid and kept for twenty four hours (24hrs) with intermittent stirring at ambient temperature. After acidification the slurry of each sample was placed in a reactor made of 500 ml tubular pyrex glass which was developed for the reduction of chromium in the sample mixture. The reactor consisted of a steam generator which supplies steam through a delivery tube (Figure 1) to the reactor which was heated at100^{o}C for period of thirty minutes by a thermostated hotplate

The reactor was intermittently agitated to ensure uniform distribution of steam and heat as they come in contact with each sample. The steam from the reactor passes through a condenser. The reduction process was carried out for a period of 30 minutes after which, samples were removed and kept in a dissicator for a period of eight hours.

2.7. Effect of Acid Concentration of Extraction of Chromium in Samples

To determine the effect of acid concentration on recoverable chromium from both samples, ten grammes (10g) each of chromium containing carbonized ash sample was impregnated, slurried with 100cm^3 of 0.2M, 0.4M, 0.6M, 0.8M, and 1.0M solution of sulphuric acid in separate 250cm^{3}cornical flasks and kept for twenty four hours (24hrs) with intermittent stirring at ambient temperature. Thereafter the samples were subjected to similar treatment of steam, heat treatment and determination of chromium concentration as above. The percentage recovery of chromium in each acidified ash sample was determined and expressed in percentage using the formula:

$$\%\,Ce \;=\; Cra - \,Crex\;100/Cra$$

Where:

%Ce = Percentage Chromium Extract

Cr_b= Chromium concentration in ash sample before extraction

Cr_a= Chromium concentration in extract

2.8. Effect of Contact Time on Chromium Recovery from Acidified Samples

This test was carried out to ascertain the maximum period required for optimum recovery of chromium on samples of both leather wastes with the highest chromium concentration

In this study, 10g of each alkaline treated and carbonized sample was acidified with 1M sulphuric acid and contacted separately with steam in the reactor at 100°C for a period of two (2) hours (120minutes) at intervals of thirty (30) minutes after which it was agitated with 100 cm^{3}water and filtered. The concentration of chromium in ash before contact at each stipulated period and that in the filtrate was determined using a spectrophotometer. The result of analysis at the stated periods for each sample was recorded and the percentage chromium recovered from the samples determined.

3. Result and Discussion

3.1. Proximate Analysis and Determination of pH and Initial Chromium in Untreated Samples

The result of proximate analysis, pH and amount of chromium in sample of solid wastes from leather buffing and shavings is presented in Table 1.

Table 1. *Proximate Analysis pH and Chromium concentration in Samples of Leather Buffing Waste (LBW) and Leather Shaving Wastes (LSW).*

Parameter	Sample	
	LBW	LSW
Moisture (%)	65.13	60.17
Ash (%)	32.75	37.82
V/matter (%)	2.12	2.01
pH	3.8	4.2
Chromium (mg/kg)	2865.063	3398.451

The amount of moisture and volatile matter in leather buffing waste was higher than that in leather shaving waste. Conversely the amount of ash and chromium in leather shaving waste was observed to be higher than that of leather buffing waste. This is expected because the leather buffing are usually obtained from loose and porous subcutaneous layer of the leather after tanning while the shavings consist of denser fibre network which absorbs less moisture and may be less in volatile matter. Moreover leather shavings being waste from full chrome tanned leathers are more hydrophobic than leather buffing which is obtained during post tanning operations. Leather shavings wastes have more chromium concentration and ash content than the leather buffing waste because much part of the leather particularly the dermis in which chromium is absorbed is shaved off during the shaving operation. The high recorded ash contain in this sample can also attributed to the high chromium contain due to the fact that it is an inorganic matter. The low ash and chromium concentration in leather buffing waste can also be attributed to the reduction in amount of chromium during retanning and post tanning operations. Shaving operation unlike buffing operation is conventionally carried out immediately after chrome tanning hence high amounts of ash and chromium is expected as reflected in this study.

3.2. Determination of Chromium Concentration in Alkaline Treated Samples

The concentration of chromium in both alkaline treated samples of leather buffing waste and leather shaving waste is shown in Figure 1.

This result indicates that there is an increase in concentration of chromium with increase in concentration of sodium carbonate in both leather buffing and shaving wastes. The rate of increase was however observed to decrease at higher concentrations of sodium carbonate. The observed increase in chromium concentration with increase in the concentration of alkali could be as a result of ability of sodium carbonate to precipitate the chromium. This shows that the higher the concentration of alkali the higher the concentration of chromium recovered. This is not surprising because chromium has been reported to be precipitated by several precipitating agents including sodium carbonate in the removal of chromium as chromium salts (Langerwerri and Daverji, 1977; Bishop, 1978; Patheet *al*, 1996)

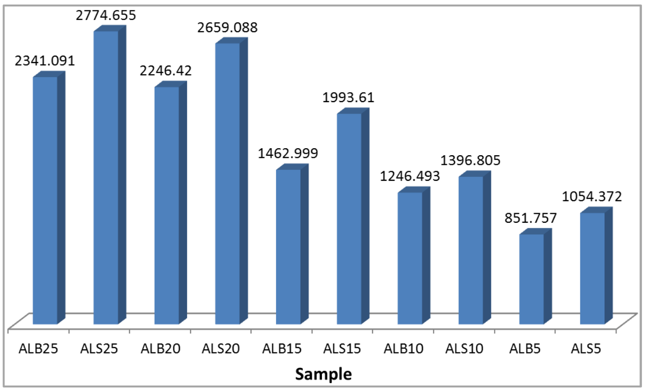

Figure 1. *Chromium Concentration (ppm) in Samples Pretreated with 5 - 25% Na_2CO_3.*

3.3. Effect of Acid Concentration of Recovery of Chromium in Samples

The effect of various acid concentrations on the recovery of chromium from both samples is presented in Figure 2.

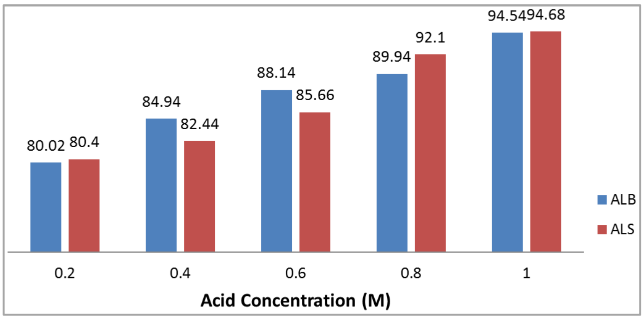

Figure 2. *Effect of Acid Concentration on PercentageChromium Recovery from Samples.*

It can be observed from this result that samples treated with higher acid concentration gave higher percentage recovery. However the rate of increase declined with increase in acid concentration as from the addition of 0.6M sulphuric acid on leather buffing waste and 0.8M of the acid on leather shaving waste. This may be attributed to the difference in concentration of chromium in the individual samples. As earlier stated more chromium is usually contained in the solid wastes obtained during shaving operation than that obtained during buffing operation in the tannery, hence the result of which is reflected in this study.

3.4. Effect of Contact Time on Chromium Recovery from Samples

There was an insignificant variation in the amount of chromium recovered from both samples over the time (Figure 3).

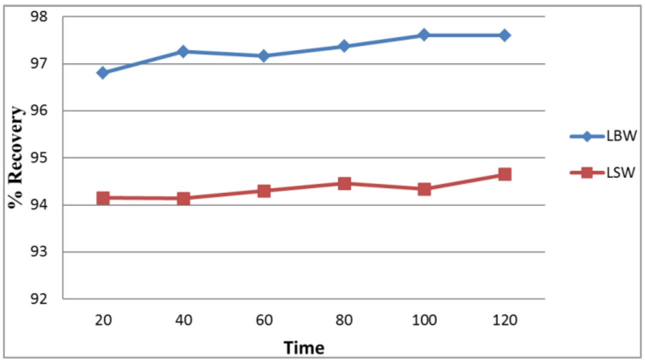

Figure 3. *Percentage Recovery of Chromium from Samples over Period of 120 Minutes.*

This shows that there was an instantaneous removal of chromium from the samples.This can be attributed to the solubility of the metal in solution especially after the samples were treated with sodium carbonate which might have increased its solubility. The rapid extraction of chromium over a short period of time can obviously lead to greater output.

This therefore means that there is no use extending the period or contact time during acidification/reduction process. Twenty minutes of contact time with the acid in the reactor would be adequate during which significant amount of 94 to 97% of chromium can be recovered from both samples of solid leather waste. This result is consistent with that obtained and observed by Pathe*et al* (1996).

4. Conclusion

It can be concluded from this study that although more chromium was found in leather shaving waste than leather buffing waste, the percentage recovery of the metal from leather buffing waste was higher considering the parameters used in this study. Optimum extraction of chromium III from both samples was however achieved when they were treated with 25% solution of sodium carbonate, carbonized at 600°C, acidified with 1.0M sulphuric acid, contacted with steam at temperature of 100°Cin the reactor for a minimum contact period of 40 minutes.

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