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Converting Leather Chrome Shaving Waste Into Free-Chrome Char As A Fuel

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Abstract

Chrome shaving wastes (CSW) are categorized as solid wastes with large quantities in tanneries, causing environmental damage when disposed by incinerating or landfilling. This study focused on converting CSW into free-chrome char that could be used as a fuel for energy production allowing recycling of recovered chrome again in leather processing. In this study, CSW were carbonized by incineration or pyrolysis at different temperatures (400, 500, 600 or 700°C). Thereafter, chrome was recovered from char using sulfuric, hydrochloric, or nitric acids at three level of concentrations (0.2M, 0.6M and 1.0M), soon after the recovered chrome was re-used for tanning pickled sheep skins' samples. The results showed that char yield was improved in pyrolysis and by the lowest temperature. Additionally, the increment in acid concentration and using sulfuric acid had the best effect for chrome recovery. Therefore, CSW pyrolysis at 400°C produced the highest char yield (44.58%) with chrome recovery rate of > 88% when using sulfuric acid with concentration ≥ 0.6M. The produced char contained 5172 kcal/kg that could be used as fuel, as well as the recycled chrome was successfully re-used in leather tanning process with no changes in leather properties as compared with traditional chrome tanning.

Keywords: Chromium sulfate; Environment; Extraction; Pyrolysis; Recycling.

Introduction

Leather tanning is the only way to convert raw animal skins or hides into valuable leathers. Due to applying different mechanical and chemical treatments during leather tanning, large wastes are produced which are classified mainly into liquid and solid wastes. Around 20 % of raw skins' or hides' weights are converted into leather while the rest are converted into tanned and non-tanned wastes [1, 2].

Although various tanning materials are used in leather tanning, chrome tanning is still the most popular method. Therefore, the chrome tanned solid wastes are the most hazard waste that leads to health and environmental problems such as air, soil and water pollution when unsafely disposed by incinerating, deep burial or landfilling [3].

Chrome shaving wastes (CSW) are unavoidable solid wastes that are produced when adjusting leather thickness mechanically. CSW is small and thin pieces of leather which composed of collagenous material cross-linked with about 4% of chromium salts [4]. Converting CSW into eco-friendly materials is the only way for valorizing it when using in other useful proposes. Previous attempts to earn added value of CSW were conducted [5], which included energy production [6, 7], protein hydrolysate [8, 9] and panels production [10, 11]. Recently, char production from CSW was emerged as a promised by-product that could be utilized in generating energy [12]. Approaching any of these goals depends mainly on the efficiency of chromium salts recovery from CSW. Chemical hydrolysis is the common way to recover chromium salts directly from CSW or obtaining it from its ash. Although, alkaline hydrolysis is more popular than acid hydrolysis in this issue, using mineral acids could have many advantages in this process for its ease of application, lowers costs and

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the capability of recycling the recovered chromium in tanning industry [13-15].

This work aimed to convert CSW to free-chrome char and recycling recovered chromium in leather tanning process. Decreasing energy consumption, increasing the yield of produced free-chrome char and enhancing the efficiency of chromium recovery were investigated in this study.

Experimental

Materials:

- Chrome shaving wastes:

The chrome shaving wastes used in this study were supplied by Elshafei Sons' Tannery, El-Max region, Alexandria, Egypt. CSW was dried at 25±3°C for five days in an open and shaded place without the use of any of thermal drying methods.

- Chemicals:

All chemicals used for chromium extraction from CSW chars and for preparing chromium sulfate for leather tanning were obtained from El-Gomhouria Company for Chemicals. Other chemicals used in tanning leathers' samples were commercial grade products routinely used in leather industry.

Methods:

- Experimental design:

The study was divided into three stages;

Carbonization of CSW:

At the beginning, characteristics of collected CSW were determined and thermogravimetric analysis (TGA) was performed. CSW was combusted using closed laboratory furnaces for incineration either by pyrolysis in opened or closed crucibles, respectively. The heating temperatures were 400, 500, 600 or 700 ℃ for two hours. The burned materials from furnaces were collected and then char yield (%) was calculated and chromium content (%) was determined in each sample.

Chrome leaching from chars:

Depending on the highest char yield from carbonization treatments, the pyrolysis was selected to extract chromium salts from chars, at the same heating temperatures, using solutions of sulfuric, hydrochloric or nitric acids at three concentrations 0.2M, 0.6M and 1.0M. Five grams from each char sample were taken in a beaker with 100 ml of desired acid and stirred for 2hrs at room temperature, then after washed twice with distilled water. The characteristics of de-chromed char were determined. Later, the optimum treatment in chrome recovery (0.6M H_2SO_4) was repeated to obtain enough exhausted solution could be re-using in leather tanning.

Re-using extracted chromium in leather tanning:

The exhausted solution was collected and chromium sulfate (33% basicity) was prepared using sulfuric acid and sugar according to Sharaf *et al*. [16]. The prepared chromium sulfate was used in tanning pieces of pickled sheep samples (20 cm × 20 cm) and compared with other samples tanned with normally commercial 33% basicity of chromium sulfate.

- Properties determination:

Chrome shaving waste characterization:

Characterization of CSW was determined. Volatile matter, ash, fat, total Kjeldahl nitrogen, chrome contents, total energy and pH values of CSW were determined according to ASTM [17].

Thermogravimetric analysis (TGA)

Thermogravimetric analysis of CSW was carried out by using a thermobalance model Shimadzu TGA-50/DTA-50. The analysis was performed by heating the samples in range (20℃ to 800 ℃) at a heating rate of 10 ℃/min under nitrogen (N_2) flow of 50 mL/min.

Char yield:

The following equation (1) was used to calculate char yield:

$$Y_c = (m/M) * 100 \quad \ldots\ldots\ldots(1)$$

where Y_c is the char yield (%); m is the char mass obtained after incineration or pyrolysis (g) and M is the mass of leather shaving waste (g).

Scanning electron micrographs and elemental analysis (SEM)

The particle morphology of chars' samples was observed and elemental analysis was performed using electron microscope model JEOL JSM-IT Series.

Textural properties of char:

The obtained char was analyzed for its surface area, pore volume, and pore diameter by N_2 adsorption/desorption isotherms at 77.3K in a surface area and porosimetry analyzer (MICROMERITICS ASAP 2020). The surface area was determined by Brunauer-Emmett-Teller (BET) and pore size distribution by the Barrett-Joyner-Halenda (BJH). Total pore volume (V 0.98) was determined from the adsorbed amount of nitrogen at P/P_0= 0.98.

Tanned leather properties:

Tanned leathers' samples were assessed physically and chemically for thickness, tensile strength, elongation, split tear strength, water absorption, permeability to water vapor, pH, and contents of ash, chrome and moisture were analyzed according to ASTM [17].

- Statistical analysis:

Data were analyzed using GLM procedure of SAS [18] to evaluate the differences among different treatments. Equation (2) explain the fixed model that used in the analysis of carbonization experiment, while equation (3) is the fixed model that used in the analysis of chromium extraction experiment.

$$Y_{ijk} = \mu + A_i + B_j + AB_{ij} + e_{ijk} \quad \text{.........(2)}$$

Where Y_{ijk} is the observation taken (k), μ is an overall mean, A_i is a fixed effect of the (i) burning method (incineration and pyrolysis), B_j is a fixed effect of the (j) burning temperature (400, 500, 600 and 700°C), AB_{ij} is an interaction effect between burning method and temperature, e_{ijk} is a random error assumed to be normally distributed with mean=0 and variance=σ^2e.

$$Y_{ijkl} = \mu + A_i + B_j + C_k + AB_{ij} + AC_{ik} + BC_{jk} + ABC_{ijk} + e_{ijkl} \quad \text{.........(3)}$$

Where Y_{ijk} is the observation taken (k), μ is an overall mean, A_i is a fixed effect of the (i) pyrolysis temperature (400, 500, 600 and 700°C)), B_j is a fixed effect of the (j) acid type (sulfuric, hydrochloric and nitric), C_k is a fixed effect of the (k) acid concentration (0.2M, 0.6M and 1.0M), AB_{ij}, AC_{ik}, BC_{jk} and ABC_{ijk} are the interaction effects among fixed effects, e_{ijkl} is a random error assumed to be normally distributed with mean=0 and variance=σ^2e.

Results and Discussion

Characterization of CSW:

Results for CSW analysis are presented in Table (1). High concentration of nitrogen (12.14%) was found in CSW as a protein substance consisting mainly of collagen fibres. Low fat content (0.29%), low pH (3.81 ml mol/L) and high chromium content (3.72%) were found in CSW due to tanning processing steps, in which the fat is removed by the action of alkalis in unhairing step to facilitate the access of tanning material into collagen fibres, which usually react to the chromium sulfate at low value of pH. The total ash content was 10.31% due to the different elements in collagen fibres such as carbon, nitrogen and sulfur, in addition to other elements comes from different chemical used in tanning especially chromium salts. The obtained values of CSW properties were in accordance with previous investigations [5, 19], while the heating value was 3515 kcal/g indicating the possibility of using it for energy production [6, 20].

Table (1): Chrome shaving waste properties.

Parameter	Value	ASTM
Volatile matter (%)	21.13	D-6403
Fat (%)	0.29	D-3495
Total Kjeldahl nitrogen (TKN)	12.14	D-2868
Total ash (%)	10.31	D-2617
Cr (%)	3.72	D-6714
pH (ml mol/L)	3.81	D-2810
Heating value (kcal/g)	3515	D-5865

Carbonization of CSW:

The thermal behavior of CSW under nitrogen atmosphere is shown in Figure (1). Thermogravimetric analysis (TGA) pointed to three stages of thermal degradation, namely;

- First stage (thermal temperatures < 80 °C): The degradation was in a medium slope and the decrease in weight was about 15% of total weight loss due to moisture loss from CSW then the weight loss stabilized at approximately the same level by increasing temperature till 270 °C.
- Second stage: (thermal temperature between 270 °C to 400 °C): The degradation was in high slope where the weight decreased by about 45% of total weight loss. The maximum value of CSW thermal degradation was reached at 320 °C. This might be due to an intensive modification of the biomass structure occurs when CSW pyrolysis or incinerated under anoxic conditions between 200 °C and 500 °C, which accompanied by formation of condensable compounds and emission of gases [6, 21].
- Third stage (thermal temperature > 400 °C): The degradation was in a medium slope and the decrease in weight declined slightly to about 40% of total weight loss due to the pyrolysis process of CSW as the formation of condensable compounds continued at a slower rate [6, 21].

The results of TGA analysis coincided with those of previous studies [15, 22] in which the behaviour of weight changes with increasing burning temperature was referred to the nature of CSW as a proteinous material of collagen fibres. The results indicated the capability of burning CSW in the range between 400 °C and 700 °C either incineration or pyrolysis conditions to obtain the highest amount of char at the next step of this work.

Table (2) shows significant effects of burning method (P<0.01) and the interaction effect between burning method and burning temperature (P<0.01) on both char yield and chrome content.

Char yield was 10.91% and 40.06% in incineration and pyrolysis, respectively, which may be attributed to the higher loss of condensable compounds and emitted gases in incineration method [23]. In contrast, chrome content was higher (P<0.01) in incineration (16.08%) than pyrolysis (3.94%). These results may be due to temperature limits used in this study which were relatively lower than those required for melting and boiling chrome element at 1907 ℃ and 2671 ℃, respectively [24].

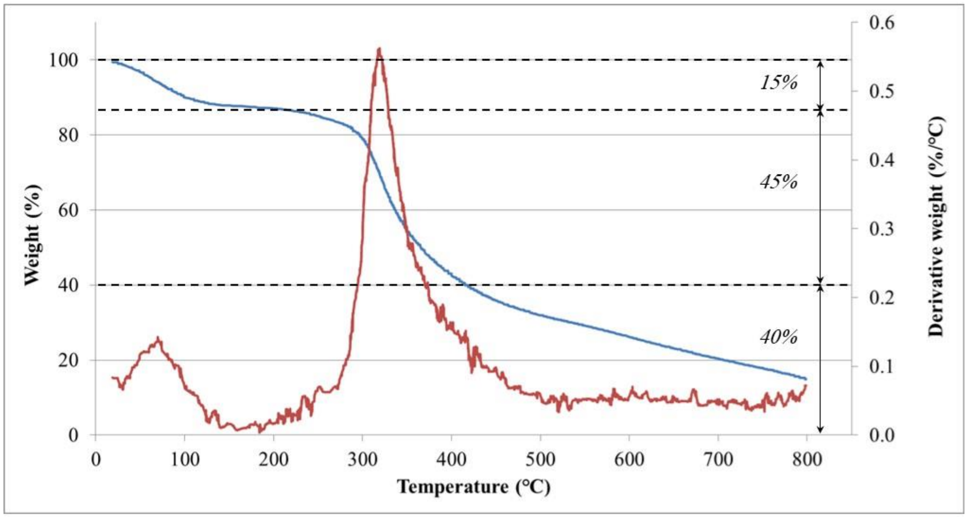

Figure (1): Thermogravimetric analysis (TGA) for chrome shaving waste.

Table (2): Means of char yield (%) and chrome content (%) as affected by burning method, burning temperature and their interaction.

Item		Char yield (%)	Chrome content (%)
Burning method			
Incineration (presence of oxygen)		10.91[a]	16.075[a]
Pyrolysis (absence of oxygen)		40.06[b]	3.939[b]
P-value		*<0.0001*	*<0.0001*
Burning temperature			
400℃		28.73	6.975
500℃		26.63	9.429
600℃		24.00	10.658
700℃		22.58	12.966
P-value		0.9146	0.562
Interaction effect (Burning method × Temperature)			
Incineration	400℃	12.89[d]	10.439[c]
	500℃	11.16[d]	15.137[b]
	600℃	10.16[d]	17.176[b]
	700℃	9.45[d]	21.549[a]
Pyrolysis	400℃	44.58[a]	3.512[d]
	500℃	42.11[ab]	3.720[d]
	600℃	37.83[bc]	4.141[d]
	700℃	35.72[c]	4.384[d]
P-value		*<0.0001*	*<0.0001*
Overall of means		25.49	10.007
Standard error of mean		2.13	1.461

Means in the same column having different superscripts are significantly different (P<0.05).

On the other hand, insignificant effect of burning temperature on both of char yield and chrome content was detected where the difference among different burning temperatures ranked in a narrow range. An inversely proportional was found between char yield and burning temperature where the highest char yield was at 400 ℃ (28.73%) and the lowest was at 700 ℃ (22.58%). These results were in accordance with previous investigation [25].

In respect to the thermal effect on chromium salts, the pyrolysis of chrome-rich tannery waste reduces significantly the oxidation of trivalent chromium to hexavalent, as well as the hazardous nature of the produced ash [15]. Therefore, this carbonization experiment recommended pyrolysis CSW at 400 ℃ as the most prober examined methods to maximize char yield and minimize energy consumption, in addition avoiding chromium oxidation.

Chrome leaching from char

Table (3) presents data of treating CSW char with different concentrations of sulfuric, hydrochloric or nitric acids at different pyrolysis temperatures for leaching chromium salts. Significant effects of acid type ($P<0.01$) and acid concentration ($P<0.05$) on both chrome content and chrome recovery were detected. Moreover, all interactions effects were significant ($P<0.01$) except the interaction effect between pyrolysis temperature and acid concentration. The use of sulfuric acid resulted in the highest recovery of chromium (87.62%), followed by hydrochloric acid (65.86%), then nitric acid (57.11%) in the last order. This arrangement was in agreement with some previous studies [14, 26, 27], while it was contrary to other studies [13, 28]. Physically, chromium nitrate has the highest solubility, followed by chromium sulfate and then chromium chloride [29]. However, equilibrium conditions, especially pH level and acid concentrations [30], in addition to the presence of some oxidizing elements, present in tanneries waste [27] may explain these results.

Regarding the effect of acid concentration, the significant difference was noticed only between the lowest (0.2M) and highest (1M) acid concentrations. Generally, increment in acid concentration declined chrome content and increased chrome recovery in coincided with other investigations [13, 26-28]. These results indicated that using medium acid concentration (0.6M) is sufficient for chrome recovery.

Figure (2) shows the changes in chrome recovery due to the interaction effect among pyrolysis temperature, acid type and acid concentration, showing the superiority of sulfuric acid with concentrations 0.6M and 1M at different pyrolysis temperatures. Since the values of chrome recovery for these two concentrations of sulfuric acid were in narrow range (88%-94%), it was recommended to pyrolysis CSW at 400℃ and use 0.6M of sulfuric acid for recovering about 88% of chromium salts from char with the least cost and energy consumption. Additionally, using sulfuric acid was reported to maintain low pH of leaching medium that ensures the presence of chromium salts in its trivalent form with minimal toxicity [14, 31].

Table (3): Means of chrome content (%) and chrome recovery (%) as affected by pyrolysis temperature, acid type, acid concentration and their interactions.

Item		Cr content (%)	Cr recovery (%)
Pyrolysis temperature	400℃	1.07	69.40
	500℃	1.12	69.97
	600℃	1.23	70.42
	700℃	1.27	71.00
P-value		*0.5365*	*0.9792*
Acid type	Sulfuric	0.48^{c}	87.62^{a}
	Hydrochloric	1.34^{b}	65.86^{b}
	Nitric	1.69^{a}	57.11^{c}
P-value		*< 0.0001*	*< 0.0001*
Acid concentration	0.2 M	1.36^{a}	65.36^{b}
	0.6 M	1.16^{ab}	70.37^{ab}
	1 M	0.99^{b}	74.87^{a}
P-value		*0.015*	*0.013*
Temperature × Acid type	*P-value*	*< 0.0001*	*< 0.0001*
Temperature × Acid concentration	*P-value*	*0.4955*	*0.6662*
Acid type × Acid concentration	*P-value*	*< 0.0001*	*< 0.0001*
Temperature × Acid type × Acid concentration	*P-value*	*< 0.0001*	*< 0.0001*
Over all of means		1.172	70.20
Standard error of mean		0.053	1.332

Means in the same column having different superscripts are significantly different ($P<0.05$).

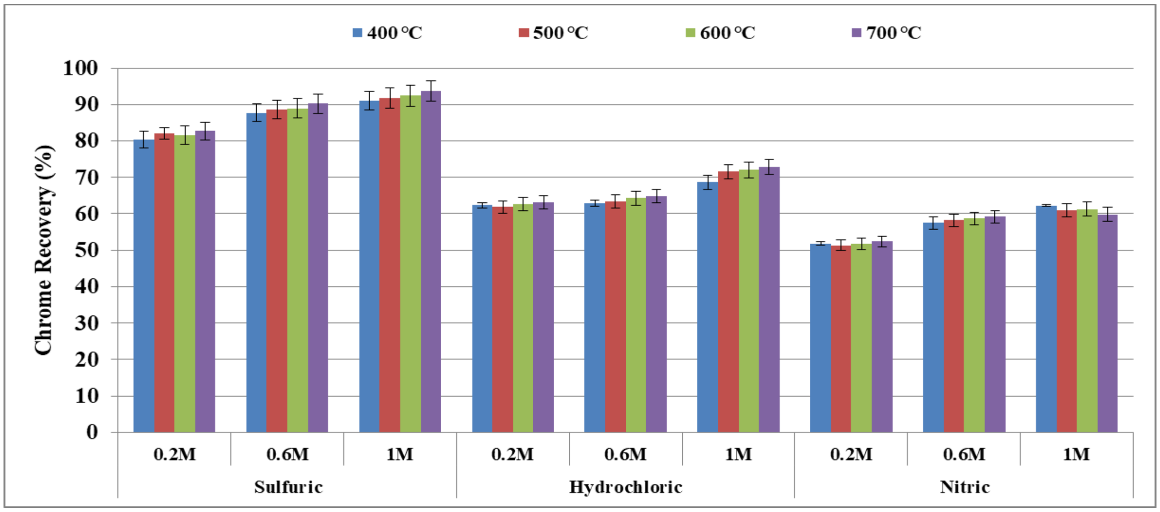

Figure (2): Chrome recovery from char as affected by pyrolysis temperature, acid type and acid concentration.

Char characteristics:

Figure (3) shows scanning electron micrographs of chrome shaving waste char. The untreated group contained inclusions sticking to the surface of its particles, which were not observed in chars that were treated with different acids. The chars' particles treated with sulfuric and hydrochloric acids were similar in both shape and size, while those treated with nitric acid were smaller in size and had a different shape.

The changes in particles' shapes among untreated and treated chars were reflexed on adsorption-desorption isotherms of chrome shaving waste char (Figure 4) and their properties (Table 4). The behavior of obtained char is typical of isotherm type I, indicating that this is a solid material with small pores formed by micro and mesopores, this was in agreement with previous investigation [6]. Treating chars with acids, especially nitric acid, improved adsorption-desorption behavior and other physical properties, while the effects of sulfuric and hydrochloric acids were similar.

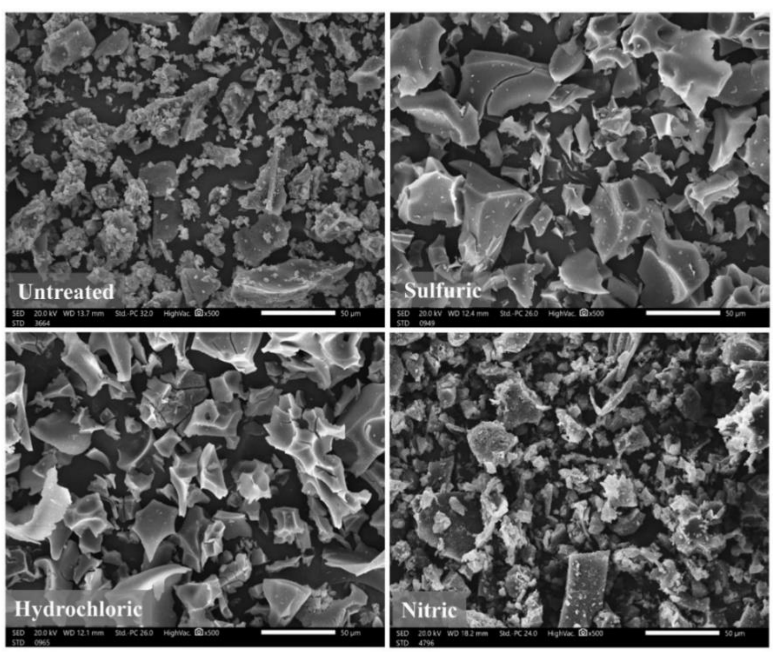

Figure (3): Scanning electron micrographs (SEM) of chrome shaving waste char (x500).

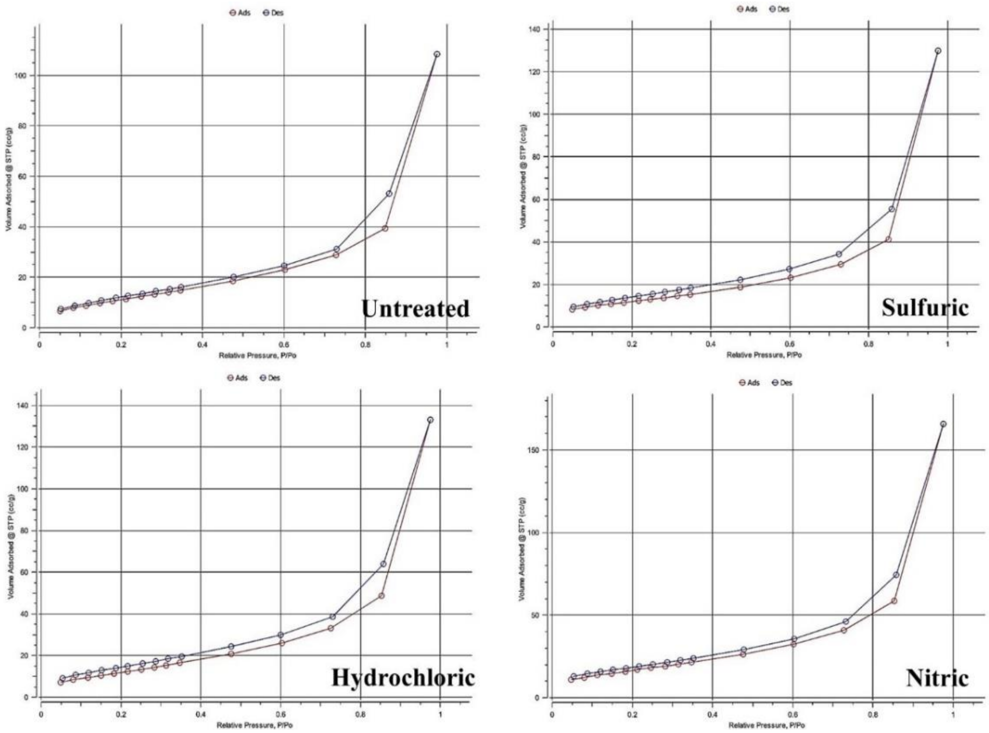

Figure (4): Adsorption-desorption isotherms of chrome shaving waste char.

Table (4): Characteristics of chrome shaving waste char.

Parameters	Untreated	H_2SO_4	HCL	HNO_3
BET surface area (m^2/gm)	44.92	45.80	49.23	63.30
Average particle radius (nm)	30.04	28.44	27.97	21.54
Total pore volume (cm^3/g)	0.168	0.201	0.206	0.257
Average pore size (nm)	7.48	8.99	8.38	8.12
Elemental composition (weight % as dry basis)				
C	39.89	46.61	46.89	46.74
O	19.32	26.25	26.82	29.67
N	13.27	20.53	19.79	19.47
Cr	7.68	4.20	4.82	3.66
Cl	11.47	0.66	1.23	0.46
S	2.75	1.75	0.45	0.00
Na	5.62	0.00	0.00	0.00
Energy (kcal/kg)	5172	5255	5320	5280

Char treated with nitric acid had the highest BET surface area (63.30 m^2/gm) followed by hydrochloric (49.23 m^2/gm) and sulfuric acids (45.80 m^2/gm). The treatment with nitric acid decreased average radius of the particles, average pore size and increased its total pore volume. The obtained values of BET surface area appeared to be normal for the values of inactive carbon which is an inessential characteristic when using carbon as an energy source, although they were lower than the corresponding values of active carbon in previous studies [6, 32, 33].

The elemental analysis in Table (4) showed that acids treatment caused an increment in carbon, oxygen and nitrogen percentages at the expense of partly or totally removing other elements such as chromium, sodium, chloride and sulfur. The values of elemental analysis on dry bases for carbon, oxygen and nitrogen percentages were in agreement with those reported by other investigators [7, 20, 34-36]. A slight increase in the energy content as a result of the treatment was also observed. Increment of carbon concentration in char increases energy content as an energy value of 5256 kcal/kg was reported to give the char privilege to be used as a fuel [6]. In the current work, this advantage was achieved, as the energy value ranged between 5255 to 5320 kcal/kg.

Table (5): Leather properties of tanned leather samples.

Group	Traditional leathers (control)	Recovered leathers	Overall of means	Standard error of mean	*P-value*	ASTM
			Physical properties			
Thickness (mm)	0.91	0.90	0.91	0.002	*0.519*	D-1813
Tensile (kg/cm^2)	161.84	170.39	166.12	2.720	*0.119*	D-2209
Tear (kg/cm)	35.39	34.29	34.84	0.445	*0.255*	D-4704
Elongation (%)	60.99	61.31	61.15	0.674	*0.841*	D-2211
WAbs (%)	212.54	212.58	212.56	0.498	*0.975*	D-6015
PWV ($mg/mm^2/h$)	5.49	5.54	5.52	0.088	*0.835*	D-5052
			Chemical properties			
Moisture (%)	15.19	15.22	15.21	0.164	*0.939*	D-6403
Ash (%)	6.25	6.46	6.36	0.197	*0.649*	D-2617
Cr (%)	3.13	3.08	3.11	0.042	*0.947*	D-6714
pH (ml mol/L)	3.70	3.67	3.69	0.029	*0.585*	D2810

ASTM: determination method according to American Society for Testing and Materials.
WAbs: Water absorption.
PWV: permeability to water vapor.

Using extracted chromium in leather tanning

The direct reduction of chromium salts with sugar-sulfuric acid mixture ensured obtaining basic chromium sulfate (33% basicity), which is normally used for traditional chrome tanning in leather processing [16, 37, 38]. Physical and chemical properties of tanned leather samples are presented in Table (5). Depending on the presented data, usage of recovered chromium did not degrade the properties of produced leather which had similar properties to that tanned with traditional basic chrome sulfate tanning. Therefore, recycling chrome from CSW could be a promised practice to achieve additional environmental and economic benefits.

Conclusion

Chemical converting of chrome shaving waste into free-chrome char rather than traditional disposing avoids the harmful environmental impact. Recycling chrome shaving waste by pyrolysis at 400 °C followed by chrome recovery with 0.6M sulfuric acid might be a recommended technique to produce char as valuable source of energy. Meanwhile, extracted basic chromium sulfate could be re-used for leather tanning process. Further large-scale application for this work is necessary to be realizable and taking into account the economic feasibility study

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