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Ahmed Ibrahim Nasr

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Conversion of Chromium Shaving Waste from Leather Processing into Activated Carbon

Ahmed Ibrahim NASR

Wool Production and Technology Research Department, Animal and Poultry Production Division, Desert Research Center, Cairo, Egypt

*ainasr@yahoo.com

Article

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ABSTRACT

This study aimed to convert chrome shaving waste (CSW) generated from leather processing into valuable materials, such as de-chromed activated carbon and basic chromium sulphate. CSW was de-chromed using three levels of leaching solution of potassium carbonate, hydrogen peroxide, and water (0.25:0.1:5, 0.5:0.2:5, and 0.75:0.3:5, respectively), and the resulting potassium chromate was converted into basic chromium sulphate using sugar reduction method. De-chromed shaving waste (DSW) was pyrolyzed at three temperatures levels (400, 500, and 600 °C) to obtain de-chroming shaving ash (DSA), which then was chemically activated using three levels of potassium hydroxide (3:1, 2:1, and 1:1 of DSA: KOH, respectively). The results showed that up to 21% of de-chroming activated carbon (DAC) was produced, containing 71.22% carbon with a surface area of 731 m^2/g, total pore volume of 0.385 cm^3/g, and an average pore diameter of 2.106 nm. The produced basic chromium sulphate was suitable for reuse in leather processing. Therefore, this study provides an effective way to convert CSW into valuable materials, reducing the environmental impact of leather processing and promoting sustainability.

KEYWORDS

chromium shaving waste, leather processing, activated carbon, pyrolysis, carbonization, de-chroming

INTRODUCTION

The leather tanning industry is a significant global industry that is expected to grow at a compound annual growth rate (CAGR) of 5.9% from 2021 to 2028 with an estimated trade value of USD 624.08 billion in 2028. The global annual production of leather is estimated to be around 23 billion square feet per year [1]. Approximately half of the world's leather production occurs in low and middle-income countries. The largest leather-producing nations include China, Brazil, India, Italy, Korea, Argentina, Mexico, Spain, Bangladesh, Japan, and Pakistan [2]. Africa is also a significant producer of leather, although its share is relatively small in terms of global production. The top leather-producing countries in Africa include South Africa, Egypt, Sudan and Morocco [3]. Therefore, the leather tanning industry is witnessing a global expansion, despite the environmental impacts it causes [4].

The leather tanning process involves treating raw animal skins/hides with chemicals to transform them into a durable material that can be used for various purposes, such as clothing, footwear, and

upholstery. There are different tanning methods, including chrome, vegetable, and synthetic tanning [5]. Chrome-tanned leather has unique properties, making it the most widely used choice in the industry worldwide [2,6-8]. However, the tanning process generates various liquid, solid, and gaseous wastes [2].

One of the largest solid wastes produced is chrome shaving waste (CSW), a narrow leather strip material created during the wet blue leather thickness adjustment process before wet finishing [9]. CSW accounts for approximately 10% of the total weight of processed raw hides/skins and has an annual global production of roughly 0.8 million tons [9,10]. The chromium content in CSW varies between 2.5% to 5.0%, depending on the tanning process used [11]. The dominant form of chromium in CSW is Cr(III), which is less toxic than the hexavalent form [12,13]. However, the unsafe disposal of such wastes poses a significant risk of environmental pollution. As a result, the leather industry is under pressure to adopt more sustainable and environmentally friendly practices to minimize its negative environmental impact [4]. Parisi et al. reviewed recent studies that have focused on converting leather tanning wastes into value-added and eco-friendly products as a safe disposal method [14]. Activated carbon is one such value-added product that can be generated from leather wastes through a pyrolysis process [16]. Pyrolysis involves heating the waste material in the absence of oxygen, which results in the breakdown of complex organic compounds into simpler molecules. The resulting material is then activated using a chemical or physical process to create a form of carbon with a high surface area due to its small particle diameter containing many low-volume pores [17]. It can be derived to be converted into charcoal or char before being activated [18]. Compared to physical activation, chemical activation is more advantageous because it requires lower temperatures and shorter activation times, resulting in higher quality and consistency of the activated carbon produced [19,20].

Previous studies from around the world have shown that the production of activated carbon from leather waste involves several consecutive steps, including carbonization followed by activation, and sometimes demineralization/de-chroming [9,16,19,21-23]. Parisi et al. [14] and Scopel et al. [15] reviewed previous investigations on the removal of chromium from CSW and reported that chromium removal relies primarily on hydrolysis processes using acids, alkaline solutions, or enzymes, as well as alkali oxidative extraction, which is characterized by its ease of application and efficiency in separating chromium.

Regarding the carbonization step, it is typically conducted within the temperature range of 400-1000 °C [24-28]. While higher temperatures are not commonly used as they may result in lower yields, using higher temperatures is still economically feasible as long as the yield is above 20% [19,29-31]. The demineralization step, which involves removing inorganic salts including chromium, can also contribute to a reduction in the final yield [21,30,31].

In the activation step, the activation agents used have either an alkaline nature, such as sodium hydroxide, calcium carbonate, and potassium carbonate, or an acidic nature, such as zinc chloride and pyrophosphoric acid. The most commonly used agent for activation is potassium hydroxide at various temperatures [32].

Complementing our previous work on CSW [18] and considering the above-mentioned facts, the main objective of the current study is to produce value-added active carbon from leather residues using higher-efficiency chemical and thermal treatments. Therefore, it aims to determine the most suitable (a) chemical concentration for de-chroming CSW and recycling of extracted chromium, (b) carbonization temperature for the resulting de-chroming shaving waste, and (c) chemical concentration for activating the charcoal produced from carbonization.

EXPERIMENTAL

Materials

Chrome shaving wastes (CSW)

The dried chrome shaving wastes used in the study were obtained from Elshafei Sons' Tannery, which is located in the El-Max region, Alexandria, Egypt.

Chemicals

The El-Gomhouria Company for Chemicals was the source of all the chemicals utilized.

Methods

The laboratory work of this study was done in the chemical laboratory of Mariout Research Station, Desert Research Center, Alexandria, Egypt. Free-chrome activated carbon and basic chromium sulphate were prepared from CSW through four steps; de-chroming, carbonization, activation and converting the chromium salts to basic chromium sulphate.

De-chroming CSW (pre-carbonization)

CSW was mechanically treated with a leaching solution using occasional stirring for 45 min at room temperature. According to Siska [33], a leaching solution was prepared with three levels of potassium carbonate, hydrogen peroxide and water as shown in Table 1. After treatment with leaching solution, CSW was filtered and rinsed twice with water. De-chromed CSW (DSW) was obtained after rinsing by pressing, whereas the filtrate, containing chromium salts was collected for subsequent basic chromium sulphate preparation.

Table 1. Factors and respective levels evaluated in the experimental design for activated carbon preparation

Step	Corresponding level	Level		
		Low	Medium	High
De-chroming	CSW: K_2CO_3: H_2O_2*: H_2O ratio (w/w)	1:0.25:0.1:5	1:0.5:0.2:5	1:0.75:0.3:5
Carbonization	Pyrolysis temperature (℃)	400	500	600
Activation	DSA: KOH ratio (w/w)	3:1	2:1	1:1

* H_2O_2 that was used was in concentration 30%. CSW chrome shaving waste, DSA de-chroming shaving ash.

Carbonization of DSW

Based on the data obtained from the de-chroming step, the resulting DSW from the medium concentration of a 1:0.5:0.2:5 ratio of CSW: K_2CO_3: H_2O_2: H_2O (w/w) was used for carbonization. DSW was weighted and dried at 105 °C until the weight was constant, thereafter it was put in a closed crucible and then heated up in a muffle furnace with a rate of 5 °C/min. Three pyrolysis temperatures were used in this step (Table 1). Once the pyrolysis temperatures reached the required levels; pyrolysis time began to run for 90 min and de-chroming shaving ash (DSA) was obtained.

Activation of DSA

Based on obtained carbonization data, the DSA of medium pyrolysis temperature (500 °C) was used for the activation step. DSA was activated chemically using three ratios of KOH: DSA (W/W), presented in Table 1. The mixing was done for 120 min and then the slurry was dried at 105 °C for 120 min. The resulting mixture was activated in a furnace at 700 °C for 90 min in the closed crucible. After cooling, obtained de-chroming activated carbon (DAC) was washed with hot water until it reached the neutral pH and then dried at 105 °C for 120 min.

Preparing basic chromium sulphate

After the extraction of chromium; potassium chromate was then converted into basic chromium sulphate using the sugar reduction method [11]. The basicity of prepared basic chromium sulphate was determined for evaluating its possibility in the leather tanning process according to ASTM (D-3897) [34].

CSW characterization

The characterization of CSW was previously determined in our collaborative work with this study [18]. The characteristics were evaluated by measuring parameters such as volatile matter, ash, fat, total Kjeldahl nitrogen, chromium content, and pH values, in accordance with ASTM specifications [34].

Thermogravimetric analysis (TGA)

The thermogravimetric analysis of CSW was determined in our previous work [18], as conducted using a Shimadzu TGA-50/DTA-50 thermobalance model. The analysis involved heating the samples from 20 °C to 800 °C at a heating rate of 10 °C/min under a nitrogen (N_2) flow of 50 mL/min.

Yield determination

The following equation 1 was used to calculate the yield in different steps:

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

where Y is the yield (%); m is the mass obtained after finishing the desired step (g) and M is the mass of leather shaving waste (g).

Scanning electron micrographs and elemental analysis

The ash and activated carbon samples were examined for particle morphology and elemental analysis using an electron microscope model JEOL JSM-IT Series.

Textural properties of Ash and activated carbon

The obtained de-chroming char and activated carbon were analysed for their surface area, pore volume and pore diameter by N_2 adsorption/desorption isotherms at 77.3 K in a surface area and porosimetry analyser (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.

Statistical analysis

The data were subjected to analysis using the SAS GLM procedure to assess the variations among the various treatments [35]. Equation 2 describes the fixed model employed in the analysis of the de-chroming and carbonization stages:

$$Y_{ij} = \mu + A_i + e_i \quad (2)$$

Where Y_{ij} is the observation taken (k), μ is an overall mean, Ai is a fixed effect of the (i) de-chroming level (low, medium or high), carbonization temperature (400, 500 or 600°C) or activation level (low, medium or high), e_{ij} is a random error assumed to be normally distributed with mean=0 and variance=$\sigma^2 e$.

RESULTS AND DISCUSSION

Characteristics of chrome shaving waste

CSW has a high nitrogen concentration (12.14%), low-fat content (0.29%), low pH (3.81), and high Cr content (3.72%). These obtained values suggest that the CSW used in this experiment has similar characteristics to those reported in previous investigations [10,36]. CSW has a high protein content due to its major composition of collagen fibrils. The low fat, low pH, and high chromium content of CSW are attributed to the chrome tanning process, which involves removing fats and lowering the pH to facilitate the interaction of chromium salts with the collagen fibres of the hides/skins.

Based on the thermogravimetric analysis (TGA) of CSW, which was estimated in our previous collaborative work with this study [18], the thermal degradation of CSW can be divided into three stages. The weight loss was 15% due to moisture loss from CSW that occurred at a medium slope in the first stage, followed by a fixed weight loss (45%) until 270 °C. The thermal degradation of CSW reached its maximum value at 320 °C in the second stage, while the third stage showed a slower rate of weight loss (40%) due to the continued formation of condensable compounds. The TGA analysis results were in agreement with previous findings [16,18,37], which linked the observed weight changes to the protein-rich nature of CSW as a material composed primarily of collagen fibres. Based on these results, it was determined that the optimal temperature range for pyrolysis of CSW is between 400 °C and 600 °C, as this temperature range was shown to yield the highest amount of carbon in previous studies [24-28]. This information was taken into account in the current study when designing the carbonization stage.

De-chroming chrome shaving wastes

In this study, the oxidative alkaline extraction method was employed, which led to the rapid dissolution of chromium salts from the CSW, consistent with previous investigations [32,33]. The resulting non-degraded leather fibres had a waxy white appearance and were easily separated from the yellow-coloured filtrate containing the chromium salts. From our point of view, potassium carbonate was a base to raise the pH of the solution, while hydrogen peroxide acted as an oxidizing agent to convert trivalent chromium to hexavalent chromium, which is more soluble and easier to extract. Specifically, the trivalent chromium hydroxide in CSW reacted with potassium carbonate and hydrogen peroxide to form potassium chromate, water, and carbon dioxide. This oxidative alkaline extraction process can be represented by the following chemical equation 3:

$$2\,Cr(OH)_3 + 2\,K_2CO_3 + 3\,H_2O_2 \rightarrow 2\,K_2CrO_4 + 6\,H_2O + 2\,CO_2 \quad (3)$$

Table 2 presents the results of the chromium content, chromium recovery, and yield for DSW, affected by the de-chroming level. The study found that increased levels of potassium carbonate and hydrogen peroxide led to a significant decrease in chromium content ($P < 0.01$) and yield ($P < 0.01$), while significantly increasing the chromium recovery ($P < 0.01$). Data analysis revealed that the differences between medium and high concentrations were not significant in terms of chromium content (0.17 vs. 0.14%) and recovery (95.86 vs. 93.73%), but the high concentration significantly reduced the yield. Therefore, the optimal de-chroming level was achieved using a medium concentration of a 1:0.5:0.2:5 ratio of CSW: K_2CO_3: H_2O_2: H_2O (w/w), which resulted in the highest percentages of chromium recovery and yield. The chromium recovery values obtained in this study were consistent with some previous studies that used the oxidative alkaline extraction method [32,38]. Furthermore, the values were higher than those reported in previous research studies that used acid or alkaline hydrolysis methods [8,36,39-42]. However, Mwondu *et al*. [43] were able to extract 99.9% of the chromium salts, which is higher than the values obtained in this study. This may be due to the use of a more complex chemical extraction method, which relies on the use of orthophosphoric acid at a controlled temperature of 50 °C after preliminary extraction of chromium using formic acid and potassium oxalate, which may require better control over the extraction conditions than that used in this experiment and may also be more costly.

Table 2. Least square means ± standard error of the mean of chrome content, chrome recovery and yield for de-chroming shaving waste (DSW) as affected by the de-chroming level

Group	Cr content (%)	Cr recovery (%)	Yield (%)†
CSW (Untreated)	3.72[a]	00.18[c]	99.50[d]
DSW (Low level)	0.46[b]	87.63[b]	98.19[c]
DSW (Medium level)	0.17[c]	95.43[a]	95.86[b]
DSW (High level)	0.14[c]	96.24[a]	93.73[a]
Over all of means	1.12	69.87	96.82
Standard error of mean	0.45	12.17	0.67
Significance	**	**	**

CSW chrome shaving waste, DSW de-chroming shaving waste, Yield is calculated as a percentage of (DSW/CSW) *100.
Significance: *** P<0.01.* Means in the same column having different superscripts are significantly different (P<0.05).

Characteristics of de-chroming shaving ash

The characteristics of the resulting DSA are presented in Table 3. The yield and particle size of DSA were significantly decreased ($P < 0.01$) with increasing pyrolysis temperature as in accordance with previous investigations [18,19,29-32,37]. As shown in the scanning electron micrographs in Figure 1, the size of the ash particles in the DSA that was pyrolyzed at 500 °C or 600 °C is smaller than those pyrolyzed at 400 °C.

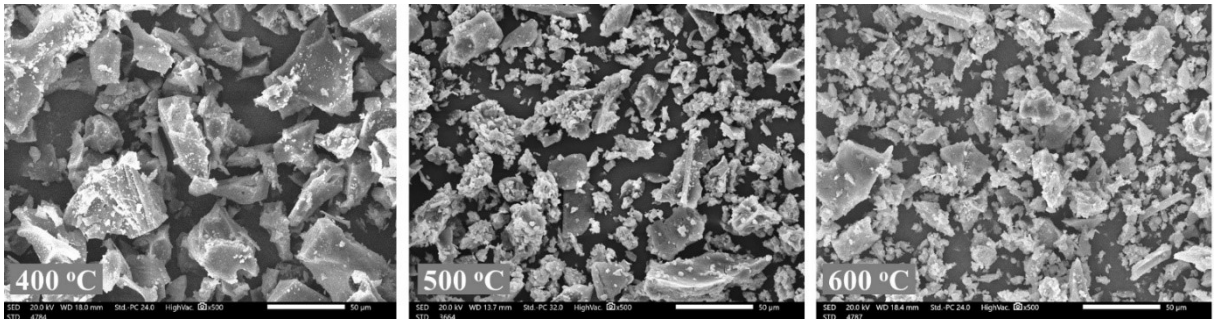

Figure 1. Scanning electron micrographs for de-chroming shaving ash (DSA) pyrolysis at three temperature levels

The decrease in particle size can be attributed to several factors; including breakdown of chemical bonds, increasing movement rate of different molecules, and decreasing viscosity of the material being burned [17,44]. Additionally, the chromium content of the ash was significantly increased ($P < 0.05$) with increasing pyrolysis temperatures. This suggests that higher temperatures led to a greater concentration of chromium in the resulting ash. Therefore, the ash obtained at 500 °C was the most suitable for the subsequent preparation of activated carbon, due to its properties being close to the average values estimated for the three levels.

Table 3. Least square means ± standard error of mean of chromium content, average particle radius and yield of de-chroming shaving ash as affected by pyrolysis temperature

Pyrolysis temperature (°C)	Cr content (%)	Average particle radius (µm)	Yield (%)
400	1.60^{b}	48.01^{a}	28.07^{a}
500	1.65^{ab}	34.40^{b}	25.94^{b}
600	1.71^{a}	25.40^{c}	23.44^{c}
Over all of means	1.65	35.94	25.82
Standard error of mean	0.02	3.45	0.68
Significance	*	**	**

Significance: *$P<0.05$. **$P<0.01$. Means in the same column having different superscripts are significantly different ($P<0.05$).

Characteristics of de-chroming activated carbon

The characteristics of the resulting DAC are detailed in Table 4. It is noticed that the final yield and particle size were decreased after activation, while the surface area and total pore volume of the particles were increased as in agreement with previous investigations [18,37,45,47].

The maximum BET surface area obtained was 731.96 m^2/g through activation with a mixture of DSA and potassium hydroxide in a weight ratio of 2:1 (w/w). The surface area achieved in this study falls within the typical range of 300 to 800 m^2/g found in most previous studies [16,21,23,30,47], although

some investigations have reported even higher specific surface areas exceeding 1000 m^2/g [22,48-50]. The reason for the rise in active carbon surface area achieved in these studies may be because that the carbonization and activation processes were conducted in a completely oxygen-free environment, specifically a nitrogen atmosphere, which was not available in this study.

Regarding the effect of KOH concentration, it was noted that raising the concentration during activation led to enhancements in the characteristics of DSA. However, the sample prepared with the highest concentration did not exhibit performance as good as the one made with a medium concentration.

Table 4. Characteristics of de-chroming activated carbon (DAC) resulting from different treatments of de-chroming shaving ash (DSA)

Parameters	DSA (Not activated)	DAC (Low level)	DAC (Medium level)	DAC (High level)
Final yield (%)*	22.464	21.038	21.044	21.076
BET surface area (m^2/g)	1.210	101.870	731.960	330.250
Total pore volume (cm^3/g)	0.016	0.103	0.385	0.182
Average pore diameter (nm)	54.088	4.043	2.106	2.201
Elemental composition (weight % as dry basis)				
C	39.98	65.95	71.22	49.79
N	27.43	18.53	12.82	24.08
O	29.24	13.85	12.37	21.28
K	0.84	1.01	1.87	2.06
Cr	1.9	0.66	0.92	1.73

* Final yield is calculated as a percentage of chrome shaving waste.

KOH is commonly used as an activating agent in the chemical activation of carbon because it is a strong base that can react with the carbon precursor material at high temperatures, leading to the formation of a porous carbon structure [51]. During chemical activation, the carbon precursor material is first partially oxidized, this creates a network of micropores and mesopores throughout the material. Then, the material is treated with a solution of KOH, which further opens up the pores and creates additional porosity. The KOH reacts with the carbon precursor material to form potassium carbonate, which is then decomposed further to form K_2O and CO_2. The chemical reaction in equation 4 was widely recognized as a potential chemistry during KOH activation [51].

$$6\,KOH + 2C \rightarrow 2\,K + 3\,H_2 + 2\,K_2CO_3 \quad (4)$$

The elemental composition data analysis indicated that the activation step increased the percentage of carbon and potassium in the samples after activation compared to the non-activated sample. This may be because activation removes impurities and some of non-carbon components from the starting material and converts them into volatile gases or solid residues [17]. Additionally, the presence of the activating agent, such as KOH, may also contribute to the increase in the percentage of potassium in the activated carbon.

Figure 2 shows a comparison of the particle shapes for samples before and after the activation steps. The figure indicates that the particle size was decreased for the activated samples compared to the non-activated sample. Additionally, the figure suggests that the particle size decreased with an increase in the concentration of KOH used in the activation process.

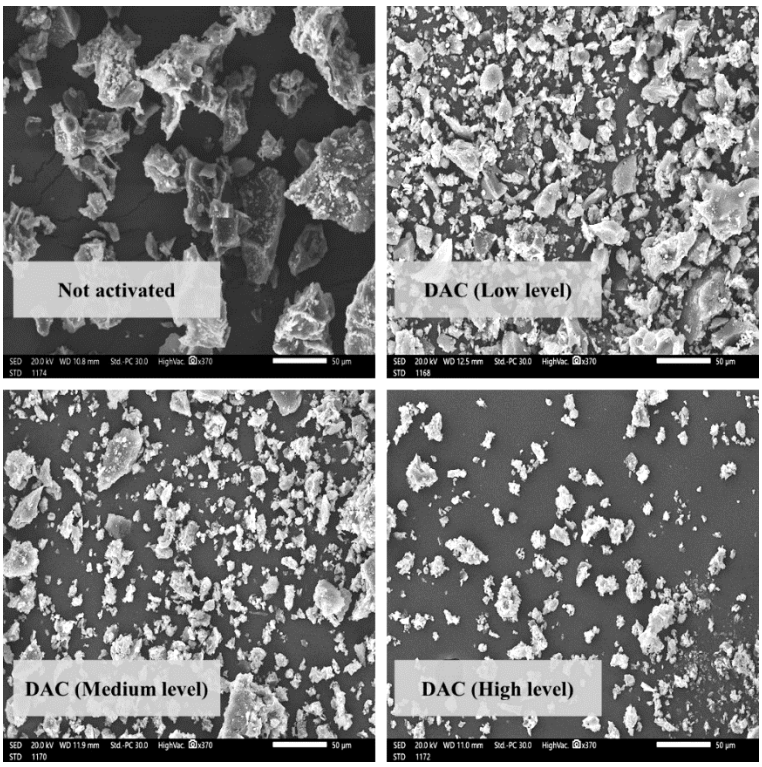

Figure 2. Scanning electron micrographs of not activated shaving ash and de-chroming activated carbon (DAC) at different activation levels

Figure (3) shows the adsorption-desorption isotherms. According to the IUPAC classification [52], the behaviour of the non-activated sample in the isotherms is typical of type I isotherms, which indicates that the extent of adsorption increases with pressure until it reaches saturation, after which no further adsorption occurs. As for the activated samples, it was observed that their behaviour follows type IV isotherms and the hysteresis may be classified as H4 type. That suggests the formation of two surface layers on the surface or on the wall of a pore that is much wider than the particle's molecular diameter. This type of isotherm is characteristic of solids formed by micro and mesoporous materials. Therefore,

it appears that the adsorption behaviour of the activated samples is different from that of the non-activated sample, and the activated samples exhibit characteristics of mesoporous materials.

With respect to the impact of KOH in the activation process, the isotherms obtained from the sample with medium KOH concentration displayed greater adsorption-desorption volume compared to the sample with high KOH concentration. On the other hand, the activated sample with low KOH concentration exhibited a lower adsorption-desorption volume. These results align with the data presented in Table (4) for the BET surface area, total pore volume, and average pore diameter.

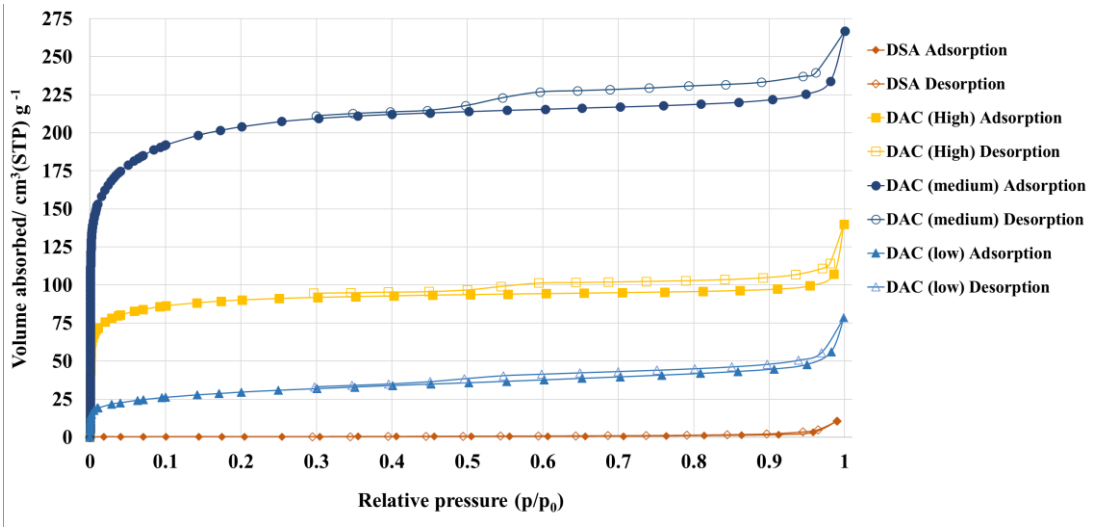

Figure 3. Adsorption-desorption isotherm of de-chroming shaving ash (DSA) and de-chroming activated carbon (DAC) at different activation levels

Preparing basic chromium sulphate

The basicity test result for the prepared basic chromium sulphate was 33%, which indicates that it is suitable for reuse in leather tanning. This finding is also consistent with previous investigations, which reported that basic chromium sulphate with a basicity of 33% can effectively bind to collagen fibres and produce stable leather products [10,18].

CONCLUSION

This study presents a simple and environmentally friendly process for extracting a high percentage of chromium from chrome shaving waste, which promotes sustainability in the leather tanning industry. The process utilizes higher-efficiency chemical and thermal treatments to obtain high-quality activated carbon from chrome shaving waste. The study used an oxidative alkaline extraction method and optimized the chromium extraction process by analysing the effects of various factors such as leaching solution concentration, pyrolysis temperature, and activating chemical agent concentration. The main findings of the study are as follows:

- The optimal CSW: K_2CO_3:H_2O_2:H_2O ratio (w/w) for chromium recovery was 1:0.5:0.2:5, which resulted in a recovery percentage of 95.43%.
- The optimal pyrolysis temperature was 500 °C, which yielded average values for ash (25.94%) and particle diameter (34.40 µm).
- In activation, the ratio of 2:1 (w/w) for ash and potassium hydroxide produced activated carbon with a final yield of 21%, a surface area of 731 m^2/g, a total pore volume of 0.385 cm^3/g, and an average pore diameter of 2.1 nm.
- The extracted chromium can be converted into chromium sulphate through a sugar reduction method for reuse in leather tanning.

Finally, further future studies can be conducted on the leather fibres resulting from this oxidative alkaline de-chroming method, as these fibres come out non-degraded and with a distinctive waxy white appearance. These fibres can be easily separated from the chrome removal solution, offering new possibilities for their utilization.

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