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Recycling tannery solid wastes as an alternative carbon resource for steelmaking: an environmentally sustainable approach

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1. INTRODUCTION

The environment is facing adverse anthropogenic and natural challenges over the past several decades. Anthropogenic pollution is a worldwide problem. Industrial production and post-consumer product wastes are one of the most potentially significant environmental risks (Desenfant et al. 2004).

Tanneries are well-known to have serious negative impacts on the environment and public health. Survival of tanneries has become a great challenge. In tannery, putrescible raw animal hides/skins are converted into imputrescible leather through a series of chemical and mechanical operations which produce significant amounts of solid and liquid wastes as well as gaseous emissions (Covington 2009). It is reported that every ton of raw hides/skins processing converts only 200 kg of raw materials into leather and more than 600 kg is produced as solid wastes (Hashem and Nur-A-Tomal 2017). Globally, every year 6 million tonnes solid waste is generated from leather processing (Masilamani et al. 2017). Moreover, considerable amounts of leather wastes are generated during the manufacturing of leather products. In developing countries like Bangladesh and India, most of the solid wastes are discharged to nearby landfill sites without proper treatment which poses environmental problems (Ravindranath et al. 2015, Ahmed et al. 2017).

To date, several technologies (e.g. biological, chemical, physical, and thermal, etc.) have been developed, but there are still deficiencies in the complete management of the wastes. It is crucial to develop novel environmentally sustainable technologies that would utilise these wastes.

On the other hand, over 70% of total global steel production directly depends on the inputs of coal. Globally, above 1.2 billion tons of coal is used in steelmaking (World Coal Association 2014). As the reserve of fossil fuel coal is limited that may be unavailable soon. Steelmaking industries have encountered supply inadequacies and rising costs (Mayyas et al. 2019). Therefore, exploring alternative carbon resources to replace coal for steelmaking is urgent.

There are some studies in the utilisation of agricultural wastes (Yunos et al 2012, Mayyas et al. 2019) as a source of carbon in steelmaking but the utilisation of solid wastes from tanneries are unprecedented

yet. The tannery solid wastes contain a high content of carbon which could be a potential source of reductant for steelmaking.

The aim of this research is to utilise the solid waste from tanneries as a source of carbon in steel making industries. This research could enable the steel industry to reduce their cost associated with traditional cokes and at the same time utilise tannery solid wastes which are rich in renewable carbon and destined to landfill.

2. EXPERIMENTAL

2.1. Materials

Chromium-containing tannery solid wastes such as shavings, buffing dust and leather cuttings were obtained from a modern tannery at Jessore, Bangladesh. Collected shavings, buffing dust and leather cuttings are illustrated in Fig. 1(a-c). The wastes were sun-dried and cut into small pieces. The collected wastes were analysed for their composition using inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF, Axios, Malvern Panalytical, UK) spectrometry. Thermogravimetric analysis of the collected wastes was also carried out. The thermal behaviour of the samples was characterised by a simultaneous thermal analyser (STA 8000, PerkinElmer, USA) under a nitrogen gas atmosphere (20 mL/min) according to ASTM D3418. The heating and cooling rates in the measurements were 20°C/min. The leather wastes were characterized using Fourier transform infrared coupled with attenuated total reflectance (ATR-FTIR). FTIR spectra of the samples were obtained using a FTIR spectrometer (Spectrum 100, PerkinElmer, USA) equipped with an attenuated total reflectance (ATR) at a resolution of 4 cm-1 and 32 scans were run for every analysis to reduce the noise.

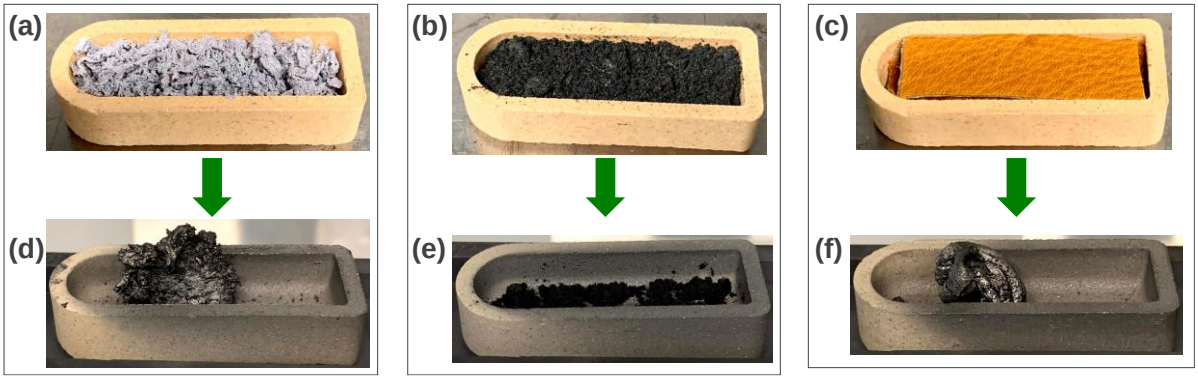


Fig. 1. Raw materials used in the present study: a) shavings, b) buffing dust and c) leather cuttings and prepared char: d) shavings char, e) buffing dust char and f) leather cuttings char.

2.2. Carbon production

Chars (hard carbon) were prepared using a horizontal tube furnace at a temperature of 800ºC. The schematic representation of the horizontal tube furnace experimental setup is illustrated in Fig. 2. Argon

gas (purity 99.99%) was continuously purged through the furnace flowing at a rate of 1L/min to confirm an inert atmosphere. The prepared char from leather wastes were presented in Fig. 1. They were analysed using inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS, PerkinElmer, USA), scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS, S3400 Hitachi, Japan), macro combustion analyser (vario MACRO cube, Elementar, Germany) and ATR-FTIR.

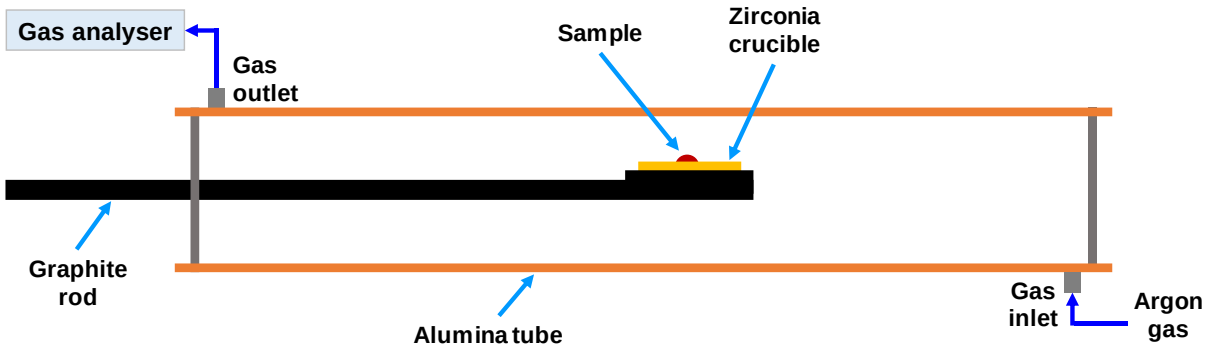


Fig. 2. Schematic diagram of the experimental setup.

2.3. Iron oxide reduction

The prepared chars were used to reduce iron oxide to demonstrate their potentiality in steelmaking as an alternative resource of carbon. The char samples were ground by a hand mortar and pestle to minimize the effect of particle size on experimental results. The char powder then used to make pellets for the reduction of iron oxide. Iron (III) oxide (Fe_2O_3, purity 99%) and char powders were mix-agglomerated (ratio of 3 mol of carbon to 2 mol of Fe_2O_3) with the addition of a little amount of water. The resultant pellets were dried in an oven at 80°C for 24 h.

Iron oxide reduction experiments were performed using a horizontal tube furnace at a temperature of 1550ºC. Argon gas (purity 99.99%) was continuously purged through the furnace flowing at a rate of 1L/min to confirm an inert atmosphere. The off-gas produced from the interaction of iron oxide-rich slag with carbon was monitored using an infrared (IR) gas analyser (AO2000, ABB, Switzerland) for 15 minutes. The microstructure of iron droplets was examined using an optical microscope (Eclipse ME-600, Nikon, Japan). The produced iron metals were subject to elemental analysis using a handheld laser-induced breakdown spectrometer (LIBS, Z-300, SciAps, USA) and SEM-EDS. A mechanical hardness test was carried out in 1HV Vickers measurement according to ASTM E140 using Struers DuraScan-20 (Struers, Denmark).

3. RESULTS AND DISCUSSION

3.1. Characteristics of used leather wastes

Leather waste samples used in the present study were first analysed for elemental composition. The concentration of elements in the samples determined using ICP-OES/MS after acid digestion is shown in Table 1. The leather wastes contain alkali metals (Na and K), alkaline-earth metals (Mg, Ca, Sr and Ba), transition metals (Ti, Cr, Fe, Co, Ni and Cu), other metals (Al, Ga and Pb) and other non-metals (B, P and S). The leather wastes contain a high content of Cr, Na and S.

Table 1. The concentration of elements in the leather wastes and chars prepared from leather wastes determined using inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) followed by acid digestion.

Element	Unit	MDL*	Raw			Char		
			Shavings	Buffing Dust	Leather cuttings	Shavings	Buffing Dust	Leather cuttings
Cr	mg/kg	5.00	18114	25213	8272	59099	138525	27376
Na	mg/kg	50.00	14194	4549	4625	54983	33597	14919
S	mg/kg	50.00	10879	17077	10801	18263	31518	10176
Mg	mg/kg	5.00	958	809	204	1877	4464	542
Si**	mg/kg	0.50	49	1983	750	223	1290	1539
Al	mg/kg	5.00	14.80	3079	39.8	56.2	26590	177
Ca	mg/kg	5.00	686	1252	3766	2512	8646	13383
Fe	mg/kg	5.00	428	530	112	1705	3801	374
B	mg/kg	0.50	258.0	13.6	3.9	754.4	78.6	16.5
K	mg/kg	5.00	137	228	481	456	1242	1503
P	mg/kg	5.00	116	619	211	265	4223	678
Cu	mg/kg	0.50	0.64	65.6	5.9	2.56	394	18.4
Ti	mg/kg	0.50	0.51	56.38	3.65	1.14	87.06	10.64
Ba	mg/kg	0.50	0.43	9.22	27.67	1.16	65.15	103.96
Sr	mg/kg	0.50	5.08	9.25	11.2	19.8	66.8	39.6
Ga	mg/kg	0.50	0.96	2.48	1.81	2.12	13.26	6.35
Ni	mg/kg	0.50	0.97	1.78	1.04	3.00	11.65	4.35
Pb	mg/kg	0.50	0.18	3.45	1.62	35.88	36.37	26.52
Co	mg/kg	0.50	0.19	0.95	0.73	7.2	13.3	27.47

*MDL = measurement detection limit.

** Soluble only, there were insoluble Si in the samples.

The ash analysis of leather waste samples was performed XRF spectroscopy. Table 2 presents the chemical analysis of the ash present in leather wastes. The ash content of shavings, buffing dust and

leather cuttings were 6.6%, 3.5% and 7.92% respectively. The ashes of leather wastes contain a high amount of chromia, sodium oxide and sulphur trioxide. Also, buffing dust contains a high content of silica and aluminium oxide whereas leather cutting also contains a high quantity of lime.

Table 2. Chemical analysis of the ash composition for raw materials used in the present study

Element oxide	Shavings	Buffing dust	Leather cuttings
Cr_2O_3 (%)	37.27	54.46	32.79
Na_2O (%)	27.32	9.14	18.82
SO_3 (%)	15.60	11.28	21.51
SiO_2 (%)	0.58	15.46	3.52
Al_2O_3 (%)	0.10	10.03	0.28
CaO (%)	1.30	2.22	13.31
MgO (%)	2.36	2.25	0.91
Fe_2O_3 (%)	0.71	0.99	0.32
K_2O (%)	2.96	0.40	2.03
P_2O_5 (%)	0.34	1.77	1.24
CuO (%)	<0.01	0.10	0.02
T_iO_2 (%)	<0.01	0.77	<0.01
SrO (%)	0.24	0.43	0.20
NiO (%)	<0.01	<0.01	<0.01
PbO (%)	<0.01	<0.01	<0.01
V_2O_5 (%)	<0.01	0.03	<0.01
Mn_3O_4 (%)	<0.01	<0.01	<0.01
ZnO (%)	<0.01	0.03	<0.01
ZrO_2 (%)	<0.01	0.03	<0.01
BaO (%)	<0.01	0.01	0.07
HfO_2 (%)	<0.01	<0.01	<0.01

FTIR spectroscopy is a rapid analytical technique that is used to identify functional groups present in materials. ATR-FTIR spectra of the leather waste samples are reported in Fig. 3. It can be observed that all the spectra of different leather wastes were nearly identical because leather is made up of collagen which is the major protein that constructs skin (Covington 2009). As shown in Fig. 3, all the samples have a peak at ~3305 cm^{-1} and ~3075 cm^{-1}, which are designated to the stretching vibration of N–H in the protein backbone. Furthermore, all the spectra depict the characteristic peaks of amide bonds, specifically a sharp peak at ~1635cm^{-1} (amide I), a peak at ~1545 cm^{-1} (amide II) and a broad shoulder at ~1030 cm^{-1} (amide III). Also, the peak at ~1450 cm^{-1} attributes to the stretching vibration of C–C

bonds, whereas the cluster of peaks at ~1450, ~1335, ~1235 cm^{-1} (amide III) is the bending vibration of C–H in protein (Vyskočilová, et al. 2019).

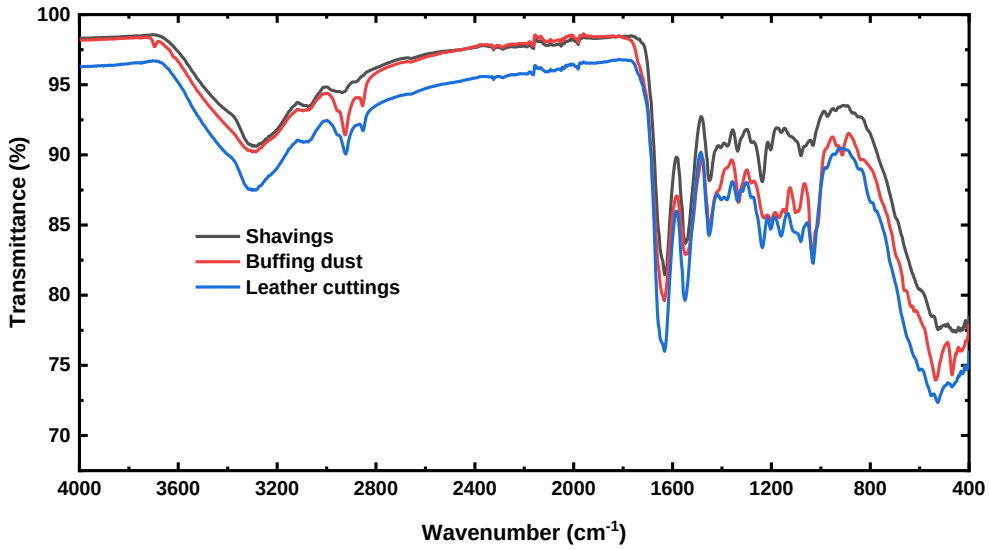


Fig. 3. Fourier transform infrared (FTIR) spectra of raw leather waste samples.

Thermal behaviour of the leather wastes was shown in Fig. 4. It is noticed that there are three degradation steps in the TGA curves of the leather wastes. The first weight loss could be due to the release of absorbed and bound water in the leather wastes, happened at about 150°C. The noticed major mass loss in the temperature range of 250–600°C could be attributed to the decomposition of the collagen. A low weight loss rate was observed from 600 to 800 °C which could be attributed to continuous pyrolysis of stable residues (Liu et al. 2019).

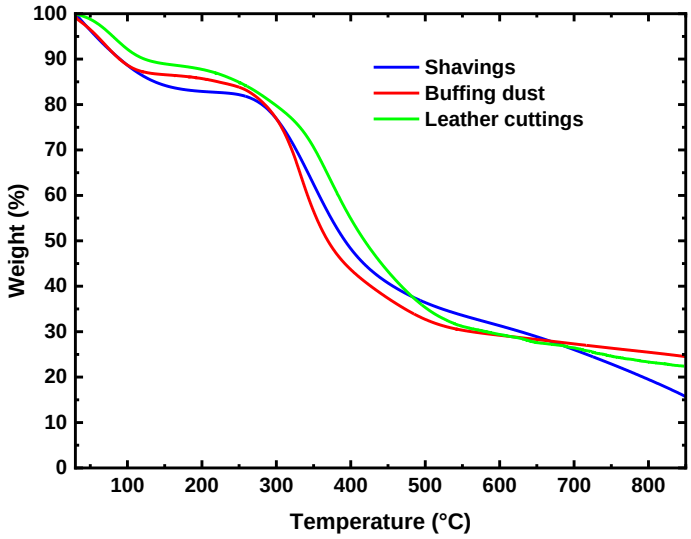


Fig. 4. Thermogravimetry curves of the raw leather waste samples at a nitrogen atmosphere.

3.2. Characteristics of prepared chars

The FTIR spectra of prepared chars from leather wastes are presented in Fig. 5. It can be seen that all the functional groups almost disappeared after charring at 800 °C (Li et al. 2017). The FTIR spectra seem like FTIR spectra of graphite.

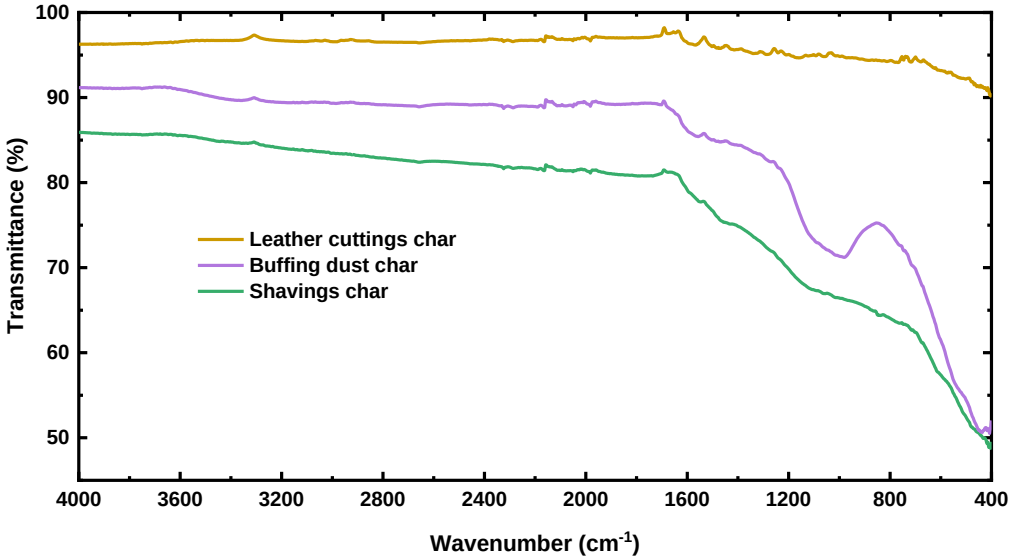


Fig. 5. Fourier transform infrared (FTIR) spectra of produced char samples.

The chemical composition of prepared char from leather wastes is presented in Table 3. The prepared char samples are a good source of carbon, as is evident from results. The carbon content of shavings char, buffing dust char and leather cuttings char were 50.01%, 38.95% and 68.92%, respectively. Additionally, the chars contain a considerable amount of hydrogen which could also aid the reduction of iron oxide.

Table 3. Chemical composition of prepared char from leather wastes

Element	Shavings char	Buffing dust char	Leather cuttings char
Carbon (%)	50.01	38.95	68.92
Nitrogen (%)	11.40	7.09	7.54
Hydrogen (%)	2.52	1.14	2.42
Sulphur (%)	1.88	2.70	1.21

The char samples also analysed using ICP-OES/MS for their elemental composition. The concentration of elements in the samples is reported in Table 1. It is noticed that the char samples contain similar elements as raw leather wastes.

SEM/EDS images of resultant chars were provided in Fig. 6. The morphology of char samples showed a three-dimensional structure with macropores. Pore formation could be attributed to the gases evolved from thermal transformation during the charring process. The elemental mapping indicates the distribution of C, Cr, Cl, O, Na and S throughout the samples.

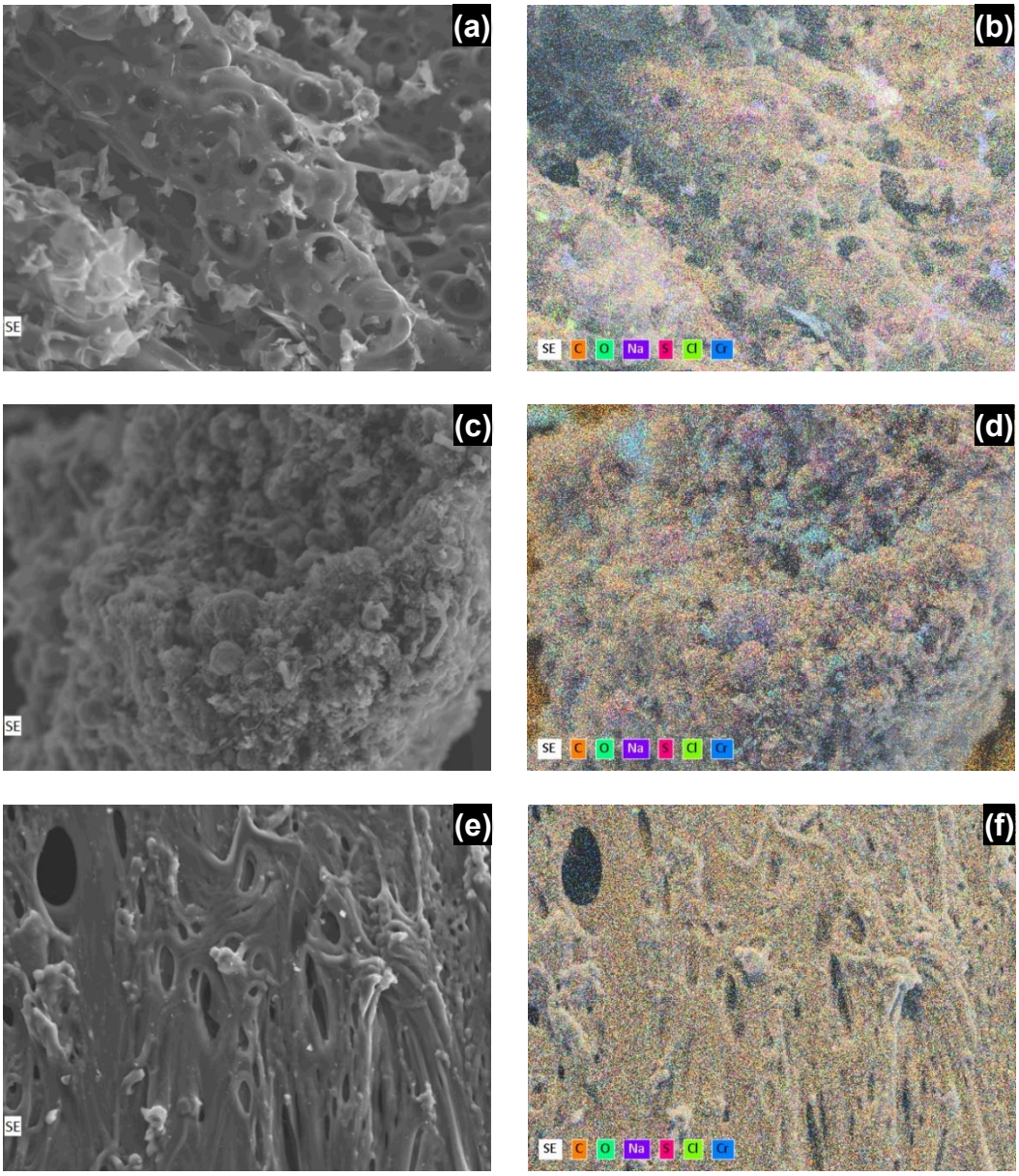


Fig. 6. Scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS) of (a and b) shavings char, (c and d) buffing dust char and (e and f) leather cuttings char at 500× magnification.

3.3. Iron oxide reduction using prepared chars

To evaluate the performance of the prepared char from leather wastes as an iron oxide reductant, pellets of iron (III) oxide and char were made and heat-treated at 1550°C. At this high temperature, the initial gas-phase reactions occur rapidly and the gases released are supposed to take part in the subsequent slag reactions which resulted in pure iron (Fe) metal (Yunos et al 2012). The gases evolved during the reduction process were recorded using gas analyser and is reported in Fig. 7. It was noticed that carbon monoxide (CO) was the major gaseous product, followed by methane (CH_4) and carbon dioxide (CO_2).

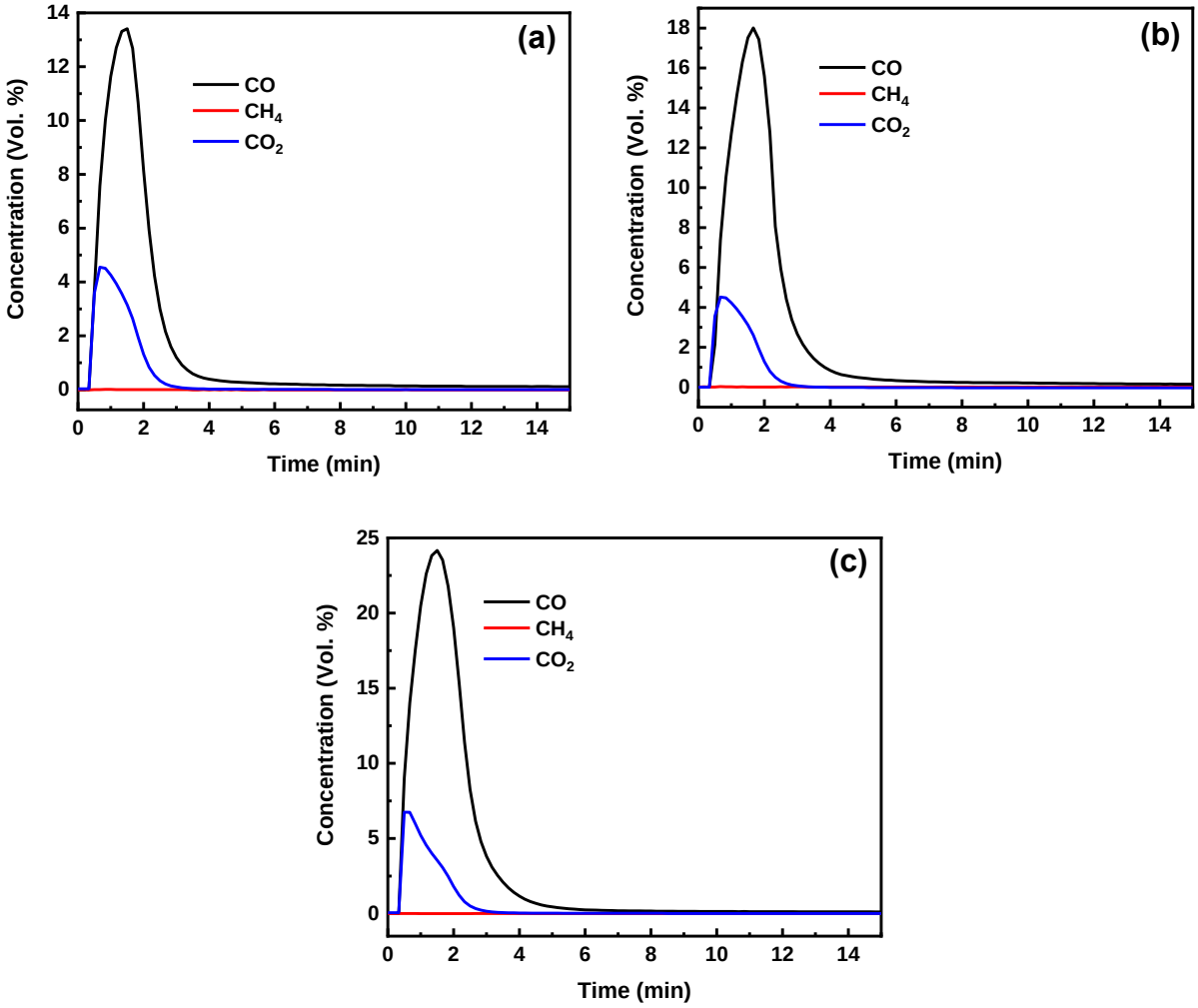


Fig. 7. The gas generated from the reduction of iron (III) oxide using a) shavings char, b) buffing dust char and c) leather cuttings char.

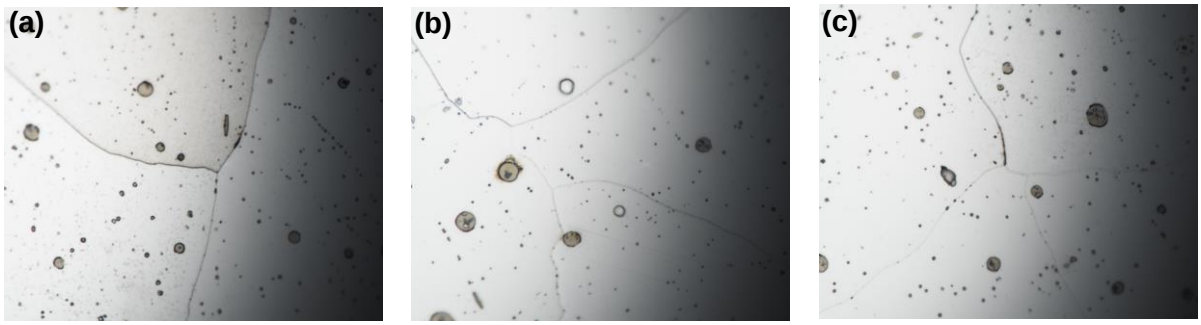


Fig. 8. Optical microscope images (at 100× magnification) of the produced iron metals using a) shavings char, b) buffing dust char and c) leather cuttings char.

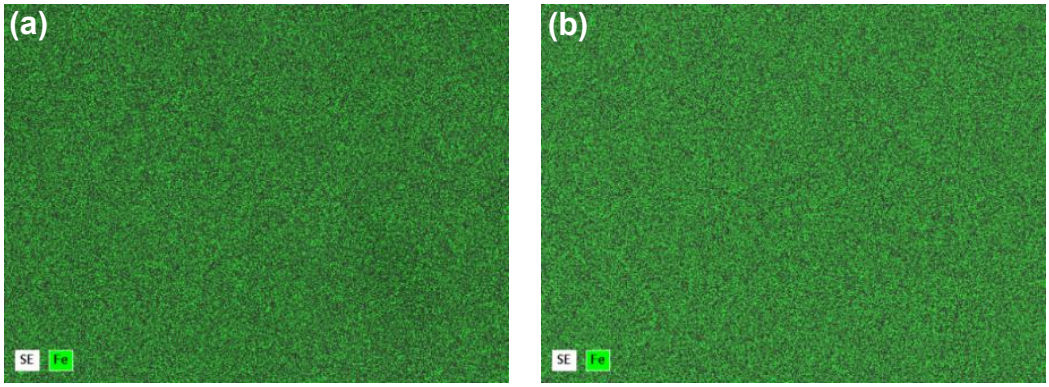
The pure iron metals produce from produced from the reduction of Fe_2O_3 and prepared chars from leather wastes mounted in resin, grinded, polished and etched to observe its microstructure. The optical microscope images of the produced iron metals are inserted in Fig. 8. The images show the

microstructure of typical low-carbon steel displaying a matrix of ferrite grains (white etching part) and pearlite (dark etching part).

Table 4. Elemental analysis of pure iron metal produced from the reduction of iron (III) oxide and prepared chars from leather wastes using laser-induced breakdown spectroscopy (LIBS).

Element	Iron metals produced using		
	Shavings char	Buffing dust char	Leather cuttings char
Fe (%)	99.7 ± 0.06	99.7 ± 0.049	99.7 ± 0.043
C (%)	0.047 ± 0.02	0.031 ± 0.012	0.025 ± 0.01
Cr (%)	0.116 ± 0.009	0.115 ± 0.116	0.024 ± 0.003
Mn (%)	0.106 ± 0.015	0.101 ± 0.012	0.122 ± 0.008
Mo (%)	0.017 ± 0.007	<0.013	0.026 ± 0.01
V (%)	0.034 ± 0.007	0.022 ± 0.005	0.018 ± 0.003
Al (%)	0.011 ± 0.004	<0.002	<0.002
Cu (%)	< 0.004	0.017 ± 0.003	0.039 ± 0.005
Si (%)	< 0.011	<0.010	<0.013
Nb (%)	< 0.004	<0.005	<0.004
Ni (%)	< 0.011	<0.009	< 0.007
Pb (%)	<0.003	<0.003	<0.002
Ti (%)	< 0.001	<0.0006	<0.0005

The produced iron metals were subject to elemental analyses. The results of laser-induced breakdown spectroscopy (LIBS) analyses are summarized in Table 4. The results imply that about 99.7% of the metal products was Fe using all the three chars. The metal droplets also contain a low content of C, Cr and Mn. The SEM/EDS analysis (shown in Fig. 9) also showed similar results, indicating a complete reduction of Fe_2O_3 to metallic iron.



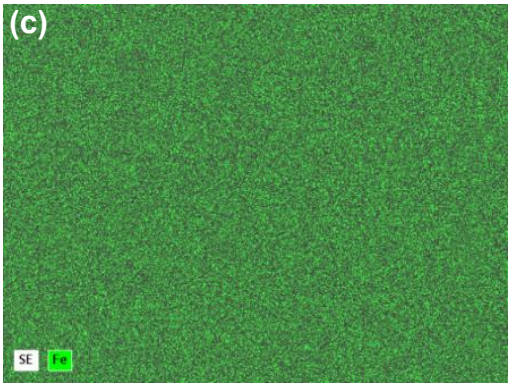


Fig. 9. Scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS) elemental mapping of produced iron metals using a) shavings char, b) buffing dust char and c) leather cuttings char at 10000× magnification.

Vickers hardness test was performed to measure the hardness of the produced iron metal. The results of hardness test are inserted in Fig. 10. Hardness value of produced iron metals using shavings char, buffing dust char and leather cuttings char was126.33 ± 1.53, 113.33 ± 3.21, 136.67 ± 2.08, respectively.

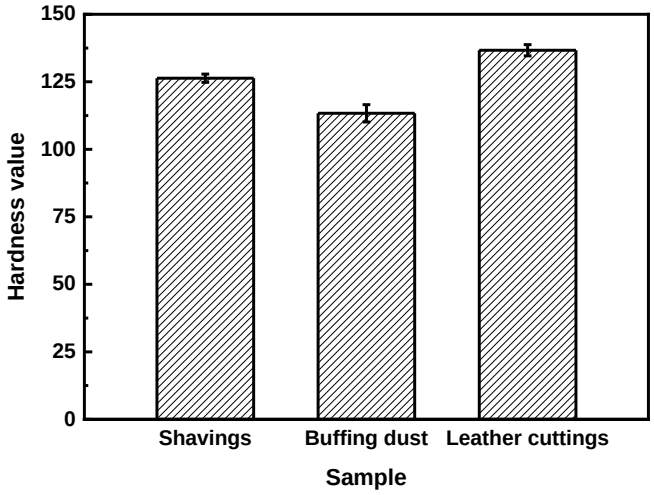


Fig. 10. Hardness values of iron metals produced using leather waste char.

The findings of LIBS, SEM/EDS and hardness analyses indicate that the char derived from tannery solid wastes could be an excellent reductant for steelmaking.

4. CONCLUSION

This study evaluated the possibility of using chromium-containing tannery solid wastes such as shavings, buffing dust and leather cuttings as a source of carbon in the steelmaking process. Thermal treatment in an argon atmosphere was employed to obtain char (hard carbon) from leather wastes. The properties of prepared chars were studied. The carbon content of shavings char, buffing dust char and leather cuttings char were 50.01%, 38.95% and 68.92%, respectively. After that, the prepared chars and

Fe_2O_3 powder were mixed and pelletised with the addition of a little amount of water to demonstrate the reduction performance of the chars. The produced iron metals from reduction reactions were characterized. The derived chars showed an excellent reduction, carburizing, and slag foaming performance. About 99.7% of the metal products was Fe using all the three chars. The obtained results suggest that chars produced from the solid wastes could be used to replace the traditional coke in steelmaking. This research can open a new path to utilising the locally source waste as input materials instead of non-renewable and expensive materials. On the other hand, it could reduce the negative effect of solid wastes from tanneries on the environment by utilising them as removable carbon source.

5. SUGGESTION FOR FUTURE WORK

This study has opened a new path to utilise solid wastes from tanneries in steelmaking. Further comprehensive research could be conducted to improve the performance of the proposed process. In addition, the process could be commercially implemented.

ACKNOWLEDGEMENT

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7 April 2020

To Whom It May Concern:

Re: **Recycling tannery solid wastes as an alternative carbon resource for steelmaking: an environmentally sustainable approach**

The aim of this project, conducted by Md. Shahruk Nur-A-Tomal, was to utilise solid wastes from tanneries as a source of carbon in steelmaking. Tannery solid wastes are rich in renewable carbon and destined to landfill without proper treatment which poses environmental problems. There are some studies in the utilisation of agricultural wastes as a carbon resource for steel industries but the utilisation of solid wastes from tanneries is unprecedented yet.

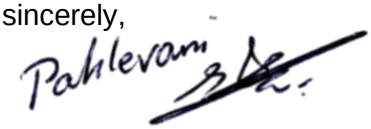
In the present study, three kinds of chromium-containing solid wastes such as shavings, buffing dust and leather cuttings were collected, sun-dried and cut into small pieces. The collected leather wastes were subject to thermal treatment at 800ºC in an argon atmosphere to prepare solid carbon. After removing the volatiles from these wastes, the remaining solid carbon content of the shavings, buffing dust and leather cuttings after heat treatment at 800 ºC was 50.01%, 38.95% and 68.92%, respectively.

These solid carbons have been used in lab scale facilities as the reducing agent for iron oxide reduction instead of conventional coke in ironmaking process. For this reason, they have been mixed with iron (III) oxide and heat-treated at 1550°C in an argon atmosphere. The chars exhibited an excellent reduction and carburizing performance. The optical microscopy images of the resultant iron metals show the microstructure of typical low-carbon steel displaying a matrix of ferrite grains and pearlite. Produced steel as the result of this process has been characterised using different technique.

The outcomes of the research suggest that the chars produced from tannery solid wastes could be recycled to replace the traditional coke in steelmaking. Thus, this research could reduce the negative effect of solid wastes from tanneries on the environment by utilising them and at the same time enable the steel industries to reduce their cost associated with traditional cokes.

We would like to thank IULTCS/IUR for the grant and their visionary approach in supporting this research.

Yours sincerely,



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