Detection of hazardous pollutants in chrome-tanned leather using locally developed laser-induced breakdown spectrometer

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Abstract Highly toxic contaminants like Cr, As, and Pb were detected in chrome-tanning process of animal skin to produce leather by applying locally developed laser-induced breakdown spectrometer. An Nd–YAG laser with 1,064 nm wavelength was focused on the surface of leather samples (natural and manufactured) to generate a plasma spark and spectrally resolved spectra were used for identification and quantification of contaminants. The leather samples were collected from a tannery located in industrial cities of Riyadh and Jeddah, Saudi Arabia. The study was carried out on fully, half manufactured (wet blue leather), and natural hide (skin). To the best of our knowledge, this is the first attempt where laser-induced breakdown spectroscopy (LIBS) technique has been applied for the analysis of leather before and after tanning process. The maximum concentration of different elements of environmental significance like chromium, lead, arsenic, sulfur, magnesium were 199, 289, 31, 38, and 39 ppm, respectively, in one of the manufactured leather samples. The limit of detection (LOD) of our LIBS system for chromium, lead, arsenic, sulfur, and magnesium were 2, 3, 1.5, 7, and 3 ppm, respectively. The safe permissible limit for tanned leather for highly toxic elements like chromium, lead, and arsenic are 1, 0.5, 0.01 ppm, respectively, as prescribed in Environmental Regulation Standards for Saudi Industries set by Royal Commission Jubail, Saudi Arabia. The LIBS technique is superior to other conventional techniques like ICP or atomic absorption that a little or no sample preparation is required, no chemicals are needed, multi-elemental analysis is possible for all kinds of samples (natural and anthropogenic materials), microgram of sample is essential, and LIBS could be applied for remote analysis. It is highly selective and sensitivity higher than ICP, and as no sample and chemicals are required, it is cost effective for multi-sample analysis per unit time as compared with other conventional techniques. The concentration of some toxic elements (Cr, Pb, As) is much higher than the safe permissible limits set by Occupational Safety and Health Administration in USA or Saudi environmental regulatory agencies. Results obtained with our LIBS systems were in close agreement with the results obtained.
using other standard analytical technique such as the inductively coupled plasma atomic emission spectroscopy.

Keywords Laser-induced breakdown spectroscopy · Chromium · Lead · Arsenic · Toxic elements detection

Introduction

Leather processing is one of the earliest industrial activities carried out by humans due to protection of their feet form harsh environment. Around 3000 a.d., ancient Egyptians were the first who were applying mineral tanning for leather processing. There are different methods of leather tanning (Josep et al. 2008; Agrawal et al. 2008). One of the effective and widely used methods is chrome tanning which was developed in the USA by Augustus Schultz in 1884. The main problem in this method is the huge amount of pollutants of waste water posing great threat to the clean environment (Wenjie et al. 2008; Amoozegar et al. 2007). In addition, it adds hazardous pollutants to the leather which is produced. The hazards effect of leather chrome-tanned shoes allergy inflammation on foot and other organs that contained contaminated leather chrome-tanned causes dermatitis. The studies using conventional analytical methods have revealed that exposure to such processed leather could expose to both Cr (III) and Cr (VI). It has been reported that Cr plays an important role in chromium allergy, because Cr is capable of eliciting eczema at low concentrations (Süreyya et al. 2005; Loveren et al. 2008). Although Cr is natural and essential for human and shortage may cause heart conditions, disruptions of metabolisms, and diabetes, its uptake caused dangerous defects like alteration of genetic material skin rashes and many kinds of other allergies. The toxic effect of arsenic is that it can cause skin disturbances, declined resistance to infections, heart disruptions, and brain damage for both men and women. Finally, inorganic arsenic can damage even DNA structure. A lethal dose of arsenic oxide, such as 100 mg if accumulated in kidneys, could damage the filtering mechanism of human body. This causes the excretion of essential proteins and sugars from the body which could cause further damage to kidney.

Previous studies demonstrated that chromium, arsenic, and lead were most abundant in the wastewater generated by a tannery (Wenjie et al. 2008; Amoozegar et al. 2007). Very little work has been reported on detection of these hazardous pollutants in the leather samples using laser-induced breakdown spectroscopy (LIBS) (Jerschow et al. 2001; Gondal et al. 2007a, b; Gondal and Hussain 2007; Gondal and Siddiqui 2007; Hussain and Gondal 2008; Siddiqui et al. 2008; Laserna 2005; Ferrero and Laserna 2008; Wu et al. 2007; Giacomo et al. 2007; Seong et al. 2008; Shuya and Kazuaki 2007; Shaikh et al. 2007), and this work is of its first kind on detection of various poisonous elements which exist in the full, half (wet blue), and natural hide/skin of animals. The basic principal of LIBS is based on the spectral analysis of radiation emitted from a plasma generated by focusing a high power pulsed laser beam on to the surface of the test sample. The characteristic emission from plasma provides information about the elements present in the target material. The unique features of LIBS (Jerschow et al. 2001; Gondal et al. 2007a, b; Gondal and Hussain 2007; Gondal and Siddiqui 2007; Hussain and Gondal 2008; Siddiqui et al. 2008; Laserna 2005; Ferrero and Laserna 2008; Wu 2007; Giacomo et al. 2007; Seong et al. 2008; Shuya and Kazuaki 2007; Shaikh et al. 2007) technique are that it requires no sample preparation and is capable of remote and in situ analysis of materials in any phase (solid, liquid, or gas). This is in contrast with conventional analytical techniques that require time-consuming sample preparation and can be employed only in well-equipped laboratory. Laser-produced plasma of solid and liquid materials are also of great interest, especially for laser diagnostic, thin film growth, and trace elemental analysis.

This study was carried out on fully manufactured, half manufactured (wet blue leather) and natural hide (skin) to detect hazardous elements like Cr, As, and Pb. LIBS results were compared with the results obtained using other analytical techniques such as the inductively coupled plasma atomic emission spectroscopy (ICP-AES).