

Research Article

Spectrochemical Analysis of Soil around Leather Tanning Industry Using Laser Induced Breakdown Spectroscopy

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We report the use of laser induced breakdown spectroscopy (LIBS) to determine the chromium contamination of soil due to effluents from leather tanning industry in Kasur District of Punjab ($+31^{\circ}6'23.21''$, $+74^{\circ}27'16.29''$) in Pakistan. Calibration curves were constructed by indigenously prepared standard sample and fitting of curves by linear regression. The limit of detection (LOD) was found to be 23.71 mg kg^{-1} . It has been found that the concentration of chromium in the soil is up to 839 mg kg^{-1} in vicinity of effluent drain and 1829 mg kg^{-1} in the area of old stagnant pool, which is much higher than the safe limits. Qualitative detection of other elements like Na, Cl, Fe, P, and Si was done from LIBS spectra. The leaching of soil contaminants due to seepage of industrial effluents from deteriorating brick lined drains in horizontal direction has also been observed.

1. Introduction

Management of industrial waste is a major concern especially in the developing countries. Due to rapid growth of industry, a huge amount of industrial waste is being dumped in the soil surface resulting in ecodamaging effects. Due to ignorance about environmental hazards, high cost of treatment plants, and lack of effective enforcement of environmental control laws, very little attention is being given to proper disposal of industrial waste [1]. Throwing waste water and dumping solid waste are causing serious health and environmental problems.

In the developing countries like Pakistan, very little work has been done for effective environmental monitoring methods despite the urgency of the matter. There have been very few reports in the literature about the environmental studies in the region. Mubin et al. [2] analyzed ten main industries of Karachi (Pakistan) and found that the leather industry was the major contributor towards damaging the environment

due to toxicity in untreated industrial waste water. Forcing this industry to have treatment plants could reduce problem up to 25% associated with industrial effluents.

The industrial waste contains large amount of contaminants like heavy metal which may enter into the food chain through vegetation in dumping areas and the areas being irrigated by the untreated/semitreated waste water from the industry [3]. It was found that vegetation grown with waste water from industry contained high concentration of heavy metals like Pd, Fe, Cu, Zn, and Cr [4]. Chromium is a pollutant that is being disposed due to several industrial processes like chromium plating, stainless steel manufacturing, wood treatment, paint industry, and tanning industry. The chromium containing effluents from tannery industry may cause serious environmental problems. US Environmental Protection Agency has designated chromium (Cr) as priority pollutant due to its adverse effects on human health [5]. Although Cr III is essential dietary mineral [6] but Cr VI is toxic form of the element mostly found in the compound

form made artificially for the use in different industries. The exposure to hexavalent chromium can cause adverse effects to warm blooded organisms [7]. Occupational Safety and Health Administration (OSHA) [8] has reported lung cancer, irritation or damaged nose, throat, and respiratory tract due to breathing in chromium polluted environmental condition, and eyes and skin rash may be the result of direct contact of chromium. The maximum dose limit set at work place for eight hours is $5 \mu\text{g m}^{-3}$ in air, in the form of dust or particles. Cr VI depresses the biological activity and the enzymatic activity of microorganisms by modifying their living environment [9]. The soil dying out by the tanning industrial waste can contain chromium concentration much higher than safe limits set by US Environmental Protection Agency.

Malek et al. [10] studied different mechanisms for removal of Cr from solid leather industrial waste for its reuse and reported 95% extraction capability. Irfan et al. [11] studied the removal of Cr from wastewater using *Thespesia populenea* with changing environmental conditions of pH, biomass dose, biomass particle size, and agitation time. The rampant discharge of untreated water from tanning industry is increasing level of chromium in soil. This causes perforation and bronchogenic carcinoma to continuously exposed humans. Chicken feeds prepared from chromium containing proteins rich tanneries solid wastes are likely to cause direct chromium entry into food chain [12]. Inclusion of chromium in the environment due to industrial activities demands a technique that can be used to monitor continuously the industrial effluents and waste *in situ* and in lab. Laser induced breakdown spectroscopy (LIBS) is atomic emission spectroscopic technique in which a laser beam is focused on the target material by a focusing lens which ablates some material (hundreds of nanogram to few microgram) from the target surface, producing microplasma which gives characteristic emission of sample on cooling [13]. The emitted radiations are analyzed by spectrometer for elemental detection. Due to simple arrangement, almost no sample preparation, rapid analysis, and capability of analyzing all states of matter (solid, liquid, or gaseous) LIBS technique is finding its niche among the modern spectroscopic techniques rapidly. The emission spectrum can be used both for qualitative and quantitative analysis [14]. N. K. Rai and A. K. Rai [15] studied Cr concentration in liquids effluents from chromium electroplating industry using LIBS.

LIBS is one of those spectroscopic techniques that are considered to have the capability of determining elements down trace level [12, 13]. It is nondestructive and is ideal for the analysis of multielements simultaneously without much sample preparation. With the help of fiber optics LIBS can be used to study hazardous environments from where carrying sample to laboratory is difficult, and remote analysis is possible as only optical access is required [13]. The technique can be used both for metallic and nonmetallic analytes with low limit of detection [16]. The specific objectives of these investigations include how LIBS can be used for analytical analysis of samples rapidly and without involving much sample preparation and how it can be used as *in situ* and online analytical technique.

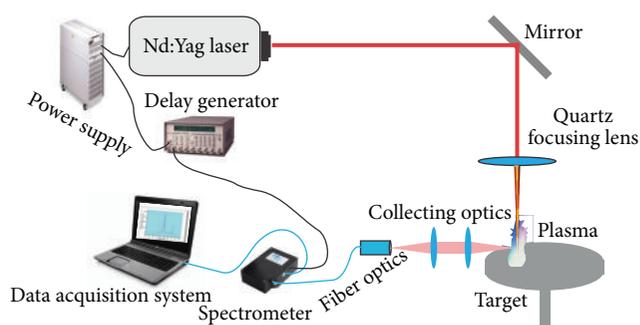


FIGURE 1: Experimental setup.

2. Materials and Methods

The experimental setup for the analysis of soil sample by LIBS is shown in Figure 1. A short pulsed (5 ns) Q-switched Nd:Yag laser operating at the fundamental mode (1064 nm) having 10 Hz repetition rate was used. A quartz biconvex lens of focal length 10 cm was used for focusing the laser beam on pelletized sample. The sample was mounted on a rotating stage, rotating at 12 RPM, to provide a fresh surface for each of the incident laser pulse. The light emitted by the hot plasma was fed to symmetrical Czerny-Turner design spectrometer (Avantes; AvaSpec-3648 USB 2 Dual channel) through collecting optics including collecting lens and fiber optics. It covers the spectrum range from 300 nm to 750 nm with optical resolution of 0.07 nm. Spectrometer is connected to a computer for storing acquired data and to a digital delay generator (DG 535 of Stanford Research System) for triggering it at a specified delay after laser pulse to start acquisition of data. The Avaspec-3648 spectrometer was operated by using Avasoft software to record spectrum. The data was analyzed by graphing software Origin. Peaks were identified and compared with NIST (National Institute of Standard and Technology) atomic spectrum database (http://physics.nist.gov/PhysRefData/ASD/lines_form.html) to identify elemental composition of the sample [17].

Samples of soil were collected from industrial area of Kasur, a district of Punjab Pakistan (Google maps shown in Figure 2). Twenty-four samples were collected from different locations (around $+31^{\circ}6'23.21''$, $+74^{\circ}27'16.29''$). First set of six samples was collected in the vicinity of discharge; the other three sets of samples, each set of six samples, were collected from 20 meter, 50 m, and 200 m from main drain. Most of the industry located there is tanning industry where raw hides are processed to finished leather. UNDP initiated Kasur Tanneries Pollution Control Project in collaboration with federal government of the Pakistan, Provincial government of the Punjab and local tannery operators. Due to these facilities stagnant pools have been vanished in the locality reducing hazardous materials in the surrounding.

Each sample was packed in polythene bags. Samples were dried at 60°C for 6 hour in oven (Shell Down Manufacturing Inc., Portland, Oregon). The samples were grinded in agate mortar and pestle and then pellets were made of each sample at 4000 bar for 5 minutes by adding polyvinyl alcohol (PVA).

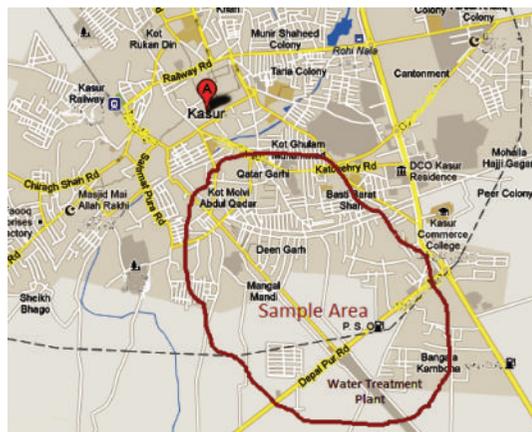


FIGURE 2: Sampling area near Kasur district of Punjab, Pakistan.

3. Results and Discussion

3.1. Calibration Curve. Instrumental calibration is an essential stage for quantitative analysis. It gives the relationship between response of the instrument (integrated intensity in arb. units) and analyte concentration (in mg kg^{-1}). We use five indigenously prepared standard samples by mixing well grinded and sieved known ratio of potassium chromate (K_2CrO_4 > 99% pure and 194.19 molecular weight, supplied by Santa Cruz Biotechnology, Inc.) and standard soil (chromium-free soil) obtained from Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad. The standard soil was also confirmed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) for absence of chromium. We started with mixing of 1.865 g (measured by scale model ATY224, from Shimadzu Corporation having readability of 0.1 mg) of K_2CrO_4 in 1000 g of clean soil to get standard sample containing Cr 500 mg kg^{-1} . The whole sample was mixed thoroughly until a homogenized sample was obtained then 100 g of sample was taken out of the homogenized sample for analysis. After that 1.685 g of powdered salt was added more to the remaining mixed sample to get standard containing Cr 1000 mg kg^{-1} . In this way, we prepared five standard samples each of 100 g. Three representative pellets from each sample were made to get average of spectra (chromium line 427.48 nm), for each standard sample. Calibration curve (shown in Figure 3) was constructed between Cr concentration and integrated intensity of the signal for 427.48 nm avoiding self-absorption and broadening effects which may rise in case of considering peak intensity for quantitative analysis. The linear regression coefficient also called coefficient of determination, $R^2 = 0.9789$, showed the good linear relationship between concentration and integrated intensity.

The analysis of variance (ANOVA) table was constructed for this linear regression model given in Table 1 to further check the statistical dependence of concentration of analyte on integrated intensity.

The small P -value in the ANOVA table shows that results have not happened by chance, but y (integrated intensity)

TABLE 1: ANOVA table for Cr calibration curve.

Item	Degrees of freedom	Sum of squares	Mean square	F statistic	P value
Model	1	556960	556960	186.79068	8.4×10^{-4}
Error	3	8945.2	2981.73333		
Total	4	565905.2			

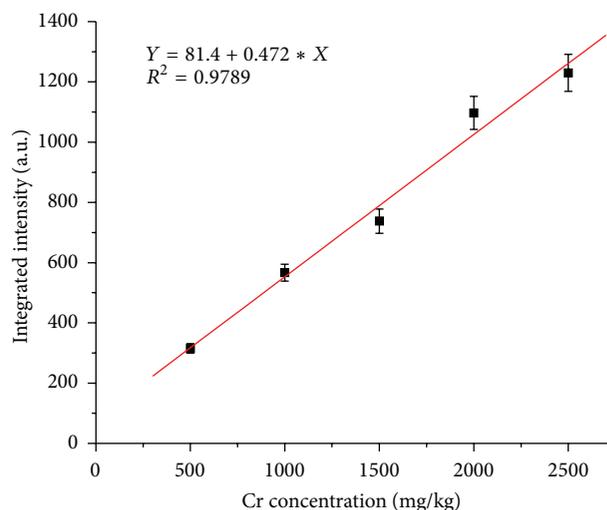


FIGURE 3: Calibration curve for Cr in soil.

and x (analyte concentration) parameters are strongly inter-related.

The limit of detection [18] for Cr was found by using the following:

$$\text{LOD} = \frac{\sqrt[3]{S^2 + S_a^2 + (a/b)^2 * S_b^2}}{b}, \quad (1)$$

where S is the standard deviation of calibration data, a is the intercept of the calibration curve at zero analyte concentration, S_a is the error in the intercept, and S_b is the indetermination on the slope of the calibration curve. The value of LOD was found 23.71 mg kg^{-1} well below the detected values in the region.

The LIBS spectrum of chromium-free soil sample is shown in Figure 4(a). In Figure 4(b) emission lines of iron (35.465 nm), chromium (427.48 nm), phosphorus (519.141 nm), sodium (588.97 nm), chlorine (499.57 nm), and so forth were identified in the spectrum. Chromium (Cr) is found in tanning industry effluents due to the use of chrome alum and chromium(III) sulphate in chrome tanning of leather. Due to its solubility it is mixed with waste water and is flushed out mostly without any effort of chrome recovery.

The concentration of the Cr in the soil samples was calculated in the area using calibration curve, and it was found that the concentration of Cr varies randomly from the minimum value of 128 mg kg^{-1} to the maximum value of 1829 mg kg^{-1} with mean value of 468 mg kg^{-1} . The range of concentration is 1701 mg kg^{-1} , and standard deviation in the concentration in samples is $371.44 \text{ mg kg}^{-1}$. The value of

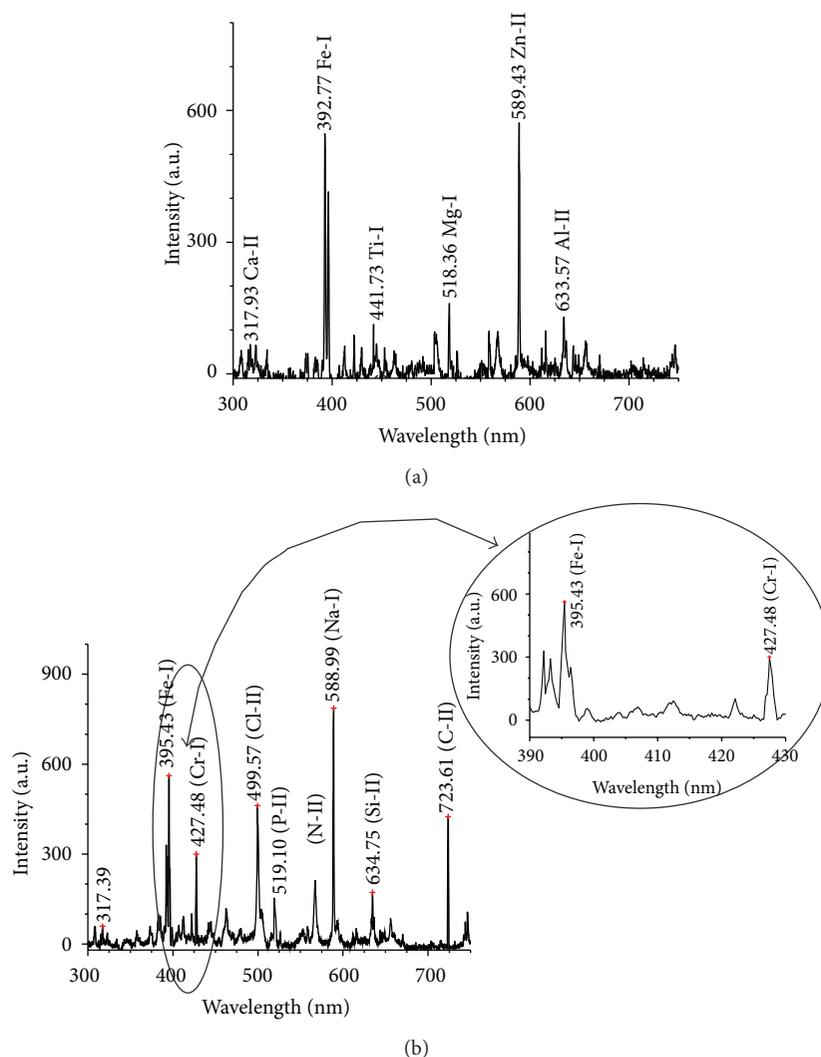


FIGURE 4: (a) Spectrum of unpolluted soil from soil sciences department (UAF). (b) Spectrum of polluted soil from sampling area.

Cr concentration near the effluent drain was found to be 839 mg kg^{-1} maximum, but at the location of old stagnant pool concentration of the Cr is very high up to 1829 mg kg^{-1} . The random distribution of Cr (shown in Figure 5) in soil in the area is due to unplanned distribution of the tanneries in the area and due to deteriorating uneven construction conditions and broken brick lining of the drains and texture of the soil causing seepage of polluted water.

The elements which can be detected in the sample along with their possible transitions are given in Table 2. The observed difference is within the narrow bandwidth of the spectrometer.

The elements sodium and chlorine were found in the soil around the tanneries because sodium chloride (NaCl) is used in large quantity for skin preservation or the pickling process of leather. Since it is highly soluble and stable so effluent treatment does not much reduce its concentration, and it remains in the effluent from which it is leached into the soil to a reasonable distance. Increased salt concentration in the water is becoming a serious issue to the environment.

Chlorides have adverse effects to the growth of plants, bacteria, and fish in surface water. When this saline water is used for irrigation purpose soil salinity increases and crop yield decreases. Calcium level in soil has high concentration of sodium which may reduce plant growth [19]. This type of soil is called sodic soil. The plants ability of water extraction from saline soil is also reduced.

4. Conclusion

Laser induced breakdown spectroscopy can be used as qualitative and quantitative analytical technique with very low limit of detection (in our study it was found to be 23.71 mg kg^{-1}). The study depicted the high concentration of Cr in the soil which in turn can be uptaken by plants and food crops in the area and ultimately can be introduced in the food chain. It has been observed that in the presence of organic acids (citric and oxalic) uptake of Cr may increase and can be toxic for the community. The salinity of the soil is also increasing due to dissolved salts in the effluents causing

TABLE 2: Important elements found in different samples with their possible transitions.

Element symbol	Wavelength (NIST) (nm)	Wavelength observed (nm)	Difference (nm)	Configuration	
Fe I	395.465	395.43	0.035	$3p^6 4f$	— $3p^6 6f$
Cr I	462.6174	462.61	0.0074	$3d^4 4s^2$	— $3d^4(^5D)4s4p(^3P^o)$
Cl II	499.5473	499.57	0.0227	$3s^2 3p^3(^2D^o)3d$	— $3s^2 3p^3(^2D^o)4p$
P II	519.141	519.10	0.041	$3s^2 3p^4s$	— $3s^2 3p^4p$
N II	567.4	567.38	0.020	$2s^2 2p^3p$	— $2s^2 2p^3d$
Na I	588.9950943	588.97	0.025094	$2p^6 3s$	— $2p^6 3p$
Si II	634.71	634.75	0.040	$1s^2 2p^4p$	— $1s^2 2p^4d$

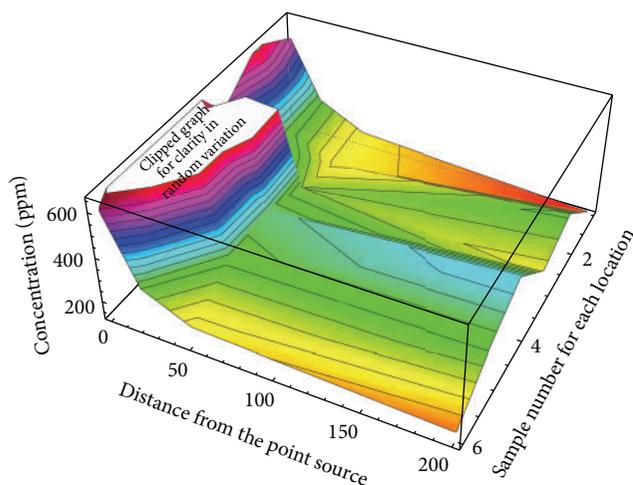


FIGURE 5: Variation of Cr concentration with distance for different samples.

low yield of crop in those areas. The soil remediation process is needed to avoid hazards of heavy metal pollution. LIBS can be used for online monitoring of the waste treatment facilities effectively and soil remediation processes due to its rapid and multielemental analysis capabilities.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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