Short communication

LIBS—An efficient approach for the determination of Cr in industrial wastewater

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Abstract

In the present paper, LIB spectra of different water samples having varying concentration of Cr (certified reference material, CRM) have been recorded by using liquid jet (fabricated in our laboratory) configuration. Calibration curves for different atomic lines of Cr are compared and it is found that calibration curve for Cr II (283.5 nm) atomic line is the best in terms of the Limit of detection (LOD) which is found to be 30 ppm. This calibration curve has been used for quantification of Cr in wastewater collected from Cr-electroplating industry where the concentration of Cr is found to be 1500 ppm. Its removal can be planned by biological system, which is in progress.
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1. Introduction

An unfortunate consequence of industrialization and industrial production is the generation and release of toxic waste which pollute our environment. The electroplating industry is one of major contributors for polluting the water and soil with poisonous elements like Pb, Cr, Cd, etc. The waste water from different type of electroplating industries such as Ni-electroplating, Cr-electroplating, Cu-electroplating, etc. were found very rich in the corresponding elements. Thus, the environmental challenges for the electroplating industry are associated with wastewater generation contaminated with toxic metals such as Ni, Cr, etc. and hence there is a great demand for the development of an analytical tool which could determine the heavy metal content in waste water accurately and rapidly, without any sample preparation. Also, the removal of such hazardous metal from wastewater is vital to make it eco-friendly.

In recent years, laser-induced breakdown spectroscopy (LIBS) is emerging as an important tool for the monitoring of trace pollutants in environment (liquid, soil, etc.) [1,2]. The principle of LIBS is based on the spectral analysis of radiation emanating from micro-plasma generated by focusing a high power pulsed laser beam on to surface of the sample. The characteristic emission from plasma provides fingerprint of constituents of target material. LIBS technique is unique in the sense that it requires no sample preparation and its capability of remote and in situ analysis of material in any phase (solid, liquid or gas) [3–8]. This is in sharp contrast with conventional analytical techniques that require time consuming sample preparation and can be employed only in laboratory. Laser produced plasma of solid and liquid materials are also of much interest, especially in the field of laser diagnostic, thin film growth, and trace element analysis [9–12].

The present work is motivated by the need for reliable Cr monitoring during the treatment of wastewater from different industries. A home made liquid jet has been chosen to record laser-induced breakdown (LIB) spectra with greater sensitivity. Calibration curves have been drawn for different Cr lines, by recording the LIB spectra of water with varying concentration of Cr and the best calibration curve has been used for quantification of Cr present in wastewater collected from the Cr-electroplating

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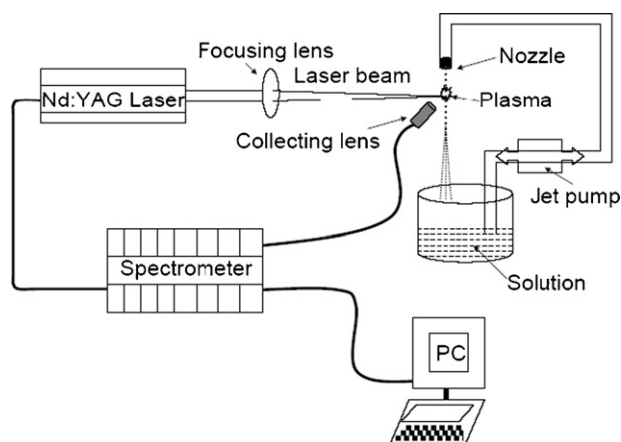
Fig. 1. Experimental setup for recording the LIB spectra of liquid sample.

Fig. 3. Variation of emission intensity of Cr II (283.5 nm) with laser energy.

industry in Kanpur which is one of the important industrial city of India.

2. Experimental

A schematic of the experimental setup, for recording the LIB spectra of liquid jet, is shown in Fig. 1. Nd:YAG (Continuum Surelite III-10) laser delivers pulsed laser energy of 425 mJ at 532 nm, with pulse width 3–4 ns and repetition rate 10 Hz. The laser beam is focused by a plano-convex quartz lens of focal length 30 cm to generate plasma on the surface of liquid stream flowing through jet from a teflon nozzle of diameter <1 mm. A jet pump, fixed in the middle of a 30 cm × 8 cm metal plate, is connected to the nozzle through a teflon tube while other end of the jet pump is in contact with solution kept in the sample cup through another teflon tube (Fig. 2). Laminar flow of jet is controlled by smoothly varying the speed of jet pump controlled by a voltage regulator. The light emission from microplasma is collected using optical fiber placed in the horizontal plane containing the laser beam (and at 45° with respect to laser beam) and fed to 4-channel spectrometer (Ocean Optics
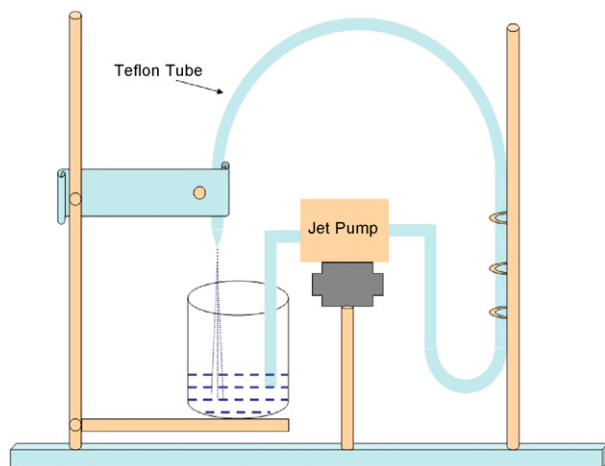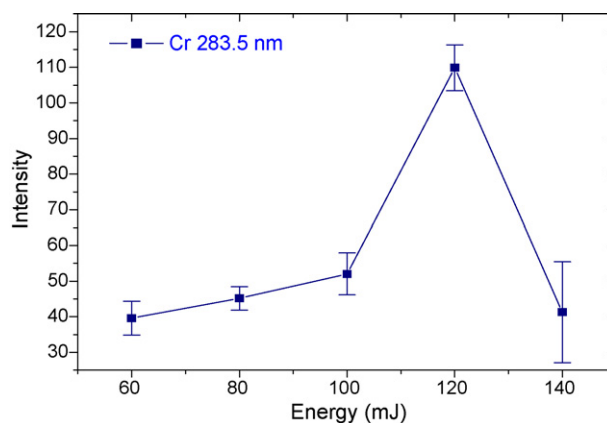
LIBS 2000+) equipped with CCD. The experimental setup was optimized by changing the experimental parameters like laser energy (measured with energy meter, Gentec-e model: UP19K-30H-VM-DO), lens to sample distance (LTSD), repetition rate of the laser and speed of liquid jet. The best LIB signals were found at laser energy 120 mJ, repetition rate 1 Hz and lens to sample distance equal to 30 cm. It is seen from Fig. 3 that LIBS signal increases monotonically with laser energy until the plasma density becomes too high for laser energy of 120 mJ. At still higher laser energy, the dense plasma formed by leading laser pulse starts absorbing energy from the later part of the laser pulse which leads to higher continuum emission [13,6] and lowers the analyte signal. Therefore, at higher energy, the decrease in LIBS signal may be due to shielding of laser light reaching to ablation surface. For calibration curve, different stoichiometric samples containing Cr were prepared by dissolving measured amount of ammonium dichromate (purchased from Merk (India) Limited, Mumbai) in double distilled water and stirring it over a period of several hours to get homogenous solution.

3. Result and discussion

The Cr-electroplating industries are one of the main sources for Cr pollution in wastewater irrigated area soil as well as ground water. Wastewater for the present study has been collected from the Cr-electroplating industry situated in Kanpur, India. The LIB spectra were recorded by focusing the pulsed laser beam just behind the laminar flow of water jet to produce plasma at its front surface. This was done to avoid breakdown in air in front of the water jet. LIB spectra of nine different standard samples of known concentration (ppm level) of Cr have been recorded. Each spectrum is average of 100 laser shots and two such spectra have been averaged to get the best signal to background (S/B) and signal to noise (S/N) ratio. Several emission lines of Cr are observed in LIB spectra in the present case but we have used Cr II lines at 283.5 and 284.3 nm, as these are non-resonant lines of Cr. Limit of detection (LOD) of Cr in water is evaluated by using the calibration curves described below.

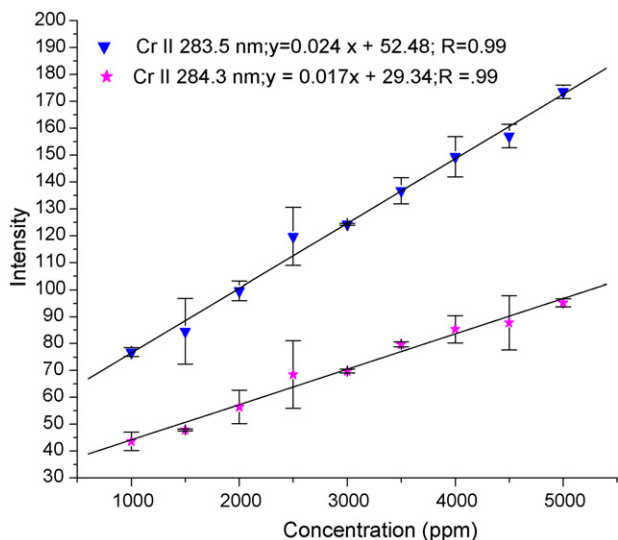
Fig. 2. Block diagram of liquid jet.

Fig. 4. Calibration curve for Cr II at 283.5 nm and Cr II at 284.3 nm.

The LOD is evaluated by using formula [4,6],

$$\text{LOD} = \frac{3\sigma}{S},$$

where σ is relative standard deviation (R.S.D.) of background and S is slope of the calibration curve.

For calculation of R.S.D. of background (σ), six pixel to pixel measurement of continuum background signal, on either side (left and right) of chosen atomic lines [Cr II (283.5 nm) and Cr II (284.3 nm)] was done and the standard deviation of these (continuum background) data was carried out separately. These measurements were made for both the spectra mentioned in the previous paragraph. Finally, mean relative standard deviation (R.S.D.) of background signal was calculated to be 0.238.

The calibration curves were drawn for Cr II 283.5 nm and Cr II 284.3 nm by plotting Cr concentration vs. emission intensity of Cr by using ORIGIN SOFTWARE and these are shown in Fig. 4. The slopes of the two calibration curves were obtained by fitting data in the linear regression functions for the two spectral lines

Cr II (283.5 nm); $y = 0.024\,x + 52.48$; $R = 0.99$
Cr II (284.3 nm); $y = 0.017x + 29.34$; $R = 0.99$

The non-zero intercept in the calibration curve is due to background signal [14]. In order to get low LOD, a calibration curve should have slope as large as possible and standard deviation should be as small as possible. Calibration curve for Cr II at 283.5 nm gives low LOD as compared to the calibration of curve of Cr II at 284.3 nm as latter has lower slope (Fig. 4). Using data for R.S.D. of background signal and slope of calibration, the LOD is found to be 30 ppm for Cr II 283.5 nm and 42 ppm for Cr II 284.3 nm. Therefore, Cr II line at 283.5 nm is best suited for quantitative determination of Cr in waste water. The LIB spectra of wastewater collected from Cr-electroplating industry (Fig. 5) is recorded under the same experimental condition as the CRM. From the measured intensity of the atomic line of Cr
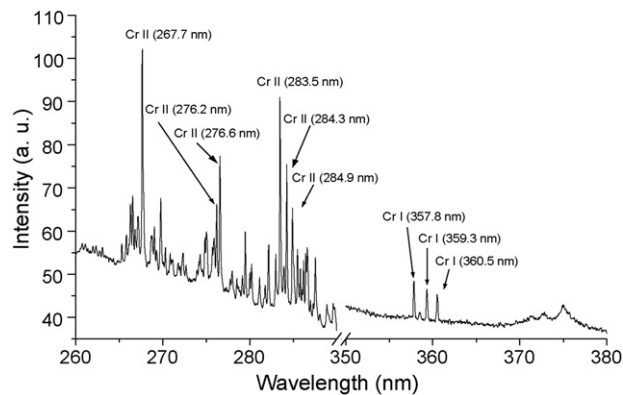

Fig. 5. LIB spectra of wastewater collected from Cr-electroplating industry.

II at 283.5 nm the concentration of Cr in wastewater is calculated, by using the above calibration curve to be 1500 ppm. This result is also compared with Cr concentration obtained from atomic absorption spectroscopy (1540 ppm), which is in close agreement. Such a high concentration Cr polluted wastewater is very dangerous to ecosystem as it might severely contaminate ground water as well as soil of that area. The removal of Cr from such wastewater by biological adsorption is in progress.

4. Conclusion

Our present results clearly demonstrate that limit of detection, which define sensitivity of any analytical technique, depends on the choice of calibration curve. Thus, the determination of suitable calibration curve is an important step in the quantification of trace elements in our environment. The calibration curve obtained in the present work is used as a reference curve to quantify the hazardous metal Cr present in wastewater. The concentration of Cr in the wastewater collected from Cr-electroplating industry is found to be 1500 ppm.

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