Utilization of Laser Induced Breakdown Spectroscopy to Investigate the Metals in Dairy Products Waste Water

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Authors’ contributions

This work was carried out in collaboration between both authors. Author NAA designed the study, wrote the protocol, and wrote the first draft of the manuscript. Author MMO managed the analyses of the study and the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

Background: Laser-induced breakdown spectroscopy (LIBS) is an atomic emission-type spectroscopy that can analyze any sample successfully and can be applied to gas, liquid, and solid samples. It can provide nonintrusive, qualitative and quantitative measurement of elements in various test environments. Due to rapid industrial growth, environmental pollution has increased tremendously over the years, especially with heavy metals. These metals, are toxic even at low concentrations, may find their way into the human body via inhalation, ingestion, and skin absorption. The analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health.

Aim: In this work Laser Induced Breakdown Spectroscopy (LIBS) was used to investigate the heavy metals in industrial water collected from dairy products processing plants.

Experimental: This study was designed to use LIBS technique to analyze the emission spectral...
lines collected from the samples plasma and to make use of this technique to determine the existence of heavy elements in waste water of dairy products.

**Place and Duration of Study:** Department of laser system, institute of laser in Sudan university of Science and Technology – Republic of the Sudan.

**Methodology:** Three water samples were irradiated by Q-switched Nd: YAG laser to produce its plasma. The emission spectra of the plasma were collected via optical fiber and analyzed by Ocean Optics 4000+ spectrometer, and the recorded spectra of the samples were analyzed using NIST data.

**Samples:** Three waste water samples, collected from dairy product plants, were used as study samples.

**Results:** The analysis of the spectra showed considerable amounts of Na, Co, Cu, Fe, Cs, Hg, Pr, Cr, Ti elements in addition to Co^{+1}, Cu^{+1}, Cs^{+1} and Fe^{+1} ions.

**Conclusions:** The analysis of the three industrial water samples led to efficient detection of different heavy metals using LIBS technique.

**Keywords:** LIBS; dairy product plant; heavy metals.

1. **INTRODUCTION**

Laser-induced breakdown spectroscopy (LIBS) is a laser based technique that can provide nonintrusive, qualitative and quantitative measurement of metals in various test environments [1]. LIBS is an emission-type technology that has been successfully applied to gas, liquid, and solid samples [2].

During the last two decades, LIBS has undergone a dramatic transformation in terms of hardware, software and application areas. It has become a powerful sensor technology for both laboratory and field use. In order to obtain a reliable quantitative elemental analysis of a sample using LIBS [2], one needs to control several parameters that can strongly affect the measurements. Some of these parameters are the laser wavelength, its irradiance, the morphology of the sample surface, the amount of ablated and vaporized sample, and the ability of the resulting plasma to absorb the optical energy. If these and related parameters are properly optimized, the spectral line intensities will be proportional to the elemental concentration.

Due to rapid industrial growth, environmental pollution has increased tremendously over the years, especially the contamination of soil and ground water with heavy metals such as chromium, lead, copper, arsenic, nickel, beryllium, antimony, zinc, magnesium, mercury, aluminum, cobalt…..etc. These metals, are toxic even at low concentrations, may find their way into the human body via inhalation, ingestion, and skin absorption [3].

The analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health [4]. If accumulation of the heavy metal ions in the body tissues is faster than the body’s detoxification, a gradual buildup of these toxins will occur. Long and even short term exposure to measurable quantities of various metals such as copper, mercury, cobalt, beryllium, zinc, chromium and antimony can lead to long term health problems and can cause irreversible damage [5].

In the dairy product industry, there is a need for an analytical technique to be able for on-line measurements of heavy metals and other trace elements in waste water coming from different processes involved. The amount of waste water generated by dairy industrial plant is of huge amount and it can have hazardous effects on environment [6].

Recent researches in laser spectroscopy suggested the technique of LIBS, beside other spectroscopic techniques, to be used for the determination of these heavy metals in our environment [7].

This work aimed to use LIBS technique in the determination of heavy metals in dairy waste water and to evaluate its efficiency in the determination of these elements.

2. **EXPERIMENTAL DETAILS**

2.1 **The Equipments**

The LIBS setup used in this work is shown in Fig (1):

The LIBS system used in this study was consisted of Ocean Optics LIBS
4000+ spectrometer, Q-switched Nd. YAG Laser (Laser Wavelength is 532 nm, pulse duration = 10ns, Pulse Energy = 30 mj, Spot size = 2-8 mm, and repetition rate = 2 Hz).

2.2 The Materials

Three industrial samples were collected from waste water in three dairy plants and investigated here.

2.3 Experimental Procedure

Each sample was put in a glass cuvette and irradiated by the Nd-YAG laser where the spark of the sample plasma was collected by a fiber optic of the spectrometer. The USB 4000 interfaces to computer with Windows operating system. The spectral range was from 200-900 nm.

In order to test the homogeneity of our samples, several LIBS measurements were performed at the surface of waste water samples.

The recorded spectra of the samples were analyzed using NIST data.

3. RESULTS AND DISCUSSION

Figs. (2), (3) and (4) show the LIBS emission spectra for the three waste water samples (1, 2, 3), respectively, in the region from 186 nm to 883 nm.

Atomic spectra database was used for the spectral analysis of the tested samples where Table (1) lists the analyzed data.

The three spectra of the samples showed different amounts of elements like (Na, Co, Cu, Fe, Cs, Hg, Pr, Cr, Ti) that were found in all the samples.

The Iron atoms (Fe) was found in the three samples with high amount in sample (3), and nearly equal amounts in samples (1) and (2). Chromium atoms (Cr) was presented in the three samples with different amounts. In sample (1) it was appeared with very high amount while it was lower in sample (3), and the lowest amount was in sample (2). Also Chromium ion (Cr$^{+3}$) presented with high amount in sample (2).

Mercury (Hg) was found with relatively little amount in the three samples, (this element is highly toxic even with little amount).

Beside neutral atoms, ions of different amounts and ionization stages also were recorded as shown in Table (1). All these ions may not present in the sample originally, where some of them are produced due to the ionization of neutral atoms by the laser power density.

Cesium ion (Cs$^{+1}$) was found with relatively little amount in the three samples. Also Cobalt ion (Co$^{+3}$) was found with high amount in samples (1) and (2) while in sample (3) it was very low.

The copper ion (Cu$^{+2}$) was found with relatively high amount in samples (1) and (2), and in less amount in sample (3).
The iron ion (Fe$^{+1}$) was found in sample (2) with very high amount compared with the other two samples. The sodium ion (Na$^{+1}$) was found in samples (1) and (2) with nearly equal amount and it was high in sample (3) compared with the two samples.

**Fig. 2.** LIBS emission spectrum of sample 1

**Fig. 3.** LIBS emission spectrum of sample (2)
Fig. 4. LIBS emission spectrum of sample (3)

| Table 1. The analyzed data of the three samples |
|-----------------------------------------------|
| **Element** | **λ nm** | **I(S1) a.u** | **I(S2) a.u** | **I(S3) a.u** |
|-------------|----------|---------------|---------------|---------------|
| Na11        | 420.87   | 140.75        | 140.97        |               |
|             | 476.85   |               | 171.44        |               |
| Na111       | 444.85   | 187.94        | 187.83        |               |
|             | 535.16   |               |               | 167.73        |
| Fe1         | 326.29   |               | 155.06        |               |
|             | 334.58   |               |               | 175.92        |
|             | 415.21   |               |               | 161.67        |
|             | 426.87   | 173.85        | 173.74        |               |
|             | 452.86   | 128.62        | 128.51        |               |
|             | 456.86   | 159.10        | 158.99        |               |
|             | 513.17   |               |               | 130.70        |
|             | 517.17   |               |               | 129.06        |
|             | 550.84   | 175.48        |               |               |
|             | 554.82   | 182.04        | 181.93        |               |
|             | 743.06   |               | 140.8         |               |
|             | 768.72   |               | 128.51        |               |
|             | 829.35   |               | 165.38        |               |
| Fe11        | 235.62   |               |               | 149.27        |
|             | 236.29   |               | 132.50        |               |
|             | 239.62   |               | 132.50        |               |
|             | 258.29   | 135.52        | 134.47        |               |
|             | 286.60   |               |               | 161.83        |
|             | 444.85   | 187.94        | 187.83        |               |
|             | 634.78   | 193.83        |               |               |
|             | 664.77   |               | 225.84        |               |
| Cr1         | 284.60   |               |               | 157.57        |
|             | 337.25   |               |               | 131.03        |
|             | 374.90   |               | 158.99        |               |
|             | 395.22   |               | 124.47        |               |
|             | 675.76   | 201.64        |               |               |
|             | 769.73   |               | 165.93        |               |
| Element | λ nm | I(S1) a.u | I(S2) a.u | I(S3) a.u |
|---------|------|----------|----------|----------|
| Cr11    | 272.27 |          |          |          |
|         | 286.60 |          |          |          |
| Ti1     | 631.20 |          |          |          |
|         | 470.86 | 187.94   | 187.83   |          |
|         | 492.84 | 177.78   | 183.89   |          |
|         | 609.12 |          |          | 141.19   |
|         | 681.19 |          |          | 175.92   |
|         | 693.09 |          |          | 138.89   |
| Cu1     | 508.82 |          |          |          |
|         | 637.78 | 196.02   | 196.13   |          |
|         | 655.09 |          | 225.73   |          |
| Cu11    | 194.97 |          |          |          |
|         | 278.60 |          |          | 135.01   |
|         | 494.84 |          | 224.96   | 124.69   |
|         | 496.51 |          |          | 143.10   |
|         | 521.16 |          |          | 126.77   |
|         | 568.81 |          | 191.87   | 192.09   |
| Hg1     | 800.71 |          | 128.51   |          |
|         | 844.33 |          |          | 132.88   |
|         | 851.35 |          | 159.15   |          |
| Cs11    | 204.64 |          |          | 132.94   |
|         | 438.87 |          | 159.10   | 158.99   |
|         | 615.12 |          |          | 126.77   |
| Ba11    | 186.98 |          |          | 157.62   |
| Mn1     | 414.88 |          | 146.97   | 146.87   |
| Mn11    | 339.24 |          |          | 149.38   |
|         | 452.53 |          |          | 161.72   |
| Pr1     | 641.11 |          |          | 129.06   |
|         | 663.10 |          |          | 222.12   |
|         | 631.76 |          | 171.17   |          |
| Pr11    | 682.76 |          |          | 167.51   |
| Kr11    | 272.94 |          | 134.52   |          |
|         | 461.52 |          |          | 170.19   |

4. CONCLUSIONS

The LIBS techniques proved to be efficient in detection of heavy metals in industrial water even those with little amounts. Also LIBS proved to be good and fast diagnostic technique that can be used for investigation of elements in liquid samples. No sample preparation is needed.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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