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Investigating Wastewater Pollution Using Laser-Induced Breakdown Spectroscopy

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Abstract

Water pollution, caused by human activities since the early 1900s, is a major concern. The metal industry, a primary contributor, releases harmful substances into the environment through wastewater, posing risks to living creatures. Conventional techniques (ICP-MS, ICP-OES, FAAS, AAS) for detecting harmful substances have drawbacks like expensive equipment and chemicals, complex sample preparation, and time-consuming procedures. Meanwhile, Laser-Induced Breakdown Spectroscopy (LIBS) faces challenges in water sample analysis: splashing, weaker spectrum, reduced plasma lifetime, and surface ripple. Two sampling techniques were explored using cadmium chloride and lead acetate as reference samples for comparing wastewater LIBS spectra to overcome them. This experiment aims to set up LIBS, collect industrial wastewater samples, and analyse them for lead (Pb) and cadmium (Cd) presence. An Nd: YAG laser (1064nm, 50 mJ, 10ns) and spectrometer (HR4000) were used to determine Cd and Pb presence in wastewater from locations near Steel Station, Paint Factory, Food Factory, and Tin Factory in Muar, Johor; Parit Jawa, Johor; Ledang, Johor; and Merlimau, Melaka, respectively. In this study, LIBS with glass slides showed significant peaks for elements in reference samples, but Cd and Pb were not detected in the wastewater. The filter paper method was ineffective. All samples met safety recommendations (3 ppb for Cd, 50 ppb for Pb) set by the Malaysian Ministry of Health (MOH) and verified by ICP-MS.

1. Introduction

Water pollution has worsened since the early 1900s due to the increase in human activities, resulting in the release of harmful substances into the environment through wastewater and needs to be concerned [1,2]. The metal industry has been the primary source of heavy metal(loid) contamination, harmful to the environment (soil, surface, and groundwater) and other living creatures, including humans [3]. The real-time and on-spot analysis becomes an urgent issue to ensure the quality of the water, most importantly the drinking water.

To precisely measure the harmful substances such as cadmium (Cd) and lead (Pb) in water and soil, a range of methods have been developed. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [4], Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [5], flame atomic absorption spectrophotometry (FAAS), and atomic absorption spectroscopy (AAS) are the standard analytical techniques. However, these techniques have limitations like expensive equipment and chemical substances, complex sample preparation procedures, and time-consuming [6]. In contrast, Laser-Induced breakdown spectroscopy (LIBS) has emerged as a useful option for fast sampling, virtually non-destructive nature in determining substance concentrations [7] and in-field analysis. LIBS, or Laser-induced breakdown spectroscopy, is a technique for identifying elements in solids, liquids, and gas states. Generally, it consists of a laser, mirrors, lenses to focus the laser, a spectrometer to divide light into wavelengths, an intensified charge-coupled device (ICCD) or camera to catch the light, a digital delay generator, and a fibre optic cable for data transfer. The laser produces plasma on the sample surface, and the spectrometer divides the light emitted into different wavelengths. This light is converted into an electrical signal by the ICCD for analysis, and data is transferred via fibre optic cable, which results in specific emission spectra that may be used to identify and measure the elemental composition of the material being examined [8].

The detection of elemental composition in liquid using LIBS has limitations, which are low sensitivity and issues like splashing, reduced plasma lifetime, weaker spectrum, and surface ripples [9]. In this study, two sampling techniques are proposed – filter paper and glass slide methods are used to overcome the challenges mentioned like splashing, reduced plasma lifetime, weaker spectrum, and surface ripples. We will investigate wastewater samples collected from the end of the sewage system in the area near the Steel Station, Upon Paint factory, WCS food factory, and Yong Shing tin factory (which is located in Muar, Johor; Parit Jawa, Johor; Ledang, Johor; and Merlimau, Melaka respectively) using LIBS. To overcome the issues for water samples mentioned before, we will convert the liquid sample to solid sample called liquid-solid conversion, which helps to remove the impacts of moisture present in the original liquid sample. The filter paper and glass slide methods are applied, with cadmium chloride and lead acetate as reference samples to compare with the LIBS spectra for wastewater samples.

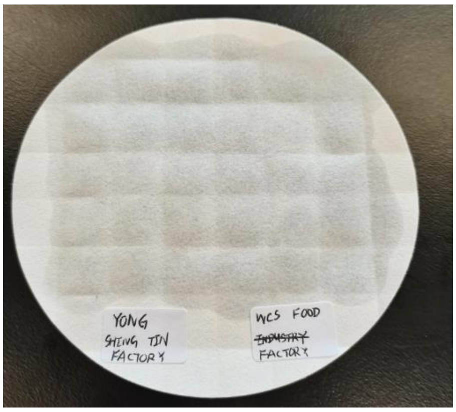
2. Materials and Methods

The wastewater samples are collected from the end of the sewage system in the region around the Steel Station, Upon Paint Factory, WCS food factory, and Yong Shing Tin factory, which is located in Muar, Johor; Parit Jawa, Johor; Ledang, Johor; and Merlimau, Melaka respectively. The Cadmium chloride and Lead acetate were used as the reference samples with a concentration of 300mg/L each.

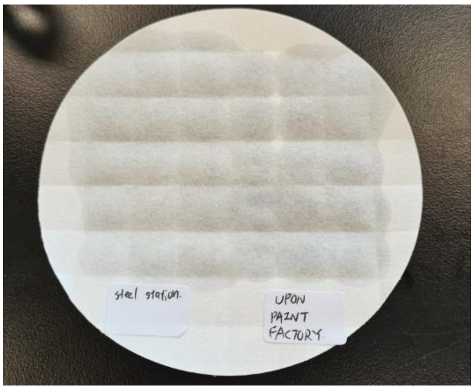
Two sampling techniques were used in this study: the filter paper and glass slide methods. For the filter paper method, a new sheet was prepared and folded to create multiple sections. Sample solution drops were pipetted onto these sections and left to dry for 2 hours. Next, set up the experiment setup as shown in Fig. 2. Once dried, the filter paper was placed on the sample stage, aligned with the laser, and shot 5 times at each sample spot. Observations were recorded, repeating the process for other samples. Besides that, the glass slide method involved cleaning and drying before pipetting the sample solution on the glass slide at different spots. Once the sample was pipetted on the glass slide, wait for 2 hours until it dried completely, and the glass slide was aligned to the laser and shot for 5 shots per spot. The result was recorded, and the experiment was repeated with other samples.

The 500ml water bottles were used to keep the wastewater samples that were collected from the end of the sewage system of the Steel station, Upon Paint Factory, Yong Shing Tin Factory Sdn Bhd, and WCS Food Industries(M) Sdn. Bhd. After that, the samples were transferred from water bottles into different small veils as shown in Fig. 1(a). During the experiments, samples were deposited on the filter paper for the LIBS experiment, respectively. Fig. 1(b) shows the wastewater droplets on the glass slide for various places which were air-dried indoors for 2 hours. The samples were pipetted into squares on the filter paper of 1.6 cm diameter (2 cm2) as shown in the Fig. 1(c) and 1(d). They were air-dried indoors for 2 h and then exposed LIBS investigations.

(a) (b)



(c)



(d)

Fig. 1 (a) *Wastewater stored in the small veils; (b) Wastewater droplets were dried on the glass slide for various places; (c) Yong Shing tin factory and WCS food factory wastewater were dropped on the filter paper respectively; (d) Steel station and Upon paint factory wastewater were dropped on the filter paper respectively.*

2.1 Sample Preparation

Fig. 2 shows the schematic diagram of the LIBS setup. The experiment was carried out with a specially configured LIBS system. A Q-switched Nd: YAG pulsed laser generated a 1064 nm laser with an energy of 50 mJ, a pulse width of approximately 10 ns, and a repetition rate of 10 Hz. This laser was directed onto a filter paper or glass slide at the sampling area using a planoconvex lens (f = 50 mm). To prevent unnecessary laser sparks in the air, the sample was placed at a distance slightly shorter than the focal length. When the laser shot the sample, it generated plasma. Spectral signals from the plasma were captured using a spectrometer (HR4000) connected to a collector set at a 45-degree angle. The spectrometer had a resolution of 0.3 nm and was able to record within a spectral range of 200nm to 1100 nm. CCD detector installed inside HR4000 converted optical signals into electrical ones, stored in a computer for further analysis. To obtain LIBS spectra from various points, the sample was placed on a sample stage and manually shifted.

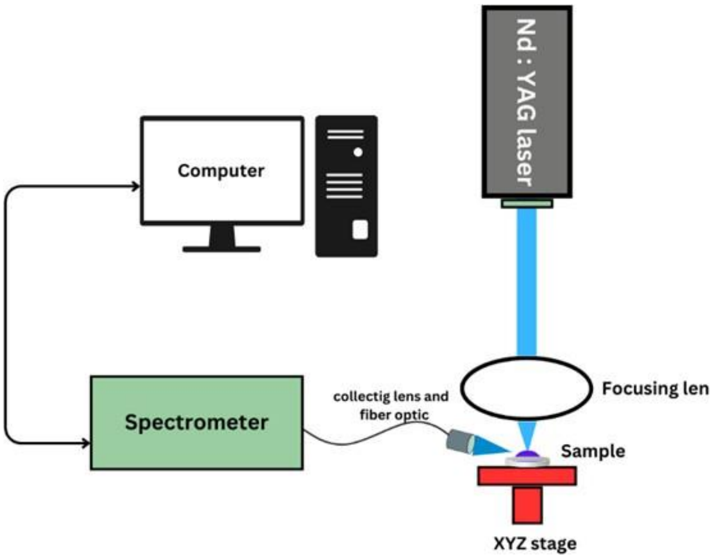


Fig. 2 *Schematic diagram of LIBS Experiment setup*

3. Results and Discussion

3.1 LIBS Analysis of Reference Samples

The Fig. 3(a) and (b) show the LIBS spectra of cadmium chloride for 2 different methods which are filter paper and glass slide methods. The concentration of cadmium chloride and lead acetate are calculated using the standard formula, C = m/V, where C is the concentration, m is the mass of the solute dissolved, and V is the total volume of the solution. In Fig. 3, we can notice that the glass slide method gives clear cadmium (Cd) peaks. The Cd II element peaks can be clearly found from the LIBS spectra which are at 214.09 and 223.42nm while the Cd I element is at 228.83, 346.56, and 361.05nm. While the Filter paper method does not show any prominent spectral lines for both LIBS spectra.

The same goes for the Lead acetate solution result. Fig. 3(c) and (d) illustrate the outcomes of lead acetate for two distinct sampling methods. According to the Fig. 3(c) and (d), the glass slide method may detect and identify clear Lead (Pb) element peaks. The LIBS spectra clearly show the Pb II element peak at 220.26 nm, while the Pb I element peaks are 261.16, 283, and 405.68 nm. Furthermore, whether the Filter paper method is used with or without Lead acetate solution, the results for both LIBS spectra are similar.

In conclusion, the filter paper method is not suitable for LIBS detection or liquid samples due to the failure of detection for lead acetate and cadmium chloride elemental compounds. For the following section, the glass slide method will be discussed only.

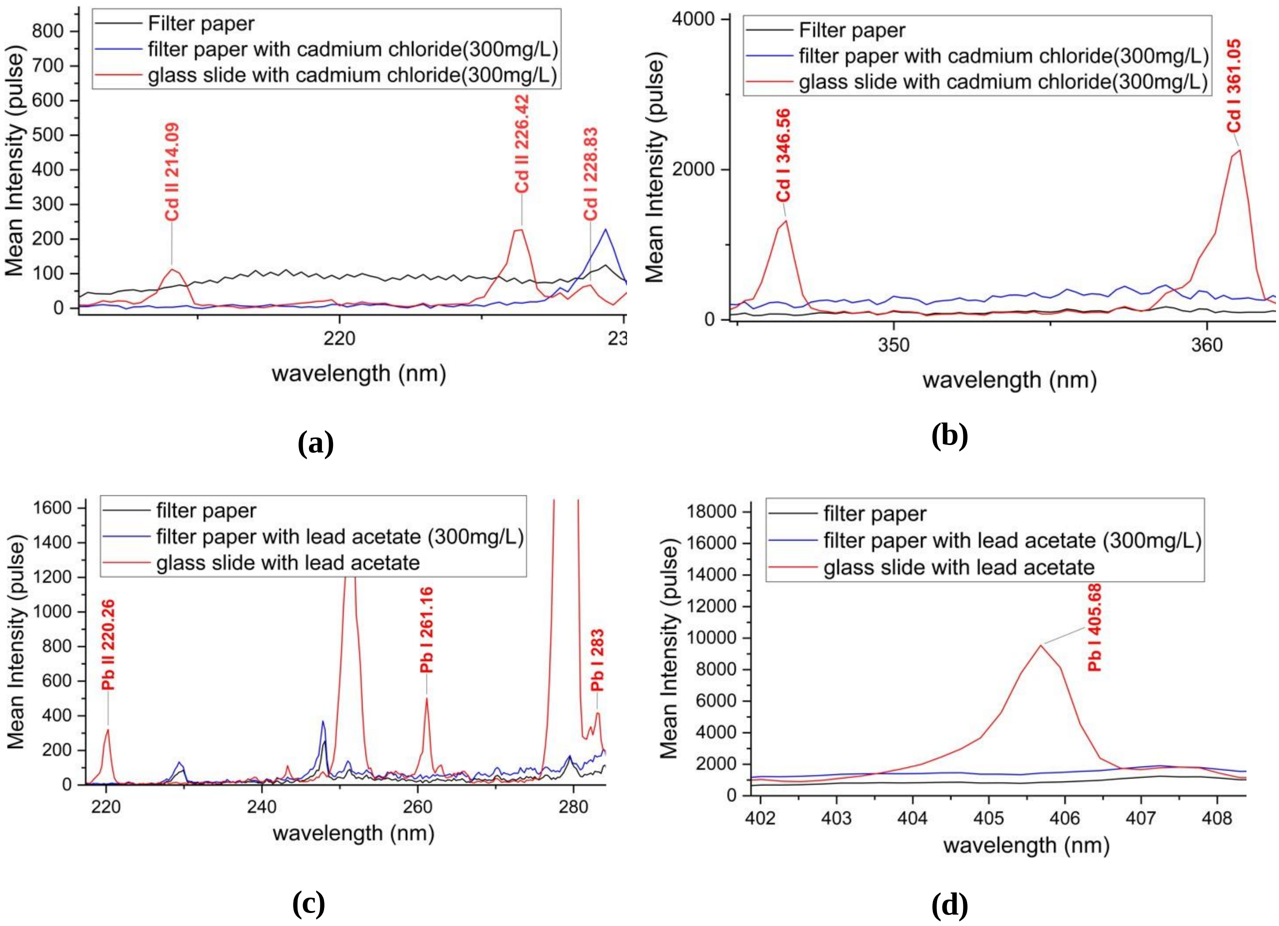


Fig. 3 (a) *LIBS spectra comparison of cadmium chloride using Filter paper and Glass slide methods (210- 230nm); (b) LIBS spectra comparison of cadmium chloride using the Filter paper and Glass slide method (345- 365nm); (c) LIBS spectra comparison of lead acetate using filter paper and glass slide method (220-285nm); (d) LIBS spectra comparison of lead acetate using filter paper and glass slide method (400-410nm).*

3.2 Elemental Analysis of Wastewater Samples Using LIBS.

From Fig. 4, no cadmium or lead element is observed in the wastewater from the Steel Station area after comparing it with the cadmium and lead LIBS spectra. In the wastewater from the Steel Station, we didn't see any clear peaks that indicate the presence of cadmium or lead elements due to the LIBS spectra of this wastewater didn't match the peaks seen in cadmium chloride and lead acetate solutions for these elements.

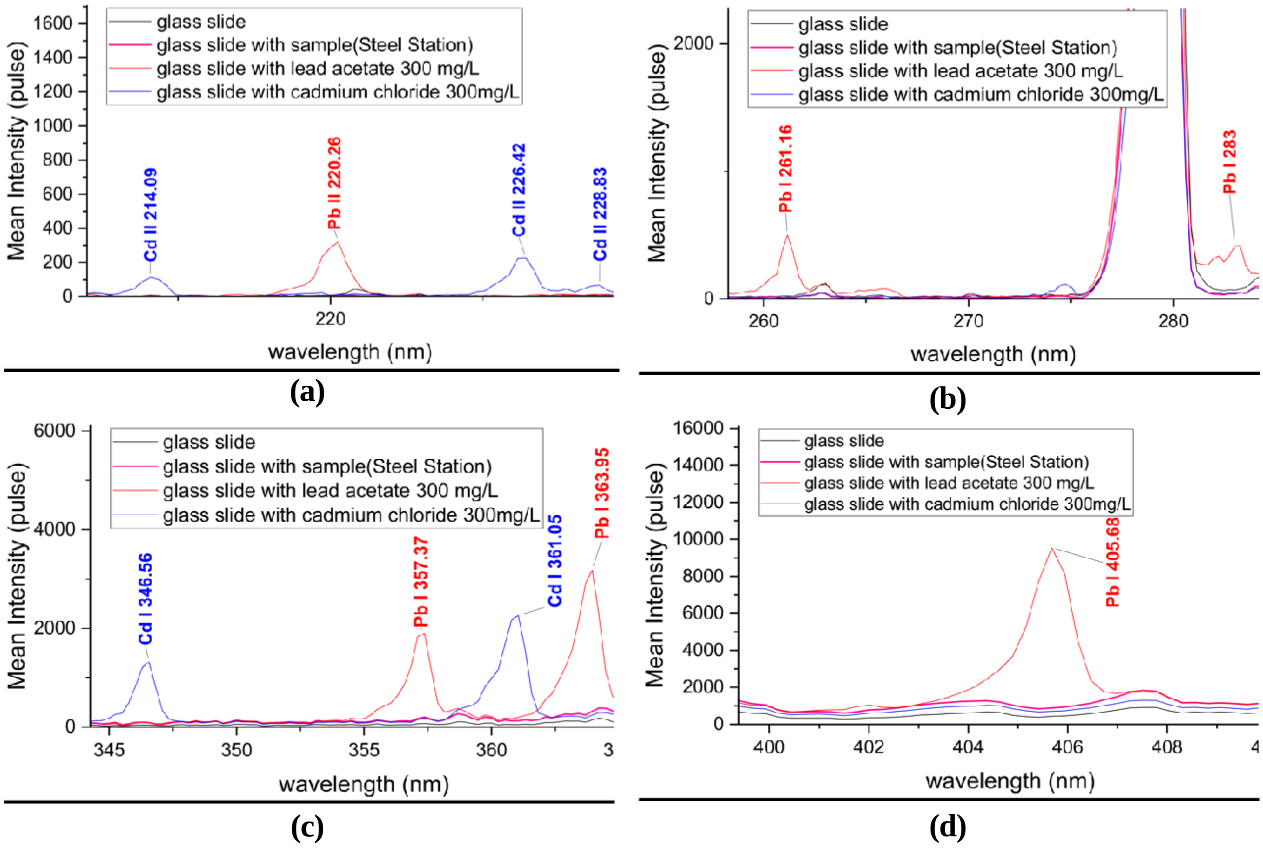
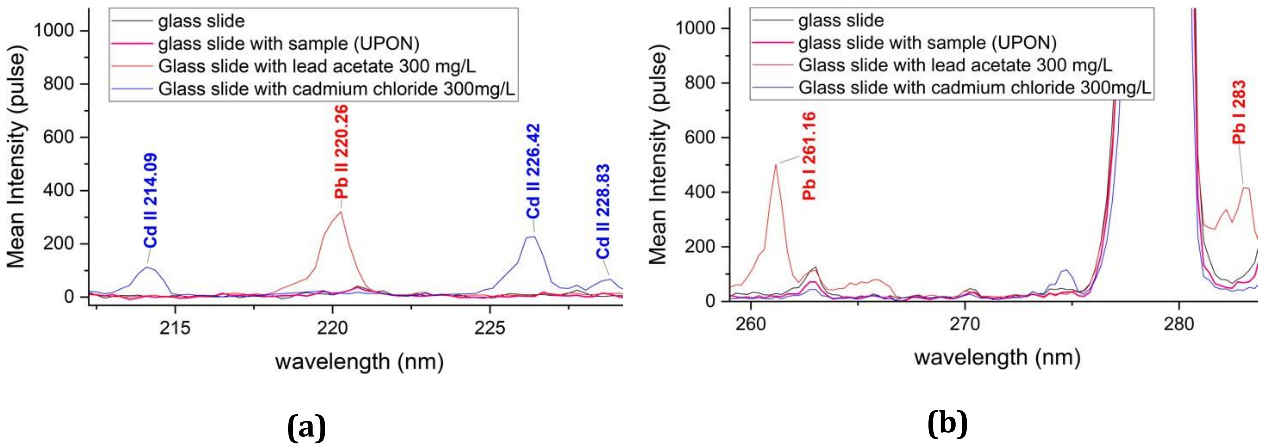
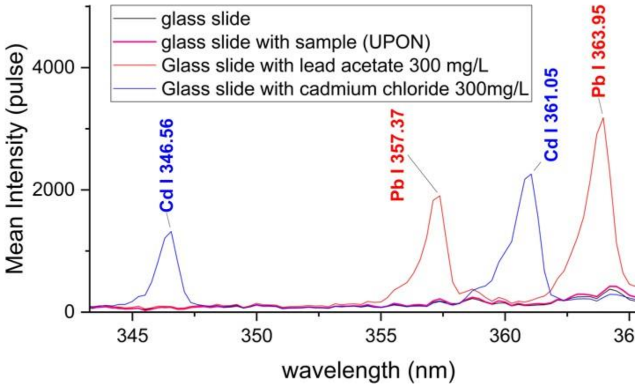


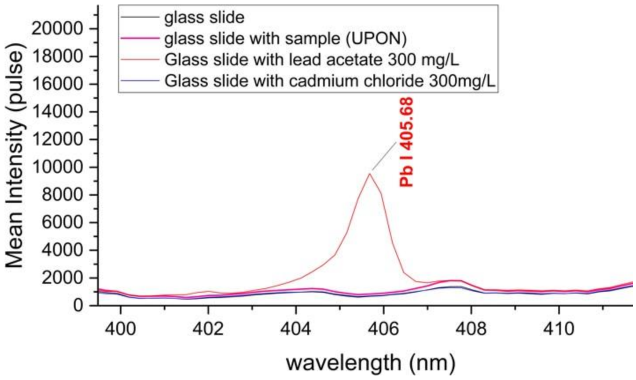
Fig. 4 *LIBS spectra of the wastewater from the Steel station for (a) 210-230nm; (b) 260-285nm; (c) 345-365nm; and (d) 400-410nm.*

As can be seen in Fig. 5, there are no peaks in the sample from Upon Paint Factory that look like they belong to the cadmium and lead elements spectra. It is evident from looking at the LIBS spectra in Fig. 5 that the wastewater from the Upon Paint facility does not include any identified peaks that match the characteristic peaks of lead and cadmium elements.





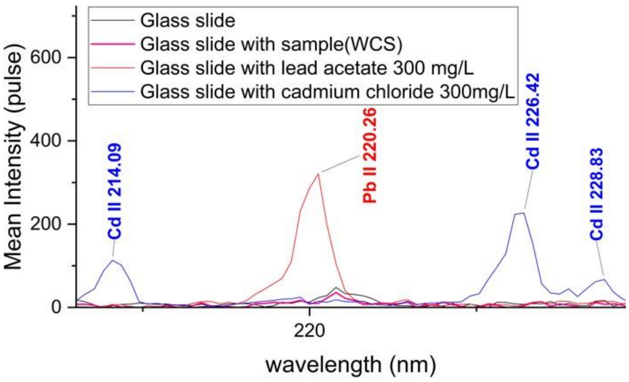
(c)



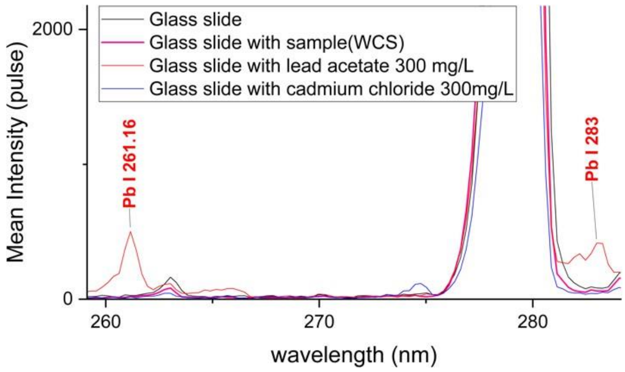
(d)

Fig. 5 *LIBS spectra of the wastewater from the Upon Paint factory for (a) 210-230nm; (b) 260-285nm; (c) 345-365nm; and (d) 400-410nm.*

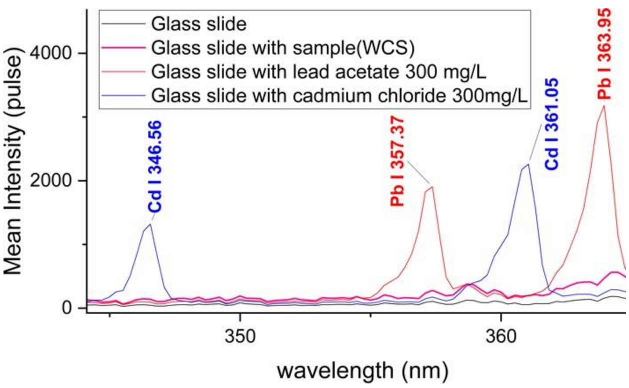
The LIBS spectra for the wastewater from the WCS food factory are quite different compared to the lead and cadmium LIBS spectra as shown in Fig. 6. The wastewater from the area of the WCS food factory does not show heavy metals like cadmium and lead. There are no similar LIBS spectral lines after comparing the cadmium and lead LIBS spectral lines with the WCS food factory LIBS spectra.



(a)



(b)



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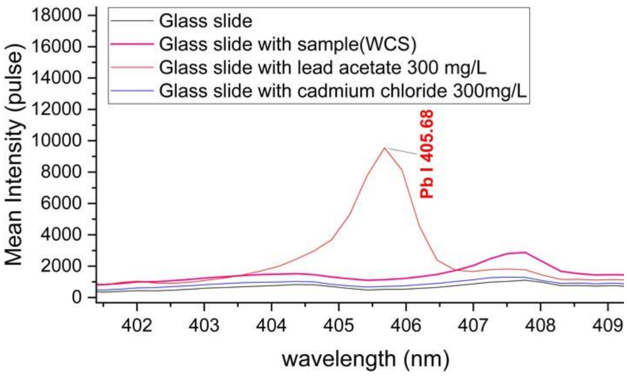

(d)

Fig. 6 *LIBS spectra of the wastewater from the WCS food factory for (a) 210-230nm; (b) 260-285nm; (c) 345-365nm; and (d) 400-410nm.*

Fig. 7(a)-(d) shows the LIBS spectra for the wastewater from Yong Shing Tin Factory compared with the cadmium and lead element LIBS spectra. Based on the spectra, it appears that there is an absence of cadmium and lead elements in the wastewater from the Yong Shing Tin factory, as shown by the LIBS spectra for these elements. So, we assume there is no lead or cadmium in the Yong Shing Tin factory's wastewater, or it is below the detection limits of LIBS.

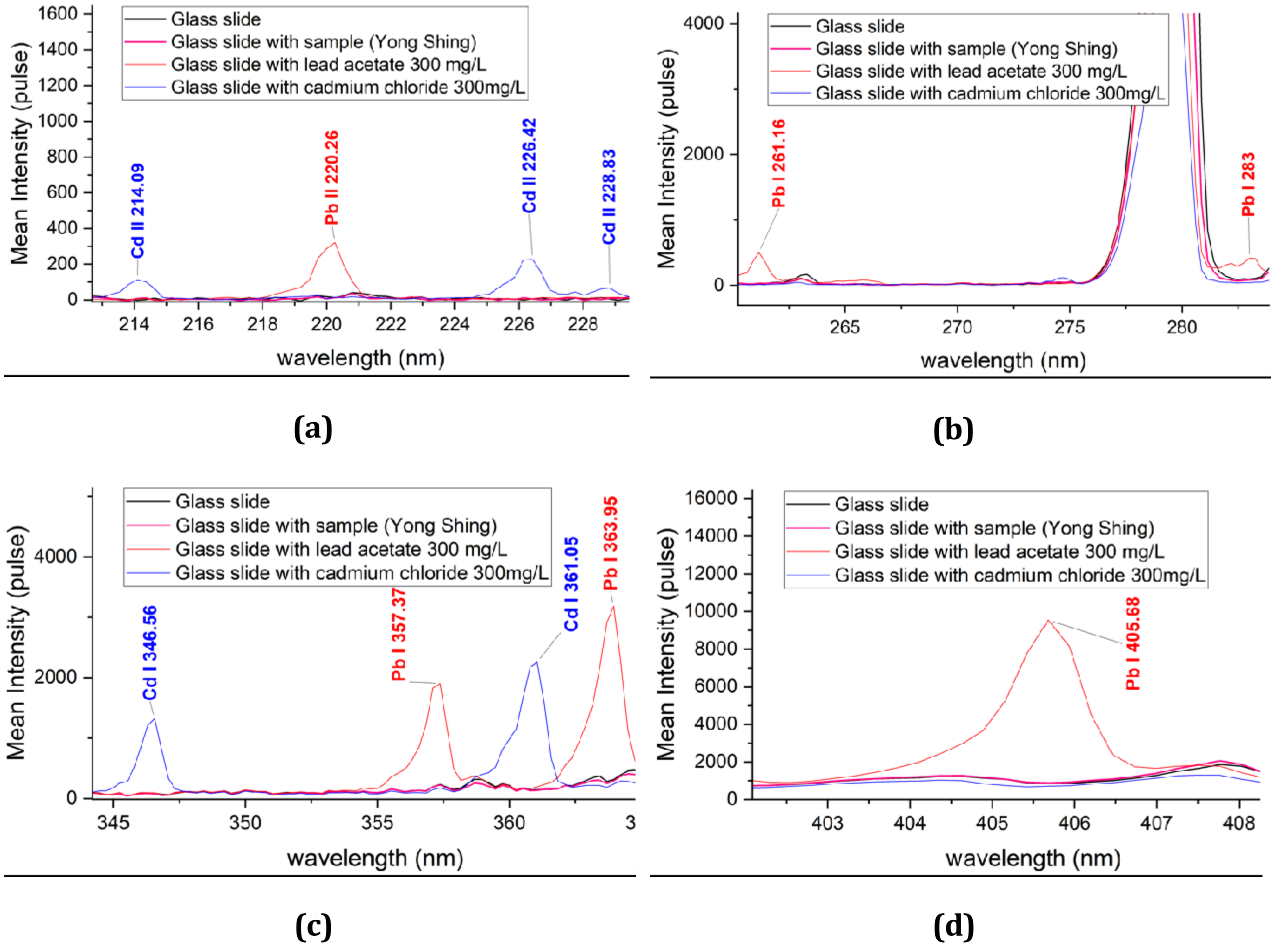

Fig. 7 *LIBS spectra of the wastewater from the Yong Shing tin factory for (a) 210-230nm; (b) 260-285nm;* **(c)***345-365nm; and (d) 400-410nm.*

Table 1 displays the Cd and Pb concentrations in wastewater from different industrial sites. The concentration from different sites was obtained by using ICP-MS. For the Steel Station, Cadmium and Lead concentrations are 0.0405 parts per billion (ppb) and 0.527 ppb, respectively. The Upon Paint factory is a factory that manufactures paint products, including protective coating, industrial coating, and car paint. It shows concentrations of 0.019 ppb for Cadmium and 0.0416 ppb for Lead in the wastewater. WCS food factory is a food factory that specializes in traditional bakery products. It exhibits the lowest Cadmium concentration at 0.0327 ppb and a Lead concentration of 0.291 ppb. Lastly, the Yong Shing tin factory is a factory that manufactures tin products, including tin bottles, doors, and window frames. It shows 0.11 ppb of Cadmium and 0.321 ppb of Lead in its wastewater.

All the wastewater samples we tested, based on the ICP-MS results, meet the Ministry of Health (MOH) Malaysia's standards. The allowed limits for cadmium and lead are 3 ppb and 50 ppb [10], respectively, and our findings show that all the samples are within these limits.

Table 1 *Concentration of cadmium and lead consist in the samples.*

Heavy metal / Sample	Cadmium (ppb)	Lead (ppb)
Steel station	0.0405	0.527
Upon paint factory	0.019	0.0416
WCS food factory	0.0327	0.291

Yong Shing Tin factory	0.11	0.321

Table 2 *Concentration of cadmium and lead acceptable by Ministry of Health Malaysia.*

Type of element	Permitted value (ppb)
Cadmium (Cd)	3
Lead (Pb)	50

In their recent study, Yan and colleagues identified the detection limit for lead across ten diverse samples, ranging notably from 0.57 to 86.72 mg/kg [11]. The unit of 1 mg/kg is equivalent to 1 ppm. In contrast, Elhassan and the team reported a distinct detection limit, specifying 5.86 ppm for lead and 8.55 ppm for cadmium [12,13,14]. For instance, our results showed that ICP-MS (Inductively Coupled Plasma Mass Spectrometry) could identify trace levels of lead and cadmium in wastewater, while LIBS (Laser-Induced Breakdown Spectroscopy) was unable to detect either of these elements. Because of ICP-MS's lower detection limit, which is expressed in ppb (parts per billion), the difference between the two methods can be attributed to LIBS's comparatively poorer sensitivity. The wastewater did include some lead and cadmium, but the concentrations were far under the safety standards set by the Ministry of Health (MOH) Malaysia, which are 50 ppb for lead and 3 ppb for cadmium.

4. Conclusion

In this present study, wastewater samples from the Steel Station, Upon Paint factory, WCS food factory, and Yong Shing tin factory were analysed, using cadmium chloride and lead acetate as reference samples. The main objective was to detect the presence of Cd and Pb in the wastewater samples. LIBS with glass slide sampling methods demonstrated significant peaks in reference samples indicating the presence of lead and cadmium elements. However, the filter paper approach did not work well for finding these elements. Besides that, LIBS was able to detect Cd and Pb for reference samples but did not find Cd and Pb in the wastewater. ICP-MS was used to verify the result claimed but LIBS. ICP-MS shows that there are trace amounts of Cd and Pb contained in the wastewater. This disparity is due to ICP-MS's higher sensitivity than LIBS. Even though the wastewater contained some cadmium and lead, the amounts remained well within the Malaysian Ministry of Health's safety recommendations of 3 ppb for cadmium and 50 ppb for lead.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design, data collection, methodology, analysis and interpretation of results:*** *Lee Kuan Yong and Syed Zuhaib. All authors reviewed the results and approved the final version of the manuscript.*

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